CHEM 260: INORGANIC CHEMISTRY



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Chem 260: Inorganic Chemistry

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This text was compiled on 06/07/2025

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Glossary

Detailed Licensing

Licensing

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

CHAPTER OVERVIEW

1: Review of Chemical Bonding

Learning Objectives

- Be able to draw Lewis dot structures, assign formal charges, predict molecular geometries (including bond angles), and calculate bond orders for molecules, including hypervalent molecules and ions.
- Describe hypervalent molecules using no-bond resonance.
- Understand and articulate how predictions of molecular structure and bonding can be experimentally verified.
- Learn to construct hybrid orbitals from s and p atomic orbitals.
- Use the isoelectronic principle to design new molecules and solids.
- Rationalize bond strength and chemical reactivity using bond polarity arguments.
- Interrelate bond length and bond strength.

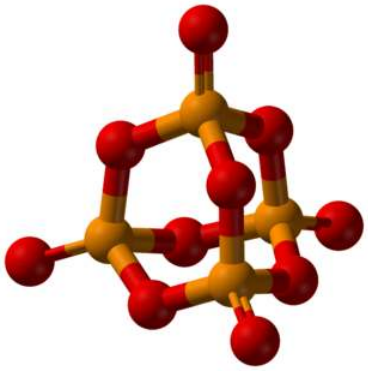
There is no topic more fundamental to Chemistry than the nature of the chemical bond, and the introduction you find here will provide you with an overview of the fundamentals and a basis for further study.

1.1: Prelude to Chemical Bonding
1.2: Waves and Electromagnetic Radiation
1.3: Quantization of Energy
1.4: Atomic Orbitals and Their Energies
1.5: Slater's Rules
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1.1: Prelude to Chemical Bonding

Molecules (and extended solids) are built from atoms that form chemical bonds. Theories of bonding seek to explain why molecules and solids form, what their structures are, why some are more stable than others, and how they react. As we will learn in Chapter 2, quantum mechanics gives us the most realistic picture of chemical bonding via molecular orbital (MO) theory. However, the MO description of bonding is conceptually difficult and mathematically intensive. This chapter will review less rigorous (but still useful) models such as Lewis dot structures and valence shell electron-pair repulsion (VSEPR) theory. When combined with a qualitative quantum mechanical description of bonding through the concepts of orbital hybridization and resonance, these simple models can help us understand a great deal about the structures, stabilities, and reactions of inorganic molecules.



Ball-and-stick representation of chemical bonding in the molecules P_4O_{10} and P_4S_{10}.

The theory of chemical bonding has a long history, dating back to ancient Greece and the atomists Democritus, Leucippus, and the Epicureans. They postulated the existence of immutable atoms moving through the void, and envisioned the physical properties of materials as arising from the kinds and shapes of atoms. In his epic poem *De rerum natura* (On the Nature of Things), the Roman poet Lucretius (c. 99 BC – c. 50 BC), drawing on his Epicurean beliefs, describes some atoms and chemical bonding in the following way:

> *What seems to us the hardened and condensed*
> *Must be of atoms among themselves more hooked,*
> *Be held compacted deep within, as 'twere*
> *By branch-like atoms -- of which sort the chief*
> *Are diamond stones, despisers of all blows*
> *And stalwart flint and strength of solid iron*
> *And brazen bars, which, budging hard in locks,*
> *Do grate and scream. But what are liquid, formed*
> *Of fluid body, they indeed must be*
> *Of elements more smooth and round -- because*
> *Their globules severally will not cohere.*

Lucretius' poem is enjoyable reading and contains some remarkable insights into the microscopic world, given the tools available at the time. Modern analytical methods show that he was off base with his ideas about hooks and spheres, however. We will revisit the nature of chemical bonding in the substances Lucretius mentions (diamond, silicates, iron, brass, and water) in the context of modern chemical theories to understand why they have the special properties they do.

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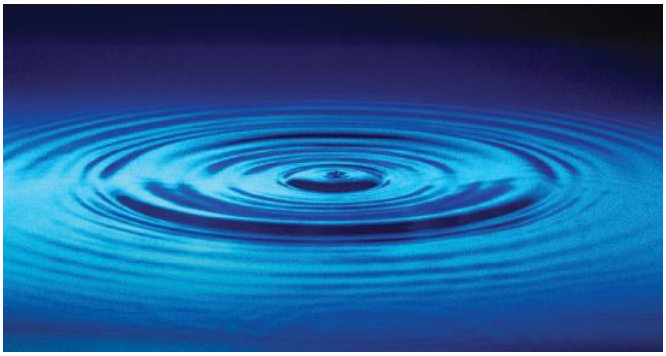
1.2: Waves and Electromagnetic Radiation

Learning Objectives

- To learn about the characteristics of electromagnetic waves.
- Types include light, X-Rays, infrared and microwaves.

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 2.1.1 A Wave in Water

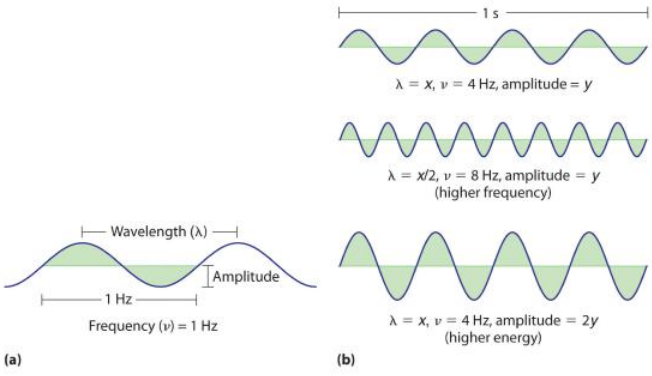


When a drop of water falls onto a smooth water surface, it generates a set of waves that travel outward in a circular direction.

Properties of Waves

A wave A periodic oscillation that transmits energy through space. 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 2.1.1). 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 2.1.2 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 2.1.2). As you may have noticed in Figure 2.1.1, waves are periodicPhenomena, such as waves, that repeat regularly in both space and time.; 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)The distance between two corresponding points in a wave—between the midpoints of two peaks or two troughs.. λ is the lowercase

Greek lambda, and ν 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 per second (1/s = s^{-1}), which in the SI system is called the hertz (Hz). It is named after German physicist Heinrich Hertz (1857–1894), a pioneer in the field of electromagnetic radiation. The amplitudeThe 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 2.1.2 , 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:

$$(wavelength)(frequency) = speed \tag{2.1.1}$$

$$\lambda\nu = v$$

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

Be careful not to confuse the symbols for the speed, *v*, with the frequency, &*nu;*.

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.

Videos



Light Speed, Wavelength, and Frequency | Dimensional Analysis by Doc Schuster



Waves in General by JaHu Productions - a bit faster. Also discusses sound waves

Figure 2.1.3 The Nature of Electromagnetic Radiation

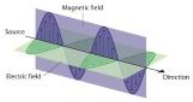


Figure 2.1.3 The Nature of Electromagnetic Radiation *All forms of electromagnetic radiation consist of perpendicular oscillating electric and magnetic fields.*

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 Energy that is transmitted, or radiated, through space in the form of periodic oscillations of electric and magnetic fields. (Figure 2.1.3). Some forms of electromagnetic radiation are shown in Figure 2.1.4. In a vacuum, all forms of electromagnetic radiation—whether microwaves, visible light, or gamma rays—travel at the speed of light (*c*)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.

Because the various kinds of electromagnetic radiation all have the same speed (*c*), they differ in only wavelength and frequency. As shown in Figure 2.1.4 and Table 2.1.1 , 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 2.1.1, we can show that the frequency of electromagnetic radiation is inversely proportional to its wavelength:

$$c = \lambda\nu$$
$$\nu = \frac{c}{\lambda} \tag{2.1.2}$$

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, wavelength increases,

Here is a video from Oxford University Press which goes through the calculation



Videos

- Calculating Frequency Given Wavelength - Johnny Cantrell
- .Wavelength Frequency Problems - Cayer Chem

Examples

- Quantum Chemistry - Ohio State
- Quantum Chemistry Quizzes - mhe education

- AP Chemistry Chapter 7 Review - Science Geek
- Quantum Theory of the Atom Practice Quiz - Northrup

Answers for these quizzes are included. There are also questions covering more topics in Chapter 2.

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

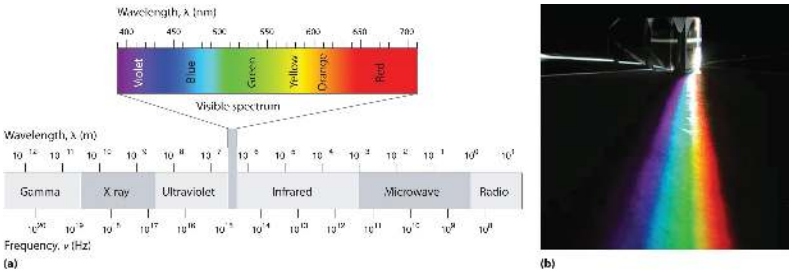


Figure 2.1.4 The Electromagnetic Spectrum *(a) This diagram shows the wavelength and frequency ranges of electromagnetic radiation. The visible portion of the electromagnetic spectrum is the narrow region with wavelengths between about 400 and 700 nm. (b) When white light is passed through a prism, it is split into light of different wavelengths, whose colors correspond to the visible spectrum.*

This video reviews the ideas in Figure 2.1.4



Table 2.1.1 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:

$$E \propto \nu \tag{2.1.3}$$

$$E \propto \frac{1}{\lambda} \tag{2.1.4}$$

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 described in Chapter 7.6 "Chemical Reactions in the Atmosphere" absorbs sunlight with wavelengths less than 350 nm, it protects us from the damaging effects of highly energetic ultraviolet radiation.

Note the Pattern

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

Example 2.1.1

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 2.1.2 to calculate the wavelength in meters.

Solution:

From Equation 2.1.2 , 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:

$$\lambda\nu = c = 2.998 \times 10^8 m/s$$

Thus the wavelength λ is given by

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

Exercise

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

In Section 2.2 "The Quantization of Energy" and Section 2.3 "Atomic Spectra and Models of the Atom", we describe how scientists developed our current understanding of the structure of atoms using the scientific method described in Chapter 1 "Introduction to Chemistry". You will discover why scientists had to rethink their classical understanding of the nature of electromagnetic energy, which clearly distinguished between the particulate behavior of matter and the wavelike nature of energy.

Key Equations

relationship between wavelength, frequency, and speed of a wave

Equation 2.1.1: $v = \lambda\nu$

relationship between wavelength, frequency, and speed of electromagnetic radiation

Equation 2.1.2: $c = \lambda\nu$

Summary

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 only in their frequencies and wavelengths.

Key Takeaway

- Understanding the electronic structure of atoms requires an understanding of the properties of waves and electromagnetic radiation.

Contributors

- Anonymous

Modified by Joshua Halpern

Light Speed Video from Doc Schuster on YouTube

Wave Video from JaHuProductions on YouTube

Wavelength and Frequency from Oxford Academic on YouTube

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1.3: Quantization of Energy

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. Electromagnetic radiation whose wavelength and color depends on the temperature of the object., the energy emitted by an object when it is heated. 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 2.2.1).



Figure 2.2.1 Blackbody Radiation *When heated, all objects emit electromagnetic radiation whose wavelength (and color) depends on the temperature of the object. A relatively low-temperature object, such as an electric stove element, on a low setting appears red, whereas a higher-temperature object, such as the filament of an incandescent light bulb, appears yellow or white.*

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 2.2.2. One of the major assumptions of classical physics was that energy increased or decreased in a smooth, continuous manner. For example, classical physics predicted that as wavelength decreased, the intensity of the radiation an object emits should increase in a smooth curve without limit at *all* temperatures, as shown by the broken line for 6000 K in Figure 2.2.2 . Thus classical physics could not explain the sharp *decrease* in the intensity of radiation emitted at shorter wavelengths (primarily in the ultraviolet region of the spectrum), which was referred to as the "ultraviolet catastrophe." In 1900, however, the German physicist Max Planck (1858–1947) explained the ultraviolet catastrophe by proposing 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 2.2.2, so the intensity does not follow a smooth curve as the temperature increases, as predicted by classical physics. Thus energy could be gained or lost only in integral multiples of some smallest unit of energy, a quantum (the smallest possible unit of energy). Energy can be gained or lost only in integral multiples of a quantum..

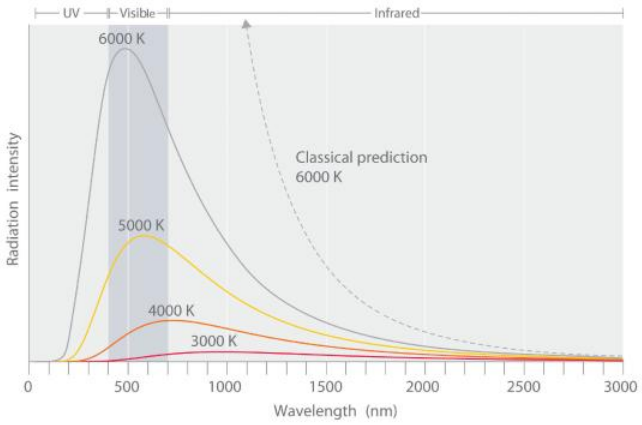


Figure 2.2.2 Relationship between the Temperature of an Object and the Spectrum of Blackbody Radiation It Emits *At relatively low temperatures, most radiation is emitted at wavelengths longer than 700 nm, which is in the infrared portion of the spectrum. The dull red glow of the electric stove element in Figure 2.2.1 is due to the small amount of radiation emitted at wavelengths less than 700 nm, which the eye can detect. As the temperature of the object increases, the maximum intensity shifts to shorter wavelengths, successively resulting in orange, yellow, and finally white light. At high temperatures, all wavelengths of visible light are emitted with approximately equal intensities. The white light spectrum shown for an object at 6000 K closely approximates the spectrum of light emitted by the sun (Figure 2.14). 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.

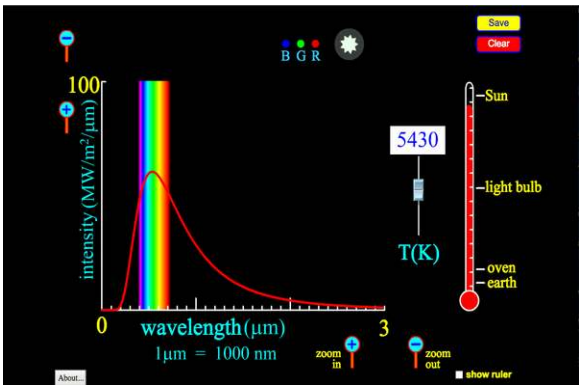
Planck postulated that the energy of a particular quantum of radiant energy could be described explicitly by the equation

$$E = h\nu \tag{2.2.1}$$

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

$$h = 6.626 \times 10^{-34}\ J \cdot s (\text{joule-seconds}) \tag{1.3.1}$$

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 *hν*, Planck devised an equation that fit the experimental data shown in Figure 2.2.2. We can understand Planck's explanation of the ultraviolet catastrophe qualitatively as follows: At low temperatures, radiation with only relatively low frequencies is emitted, corresponding to low-energy quanta. As the temperature of an object increases, there is an increased probability of emitting radiation with higher frequencies, corresponding to higher-energy quanta. At any temperature, however, it is simply more probable for an object to lose energy by emitting a large number of lower-energy quanta than a single very high-energy quantum that corresponds to ultraviolet radiation. The result is a maximum in the plot of intensity of emitted radiation versus wavelength, as shown in Figure 2.2.2, and a shift in the position of the maximum to lower wavelength (higher frequency) with increasing temperature. You can get a feel for this by clicking on the black body applet from PHeT below. (you may need to install JAVA to run the applets).



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.

Videos

- Calculating Energy of a Mole of Photons - Johnny Cantrell
- .Photons - ViaScience, an advanced explanation of the Planck radiation law and the photoelectric effect (below) as well as biological interactions with UV light.and the nature of light and quantum weirdness. Probably the first 6 minutes and the last 3 (from 12:00 on) as an introduction to wave particle duality.are useful to a beginning student.

Examples

Same as before

- Quantum Chemistry - Ohio State
- Quantum Chemistry Quizzes - mhe education
- AP Chemistry Chapter 7 Review - Science Geek
- Quantum Theory of the Atom Practice Quiz - Northrup

Answers for these quizzes are included. There are also questions covering more topics in Chapter 2.

The Photoelectric Effect

Only five years after he proposed it, Planck's quantization hypothesis was used to explain a second phenomenon that conflicted with the accepted laws of classical physics. When certain metals are exposed to light, electrons are ejected from their surface (Figure 2.2.3). Classical physics predicted that the number of electrons emitted and their kinetic energy should depend on only the intensity of the light, not its frequency. In fact, however, each metal was found to have a characteristic threshold frequency of light; below that frequency, no electrons are emitted regardless of the light's intensity. Above the threshold frequency, the number of electrons emitted was found to be proportional to the intensity of the light, and their kinetic energy was proportional to the frequency. This phenomenon was called the photoelectric effect (a phenomenon in which electrons are ejected from the surface of a metal that has been exposed to light).

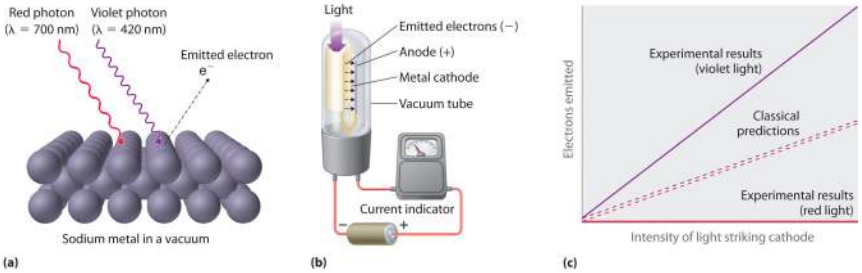


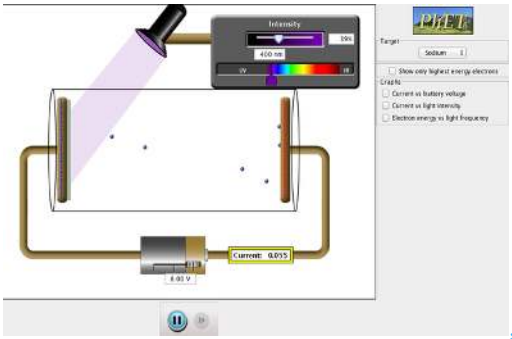
Figure 2.2.3 The Photoelectric Effect *(a) Irradiating a metal surface with photons of sufficiently high energy causes electrons to be ejected from the metal. (b) A photocell that uses the photoelectric effect, similar to those found in automatic door openers. When light strikes the metal cathode, electrons are emitted and attracted to the anode, resulting in a flow of electrical current. If the*

incoming light is interrupted by, for example, a passing person, the current drops to zero. (c) In contrast to predictions using classical physics, no electrons are emitted when photons of light with energy less than E_o, such as red light, strike the cathode. The energy of violet light is above the threshold frequency, so the number of emitted photons is proportional to the light's intensity.

Albert Einstein (1879–1955; Nobel Prize in Physics, 1921) quickly realized that Planck's hypothesis about the quantization of radiant energy could also explain the photoelectric effect. The key feature of Einstein's hypothesis was the assumption that radiant energy arrives at the metal surface in particles that we now call photons. 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:

$$kinetic\ energy\ of\ ejected\ electron = E - E_o = h\nu - h\nu_o = h\,(\nu - \nu_o) \tag{2.2.2}$$

When a metal is struck by light with energy above the threshold energy E_o, the *number* of emitted electrons is proportional to the *intensity* of the light beam, which corresponds to the number of photons per square centimeter, but the *kinetic energy* of the emitted electrons is proportional to the *frequency* of the light. Thus Einstein showed that the energy of the emitted electrons depended on the frequency of the light, contrary to the prediction of classical physics. KCVS has an applet which illustrates the photoelectric effect and here is another from PHET which you can run by clicking on (it also requires JAVA)



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 2.2.1



Figure 2.2.4 A Beam of Red Light Emitted by a Helium Neon laser reads a bar code *Originally Helium neon lasers, which emit red light at a wavelength of 632.8 nm, were used to read bar codes. Today, smaller, inexpensive diode lasers are used.*

A ruby laser, a device that produces light in a narrow range of wavelengths (Section 2.3 "Atomic Spectra and Models of the Atom"), emits red light at a wavelength of 694.3 nm (Figure 6.8). What is the energy in joules of a single photon?

Given: wavelength

Asked for: energy of single photon.

Strategy:

A Use Equation 2.1.1 and Equation 2.2.1 to calculate the energy in joules.

Solution:

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

Exercise

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

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

Answer:

1. 1.287×10^{-15} J/photon
2. 4497 times

Key Equation

quantization of energy

$$E = h\nu \tag{2.2.1}$$

Summary

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.

Key Takeaway

- The fundamental building blocks of energy are quanta and of matter are atoms.

Contributors

- Anonymous

Modified by Joshua Halpern (Howard University)

Blackbody Radiation Applet from pHet

Photoelectric Effect Applet from pHet

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1.4: Atomic Orbitals and Their Energies

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's theory today is described as quantum mechanicsA theory developed by Erwin Schrödinger that describes the energies and spatial distributions of electrons in atoms and molecules.. It successfully describes the energies and spatial distributions of electrons in atoms and molecules.

Erwin Schrödinger (1887–1961)

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

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. The Schrödinger equation is similar in form to equations for the propagation of waves, which is why originally quantum mechanics was called wave mechanics, but there are significant differences between quantum wave functions and those that describe real waves. Therefore, at this point it would be best to lean only lightly on the standing wave analogy.

Wave Functions

A wavefunction (Ψ)A mathematical function that relates the location of an electron at a given point in space to the amplitude of its wave, which corresponds to its energy., Ψ is the uppercase Greek letter psi, is a mathematical expression that can be used to calculate any property of an atom. In general, wavefunctions depend on both time and position. For atoms, solutions to the Schrödinger equation correspond to arrangements of the electrons, which, if left alone, remain unchanged and are thus only functions of position. To indicate time independence we use lower case ψ

Wavefunctions for each atom have some properties that are exact, for example each wavefunction describes an electron in quantum state with a specific energy. Each of these exact properties is associated with an integer. The energy of an electron in an atom is associated with the integer n, which turns out to be the same n that Bohr found in his model. These integers are called quantum numbers and different wavefunctions have different sets of quantum numbers. The important point about quantum numbers is that they are countable integers, not continuous variables like the number of points on a line. In the case of atoms, each electron has four quatum numbers which determine its wavefunction.

For other properties, there is a mathematical procedure by which the wavefunctions can be used to calculate average values and probabilities for anything, for example the probability of finding the electron at any point in space. Driven by the Heisenberg Uncertainy Principle, the calculation of probabilities is the best we can do for properties not associated directly with quantum numbers.

The properties of wave functions derived from quantum mechanics are summarized here. Although there are no equations there are a number of advanced concepts. Even if your math is not strong, try to understand the key concepts.:

- **A time independent wavefunction uses three variables to describe the position of an electron.** Three coordinates specify the position in space (as with the Cartesian coordinates x, y, and z, or spherical coordinates r, θ, φ). Figure 2.21 shows both Cartesian and spherical coordinates. For the motion of an electron about the massive nucleus, spherical coordinates can be more natural than Cartesian.

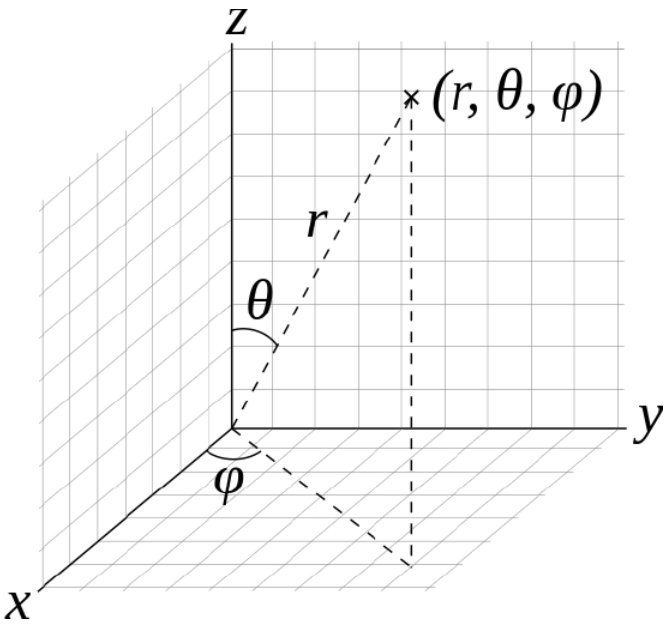


Figure 2.5.1 Cartesian (x, y, z) and spherical coordinates (r, θ, φ)

- **Wave functions have both real and imaginary parts. They are complex functions**, which is a mathematical term indicating that they contain $\sqrt{-1}$., represented as *i*. Imaginary and complex numbers have no physical significance.

Imaginary Numbers

If you need an introduction to imaginary number, here is one. To see it you will have to be attached to the INTERNET



- **The probability of finding an electron at a point 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*.** This product is called the modulus square and for wave functions it always must be a real positive number or zero. Negative, impaginary or complex probabilities of finding an electron at a point would be meaningless. This interpretation was discovered by Max Born, for which he won the Nobel prize. 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 quantum numbers specifying the wavefunction and the three coordinates specifying the position in space we are interested in. As one way of graphically representing the probability distribution, the probability of finding an electron is indicated by the density of colored dots, shown for the ground state of the hydrogen atom in Figure 2.5.2

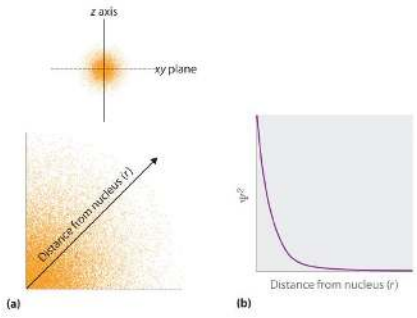


Figure 2.5.2 Probability of Finding the Electron in the Ground State of the Hydrogen Atom at Different Points in Space *(a) The density of the dots shows electron probability. (b) In this plot of Ψ^2 versus r for the ground state of the hydrogen atom, the electron probability density is greatest at r = 0 (the nucleus) and falls off with increasing r. Because the line never actually reaches the horizontal axis, the probability of finding the electron at very large values of r is very small but not zero.*

- **The total probability of finding the electron anywhere must be 100%**. It has to be somewhere. On the other hand, since there is a lot more space far away from a nucleus than near it, the probability of finding the electron at any one point as one moves away from the nucleus must eventually go to zero.
- **The relative phases of wave function for electrons in different atoms** determines bonding. This will be important in our discussion of chemical bonding in Chapter 5. As discussed in the previous section, wavefunctions like waves, can positively reinforce each other or destructively interfere. When they reinforce they are said to be in phase, and when they interfere they are said to be out of phase. The phases are indicated as positive, +, or negative, -. Do not confuse the sign of the phase with a positive or negative electrical charge.
- **Each wavefunction has a unique sets of** quantum numbersA unique set of numbers that specifies a wave function (a solution to the Schrödinger equation), which provides important information about the energy and spatial distribution of an electron.**.** The spacial patterns of the three-dimensional wave functions are 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 water world, which turn out to be solutions of the Schrödinger equation for a spherically symmetric atom.
- **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 emerges from the wave equation.

Quantum Numbers

Schrödinger's approach requires three quantum numbers (n, l, and m_l) to specify a wave function for each electron. The quantum numbers provide information about the spatial distribution of an electron. Although n can be any positive integer (NOT zero), only certain values of l and m_l are allowed for a given value of n. This is a consequence of the mathematical details of the Schrödinger equation

The Principal Quantum Number

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

Equation 2.5.1 $n = 1, 2, 3, 4,\ldots$

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 shellAll the wave functions that have the same value of because those electrons have similar average distances from the nucleus. because those electrons have similar average distances from the nucleus. As you will see, the principal quantum number n corresponds to the n used by Bohr to describe electron orbits and by Rydberg to describe atomic energy levels.

The Azimuthal Quantum Number

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

Equation 2.5.2 $l = 0, 1, 2,\ldots, n − 1$

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 subshellA group of wave functions that have the same values of <math xml:id="av_1.0-ch02_m046" display="inline"><semantics><mi>n</mi></semantics></math> and <math xml:id="av_1.0-ch02_m047" display="inline"><semantics><mrow><mi>l</mi><mo>.</mo></mrow></semantics></math>. The regions of space occupied by electrons in the same subshell usually have the same shape, but they are oriented differently in space.

The Magnetic Quantum Number

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

Equation 2.5.3 $m_l = −l, −l + 1,\ldots, 0,\ldots, l − 1, l$

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

Example 2.5.1

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:

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

Exercise

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

Answer: three subshells; nine orbitals

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

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

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

We can summarize the relationships between the quantum numbers and the number of subshells and orbitals as follows (Table 2.5.1):

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

Note the Pattern

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

Table 2.5.1 Allowed values of n, l, and m_l through $n = 4$

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

Videos

- Quantum numbers - ChemDo

Examples

- Quantum Numbers and Electron Configurations - Purdue - tutorial
- Quantum Chemistry - Ohio State
- Quantum Chemistry Quizzes - mhe education
- AP Chemistry Chapter 7 Review - Science Geek
- Quantum Theory of the Atom Practice Quiz - Northrup

Answers for these quizzes are included. There are also questions covering more topics in Chapter 2.

Orbital Shapes

An orbital is the quantum mechanical generalization of Bohr's orbit. In contrast to his concept of a simple circular orbit with a fixed radius, orbitals are mathematically derived regions of space with different *probabilities* of having an electron.

One way of representing electron probability distributions was illustrated in Figure 2.5.1 for the 1*s* orbital of hydrogen. The probability of finding an electron in a region of space with volume V (such as a cubic picometer) is the product of the volume with $\psi\psi^*$(we can write this as $|\psi|^2$). From our consideration of the properties of the wavefunction, we know that adding up the probability from every such small volume over all space will sum to unity, or a 100% probability that the electron is somewhere. A plot of $|\psi|^2$ versus distance from the nucleus (r) is a plot of the *probability density*. The 1*s* orbital is spherically symmetrical, so the probability of finding a 1*s* electron at any given point depends *only* on its distance from the nucleus. The probability density is greatest at $r = 0$ (at the nucleus) and decreases steadily with increasing distance. At very large values of r, the electron probability density is tiny but *not* eactly zero.

In contrast to the probability density, we can calculate the *radial probability* (the probability of finding a 1*s* electron at a distance r from the nucleus) by adding together the probabilities of an electron being at all points on a series of x spherical shells of radius r_1, r_2, r_3,…, r_{x-1}, r_x. In effect, we are dividing the atom into very thin concentric shells, much like the layers of an onion (part (a) in Figure 2.5.2), and calculating the probability of finding an electron on each spherical shell. Recall that the electron probability density is greatest at $r = 0$ (part (b) in Figure 2.5.3), so the density of dots is greatest for the smallest spherical shells in part (a) in Figure 2.5.3

By contrast, the surface area of each spherical shell is equal to $4\pi r^2$, which increases rapidly with increasing r (part (c) in Figure 2.5.3). Because the surface area of the spherical shells increases at first more rapidly with increasing r than the electron probability density decreases, the plot of radial probability has a maximum at a particular distance (part (d) in Figure 2.5.3). As important, when r is very small, the surface area of a spherical shell is so small that the *total* probability of finding an electron close to the nucleus is very low; at the nucleus, the electron probability vanishes because the surface area of the shell is zero (part (d) in Figure 2.5.2).

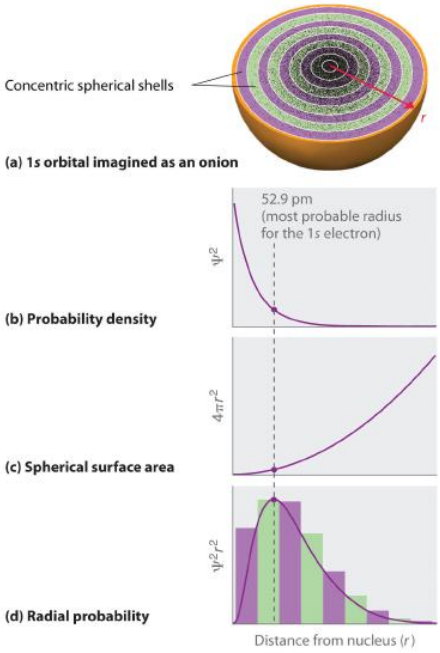


Figure 2.5.3 Most Probable Radius for the Electron in the Ground State of the Hydrogen Atom *(a) Imagine dividing the atom's total volume into very thin concentric shells as shown in the onion drawing. (b) A plot of electron probability density Ψ^2 versus r shows that the electron probability density is greatest at r = 0 and falls off smoothly with increasing r. The density of the dots is therefore greatest in the innermost shells of the onion. (c) The surface area of each shell, given by $4\pi r^2$, increases rapidly with increasing r. (d) If we count the number of dots in each spherical shell, we obtain the total probability of finding the electron at a given value of r. Because the surface area of each shell increases more rapidly with increasing r than the electron probability*

density decreases, a plot of electron probability versus r (the radial probability) shows a peak. This peak corresponds to the most probable radius for the electron, 52.9 pm, which is exactly the radius predicted by Bohr's model of the hydrogen atom.

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

Figure 2.5,4 compares the electron probability densities for the hydrogen 1*s*, 2*s*, and 3*s* orbitals. Note that all three are spherically symmetrical. For the 2*s* and 3*s* orbitals, however (and for all other *s* orbitals as well), the electron probability density does not fall off smoothly with increasing *r*. Instead, a series of minima and maxima are observed in the radial probability plots (part (c) in Figure 2.5.4). The minima correspond to spherical nodes (regions of zero electron probability), which alternate with spherical regions of nonzero electron probability.

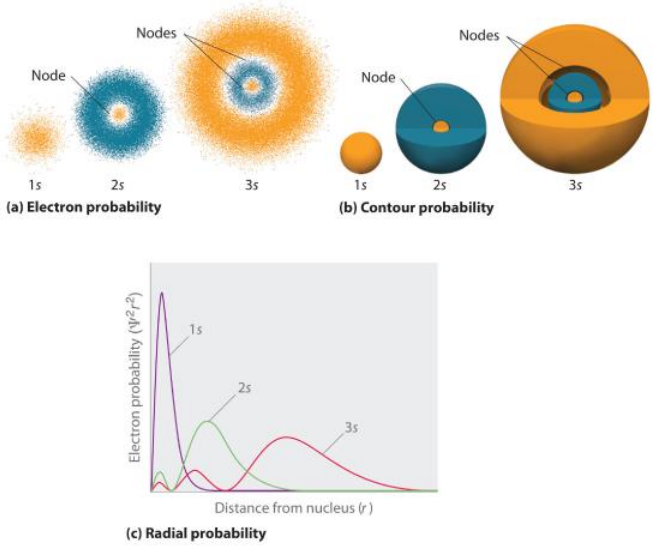


Figure 2.5.4 Probability Densities for the 1*s*, 2*s*, and 3*s* Orbitals of the Hydrogen Atom *(a) The electron probability density in any plane that contains the nucleus is shown. Note the presence of circular regions, or nodes, where the probability density is zero. (b) Contour surfaces enclose 90% of the electron probability, which illustrates the different sizes of the 1s, 2s, and 3s orbitals. The cutaway drawings give partial views of the internal spherical nodes. The orange color corresponds to regions of space where the phase of the wave function is positive, and the blue color corresponds to regions of space where the phase of the wave function is negative. (c) In these plots of electron probability as a function of distance from the nucleus (r) in all directions (radial probability), the most probable radius increases as n increases, but the 2s and 3s orbitals have regions of significant electron probability at small values of r.*

s Orbitals

Three things happen to *s* orbitals as *n* increases (Figure 2.5.4):

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

Orbitals are generally drawn as three-dimensional surfaces that enclose 90% of the electron densityElectron distributions that are represented as standing waves., as was shown for the hydrogen 1*s*, 2*s*, and 3*s* orbitals in part (b) in Figure 2.5.4 Although such drawings show the relative sizes of the orbitals, they do not normally show the spherical nodes in the 2*s* and 3*s* orbitals because the spherical nodes lie inside the 90% surface. Fortunately, the positions of the spherical nodes are not important for chemical bonding.

This makes sense because bonding is an interaction of electrons from two atoms which will be most sensitive to forces at the edges of the orbitals.

p Orbitals

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

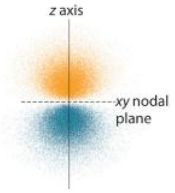


Figure 2.5.5 Electron Probability Distribution for a Hydrogen 2*p* Orbital *The nodal plane of zero electron density separates the two lobes of the 2p orbital. As in Figure 2.5.4 , the colors correspond to regions of space where the phase of the wave function is positive (orange) and negative (blue).*

The electron probability distribution for one of the hydrogen 2*p* orbitals is shown in Figure 2.5.5 . Because this orbital has two lobes of electron density arranged along the *z* axis, with an electron density of zero in the *xy* plane (i.e., the *xy* plane is a nodal plane), it is a $2p_z$ orbital. As shown in Figure 2.5.6 , the other two 2*p* orbitals have identical shapes, but they lie along the *x* axis ($2p_x$) and *y* axis ($2p_y$), respectively. Note that each *p* orbital has just one nodal plane. In each case, the phase of the wave function for each of the 2*p* orbitals is positive for the lobe that points along the positive axis and negative for the lobe that points along the negative axis. It is important to emphasize that these signs correspond to the *phase* of the wave that describes the electron motion, *not* to positive or negative charges.

In the next section when we consider the electron configuration of multielectron atoms, the geometric shapes provide an important clue about which orbitals will be occupied by different electrons. Because electrons in different *p* orbitals are geometrically distant from each other, there is less repulsion between them than would be found if two electrons were in the same *p* orbital. Thus, when the *p* orbitals are filled, it will be energetically favorable to place one electron into each *p* orbital, rather than two into one orbital.

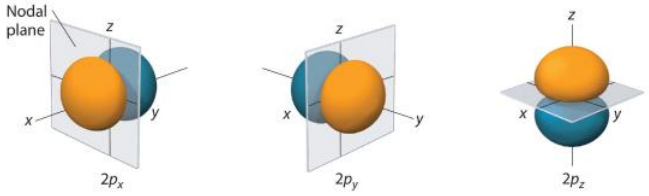


Figure 2.5.6 The Three Equivalent 2*p* Orbitals of the Hydrogen Atom*The surfaces shown enclose 90% of the total electron probability for the $2p_x$, $2p_y$, and $2p_z$ orbitals. Each orbital is oriented along the axis indicated by the subscript and a nodal plane that is perpendicular to that axis bisects each 2p orbital. The phase of the wave function is positive (orange) in the region of space where x, y, or z is positive and negative (blue) where x, y, or z is negative.*

Just as with the *s* orbitals, the size and complexity of the *p* orbitals for any atom increase as the principal quantum number *n* increases. The shapes of the 90% probability surfaces of the 3*p*, 4*p*, and higher-energy *p* orbitals are, however, essentially the same as those shown in Figure 2.5.6

d Orbitals

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

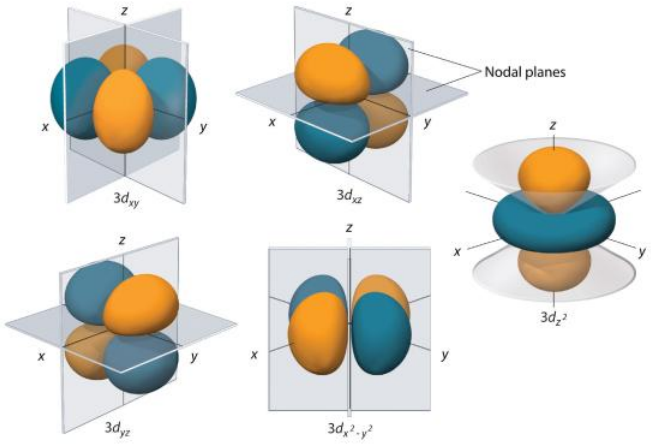


Figure 2.5.7 The Five Equivalent 3*d* Orbitals of the Hydrogen Atom *The surfaces shown enclose 90% of the total electron probability for the five hydrogen 3d orbitals. Four of the five 3d orbitals consist of four lobes arranged in a plane that is intersected by two perpendicular nodal planes. These four orbitals have the same shape but different orientations. The fifth 3d orbital,* $3d_{z^2}$ *, has a distinct shape even though it is mathematically equivalent to the others. The phase of the wave function for the different lobes is indicated by color: orange for positive and blue for negative.*

The hydrogen 3*d* orbitals, shown in Figure 2.5.7 , have more complex shapes than the 2*p* orbitals. All five 3*d* orbitals contain two nodal surfaces, as compared to one for each *p* orbital and zero for each *s* orbital. In three of the *d* orbitals, the lobes of electron density are oriented between the *x* and *y*, *x* and *z*, and *y* and *z* planes; these orbitals are referred to as the $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$ orbitals, respectively. A fourth *d* orbital has lobes lying along the *x* and *y* axes; this is the $3d_{x^2-y^2}$ orbital. The fifth 3*d* orbital, called the $3d_{z^2}$ orbital, has a unique shape: it looks like a $2p_z$ orbital combined with an additional doughnut of electron probability lying in the *xy* plane. Despite its peculiar shape, the $3d_{z^2}$ orbital is mathematically equivalent to the other four and has the same energy. In contrast to *p* orbitals, the phase of the wave function for *d* orbitals is the same for opposite pairs of lobes. As shown in Figure 2.5.7 , the phase of the wave function is positive for the two lobes of the $3d_{z^2}$ orbital that lie along the *z* axis, whereas the phase of the wave function is negative for the doughnut of electron density in the *xy* plane. Like the *s* and *p* orbitals, as *n* increases, the size of the *d* orbitals increases, but the overall shapes remain similar to those depicted in Figure 2.5.7 .

f Orbitals

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

Orbital Energies

Although we have discussed the shapes of orbitals, we have said little about their comparative energies. We begin our discussion of orbital energiesA particular energy associated with a given set of quantum numbers. by considering atoms or ions with only a single electron (such as H or He^+). This is the simplest case.

The relative energies of the atomic orbitals with $n \le 4$ for a hydrogen atom are plotted in Figure 2.5.8 note that the orbital energies depend on *only* the principal quantum number *n*. Consequently, the energies of the 2*s* and 2*p* orbitals of hydrogen are the same; the energies of the 3*s*, 3*p*, and 3*d* orbitals are the same; and so forth. The orbital energies obtained for hydrogen using quantum mechanics are exactly the same as the allowed energies calculated by Bohr. In contrast to Bohr's model, however, which allowed only one orbit for each energy level, quantum mechanics predicts that there are *4* orbitals with different electron density distributions in the $n = 2$ principal shell (one 2*s* and three 2*p* orbitals), *9* in the $n = 3$ principal shell, and *16* in the $n = 4$ principal shell.The different values of *l* and m_l for the individual orbitals within a given principal shell are not important for understanding the emission or absorption spectra of the hydrogen atom under most conditions, but they do explain the splittings of the main lines that are observed when hydrogen atoms are placed in a magnetic field. As we have just seen, however, quantum mechanics also predicts that in the hydrogen atom, all orbitals with the same value of *n* (e.g., the three 2*p* orbitals) are degenerateHaving the same

energy., meaning that they have the same energy. Figure 2.5.8 shows that the energy levels become closer and closer together as the value of *n* increases, as expected because of the $1/n^2$ dependence of orbital energies.

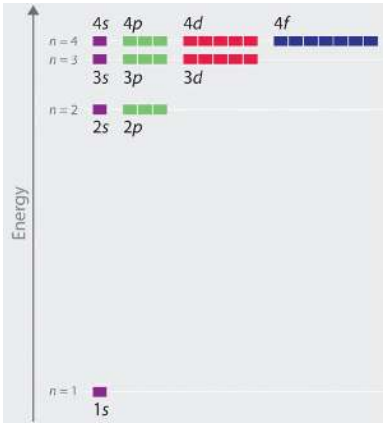


Figure 2.5.8 Orbital Energy Level Diagram for the Hydrogen Atom *Each box corresponds to one orbital. Note that the difference in energy between orbitals decreases rapidly with increasing values of n.*

The energies of the orbitals in any species with only one electron can be calculated by a minor variation of Bohr's equation (Equation 2.3.3), which can be extended to other single-electron species by incorporating the nuclear charge *Z* (the number of protons in the nucleus):

Equation 2.5.4 $E = -\frac{Z^2}{n^2}\mathcal{R}hc$

In general, both energy and radius decrease as the nuclear charge increases. As a result of the Z^2 dependence of energy in Equation 2.24, electrons in the 1s orbital of carbon, which has a nuclear charge of +6, lie roughly 36 times lower in energy than those in the hydrogen 1s orbital, and the 1s orbital of tin, with an atomic number of 50 is roughly 2500 times lower still. The most stable and tightly bound electrons are in orbitals (those with the lowest energy) closest to the nucleus.

For example, in the ground state of the hydrogen atom, the single electron is in the 1*s* orbital, whereas in the first excited state, the atom has absorbed energy and the electron has been promoted to one of the $n = 2$ orbitals. In ions with only a single electron, the energy of a given orbital depends on only *n*, and all subshells within a principal shell, such as the p_x, p_y, and p_z orbitals, are degenerate.

Videos

- Quantum Mechanics 6a- Hydrogen - via science (don't bother with the first 3 minutes which are advanced math heavy, but the stunning illustrations of orbital shapes afterwards are great)
- Electron Spin and the Pauli Principle - via science.(does an excellent job explaining why electron spin is not a spinning electron)
- Electron Orbitals - Anna Tanczos - more visualizations

Examples

- Quantum Chemistry - Ohio State
- Quantum Chemistry Quizzes - mhe education
- AP Chemistry Chapter 7 Review - Science Geek
- Quantum Theory of the Atom Practice Quiz - Northrup

Answers for these quizzes are included. There are also questions covering more topics in Chapter 2.

Effective Nuclear Charges

For an atom or an ion with only a single electron, we can calculate the potential energy by considering only the electrostatic attraction between the positively charged nucleus and the negatively charged electron. When more than one electron is present, however, the total energy of the atom or the ion depends not only on attractive electron-nucleus interactions but also on repulsive electron-electron interactions. When there are two electrons, the repulsive interactions depend on the positions of *both* electrons at a given instant, but because we cannot specify the exact positions of the electrons, it is impossible to exactly calculate the repulsive

interactions. Consequently, we must use approximate methods to deal with the effect of electron-electron repulsions on orbital energies.

If an electron is far from the nucleus (i.e., if the distance r between the nucleus and the electron is large), then at any given moment, most of the other electrons will be *between* that electron and the nucleus. Hence the electrons will cancel a portion of the positive charge of the nucleus and thereby decrease the attractive interaction between it and the electron farther away. As a result, the electron farther away experiences an effective nuclear charge (Z_{eff})The nuclear charge an electron actually experiences because of shielding from other electrons closer to the nucleus. that is *less* than the actual nuclear charge Z. This effect is called electron shieldingThe effect by which electrons closer to the nucleus neutralize a portion of the positive charge of the nucleus and thereby decrease the attractive interaction between the nucleus and an electron father away.. As the distance between an electron and the nucleus approaches infinity, Z_{eff} approaches a value of 1 because all the other $(Z - 1)$ electrons in the neutral atom are, on the average, between it and the nucleus. If, on the other hand, an electron is very close to the nucleus, then at any given moment most of the other electrons are farther from the nucleus and do not shield the nuclear charge. At $r \approx 0$, the positive charge experienced by an electron is approximately the full nuclear charge, or $Z_{eff} \approx Z$. At intermediate values of r, the effective nuclear charge is somewhere between 1 and Z: $1 \le Z_{eff} \le Z$. Thus the actual Z_{eff} experienced by an electron in a given orbital depends not only on the spatial distribution of the electron in that orbital but also on the distribution of all the other electrons present. This leads to large differences in Z_{eff} for different elements, as shown in Figure 2.5.9 for the elements of the first three rows of the periodic table. Notice that only for hydrogen does $Z_{eff} = Z$, and only for helium are Z_{eff} and Z comparable in magnitude.

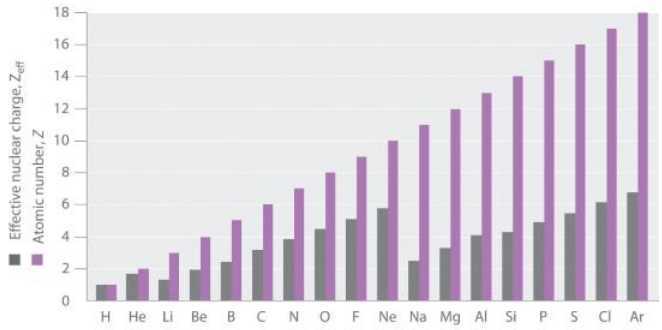


Figure 2.5.9 Relationship between the Effective Nuclear Charge Z_{eff} and the Atomic Number Z for the Outer Electrons of the Elements of the First Three Rows of the Periodic Table *Except for hydrogen, Z_{eff} is always less than Z, and Z_{eff} increases from left to right as you go across a row.*

The trend that you see in Figure 2.5.9 for the first three principal shells corresponding to n= 1, 2, and 3, continues in the further shells. The atomic number and thus the nuclear charge increase linearly, but the sawtooth pattern for Z_{eff} repeats itself, resetting as the quantum number n changes. Chemical bonding and reactivity involves the sharing or exchange of electrons between atoms. Those electrons which can participate are those held least strongly by the atom, the outermost electrons, which, no matter what the atomic number, and nuclear charge, are bound to their atom by roughly the same energy range because of the shielding effect.

In multielectron atoms this shifts the energies of the different orbitals for a typical multielectron atom as shown in Figure 2.5.10 . Within a given principal shell of a multielectron atom, the orbital energies increase with increasing l. An ns orbital always lies below the corresponding np orbital, which in turn lies below the nd orbital. These energy differences are caused by the effects of shielding and *penetration*, the extent to which a given orbital lies inside other filled orbitals. As shown in Figure 2.5.11 for example, an electron in the 2s orbital penetrates inside a filled 1s orbital more than an electron in a 2p orbital does. Hence in an atom with a filled 1s orbital, the Z_{eff} experienced by a 2s electron is greater than the Z_{eff} experienced by a 2p electron. Consequently, the 2s electron is more tightly bound to the nucleus and has a lower energy, consistent with the order of energies shown in Figure 2.5.10

Note the Pattern

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

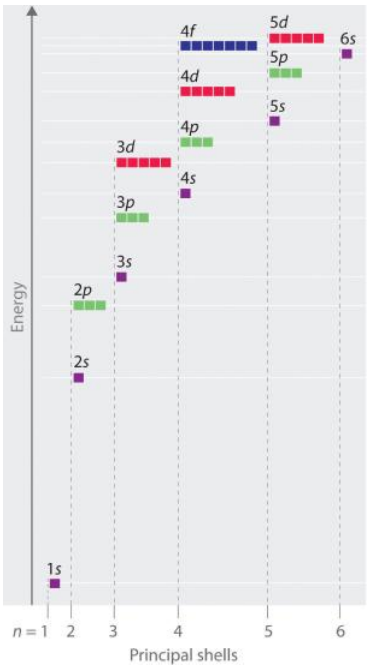


Figure 2.5.10 Orbital Energy Level Diagram for a Typical Multielectron Atom

Because of the effects of shielding and the different radial distributions of orbitals with the same value of *n* but different values of *l*, the different subshells are not degenerate in a multielectron atom. (Compare this with Figure 2.5.8 For a given value of *n*, the *ns* orbital is always lower in energy than the *np* orbitals, which are lower in energy than the *nd* orbitals, and so forth. As a result, some subshells with higher principal quantum numbers are actually lower in energy than subshells with a lower value of *n*; for example, the 4*s* orbital is lower in energy than the 3*d* orbitals for most atoms.

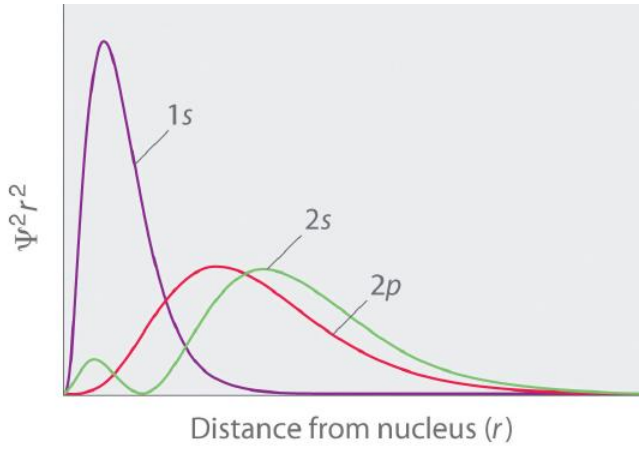


Figure 2.5.11 Orbital Penetration *A comparison of the radial probability distribution of the 2s and 2p orbitals for various states of the hydrogen atom shows that the 2s orbital penetrates inside the 1s orbital more than the 2p orbital does. Consequently, when an electron is in the small inner lobe of the 2s orbital, it experiences a relatively large value of Z_{eff}, which causes the energy of the 2s orbital to be lower than the energy of the 2p orbital.*

Notice in Figure 2.5.10 that the difference in energies between subshells can be so large that the energies of orbitals from different principal shells can become approximately equal. For example, the energy of the 3*d* orbitals in most atoms is actually *between* the energies of the 4*s* and the 4*p* orbitals.

Key Equation

energy of hydrogen-like orbitals

Equation 2.5.4: $E = -\frac{Z^2}{n^2}\mathcal{R}hc$

Summary

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**.

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

Because its average distance from the nucleus determines the energy of an electron, each atomic orbital with a given set of quantum numbers has a particular energy associated with it, the **orbital energy**. In atoms or ions with only a single electron, all orbitals with the same value of *n* have the same energy (they are **degenerate**), and the energies of the principal shells increase smoothly as *n* increases. An atom or ion with the electron(s) in the lowest-energy orbital(s) is said to be in its ground state, whereas an atom or ion in which one or more electrons occupy higher-energy orbitals is said to be in an excited state.

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

Key Takeaway

- There is a relationship between the motions of electrons in atoms and molecules and their energies that is described by quantum mechanics.

Conceptual Problems

1. Why does an electron in an orbital with $n = 1$ in a hydrogen atom have a lower energy than a free electron ($n = \infty$)?
2. What four variables are required to fully describe the position of any object in space? In quantum mechanics, one of these variables is not explicitly considered. Which one and why?
3. Chemists generally refer to the square of the wave function rather than to the wave function itself. Why?

4. Orbital energies of species with only one electron are defined by only one quantum number. Which one? In such a species, is the energy of an orbital with $n = 2$ greater than, less than, or equal to the energy of an orbital with $n = 4$? Justify your answer.
5. In each pair of subshells for a hydrogen atom, which has the higher energy? Give the principal and the azimuthal quantum number for each pair.
    1. 1*s*, 2*p*
    2. 2*p*, 2*s*
    3. 2*s*, 3*s*
    4. 3*d*, 4*s*
6. What is the relationship between the energy of an orbital and its average radius? If an electron made a transition from an orbital with an average radius of 846.4 pm to an orbital with an average radius of 476.1 pm, would an emission spectrum or an absorption spectrum be produced? Why?
7. In making a transition from an orbital with a principal quantum number of 4 to an orbital with a principal quantum number of 7, does the electron of a hydrogen atom emit or absorb a photon of energy? What would be the energy of the photon? To what region of the electromagnetic spectrum does this energy correspond?
8. What quantum number defines each of the following?
    1. the overall shape of an orbital
    2. the orientation of an electron with respect to a magnetic field
    3. the orientation of an orbital in space
    4. the average energy and distance of an electron from the nucleus
9. In an attempt to explain the properties of the elements, Niels Bohr initially proposed electronic structures for several elements with orbits holding a certain number of electrons, some of which are in the following table:

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

    1. Draw the electron configuration of each atom based only on the information given in the table. What are the differences between Bohr's initially proposed structures and those accepted today?
    2. Using Bohr's model, what are the implications for the reactivity of each element?
    3. Give the actual electron configuration of each element in the table.
10. What happens to the energy of a given orbital as the nuclear charge Z of a species increases? In a multielectron atom and for a given nuclear charge, the Z_{eff} experienced by an electron depends on its value of l. Why?
11. The electron density of a particular atom is divided into two general regions. Name these two regions and describe what each represents.
12. As the principal quantum number increases, the energy difference between successive energy levels decreases. Why? What would happen to the electron configurations of the transition metals if this decrease did not occur?

13. Describe the relationship between electron shielding and Z_{eff} on the outermost electrons of an atom. Predict how chemical reactivity is affected by a decreased effective nuclear charge.
14. If a given atom or ion has a single electron in each of the following subshells, which electron is easier to remove?
    1. 2*s*, 3*s*
    2. 3*p*, 4*d*
    3. 2*p*, 1*s*
    4. 3*d*, 4*s*

Numerical Problems

1. How many subshells are possible for $n = 3$? What are they?
2. How many subshells are possible for $n = 5$? What are they?
3. What value of l corresponds to a *d* subshell? How many orbitals are in this subshell?
4. What value of l corresponds to an *f* subshell? How many orbitals are in this subshell?
5. State the number of orbitals and electrons that can occupy each subshell.
    1. 2*s*
    2. 3*p*
    3. 4*d*
    4. 6*f*
6. State the number of orbitals and electrons that can occupy each subshell.
    1. 1*s*
    2. 4*p*
    3. 5*d*
    4. 4*f*
7. How many orbitals and subshells are found within the principal shell $n = 6$? How do these orbital energies compare with those for $n = 4$?
8. How many nodes would you expect a 4*p* orbital to have? A 5*s* orbital?
9. A *p* orbital is found to have one node in addition to the nodal plane that bisects the lobes. What would you predict to be the value of *n*? If an *s* orbital has two nodes, what is the value of *n*?

Answers

1. Three subshells, with $l = 0$ (*s*), $l = 1$ (*p*), and $l = 2$ (*d*).
2.
3. A *d* subshell has $l = 2$ and contains 5 orbitals.
4.
5.
    1. 2 electrons; 1 orbital
    2. 6 electrons; 3 orbitals
    3. 10 electrons; 5 orbitals
    4. 14 electrons; 7 orbitals
6.
7. A principal shell with $n = 6$ contains six subshells, with $l = 0$, 1, 2, 3, 4, and 5, respectively. These subshells contain 1, 3, 5, 7, 9, and 11 orbitals, respectively, for a total of 36 orbitals. The energies of the orbitals with $n = 6$ are higher than those of the corresponding orbitals with the same value of l for $n = 4$.
8.
9.

Contributors

- Anonymous

Modified by Joshua Halpern

Imaginary Number Video from IceDave33 on YouTube

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1.5: Slater's Rules

Learning Objective

- To quantify the shielding effect experienced by atomic electrons.

We have previously described the concepts of electron shielding, orbital penetration and effective nuclear charge, but we did so in a qualitative manner. In this section, we explore one model for quantitatively estimating the impact of electron shielding, and then use that to calculate the effective nuclear charge experienced by an electron in an atom. The model we will use is known as Slater's Rules (J.C. Slater, *Phys Rev* **1930**, *36*, 57).

Slater's Rules

The general principle behind Slater's Rule is that the actual charge felt by an electron is equal to what you'd expect the charge to be from a certain number of protons, but minus a certain amount of charge from other electrons. Slater's rules allow you to estimate the effective nuclear charge Z_{eff} from the real number of protons in the nucleus and the effective shielding of electrons in each orbital "shell" (e.g., to compare the effective nuclear charge and shielding 3d and 4s in transition metals). Slater's rules are fairly simple and produce fairly accurate predictions of things like the electron configurations and ionization energies.

Slater's Rules

- **Step 1**: Write the electron configuration of the atom in the following form:

  (1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 5p) . . .

- **Step 2**: Identify the electron of interest, and ignore all electrons in higher groups (to the right in the list from Step 1). These do not shield electrons in lower groups
- **Step 3**: Slater's Rules is now broken into two cases:
  - the shielding experienced by an s- or p- electron,
    - electrons within same group shield **0.35**, except the 1*s* which shield **0.30**
    - electrons within the n-1 group shield **0.85**
    - electrons within the n-2 or lower groups shield **1.00**
  - the shielding experienced by n*d* or n*f* valence electrons
    - electrons within same group shield **0.35**
    - electrons within the lower groups shield **1.00**

These rules are summarized in Figure 1.5.1 and Table 1.5.1.

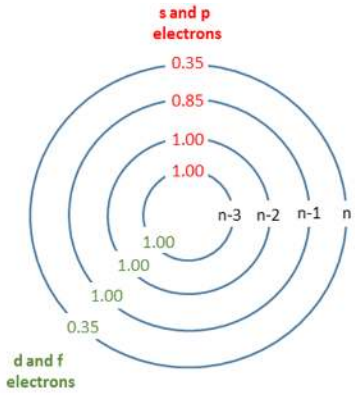


Figure 1.5.1: Graphical depiction of Slater's rules with shielding constants indicated.

Shielding happens when electrons in lower valence shells (or the same valence shell) provide a repulsive force to valence electrons, thereby "negating" some of the attractive force from the positive nucleus. Electrons really close to the atom (n-2 or lower) pretty much just look like protons, so they completely negate. As electrons get closer to the electron of interest, some more complex interactions happen that reduce this shielding.

Table 1.5.1: Slater's Rules for calculating shieldings

Group	Other electrons in the same group	Electrons in group(s) with principal quantum number n and azimuthal quantum number < l	Electrons in group(s) with principal quantum number n-1	Electrons in all group(s) with principal quantum number < n-1
[1s]	0.30	-	-	-
[*n*s,*n*p]	0.35	-	0.85	1
[*n*d] or [*n*f]	0.35	1	1	1

The shielding numbers in Table 1.5.1 were derived semi-empirically (i.e., derived from experiments) as opposed to theoretical calculations. This is because quantum mechanics makes calculating shielding effects quite difficult, which is outside the scope of this Module.

Calculating *S*

Sum together the contributions as described in the appropriate rule above to obtain an estimate of the shielding constant, S, which is found by totaling the screening by **all electrons** except the one in question.

$$S = \sum n_i S_i \tag{1.5.1}$$

where

- n_i is the number of electrons in a specific shell and subshell and
- S_i is the shielding of the electrons subject to Slater's rules (Table 1.5.1)

Example 1.5.1: The Shielding of 3*p* Electrons of Nitrogen Atoms

What is the shielding constant experienced by a 2*p* electron in the nitrogen atom?

Given: Nitrogen (N)

Asked for: S, the shielding constant, for a 2*p* electron (Equation 1.5.1)

Strategy:

A. Determine the electron configuration of nitrogen, then write it in the appropriate form.
B. Use the appropriate Slater Rule to calculate the shielding constant for the electron.

Solution A N: $1s^2\ 2s^2\ 2p^3$

N: $(1s^2)(2s^2,2p^3)$

Solution B

$$S[2p] = \underbrace{0.85(2)}_{\text{the 1s electrons}} + \underbrace{0.35(4)}_{\text{the 2s and 2p electrons}} = 3.10$$

As Table 1.5.1 indicates,

- the 1s electrons shield the other 2p electron to 0.85 "charges".
- the 2s and 2p electrons shield the other 2p electron equally at 0.35 "charges".

Exercise 1.5.1: The Shielding of valence *p* Electrons of Bromine Atoms

What is the shielding constant experienced by a valence *p*-electron in the bromine atom?

Answer

$$S = 2 + 8 + 8 \times 0.85 + 10 + 4 \times 0.35 = 28.20$$

Example 1.5.2: The Shielding of 3*d* Electrons of Bromine Atoms

What is the shielding constant experienced by a 3*d* electron in the bromine atom?

Given: Bromine (Br)

Asked for: *S*, the shielding constant, for a 3*d* electron

Strategy:

A. Determine the electron configuration of bromine, then write it in the appropriate form.
B. Use the appropriate Slater Rule to calculate the shielding constant for the electron.

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

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

Ignore the group to the right of the 3d electrons. These do not contribute to the shielding constant.

Solution B *S*[3d] = 1.00(18) + 0.35(9) = 21.15

Exercise 1.5.2: The Shielding of 3*d* Electrons of Copper Atoms

What is the shielding constant experienced by a valence *d*-electron in the copper atom?

Answer

S = 21.15

Calculating Z_{eff}

One set of estimates for the effective nuclear charge (Z_{eff}) was presented in Figure 2.5.1. Previously, we described Z_{eff} as being less than the actual nuclear charge (Z) because of the repulsive interaction between core and valence electrons. We can quantitatively represent this difference between Z and Z_{eff} as follows:

$$S = Z - Z_{eff} \tag{1.5.2}$$

Rearranging this formula to solve for Z_{eff} we obtain:

$$Z_{eff} = Z - S \tag{1.5.3}$$

We can then substitute the shielding constant obtained using Equation 1.5.3 to calculate an estimate of Z_{eff} for the corresponding atomic electron.

Example 1.5.3: The Effective Charge of p Electrons of Boron Atoms

What is the effective nuclear charge experienced by a valence *p*- electron in boron?

Given: Boron (B)

Asked for: Z_{eff} for a valence *p*- electron

Strategy:

A. Determine the electron configuration of boron and identify the electron of interest.
B. Use the appropriate Slater Rule to calculate the shielding constant for the electron.
C. Use the Periodic Table to determine the actual nuclear charge for boron.
D. Determine the effective nuclear constant.

Solution:

A B: $1s^2\ 2s^2\ 2p^1$. The valence p- electron in boron resides in the 2*p* subshell.

B: $(1s^2)(2s^2,2p^1)$

B *S*[2*p*] = 1.00(0) + 0.85(2) + 0.35(2) = 2.40

C *Z* = 5

D Using Equation 1.5.3, $Z_{eff} = 2.60$

Exercise 1.5.3

What is the effective nuclear charge experienced by a valence d-electron in copper?

Answer

$Z_{eff} = 7.85$

Summary

Slater's Rules can be used as a model of shielding. This permits us to quantify both the amount of shielding experienced by an electron and the resulting effective nuclear charge. Others performed better optimizations of Z_{eff} using variational Hartree-Fock methods. For example, Clementi and Raimondi published "Atomic Screening Constants from SCF Functions." J Chem Phys (1963) 38, 2686–2689.

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CHAPTER OVERVIEW

2: Molecular Orbital Theory

Learning Objectives

- Be able to construct molecular orbital diagrams for homonuclear diatomic, heteronuclear diatomic, homonuclear triatomic, and heteronuclear triatomic molecules.
- Understand and be able to articulate how molecular orbitals form – conceptually, visually, graphically, and (semi)mathematically.
- Interrelate bond order, bond length, and bond strength for diatomic and triatomic molecules, including neutral and ionized forms.
- Use molecular orbital theory to predict molecular geometry for simple triatomic systems
- Rationalize molecular structure for several specific systems in terms of orbital overlap and bonding.
- Understand the origin of aromaticity and anti-aromaticity in molecules with π-bonding.

Valence bond (VB) theory gave us a qualitative picture of chemical bonding, which was useful for predicting the shapes of molecules, bond strengths, etc. It fails to describe some bonding situations accurately because it ignores the wave nature of the electrons. Molecular orbital (MO) theory has the potential to be more quantitative. With it we can also get a picture of where the electrons are in the molecule, as shown in the image at the right. This can help us understand patterns of bonding and reactivity that are otherwise difficult to explain.

2.1: Valence Bond Theory- Lewis Dot Structures, the Octet Rule, Formal Charge, Resonance, and the Isoelectronic Principle
2.2: The Shapes of Molecules (VSEPR Theory) and Orbital Hybridization
2.3: Prelude to Molecular Orbital Theory
2.4: Molecular Orbital Theory
2.5: Constructing Molecular Orbitals from Atomic Orbitals
2.6: Orbital Symmetry
2.7: σ, π, and δ orbitals
2.8: Diatomic Molecules
2.9: Orbital Filling
2.10: Second-Row Diatomic Molecules
2.11: Periodic Trends in π Bonding
2.12: References

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2.1: Valence Bond Theory- Lewis Dot Structures, the Octet Rule, Formal Charge, Resonance, and the Isoelectronic Principle

Atoms and Molecules

Atomism, because it was dismissed by Aristotle, enjoyed a long sleep in scientific discourse until it was reconsidered by Galileo, Decartes, and Gassendi in the 1600s. Dalton postulated the modern atomic theory in 1808 based on his observation that elements such as hydrogen and oxygen combined in specific ratios (the Law of Definite Proportions), but the atomic theory remained contentious throughout most of the 19th century. Thompson, Rutherford, Bohr, and others around the turn of the 20th century established that matter was indeed composed of atoms that contained heavy nuclei and light electrons, and that atoms could exist in excited states that could be interpreted as excitations of their electrons to different energy levels. However the atomic theory did not provide a ready explanation for the bonded states of atoms in molecules.

In 1916, still more than a decade before modern quantum theory would adequately describe the shapes of atomic orbitals, Lewis proposed the octet theory based on the empirically observed rules of valence, i.e., the combining ratios of atoms in molecules.[1] This theory, in hindsight, can be rationalized for s- and p-block elements by observing that main-group atoms can use their four valence orbitals (s, p_x, p_y, and p_z) to accommodate up to eight electrons, some or all of which may be shared with other atoms. In Lewis' model, the valence electrons of an atom were situated at the corners of a cube, and the cubes could share edges or faces to complete their octets. Lewis developed a shorthand notation for these structures based on dots that represented the valence electrons, as illustrated in Fig. 2.1.1. A pair of electrons shared between atoms constitutes a chemical bond, and can also be represented as a line joining the atoms. Four electrons shared between atoms, represented by two lines, is a double bond, and so forth. Any pairs of electrons not involved in bonding form "lone pairs" that belong to one atom only and are thus not involved in bonding.

The Lewis picture is powerful in its simplicity. It can be readily used to rationalize or predict the combining ratios of atoms, to sort plausible and unlikely structures for molecules (including large ones), and to rationalize the acid-base properties of many molecules. It is important to remember that the model is built on a shaky, pre-quantum mechanical description of atoms and so with it, we will make mistakes. Nevertheless it is useful to see how far we can go with the Lewis model.

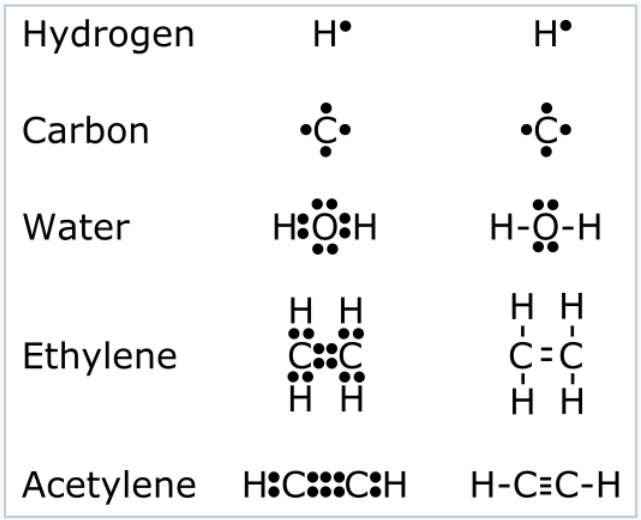


Figure 2.1.1: Examples of Lewis dot diagrams showing chemical bonds between carbon, hydrogen, and oxygen, and non-bonding electron pairs.

Constructing the octet valence bond picture for a molecule

We can construct an octet picture for any molecule using the **N-V method:**

Number of electrons *needed* to make separate octets around all atoms = **N**

(N = 8 for non-H atoms, N = 2 for H)

Number of *valence* electrons = **V** (add up using group numbers; don't forget to add or subtract for charges on ions)

Number of *shared* electrons = **S** = N-V; and therefore the number of bonds = S/2

Fill in lone pairs everywhere else to complete octets

Example: nitrate anion, NO_3^-

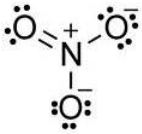
N = 4 atoms x 8 electrons = 32

V = 5 + 6 + 6 + 6 + 1 = 24 (N + O + O + O + charge)

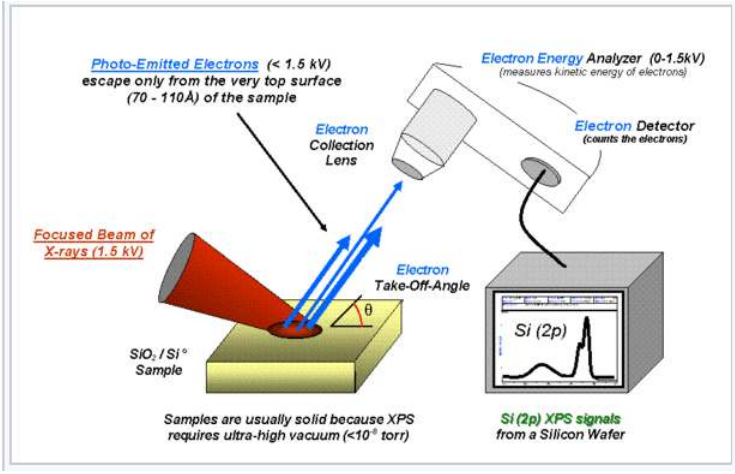
S = 32-24 = 8 shared electrons = **4 bonds**

The number of lone pairs is obtained by difference: (V-S)/2 = (24-8)/2 = 8

Now draw the molecule, starting with the four bonds and adding eight lone pairs to complete the octets:



Count the shared and unshared electrons around each atom in the nitrate ion and you will see that all atoms are **octet** and that the total number of valence electrons (V) is 24. If you do the N-V calculation according to the rules above, you should always get an octet structure.



The charges on atoms in a molecule (or an extended solid such as SiO_2) can be estimated from X-ray photoelectron spectra (XPS). Energetic X-rays ionize atoms by kicking out electrons from their core orbitals. By conservation of energy, the kinetic energy (KE) of an emitted electron is related to its binding energy (BE) and the energy of the incoming X-ray photon (hν) by BE = hν - KE. Electrons are harder to remove from positively charged atoms (higher BE), and easier to remove from negatively charged atoms (lower BE), relative to the neutral element.

The **formal charge** distribution is assigned by dividing the shared (bonding) electrons equally between atoms. Thus, the singly bonded O atoms each possess 7 electrons, and because O is in group 6, their formal charge is -1. The doubly bonded O has a formal charge of zero. The N atom has a formal charge of +1 because it "owns" 4 valence electrons and is in group 5.

Note that the **formal charge** is **not** the same thing as the **oxidation number** (or **oxidation state**). In the nitrate ion, the oxidation state of nitrogen is +5 and the oxidation state of oxygen is -2. The formal charge is typically closer to the "real" charge on the atom (as measured, e.g., by X-ray photoelectron spectroscopy). Oxidation states are a useful bookkeeping device for keeping track of

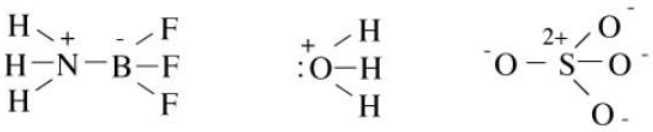
oxidation-reduction reactions, as we will discuss in Chapter 4. Like oxidation states, the formal charges on the atoms in a molecule or ion must *add up to its overall charge*.

We can similarly draw the Lewis structure for ammonia as shown below:



When we divide the shared electrons equally between the atoms, we see that the N atom has five electrons and each H atom has one. These are the same as their group numbers, and thus, all the formal charges in the ammonia molecule are zero.

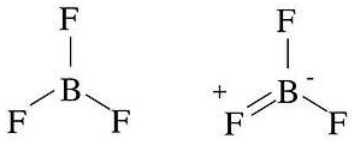
Octet structures of the Lewis acid-base adduct NH_3BF_3, the hydronium ion H_3O^+, and the sulfate anion SO_4^{2-} are shown below. In this case (and in many Lewis structures we will draw), we leave off the implied lone pairs around the peripheral atoms. Try calculating the number of bonds in each of these molecules using the N-V method, and fill in the lone pairs that are not explicitly drawn in.



In cases where more than one valence bond structure is possible, we can use formal charges to decide which structures should be more or less stable. The rules are:

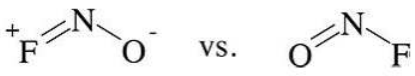
- The formal charges on atoms are minimized in stable structures, zero being the best case.
- Negative formal charges should be placed on the most electronegative atom(s).
- Positive formal charges should be placed on the least electronegative atom(s).
- It is unfavorable to place like charges (++ or --) on neighboring atoms in a molecule.

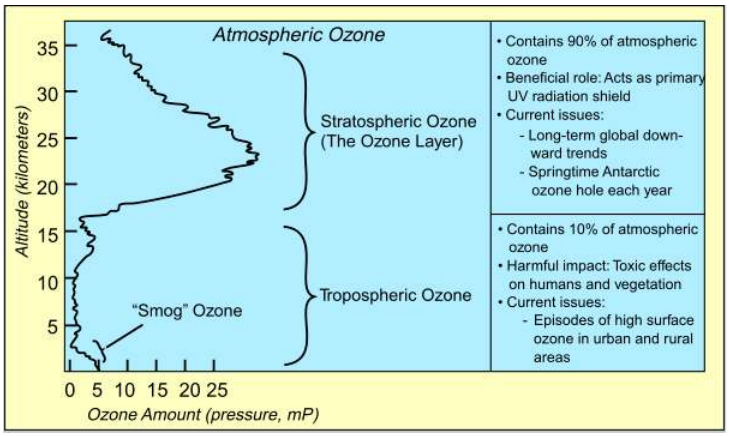
Examples of these rules are shown below for alternative structures of BF_3 and ONF.



In the BF_3 case, the structure on the left is non-octet, because there are only six electrons (three bonds) in the valence shell of B. Such structures are said to be *electron deficient.* An octet structure (right) can be drawn, but it places a positive formal charge on F, the most electronegative atom in the molecule. Thus, neither structure is completely "happy," but the formal charge rules tell us that the electron-deficient structure on the left is more stable. The electron deficiency of BF_3makes it a powerful Lewis acid.

In the case of ONF, the structure on the left is unfavorable for two reasons. First, it places a positive formal charge on F, the most electronegative atom. Second, there is another possible structure (right) that has zero formal charge, which is preferable to one with non-zero charge. This means that the structure on the right, with a double bond between N and O, is more reasonable.

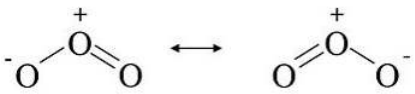




Life outside of the ocean owes its existence to the presence of ozone (O_3) in the stratosphere. Ozone absorbs the ultraviolet light in the solar spectrum, which otherwise would cause catastrophic damage to DNA and other biological molecules. Because ozone is produced photochemically from O_2, which is itself generated by photosynthesis, the spectroscopic signature of ozone in the atmosphere of distant planets is one possible way to look for extraterrestrial life.

Resonance structures

The ozone (O_3) molecule has two equivalent octet structures, shown below:

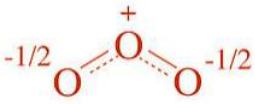


In both cases, the Lewis dot diagram suggests that there are three kinds of oxygen atoms in the molecule, with +1, 0, and -1 formal charges. These structures also suggest that ozone should have one single and one double bond. Experimentally (by electron diffraction), however, we find that the molecule is symmetric, with both O-O bond lengths the same. The real (instantaneous) structure is the average of the two forms, as shown below. In the classical Lewis picture of the molecule, we can rationalize resonance by observing that electrons, being thousands of times lighter than the nuclei of atoms, move very fast on the timescale of molecular vibrations. Thus, in the time it takes for the oxygen atoms to adjust their positions, the electrons can move back and forth many times. In the quantum mechanical MO picture (Chapter 2), we will see that resonance involves electrons that are fully delocalized over the atoms in the molecule. We represent resonance structures with a double-headed arrow to signify that the only difference between the Lewis structures is the distribution of electrons.

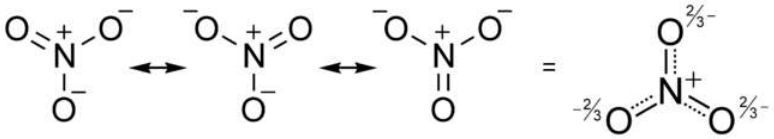


Susan Solomon discovered the heterogeneous catalytic mechanism whereby ozone is decomposed by chlorofluorocarbons (freons), creating the Antarctic ozone hole. Her work formed the basis of the U.N. Montreal Protocol, an international agreement to protect the ozone layer by regulating damaging chemicals.

In the instantaneous structure of ozone, the formal (-) charge is shared between the two terminal oxygen atoms and therefore each one has a formal charge of -1/2. The O-O bonds are the average of a single and a double bond, i.e., each O-O bond order is 1.5.

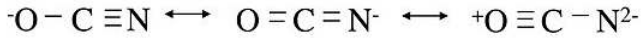


Similarly, the nitrate anion has three resonance structures, and experimentally (by X-ray crystallography of nitrate salts) we find that all the N-O bonds in the ion are the same. In this case, in the averaged structure, each O atom has a formal charge of -2/3 and the N-O bond order is 4/3 (=1.33...).



Inequivalent resonance structures

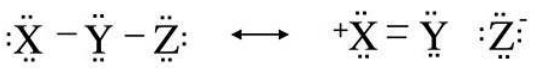
The rules of resonance also apply to inequivalent structures, which in general will have different energies from each other. In this case the structure of the molecule represents a weighted average of the low energy structures. A good example is the cyanate ion, OCN^-. We can write three inequivalent octet structures for the molecule:



The first two are reasonable resonance structures, although we suspect the one on the left is the best because it puts the negative formal charge on the most electronegative atom. The last one is clearly a bad resonance structure, because the formal charges are high and there is a positive charge on the oxygen atom. The real structure is thus a weighted average of the first two.

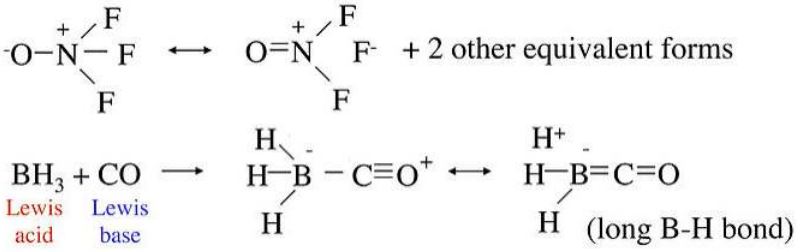
No-bond resonance

An interesting and useful kind of inequivalent resonance structure is one in which there is a bond order of *zero* between two of the atoms. This concept of **no-bond resonance** is important in understanding the bonding in many halogen- and hydrogen-containing compounds. The idea is illustrated below for the generic molecule X-Y-Z, where Z might be an electronegative halogen atom such as F. By moving the bonding electrons from the Y-Z bond onto the Z atom, and moving a lone pair from X into the X-Y bond, we generate the resonance structure shown on the right in which all atoms remain octet, but there is no bond between Y and Z.

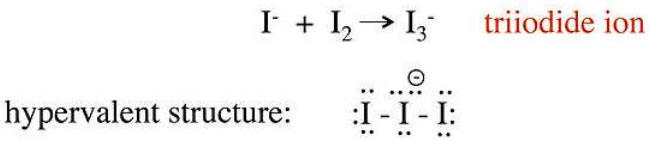


It is important to recognize in this example that the no-bond form is only one resonance structure, and therefore the Z atom is still bound to Y. If the two resonance structures in this example have the same energy, we would expect the X-Y bond order to be 1.5 and the Y-Z bond order to be 0.5. Therefore the Y-Z bond should be longer than it is in a compound where the bond order is one, and it should be relatively easy to break the Y-Z bond.

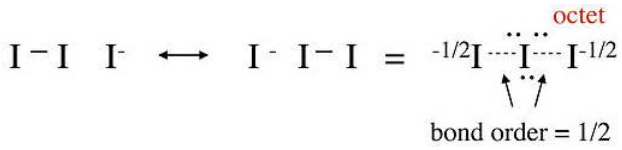
Some molecular examples of no-bond resonance are shown below. In the molecule ONF_3, the N-F bond is unusually long relative to the N-F bond in NF_3, in which the bond order is 1. This can be explained by the no-bond resonance forms shown on the right. Similarly, in the Lewis acid-base adduct formed by combining BH_3 with CO, we can explain the long B-H bonds using no-bond resonance forms that place a partial positive charge on the H atoms.



No-bond resonance is often used to provide an octet bonding picture for so-called **hypervalent compounds**, which are compounds that appear to have more than 8 valence electrons in the bonding shell of the central atom. For example, we can consider two different valence bond structures for the triiodide ion, I_3^-, which is formed by reaction of I^- with I_2 in water:

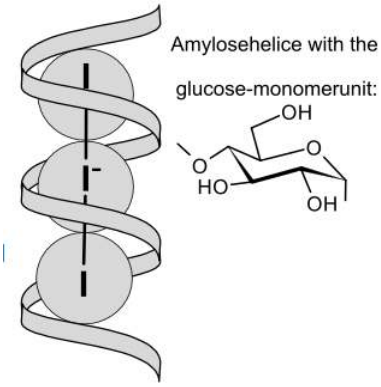


In this structure, the central iodine atom has 10 electrons in its valence shell, in violation of the octet rule. Raman spectra of the triiodide ion show that the I-I bond is weaker than the I-I single bond in I_2, suggesting that this picture is not an accurate description of the bonding. A better representation of I_3^- can be obtained with no-bond resonance structures, as shown below. We will see that this picture is consistent with the MO description of I_3^- in Chapter 2:





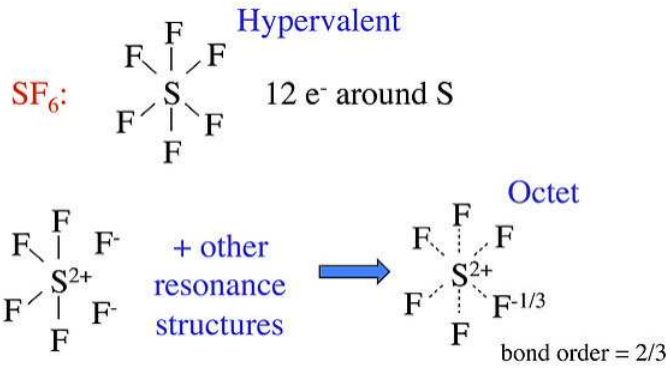
The deep blue color of starch-iodine solutions results from the complexation of linear polyiodide ions (I_n^-) by the starch (amylose) left-handed helix. The interior of the helix is hydrophobic. In electron donor solvents such as ethanol and water, I_2 and salts of I_3^- have a brown color, the result of a charge transfer interaction between the solvent and solute.[2][3]

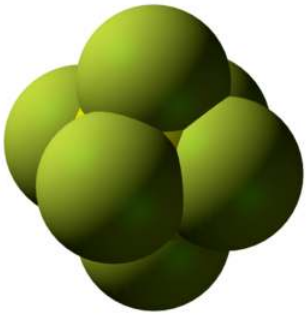


We can draw a similar picture for the XeF_2 molecule, which has the same number of valence electrons as I_3^-. This picture is consistent with XPS data, which show a partial negative charge on the F atoms, as well as vibrational spectra, which show that the Xe-F bond is weaker in XeF_2 than it is in the singly-bonded cation $Xe\text{-}F^+$.

$$^{-1/2}F\text{-------}Xe^{+}\text{-------}F^{-1/2}$$

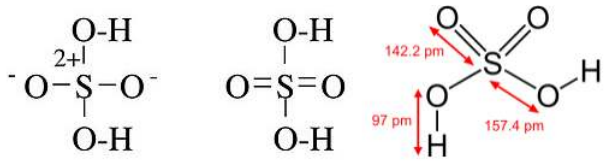
Other well known examples of hypervalent compounds are PF_5, $P(CH_3)_5$, and SF_6, as well as oxyacids such as H_2SO_4 and $HClO_4$. The hypervalent structure is often drawn for these molecules, with the explanation that d-orbitals on the central atom contribute to the bonding in dsp^3 and d^2sp^3 hybrids for 5- and 6-coordinate molecules, respectively. However, realistic molecular orbital calculations show that the phosphorus and sulfur 3d orbitals are too high in energy to contribute significantly to bonding in PF_5 and SF_6. For these molecules, we can use no-bond resonance to make reasonable octet structures that predict polar bonds between the central atom and F.





Space-filling model of sulfur hexafluoride. SF_6 is surprisingly unreactive with water, relative to other compounds that contain S-F bonds. The tight packing of F atoms around S prevents nucleophilic attack by water.

In other cases, such as $P(CH_3)_5$, the octet structure is unreasonable because it suggests a polar bond between P and C, with a partial negative charge on C. Further, in the case of oxyacids such as H_2SO_4 and $HClO_4$, X-ray crystallographic data establish that the S-O and Cl-O bonds are shorter for the oxygen atoms not bonded to hydrogen, which is more consistent with the hypervalent picture:

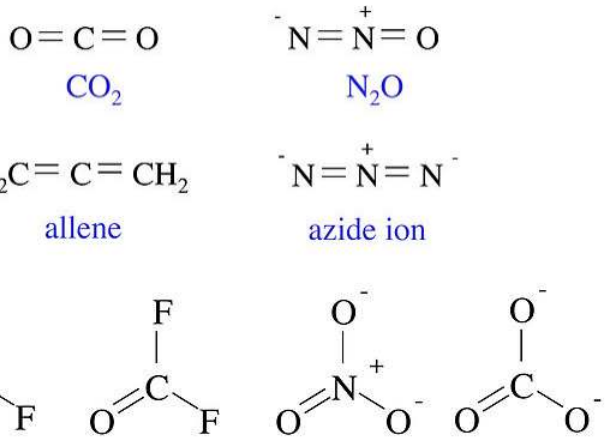


The question of whether hypervalency and the octet rule are really useful descriptions of the bonding in these compounds has been considered in a number of computational studies, which have used increasingly accurate quantum mechanical calculations to determine the number of electrons associated with the central atom. In a 2002 study, Gillespie and Silvi[4] found that the population of the valence shell is greater than eight for compounds with electropositive ligands, such as $P(CH_3)_5$, and less than eight for compounds such as PF_5. They concluded that these valence electron shell populations depend primarily on the coordination numbers and electronegativities of the central atoms and their ligands, and that there is no fundamental difference between the bonding in hypervalent and non-hypervalent (Lewis octet) molecules. This reminds us that the octet rule is not a law of nature, but rather an empirical rule that is useful within certain limits.

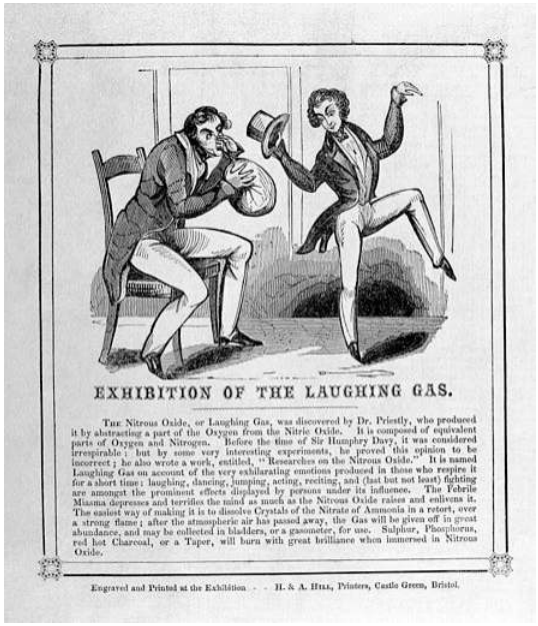
The isoelectronic principle

In calculating the octet structures of molecules using the N-V method, we needed to know only the number of atoms and the number of electrons, not the identities of the atoms themselves. This means that we will get the same answer (and the same set of octet and resonance structures) for *any* molecule or ion that contains (a) the same number of non-hydrogen atoms, and (b) the same total number of valence electrons. Such molecules are said to be *isoelectronic*. This is a powerful conclusion because, once we have determined the electronic structure of one molecule, we can write down the same solution for *all other molecules* that are isoelectronic. For example, we noted above that I_3^- and XeF_2, which both have 22 valence electrons, have the same valence bond structure. We can further expect that isoelectronic molecules will have the same shapes and, very often, similar physical properties.

The four molecules and ions below all contain three non-hydrogen atoms and 16 valence electrons. All of them are linear molecules with two double bonds. The four molecules and ions shown below them all contain four non-hydrogen atoms and 24 valence electrons. These four have a trigonal planar shape. While BF_3 is a member of this isoelectronic series, we do not write it in the resonance form that contains a B=F double bond, because that would put a positive formal charge on F.



Similarly we can show that CH_4, NH_3, NH_4^+, H_2O, H_3O^+, HF, F^-, and OH^- are all isoelectronic with one non-H atom and eight valence electrons. In the next section we will see that this gives rise to nearly identical electronic shapes for these molecules.



Nitrous oxide (N_2O), or laughing gas, is isoelectronic with CO_2. The two molecules have the same shape (linear) and similar physical properties. CO_2 sublimes at -78 °C, whereas N_2O melts at -91 °C and boils at -88 °C.

Isoelectronic solids

The isoelectronic principle works not just for molecules but for extended solids as well. One technologically important set of isoelectronic solids are the p-block semiconductors. The group 14 element Si is the most widely used semiconductor for electronics, but, as we will discuss later, it is not a good light emitter. Light-emitting diodes (LEDs), which are used in lasers, high efficiency lighting, and display technologies, are made from compounds that are isoelectronic with Si and Ge, especially GaAs, GaP, AlAs, and GaN (all contain four valence electrons per atom). CdTe and $CuIn_{1-x}Ga_xSe_2$ (CIGS) are promising solar cell materials that also have the same number of valence electrons per atom. Like Si and Ge, these compounds have tetrahedrally bonded structures in the solid state and absorb light across most of the solar spectrum, as we will discuss in more detail in Chapters 8 and 10.

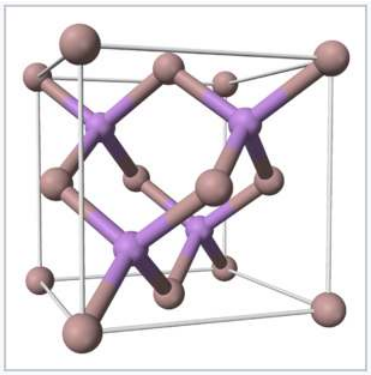


Figure 2.1.2: The tetrahedral bonding in crystals of GaAs, CdTe, $CuIn_{1-x}Ga_xSe_2$ and other semiconductors is similar to that in isoelectronic Si and Ge.

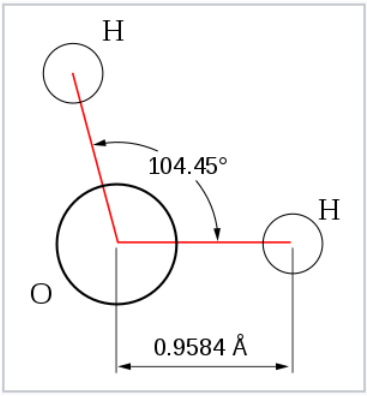
The isoelectronic principle is also a powerful tool in materials research, because it provides guidance about where to look for new materials with similar and perhaps improved properties. For example, the discovery that 8.5% efficient thin layer solar cells could be made with the compound $CsSnI_3$[5] stimulated the exploration of many isoelectronic ABX_3 compounds with the same perovskite crystal structure. Very recently thin film solar cells based on light absorbers in this structural family $(MA)PbI_{3-x}Cl_x$ and $FA_xMA_{1-x}PbBr_yI_{3-y}$ (MA^+ = methylammonium, $CH_3NH_3^+$; FA^+ = formamidinium, $HC(NH_2)_2^+$) have been reported with efficiencies as high as 22%.[6][7][8]

2.1: Valence Bond Theory- Lewis Dot Structures, the Octet Rule, Formal Charge, Resonance, and the Isoelectronic Principle is shared under a CC BY-SA license and was authored, remixed, and/or curated by LibreTexts.

- **1.2: Valence Bond Theory- Lewis Dot Structures, the Octet Rule, Formal Charge, Resonance, and the Isoelectronic Principle** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

2.2: The Shapes of Molecules (VSEPR Theory) and Orbital Hybridization

The Valence Shell Electron Pair Repulsion (VSEPR) theory is a simple and useful way to predict and rationalize the shapes of molecules. The theory is based on the idea of minimizing the electrostatic repulsion between electron pairs, as first proposed by Sidgwick and Powell in 1940,[9] then generalized by Gillespie and Nyholm in 1957,[10] and then broadly applied over the intervening 50+ years.[11]



Geometry of the water molecule

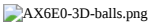
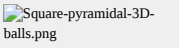
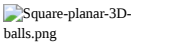
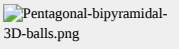
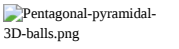
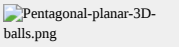
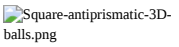
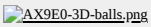
To use the VSEPR model, one begins with the Lewis dot picture to determine the number of lone pairs and bonding domains around a central atom. Because VSEPR considers all bonding domains equally (i.e., a single bond, a double bond, and a half bond all count as one electron domain), one can use either an octet or hypervalent structure, provided that the number of lone pairs (which should be the same in both) is calculated correctly. For example, in either the hypervalent or octet structure of the I_3^- ion above, there are three lone pairs on the central I atom and two bonding domains. We then follow these steps to obtain the **electronic geometry**:

- Determine the number of lone pairs on the central atom in the molecule, and add the number of bonded atoms (a.k.a. bonding domains)
- This number (the *steric number*) defines the electronic shape of the molecule by minimizing repulsion. For example a steric number of three gives a trigonal planar electronic shape.
- The angles between electron domains are determined primarily by the electronic geometry (e.g., 109.5° for a steric number of 4, which implies that the electronic shape is a tetrahedron)
- These angles are adjusted by the hierarchy of repulsions: (lone pair - lone pair) > (lone pair - bond) > (bond - bond)

The **molecular geometry** is deduced from the electronic geometry by considering the lone pairs to be present but invisible. The most commonly used methods to determine molecular structure - X-ray diffraction, neutron diffraction, and electron diffraction - have a hard time seeing lone pairs, but they can accurately determine the lengths of bonds between atoms and the bond angles.

The table below gives examples of electronic and molecular shapes for steric numbers between 2 and 9. We are most often concerned with molecules that have steric numbers between 2 and 6.

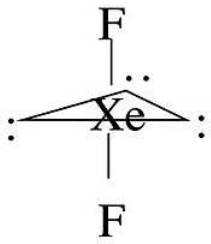
Bonding electron pairs	Lone pairs	Electron domains (Steric #)	Shape	Ideal bond angle (example's bond angle)	Example	Image
2	0	2	linear	180°	CO_2	Linear-3D-balls.png
3	0	3	trigonal planar	120°	BF_3	Trigonal-3D-balls.png
2	1	3	bent	120° (119°)	SO_2	Bent-3D-balls.png
4	0	4	tetrahedral	109.5°	CH_4	AX4E0-3D-balls.png
3	1	4	trigonal pyramidal	109.5° (107°)	NH_3	Pyramidal-3D-balls.png

Bonding electron pairs	Lone pairs	Electron domains (Steric #)	Shape	Ideal bond angle (example's bond angle)	Example	Image
2	2	4	bent	109.5° (104.5°)	H_2O	
5	0	5	trigonal bipyramidal	90°, 120°, 180°	PCl_5	
4	1	5	seesaw	180°, 120°, 90° (173.1°, 101.6°)	SF_4	
3	2	5	T-shaped	90°, 180° (87.5°, < 180°)	ClF_3	
2	3	5	linear	180°	XeF_2	
6	0	6	octahedral	90°, 180°	SF_6	
5	1	6	square pyramidal	90° (84.8°), 180°	BrF_5	
4	2	6	square planar	90°, 180°	XeF_4	
7	0	7	pentagonal bipyramidal	90°, 72°, 180°	IF_7	
6	1	7	pentagonal pyramidal	72°, 90°, 144°	$XeOF_5^-$	
5	2	7	planar pentagonal	72°, 144°	XeF_5^-	
8	0	8	square antiprismatic		XeF_8^{2-}	
9	0	9	tricapped trigonal prismatic		ReH_9^{2-}	

From the Table, we see that some of the molecules shown as examples have bond angles that depart from the ideal electronic geometry. For example, the H-N-H bond angle in ammonia is 107°, and the H-O-H angle in water is 104.5°. We can rationalize this in terms of the last rule above. The lone pair in ammonia repels the electrons in the N-H bonds more than they repel each other. This lone pair repulsion exerts even more steric influence in the case of water, where there are two lone pairs. Similarly, the axial F-S-F angle in the "seesaw" molecule SF_4 is a few degrees less than 180° because of repulsion by the lone pair in the molecule.

Geometrical isomers

For some molecules in the Table, we note that there is more than one possible shape that would satisfy the VSEPR rules. For example, the XeF_2 molecule has a steric number of five and a trigonal bipyramidal geometry. There are three possible stereoisomers: one in which the F atoms occupy axial sites, resulting in linear molecule, one in which the F atoms occupy one equatorial and one axial site (resulting in a 90° bond angle), and one in which the F atoms are both on equatorial sites, with a F-Xe-F bond angle of 120°.



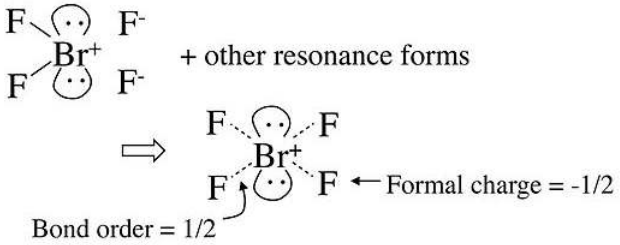
The observed geometry of XeF_2 is linear, which can be rationalized by considering the orbitals that are used to make bonds (or lone pairs) in the axial and equatorial positions. There are four available orbitals, s, p_x, p_y, and p_z. If we choose the z-axis as the axial direction, we can see that the p_x and p_y orbitals lie in the equatorial plane. We assume that the spherical s orbital is shared equally by the five electron domains in the molecule, the two axial bonds share the p_z orbital, and the three equatorial bonds share the p_x and p_y orbitals. We can then calculate the bond orders to axial and equatorial F atoms as follows:

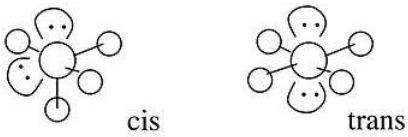
$axial:\ \frac{1}{5}+\frac{1}{2}p_z = 0.7\ bond(formal\ charge = -0.3)$

$equatorial:\ \frac{1}{5}s+\frac{1}{3}p_x+\frac{1}{3}p_y = 0.867\ bond(formal\ charge = -0.122)$

Because fluorine is more electronegative than a lone pair, it prefers the axial site where it will have more negative formal charge. In general, by this reasoning, lone pairs and electropositive ligands such as CH_3 will always prefer the equatorial sites in the trigonal bipyramidal geometry. Electronegative ligands such as F will always go to the axial sites.

In the case of the BrF_4^- anion, which is isoelectronic with XeF_4 in the Table, the electronic geometry is octahedral and there are two possible isomers in which the two lone pairs are *cis* or *trans* to each other. In this case, lone pair - lone pair repulsion dominates and we obtain the *trans* arrangement of lone pairs, giving a square planar molecular geometry.





Orbital hybridization

The observation of molecules in the various electronic shapes shown above is, at first blush, in conflict with our picture of atomic orbitals. For an atom such as oxygen, we know that the 2s orbital is spherical, and that the $2p_x$, $2p_y$, and $2p_z$ orbitals are dumbell-shaped and point along the Cartesian axes. The water molecule contains two hydrogen atoms bound to oxygen not at a 90° angle, but at an angle of 104.5°. Given the relative orientations of the atomic orbitals, how do we arrive at angles between electron domains of 104.5°, 120°, and so on? To understand this we will need to learn a little bit about the quantum mechanics of electrons in atoms and molecules.

The atomic orbitals ψ represent solutions to the **Schrödinger wave equation**,

$$E\psi = \hat{H}\psi \tag{2.2.1}$$

Here E is the energy of an electron in the orbital, and $\hat{H}$ is the Hamiltonian operator.

By analogy with classical mechanics, the Hamiltonian is commonly expressed as the sum of operators corresponding to the kinetic and potential energies of a system in the form

$$\hat{H} = \hat{T} + \hat{V} \tag{2.2.2}$$

where $\hat{V} = V(\mathbf{r}, t)$ is the potential energy, and

$$\hat{T} = \frac{\hat{\mathbf{p}} \cdot \hat{\mathbf{p}}}{2m} = \frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m}\nabla^2, \tag{2.2.3}$$

is the kinetic energy operator in which *m* is the mass of the particle and the momentum operator is:

$$\hat{p} = -i\hbar\nabla, \text{where} \nabla = \frac{\delta}{\delta x} + \frac{\delta}{\delta y} + \frac{\delta}{\delta z} \tag{2.2.4}$$

Here $\hbar$ is h/2π, where h is Planck's constant, and the Laplacian operator ∇^2 is:

$$\nabla^2 = \frac{\delta^2}{\delta x^2} + \frac{\delta^2}{\delta y^2} + \frac{\delta^2}{\delta z^2} \tag{2.2.5}$$

Although this is not the technical definition of the Hamiltonian in classical mechanics, it is the form it most commonly takes in quantum mechanics. Combining these together yields the familiar form used in the Schrödinger equation:

$$\hat{H} = \hat{T} + \hat{V} = \frac{\hat{\mathbf{p}} \cdot \hat{\mathbf{p}}}{2m} + V(\mathbf{r}, t) = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r}, t) \tag{2.2.6}$$

For hydrogen-like (one-electron) atoms, the Schrödinger equation can be written as:

$$E\psi = -\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{Ze^2}{4\pi\epsilon_0 r}\psi \tag{2.2.7}$$

where **Z** is the nuclear charge, *e* is the electron charge, and **r** is the position of the electron. The radial potential term on the right side of the equation is due to the Coulomb interaction, i.e., the electrostatic attraction between the nucleus and the electron, in which ε_0 is the dielectric constant (permittivity of free space) and

$$\mu = \frac{m_e m_n}{m_e + m_n} \tag{2.2.8}$$

is the 2-body reduced mass of the nucleus of mass m_n and the electron of mass m_e. To a good approximation, $\mu \approx m_e$.



Erwin Schrödinger as a young scientist

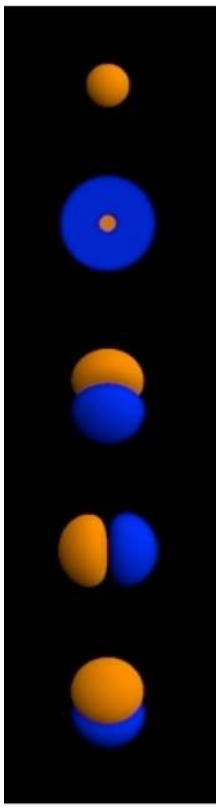
This is the equation that Erwin Schrödinger famously derived in 1926 to solve for the energies and shapes of the s, p, d, and f atomic orbitals in hydrogen-like atoms. It was a huge conceptual leap for both physics and chemistry because it not only explained the quantized energy levels of the hydrogen atom, but also provided the theoretical basis for the octet rule and the arrangement of elements in the periodic table.

The Schrödinger equation can be used to describe chemical systems that are more complicated than the hydrogen atom (e.g., multi-electron atoms, molecules, infinite crystals, and the dynamics of those systems) if we substitute the appropriate potential energy function V(r,t) into the Hamiltonian. The math becomes more complicated and the equation must be solved numerically in those cases, so for our purposes we will stick with the simplest case of time-invariant, one-electron, hydrogen-like atoms.

Without going into too much detail about the Schrödinger equation, we can point out some of its most important properties:

$$E\psi = -\frac{\hbar^2}{2\mu}\nabla^2\psi - \frac{Ze^2}{4\pi\epsilon_0 r}\psi \tag{2.2.9}$$

- The equation derives from the fact that the total energy (E) is the sum of the kinetic energy (KE) and the potential energy (PE). These three quantities are represented mathematically as **operators** in the equation.
- On the left side of the equation, the total energy operator (E) is a scalar that is multiplied by the wavefunction ψ. ψ is a function of the spatial coordinates (x,y,z) and is related to the probability that the electron is at that point in space.
- The first term on the right side of the equation represents the kinetic energy (KE). The kinetic energy operator is proportional to ∇^2 (the Laplacian operator) which takes the second derivative (with respect to three spatial coordinates) of ψ. Thus, the Schrödinger equation is a **differential equation**.
- The second term on the right side of the equation represents the Coulomb potential (PE), i.e. the attractive energy between the positively charged nucleus and the negatively charged electron.
- The solutions to the Schrödinger equation are a set of **energies** E (which are scalar quantities) and **wavefunctions** (a.k.a. **atomic orbitals**) ψ, which are functions of the spatial coordinates. You will sometimes see the energies referred to as *eigenvalues* and the orbitals as *eigenfunctions*, because mathematically the Schrödinger equation is an eigenfunction-eigenvalue equation. Although ψ is a function of the coordinates, E is not. So an electron in a $2p_z$ orbital has the same total energy E (= PE + KE) no matter where it is in space.
- These E values and their associated wavefunctions ψ are catalogued according to their **quantum numbers** *n*, *l*, and m_l. That is, there are many solutions to the differential equation, and each solution (ψ(xyz) and E) has a unique set of quantum numbers. Some sets of orbitals are **degenerate**, meaning that they have the same energy (e.g., $2p_x$, $2p_y$, and $2p_z$).
- The solutions ψ(xyz) to the Schrödinger equation (e.g., the 1s, 2s, $2p_x$, $2p_y$, and $2p_z$ orbitals) represent **probability amplitudes** for finding the electron at a particular point (x,y,z) in space. A probability amplitude can have either **+ or - sign**. We typically represent the different signs by shading or by + and - signs on the two lobes of a 2p orbital.
- The square of the probability amplitude, ψ^2, is always a positive number and represents the **probability** of finding the electron at a point x,y,z in space. Because the total probability of finding the electron somewhere is 1, the wavefunction must be **normalized** so that the integral of ψ^2 over the spatial coordinates (from -∞ to +∞) is 1.
- The solutions to the Schrödinger equation are **orthogonal**, meaning that the product of any two (integrated over all space) is zero. For example the product of the 2s and $2p_x$ orbitals, integrated over the spatial coordinates from -∞ to +∞, is zero.



The shapes of the first five atomic orbitals: 1s, 2s, $2p_x$, $2p_y$, and $2p_z$. The colors denote the sign of the wave function.

Orbital hybridization involves making *linear combinations* of the atomic orbitals that are solutions to the Schrödinger equation. Mathematically, this is justified by recognizing that the Schrödinger equation is a *linear* differential equation. As such, any sum of solutions to the Schrödinger equation is also a valid solution. However, we still impose the constraint that our hybrid orbitals must be **orthogonal** and **normalized**.

Rules for orbital hybridization:

- Add and subtract atomic orbitals to get hybrid orbitals.
- We get the same number of orbitals out as we put in.
- The energy of a hybrid orbital is the weighted average of the atomic orbitals that make it up.
- The coefficients are determined by the constraints that the hybrid orbitals must be orthogonal and normalized.

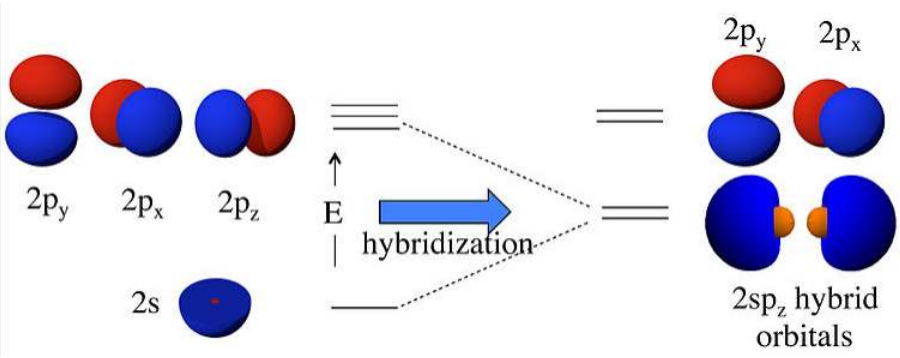
For **sp hybridization**, as in the BeF_2 or CO_2 molecule, we make two linear combinations of the 2s and $2p_z$ orbitals (assigning z as the axis of the Be-F bond):

$$\psi_1 = \frac{1}{\sqrt{2}}(2s) + \frac{1}{\sqrt{2}}(2p_z) \tag{2.2.10}$$

$$\psi_2 = \frac{1}{\sqrt{2}}(2s) - \frac{1}{\sqrt{2}}(2p_z) \tag{2.2.11}$$

Here we have simply added and subtracted the 2s and 2pz orbitals; we leave it as an exercise for the interested student to show that both orbitals are normalized (i.e., $\int \psi_1^2 d\tau = \int \psi_2^2 d\tau = 1$) and orthogonal (i.e., $\int \psi_1 \psi_2 d\tau = 0$) .

What this means physically is explained in the figure below. By combining the 2s and $2p_z$ orbitals we have created two new orbitals with large lobes (high electron probability) pointing along the z-axis. These two orbitals are degenerate and have an energy that is halfway between the energy of the 2s and $2p_z$ orbitals.



Linear combinations of the 2s and $2p_z$ atomic orbitals make two $2sp_z$ hybrids. The $2p_x$and $2p_y$ orbitals are unchanged.

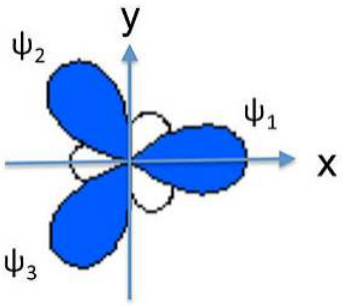
For an isolated Be atom, which has two valence electrons, the lowest energy state would have two electrons spin-paired in the 2s orbital. However, these electrons would not be available for bonding. By **promoting** these electrons to the degenerate $2sp_z$ hybrid orbitals, they become unpaired and are prepared for bonding to the F atoms in BeF_2. This will occur if the **bonding energy** (in the promoted state) exceeds the promotion energy. The **overall bonding energy**, i.e., the energy released by combining a Be atom in its ground state with two F atoms, is the difference between the bonding and promotion energies.

We can similarly construct **sp^2 hybrids** (e.g., for the BF_3 molecule or the NO_3^- anion) from one 2s and two 2p atomic orbitals. Taking the plane of the molecule as the xy plane, we obtain three hybrid orbitals at 120° to each other. The three hybrids are:

$$\psi_1 = \frac{1}{\sqrt{3}}(2s) + \frac{\sqrt{2}}{\sqrt{3}}(2p_x) \tag{2.2.12}$$

$$\psi_2 = \frac{1}{\sqrt{3}}(2s) - \frac{1}{\sqrt{6}}(2p_x) + \frac{1}{\sqrt{2}}(2p_y) \tag{2.2.13}$$

$$\psi_3 = \frac{1}{\sqrt{3}}(2s) - \frac{1}{\sqrt{6}}(2p_x) - \frac{1}{\sqrt{2}}(2p_y) \tag{2.2.14}$$



These orbitals are again degenerate and their energy is the weighted average of the energies of the 2s, $2p_x$, and $2p_y$ atomic orbitals.

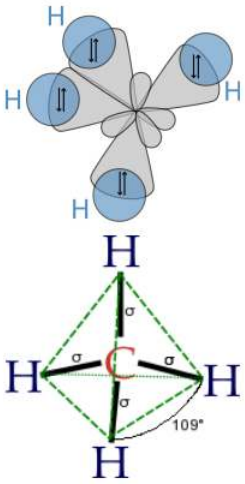
Finally, to make a sp^3 hybrid, as in CH_4, H_2O, etc., we combine all four atomic orbitals to make four degenerate hybrids:

$$\psi_1 = \frac{1}{2}(2s + 2p_x + 2p_y + 2p_z) \tag{2.2.15}$$

$$\psi_2 = \frac{1}{2}(2s - 2p_x - 2p_y + 2p_z) \tag{2.2.16}$$

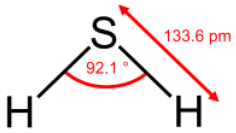
$$\psi_3 = \frac{1}{2}(2s + 2p_x - 2p_y - 2p_z) \tag{2.2.17}$$

$$\psi_4 = \frac{1}{2}(2s - 2p_x + 2p_y - 2p_z) \tag{2.2.18}$$



The lobes of the **sp^3 hybrid** orbitals point towards the vertices of a tetrahedron (or alternate corners of a cube), consistent with the tetrahedral bond angle in CH_4 and the nearly tetrahedral angles in NH_3 and H_2O. Similarly, we can show that we can construct the trigonal bipyramidal electronic shape by making sp and sp^2 hybrids, and the octahedral geometry from three sets of sp hybrids. The picture that emerges from this is that the atomic orbitals can hybridize as required by the shape that best minimizes electron pair repulsions.

Interestingly however, the bond angles in PH_3, H_2S and H_2Se are close to 90°, suggesting that P, S, and Se primarily use their p-orbitals in bonding to H in these molecules. This is consistent with the fact that the energy difference between s and p orbitals stays roughly constant going down the periodic table, but the bond energy *decreases* as the valence electrons get farther away from the nucleus. In compounds of elements in the 3rd, 4th, and 5th rows of the periodic table, there thus is a *decreasing tendency to use s-p orbital hybrids in bonding*. For these heavier elements, the bonding energy is not enough to offset the energy needed to promote the s electrons to s-p hybrid orbitals.



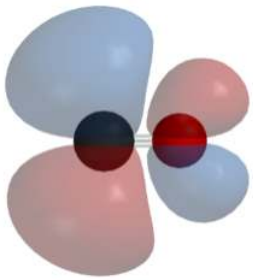
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2.3: Prelude to Molecular Orbital Theory

Valence bond (VB) theory gave us a qualitative picture of chemical bonding, which was useful for predicting the shapes of molecules, bond strengths, etc. It fails to describe some bonding situations accurately because it ignores the wave nature of the electrons. Molecular orbital (MO) theory has the potential to be more quantitative. With it we can also get a picture of where the electrons are in the molecule, as shown in the image at the right. This can help us understand patterns of bonding and reactivity that are otherwise difficult to explain.

Although MO theory in principle gives us a way to calculate the energies and wavefunctions of electrons in molecules very precisely, usually we settle for simplified models here too. These simple models do not give very accurate orbital and bond energies, but they do explain concepts such as resonance (e.g., in the ferrocene molecule) that are hard to represent otherwise. We can get more accurate energies from MO theory by computational "number crunching." While MO theory is more correct than VB theory and can be very accurate in predicting the properties of molecules, it is also rather complicated even for fairly simple molecules. For example, you should have no trouble drawing the VB pictures for CO, NH_3, and benzene, but we will find that these are increasingly challenging with MO theory.



The lowest unoccupied molecular orbital of the carbon monoxide molecule is a π antibonding orbital that derives from the 2p orbitals of carbon (left) and oxygen (right)

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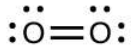
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2.4: Molecular Orbital Theory

Skills to Develop

- Outline the basic quantum-mechanical approach to deriving molecular orbitals from atomic orbitals
- Describe traits of bonding and antibonding molecular orbitals
- Calculate bond orders based on molecular electron configurations
- Write molecular electron configurations for first- and second-row diatomic molecules
- Relate these electron configurations to the molecules' stabilities and magnetic properties

For almost every covalent molecule that exists, we can now draw the Lewis structure, predict the electron-pair geometry, predict the molecular geometry, and come close to predicting bond angles. However, one of the most important molecules we know, the oxygen molecule O_2, presents a problem with respect to its Lewis structure. We would write the following Lewis structure for O_2:



This electronic structure adheres to all the rules governing Lewis theory. There is an O=O double bond, and each oxygen atom has eight electrons around it. However, this picture is at odds with the magnetic behavior of oxygen. By itself, O_2 is not magnetic, but it is attracted to magnetic fields. Thus, when we pour liquid oxygen past a strong magnet, it collects between the poles of the magnet and defies gravity. Such attraction to a magnetic field is called paramagnetism, and it arises in molecules that have unpaired electrons. And yet, the Lewis structure of O_2 indicates that all electrons are paired. How do we account for this discrepancy?

Magnetic susceptibility measures the force experienced by a substance in a magnetic field. When we compare the weight of a sample to the weight measured in a magnetic field (Figure 2.4.1), paramagnetic samples that are attracted to the magnet will appear heavier because of the force exerted by the magnetic field. We can calculate the number of unpaired electrons based on the increase in weight.

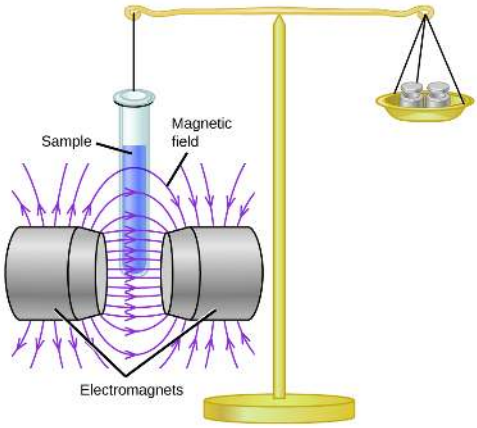


Figure 2.4.1: *A Gouy balance compares the mass of a sample in the presence of a magnetic field with the mass with the electromagnet turned off to determine the number of unpaired electrons in a sample.*

Experiments show that each O_2 molecule has two unpaired electrons. The Lewis-structure model does not predict the presence of these two unpaired electrons. Unlike oxygen, the apparent weight of most molecules decreases slightly in the presence of an inhomogeneous magnetic field. Materials in which all of the electrons are paired are diamagnetic and weakly repel a magnetic field. Paramagnetic and diamagnetic materials do not act as permanent magnets. Only in the presence of an applied magnetic field do they demonstrate attraction or repulsion.



***Video* 2.4.1**: *Water, like most molecules, contains all paired electrons. Living things contain a large percentage of water, so they demonstrate diamagnetic behavior. If you place a frog near a sufficiently large magnet, it will levitate. You can see videos of diamagnetic floating frogs, strawberries, and more (https://www.youtube.com/watch?v=A1vyB-O5i6E)*

Molecular orbital theory (MO theory) provides an explanation of chemical bonding that accounts for the paramagnetism of the oxygen molecule. It also explains the bonding in a number of other molecules, such as violations of the octet rule and more molecules with more complicated bonding (beyond the scope of this text) that are difficult to describe with Lewis structures. Additionally, it provides a model for describing the energies of electrons in a molecule and the probable location of these electrons. Unlike valence bond theory, which uses hybrid orbitals that are assigned to one specific atom, MO theory uses the combination of atomic orbitals to yield molecular orbitals that are delocalized over the entire molecule rather than being localized on its constituent atoms. MO theory also helps us understand why some substances are electrical conductors, others are semiconductors, and still others are insulators. Table 2.4.1 summarizes the main points of the two complementary bonding theories. Both theories provide different, useful ways of describing molecular structure.

***Table* 2.4.1**: *Comparison of Bonding Theories*

Valence Bond Theory	Molecular Orbital Theory
considers bonds as localized between one pair of atoms	considers electrons delocalized throughout the entire molecule
creates bonds from overlap of atomic orbitals (*s*, *p*, *d*…) and hybrid orbitals (*sp*, sp^2, sp^3…)	combines atomic orbitals to form molecular orbitals (σ, σ*, π, π*)
forms σ or π bonds	creates bonding and antibonding interactions based on which orbitals are filled
predicts molecular shape based on the number of regions of electron density	predicts the arrangement of electrons in molecules
needs multiple structures to describe resonance	

Molecular orbital theory describes the distribution of electrons in molecules in much the same way that the distribution of electrons in atoms is described using atomic orbitals. Using quantum mechanics, the behavior of an electron in a molecule is still described by a wave function, Ψ, analogous to the behavior in an atom. Just like electrons around isolated atoms, electrons around atoms in molecules are limited to discrete (quantized) energies. The region of space in which a valence electron in a molecule is likely to be found is called a molecular orbital (Ψ^2). Like an atomic orbital, a molecular orbital is full when it contains two electrons with opposite spin.

We will consider the molecular orbitals in molecules composed of two identical atoms (H_2 or Cl_2, for example). Such molecules are called homonuclear diatomic molecules. In these diatomic molecules, several types of molecular orbitals occur.

The mathematical process of combining atomic orbitals to generate molecular orbitals is called the linear combination of atomic orbitals (LCAO). The wave function describes the wavelike properties of an electron. Molecular orbitals are combinations of atomic orbital wave functions. Combining waves can lead to constructive interference, in which peaks line up with peaks, or

destructive interference, in which peaks line up with troughs (Figure 2.4.2). In orbitals, the waves are three dimensional, and they combine with in-phase waves producing regions with a higher probability of electron density and out-of-phase waves producing nodes, or regions of no electron density.



***Figure* 2.4.2:** *(a) When in-phase waves combine, constructive interference produces a wave with greater amplitude. (b) When out-of-phase waves combine, destructive interference produces a wave with less (or no) amplitude.*

There are two types of molecular orbitals that can form from the overlap of two atomic *s* orbitals on adjacent atoms. The two types are illustrated in Figure 8.4.3. The in-phase combination produces a lower energy σ_s molecular orbital (read as "sigma-s") in which most of the electron density is directly between the nuclei. The out-of-phase addition (which can also be thought of as subtracting the wave functions) produces a higher energy σ_s^* molecular orbital (read as "sigma-s-star") molecular orbital in which there is a node between the nuclei. The asterisk signifies that the orbital is an antibonding orbital. Electrons in a σ_s orbital are attracted by both nuclei at the same time and are more stable (of lower energy) than they would be in the isolated atoms. Adding electrons to these orbitals creates a force that holds the two nuclei together, so we call these orbitals bonding orbitals. Electrons in the σ_s^* orbitals are located well away from the region between the two nuclei. The attractive force between the nuclei and these electrons pulls the two nuclei apart. Hence, these orbitals are called antibonding orbitals. Electrons fill the lower-energy bonding orbital before the higher-energy antibonding orbital, just as they fill lower-energy atomic orbitals before they fill higher-energy atomic orbitals.

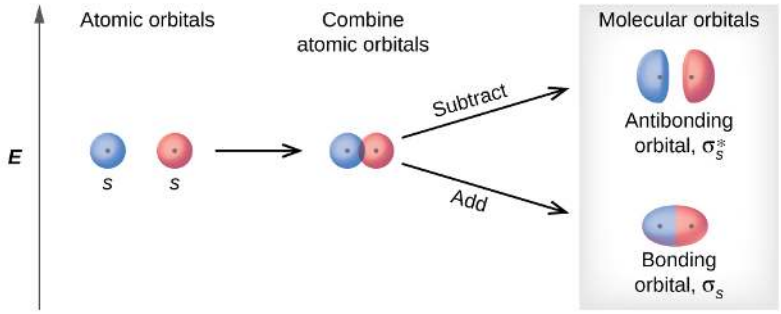


***Figure* 2.4.3:** *Sigma (σ) and sigma-star (σ*) molecular orbitals are formed by the combination of two s atomic orbitals. The plus (+) signs indicate the locations of nuclei.*

In *p* orbitals, the wave function gives rise to two lobes with opposite phases, analogous to how a two-dimensional wave has both parts above and below the average. We indicate the phases by shading the orbital lobes different colors. When orbital lobes of the same phase overlap, constructive wave interference increases the electron density. When regions of opposite phase overlap, the destructive wave interference decreases electron density and creates nodes. When *p* orbitals overlap end to end, they create σ and σ* orbitals (Figure 2.4.4). If two atoms are located along the *x*-axis in a Cartesian coordinate system, the two p_x orbitals overlap end to end and form σ_{px} (bonding) and σ_{px}^* (antibonding) (read as "sigma-p-x" and "sigma-p-x star," respectively). Just as with *s*-orbital overlap, the asterisk indicates the orbital with a node between the nuclei, which is a higher-energy, antibonding orbital.

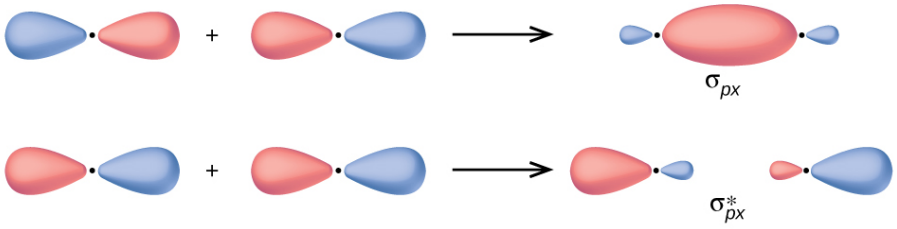


***Figure* 2.4.4:** Combining wave functions of two *p* atomic orbitals along the internuclear axis creates two molecular orbitals, σ_p and σ_p^*.

The side-by-side overlap of two *p* orbitals gives rise to a pi (π) bonding molecular orbital and a π* antibonding molecular orbital, as shown in Figure 2.4.5. In valence bond theory, we describe π bonds as containing a nodal plane containing the internuclear axis and perpendicular to the lobes of the *p* orbitals, with electron density on either side of the node. In molecular orbital theory, we describe the π orbital by this same shape, and a π bond exists when this orbital contains electrons. Electrons in this orbital interact with both nuclei and help hold the two atoms together, making it a bonding orbital. For the out-of-phase combination, there are two nodal planes created, one along the internuclear axis and a perpendicular one between the nuclei.

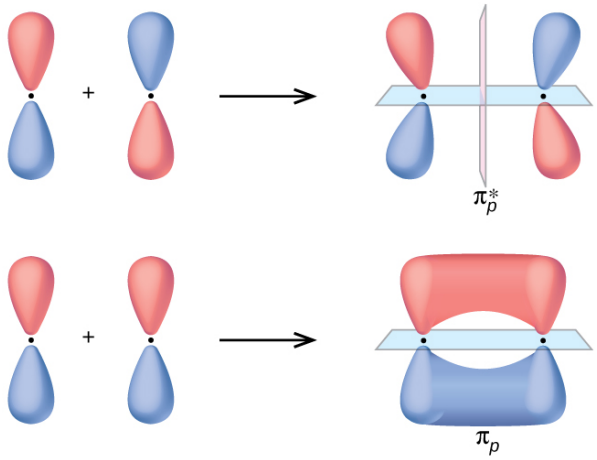
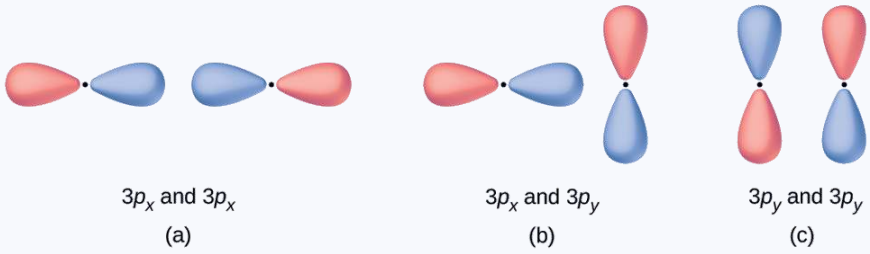


Figure* 2.4.5*: *Side-by-side overlap of each two p orbitals results in the formation of two π molecular orbitals. Combining the out-of-phase orbitals results in an antibonding molecular orbital with two nodes. One contains the internuclear axis, and one is perpendicular to the axis. Combining the in-phase orbitals results in a bonding orbital. There is a node (blue plane) containing the internuclear axis with the two lobes of the orbital located above and below this node.*

In the molecular orbitals of diatomic molecules, each atom also has two sets of *p* orbitals oriented side by side (p_y and p_z), so these four atomic orbitals combine pairwise to create two π orbitals and two π* orbitals. The π_{py} and π_{py}^* orbitals are oriented at right angles to the π_{pz} and π_{pz}^* orbitals. Except for their orientation, the π_{py} and π_{pz} orbitals are identical and have the same energy; they are degenerate orbitals. The π_{py}^* and π_{pz}^* antibonding orbitals are also degenerate and identical except for their orientation. A total of six molecular orbitals results from the combination of the six atomic *p* orbitals in two atoms: σ_{px} and σ_{px}^*, π_{py} and π_{py}^*, π_{pz} and π_{pz}^*.

Example 2.4.1

Molecular Orbitals Predict what type (if any) of molecular orbital would result from adding the wave functions so each pair of orbitals shown overlap. The orbitals are all similar in energy.



Solution

a. This is an in-phase combination, resulting in a σ_{3p} orbital
b. This will not result in a new orbital because the in-phase component (bottom) and out-of-phase component (top) cancel out. Only orbitals with the correct alignment can combine.
c. This is an out-of-phase combination, resulting in a π_{3p}^* orbital.

Exercise 2.4.1

Label the molecular orbital shown as σ or π, bonding or antibonding and indicate where the node occurs.



Answer

The orbital is located along the internuclear axis, so it is a σ orbital. There is a node bisecting the internuclear axis, so it is an antibonding orbital.



Application: Computational Chemistry in Drug Design

While the descriptions of bonding described in this chapter involve many theoretical concepts, they also have many practical, real-world applications. For example, drug design is an important field that uses our understanding of chemical bonding to develop pharmaceuticals. This interdisciplinary area of study uses biology (understanding diseases and how they operate) to identify specific targets, such as a binding site that is involved in a disease pathway. By modeling the structures of the binding site and potential drugs, computational chemists can predict which structures can fit together and how effectively they will bind (Figure 2.4.6). Thousands of potential candidates can be narrowed down to a few of the most promising candidates. These candidate molecules are then carefully tested to determine side effects, how effectively they can be transported through the body, and other factors. Dozens of important new pharmaceuticals have been discovered with the aid of computational chemistry, and new research projects are underway.

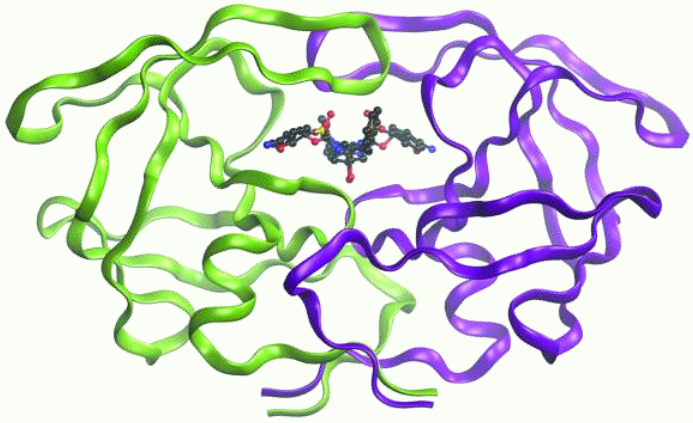


Figure 2.4.6: *The molecule shown, HIV-1 protease, is an important target for pharmaceutical research. By designing molecules that bind to this protein, scientists are able to drastically inhibit the progress of the disease.*

Molecular Orbital Energy Diagrams

The relative energy levels of atomic and molecular orbitals are typically shown in a molecular orbital diagram (Figure 2.4.7). For a diatomic molecule, the atomic orbitals of one atom are shown on the left, and those of the other atom are shown on the right. Each horizontal line represents one orbital that can hold two electrons. The molecular orbitals formed by the combination of the atomic orbitals are shown in the center. Dashed lines show which of the atomic orbitals combine to form the molecular orbitals. For each pair of atomic orbitals that combine, one lower-energy (bonding) molecular orbital and one higher-energy (antibonding) orbital result. Thus we can see that combining the six 2*p* atomic orbitals results in three bonding orbitals (one σ and two π) and three antibonding orbitals (one σ* and two π*).

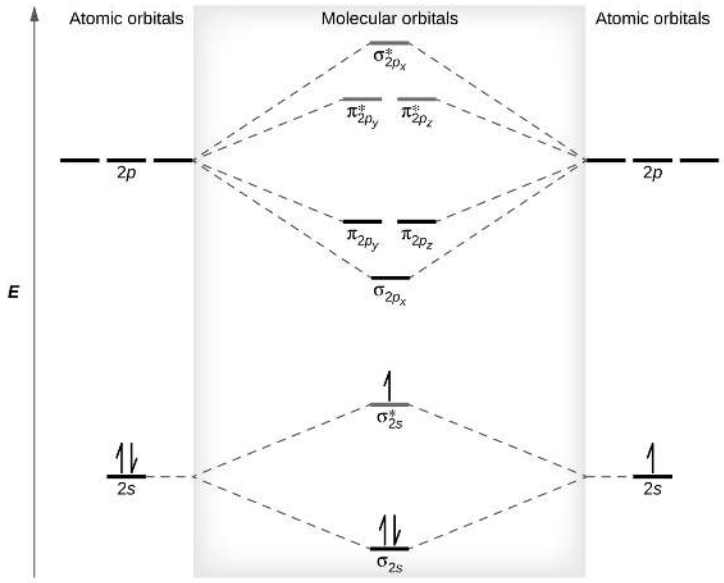


Figure 2.4.7*: This is the molecular orbital diagram for the homonuclear diatomic* Be_2^+*, showing the molecular orbitals of the valence shell only. The molecular orbitals are filled in the same manner as atomic orbitals, using the Aufbau principle and Hund's rule.*

We predict the distribution of electrons in these molecular orbitals by filling the orbitals in the same way that we fill atomic orbitals, by the Aufbau principle. Lower-energy orbitals fill first, electrons spread out among degenerate orbitals before pairing, and each orbital can hold a maximum of two electrons with opposite spins (Figure 2.4.7). Just as we write electron configurations for atoms, we can write the molecular electronic configuration by listing the orbitals with superscripts indicating the number of electrons present. For clarity, we place parentheses around molecular orbitals with the same energy. In this case, each orbital is at a different energy, so parentheses separate each orbital. Thus we would expect a diatomic molecule or ion containing seven electrons (such as Be_2^+) would have the molecular electron configuration $(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^1$. It is common to omit the core electrons from molecular orbital diagrams and configurations and include only the valence electrons.

Bond Order

The filled molecular orbital diagram shows the number of electrons in both bonding and antibonding molecular orbitals. The net contribution of the electrons to the bond strength of a molecule is identified by determining the bond order that results from the filling of the molecular orbitals by electrons.

When using Lewis structures to describe the distribution of electrons in molecules, we define bond order as the number of bonding pairs of electrons between two atoms. Thus a single bond has a bond order of 1, a double bond has a bond order of 2, and a triple bond has a bond order of 3. We define bond order differently when we use the molecular orbital description of the distribution of electrons, but the resulting bond order is usually the same. The MO technique is more accurate and can handle cases when the Lewis structure method fails, but both methods describe the same phenomenon.

In the molecular orbital model, an electron contributes to a bonding interaction if it occupies a bonding orbital and it contributes to an antibonding interaction if it occupies an antibonding orbital. The bond order is calculated by subtracting the destabilizing (antibonding) electrons from the stabilizing (bonding) electrons. Since a bond consists of two electrons, we divide by two to get the bond order. We can determine bond order with the following equation:

$$\text{bond order} = \frac{(\text{number of bonding electrons}) - (\text{number of antibonding electrons})}{2} \tag{2.4.1}$$

The order of a covalent bond is a guide to its strength; a bond between two given atoms becomes stronger as the bond order increases. If the distribution of electrons in the molecular orbitals between two atoms is such that the resulting bond would have a bond order of zero, a stable bond does not form. We next look at some specific examples of MO diagrams and bond orders.

Bonding in Diatomic Molecules

A dihydrogen molecule (H_2) forms from two hydrogen atoms. When the atomic orbitals of the two atoms combine, the electrons occupy the molecular orbital of lowest energy, the σ_{1s} bonding orbital. A dihydrogen molecule, H_2, readily forms because the energy of a H_2 molecule is lower than that of two H atoms. The σ_{1s} orbital that contains both electrons is lower in energy than either of the two 1*s* atomic orbitals.

A molecular orbital can hold two electrons, so both electrons in the H_2 molecule are in the σ_{1s} bonding orbital; the electron configuration is $(\sigma_{1s})^2$. We represent this configuration by a molecular orbital energy diagram (Figure 2.4.8) in which a single upward arrow indicates one electron in an orbital, and two (upward and downward) arrows indicate two electrons of opposite spin.

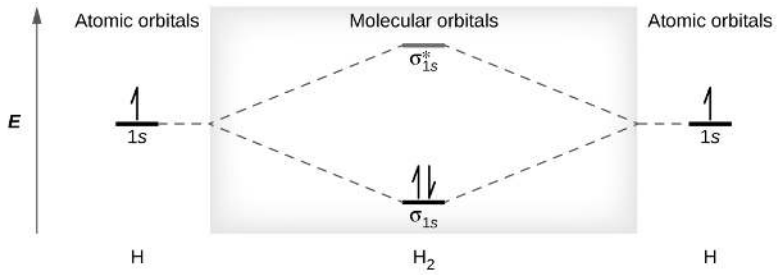


***Figure* 2.4.8**:*The molecular orbital energy diagram predicts that H_2 will be a stable molecule with lower energy than the separated atoms.*

A dihydrogen molecule contains two bonding electrons and no antibonding electrons so we have

$$\text{bond order in } H_2 = \frac{(2-0)}{2} = 1 \tag{2.4.2}$$

Because the bond order for the H–H bond is equal to 1, the bond is a single bond.

A helium atom has two electrons, both of which are in its 1*s* orbital. Two helium atoms do not combine to form a dihelium molecule, He_2, with four electrons, because the stabilizing effect of the two electrons in the lower-energy bonding orbital would be offset by the destabilizing effect of the two electrons in the higher-energy antibonding molecular orbital. We would write the hypothetical electron configuration of He_2 as $(\sigma_{1s})^2(\sigma^*_{1s})^2$ as in Figure 2.4.9. The net energy change would be zero, so there is no driving force for helium atoms to form the diatomic molecule. In fact, helium exists as discrete atoms rather than as diatomic molecules. The bond order in a hypothetical dihelium molecule would be zero.

$$\text{bond order in } He_2 = \frac{(2-2)}{2} = 0 \tag{2.4.3}$$

A bond order of zero indicates that no bond is formed between two atoms.

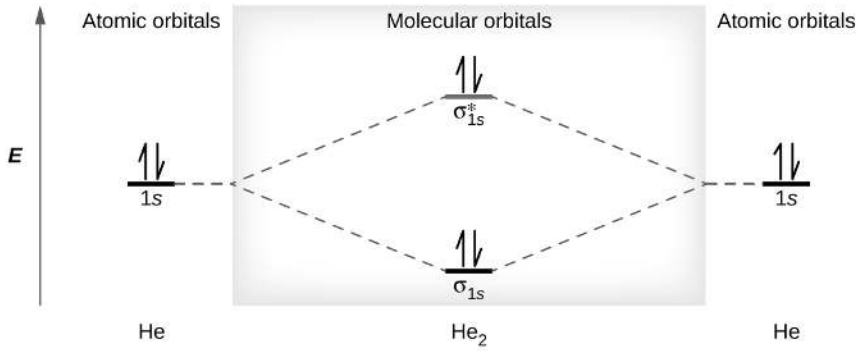


***Figure* 2.4.9**: *The molecular orbital energy diagram predicts that He_2 will not be a stable molecule, since it has equal numbers of bonding and antibonding electrons.*

The Diatomic Molecules of the Second Period

Eight possible homonuclear diatomic molecules might be formed by the atoms of the second period of the periodic table: Li_2, Be_2, B_2, C_2, N_2, O_2, F_2, and Ne_2. However, we can predict that the Be_2 molecule and the Ne_2 molecule would not be stable. We can see this by a consideration of the molecular electron configurations (Table 2.4.1).

***Table* 2.4.1**: *Electron Configuration and Bond Order for Molecular Orbitals in Homonuclear Diatomic Molecules of Period Two Elements*

Molecule	Electron Configuration	Bond Order
Li_2	$(\sigma_{2s})^2$	1
Be_2 (unstable)	$(\sigma_{2s})^2(\sigma^*_{2s})^2$	0
B_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py},\ \pi_{2pz})^2$	1
C_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py},\ \pi_{2pz})^4$	2
N_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2py},\ \pi_{2pz})^4(\sigma_{2px})^2$	3
O_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2px})^2(\pi_{2py},\ \pi_{2pz})^4(\pi^*_{2py},\pi^*_{2pz})^2$	2
F_2	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2px})^2(\pi_{2py},\ \pi_{2pz})^4(\pi^*_{2py},\ \pi^*_{2pz})^4$	1
Ne_2 (unstable)	$(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2px})^2(\pi_{2py},\ \pi_{2pz})^4(\pi^*_{2py},\pi^*_{2pz})^4(\sigma^*_{2px})^2$	0

We predict valence molecular orbital electron configurations just as we predict electron configurations of atoms. Valence electrons are assigned to valence molecular orbitals with the lowest possible energies. Consistent with Hund's rule, whenever there are two or more degenerate molecular orbitals, electrons fill each orbital of that type singly before any pairing of electrons takes place.

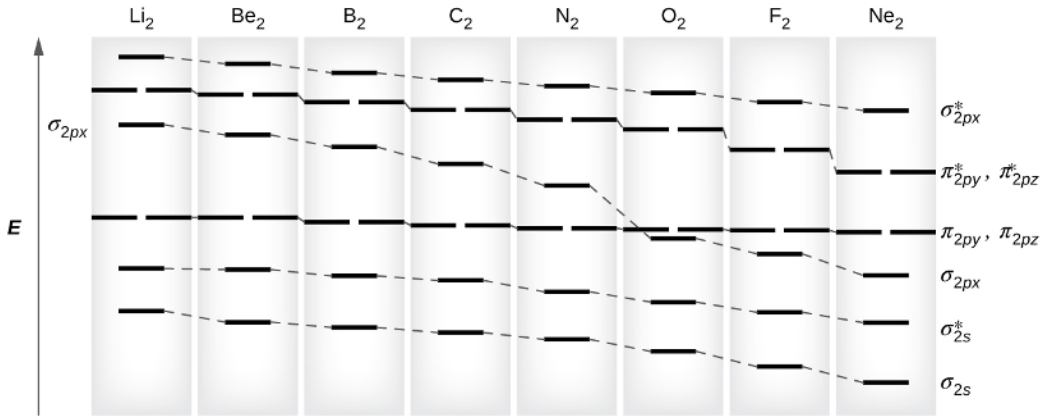


***Figure* 2.4.10**: *This shows the MO diagrams for each homonuclear diatomic molecule in the second period. The orbital energies decrease across the period as the effective nuclear charge increases and atomic radius decreases. Between N_2 and O_2, the order of the orbitals changes.*

As we saw in valence bond theory, σ bonds are generally more stable than π bonds formed from degenerate atomic orbitals. Similarly, in molecular orbital theory, σ orbitals are usually more stable than π orbitals. However, this is not always the case. The MOs for the valence orbitals of the second period are shown in Figure 2.4.10. Looking at Ne_2 molecular orbitals, we see that the order is consistent with the generic diagram shown in the previous section. However, for atoms with three or fewer electrons in the *p* orbitals (Li through N) we observe a different pattern, in which the σ_p orbital is higher in energy than the π_p set. Obtain the molecular orbital diagram for a homonuclear diatomic ion by adding or subtracting electrons from the diagram for the neutral molecule.

This switch in orbital ordering occurs because of a phenomenon called s-p mixing. s-p mixing does not create new orbitals; it merely influences the energies of the existing molecular orbitals. The σ_s wavefunction mathematically combines with the σ_p wavefunction, with the result that the σ_s orbital becomes more stable, and the σ_p orbital becomes less stable (Figure 2.4.11). Similarly, the antibonding orbitals also undergo s-p mixing, with the σ_{s*} becoming more stable and the σ_{p*} becoming less stable.

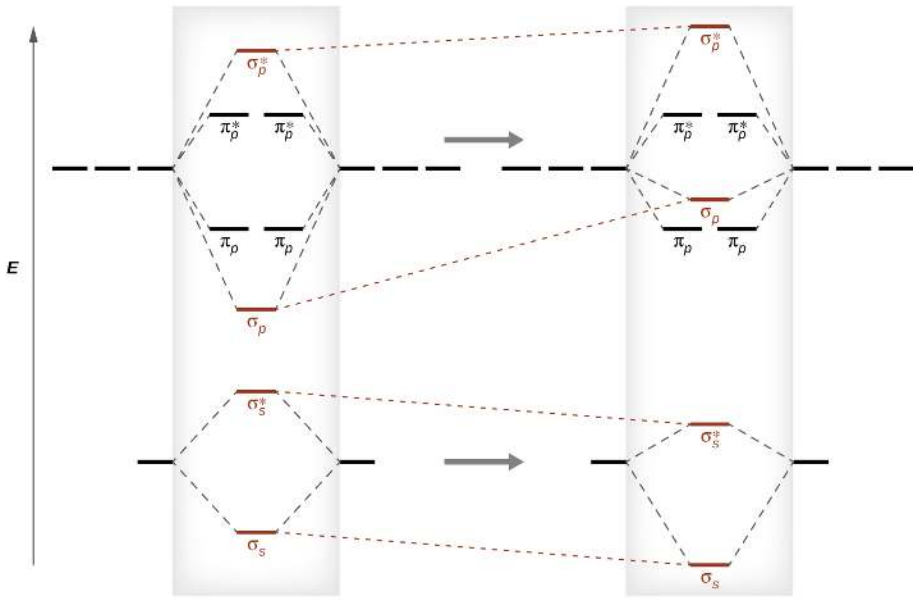


***Figure* 2.4.11**: *Without mixing, the MO pattern occurs as expected, with the σ_p orbital lower in energy than the σ_p orbitals. When s-p mixing occurs, the orbitals shift as shown, with the σ_p orbital higher in energy than the π_p orbitals.*

s-p mixing occurs when the *s* and *p* orbitals have similar energies. The energy difference between 2*s* and 2*p* orbitals in O, F, and Ne is greater than that in Li, Be, B, C, and N. Because of this, O_2, F_2, and Ne exhibit negligible s-p mixing (not sufficient to change the energy ordering), and their MO diagrams follow the normal pattern, as shown in Figure 2.4.7. All of the other period 2 diatomic molecules do have s-p mixing, which leads to the pattern where the σ_p orbital is raised above the π_p set.

Using the MO diagrams shown in Figure 2.4.11, we can add in the electrons and determine the molecular electron configuration and bond order for each of the diatomic molecules. As shown in Table 2.4.1, Be_2 and Ne_2 molecules would have a bond order of 0, and these molecules do not exist.

The combination of two lithium atoms to form a lithium molecule, Li_2, is analogous to the formation of H_2, but the atomic orbitals involved are the valence 2*s* orbitals. Each of the two lithium atoms has one valence electron. Hence, we have two valence electrons available for the σ_{2s} bonding molecular orbital. Because both valence electrons would be in a bonding orbital, we would predict the Li_2 molecule to be stable. The molecule is, in fact, present in appreciable concentration in lithium vapor at temperatures near the boiling point of the element. All of the other molecules in Table 2.4.1 with a bond order greater than zero are also known.

The O_2 molecule has enough electrons to half fill the $(\pi^*_{2py}, \pi^*_{2pz})$ level. We expect the two electrons that occupy these two degenerate orbitals to be unpaired, and this molecular electronic configuration for O_2 is in accord with the fact that the oxygen molecule has two unpaired electrons (Figure 2.4.10). The presence of two unpaired electrons has proved to be difficult to explain using Lewis structures, but the molecular orbital theory explains it quite well. In fact, the unpaired electrons of the oxygen molecule provide a strong piece of support for the molecular orbital theory.

Application: Band Theory in Extended Systems

When two identical atomic orbitals on different atoms combine, two molecular orbitals result (e.g., H_2 in Figure 2.4.8). The bonding orbital is lower in energy than the original atomic orbitals because the atomic orbitals are in-phase in the molecular orbital. The antibonding orbital is higher in energy than the original atomic orbitals because the atomic orbitals are out-of-phase.

In a solid, similar things happen, but on a much larger scale. Remember that even in a small sample there are a huge number of atoms (typically > 10^{23} atoms), and therefore a huge number of atomic orbitals that may be combined into molecular orbitals. When *N* valence atomic orbitals, all of the same energy and each containing one (1) electron, are combined, *N*/2 (filled) bonding orbitals and *N*/2 (empty) antibonding orbitals will result. Each bonding orbital will show an energy lowering as the atomic orbitals are *mostly* in-phase, but each of the bonding orbitals will be a little different and have slightly different energies. The antibonding orbitals will show an increase in energy as the atomic orbitals are *mostly* out-of-phase, but each of the antibonding orbitals will also be a little different and have slightly different energies. The allowed energy levels for all the bonding orbitals are so close together that they form a band, called the valence band. Likewise, all the antibonding orbitals are very close

together and form a band, called the conduction band. Figure 2.4.12) shows the bands for three important classes of materials: insulators, semiconductors, and conductors.

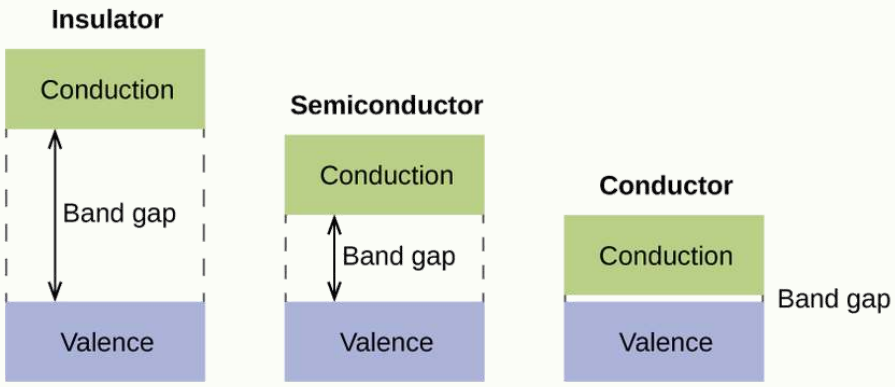


***Figure* 2.4.12**: *Molecular orbitals in solids are so closely spaced that they are described as bands. The valence band is lower in energy and the conduction band is higher in energy. The type of solid is determined by the size of the "band gap" between the valence and conduction bands. Only a very small amount of energy is required to move electrons from the valence band to the conduction band in a conductor, and so they conduct electricity well. In an insulator, the band gap is large, so that very few electrons move, and they are poor conductors of electricity. Semiconductors are in between: they conduct electricity better than insulators, but not as well as conductors.*

In order to conduct electricity, electrons must move from the filled valence band to the empty conduction band where they can move throughout the solid. The size of the band gap, or the energy difference between the top of the valence band and the bottom of the conduction band, determines how easy it is to move electrons between the bands. Only a small amount of energy is required in a conductor because the band gap is very small. This small energy difference is "easy" to overcome, so they are good conductors of electricity. In an insulator, the band gap is so "large" that very few electrons move into the conduction band; as a result, insulators are poor conductors of electricity. Semiconductors conduct electricity when "moderate" amounts of energy are provided to move electrons out of the valence band and into the conduction band. Semiconductors, such as silicon, are found in many electronics.

Semiconductors are used in devices such as computers, smartphones, and solar cells. Solar cells produce electricity when light provides the energy to move electrons out of the valence band. The electricity that is generated may then be used to power a light or tool, or it can be stored for later use by charging a battery. As of December 2014, up to 46% of the energy in sunlight could be converted into electricity using solar cells.

Example 2.4.2: Molecular Orbital Diagrams, Bond Order, and Number of Unpaired Electrons

Draw the molecular orbital diagram for the oxygen molecule, O_2. From this diagram, calculate the bond order for O_2. How does this diagram account for the paramagnetism of O_2?

Solution

We draw a molecular orbital energy diagram similar to that shown in Figure 2.4.7. Each oxygen atom contributes six electrons, so the diagram appears as shown in Figure 2.4.7.

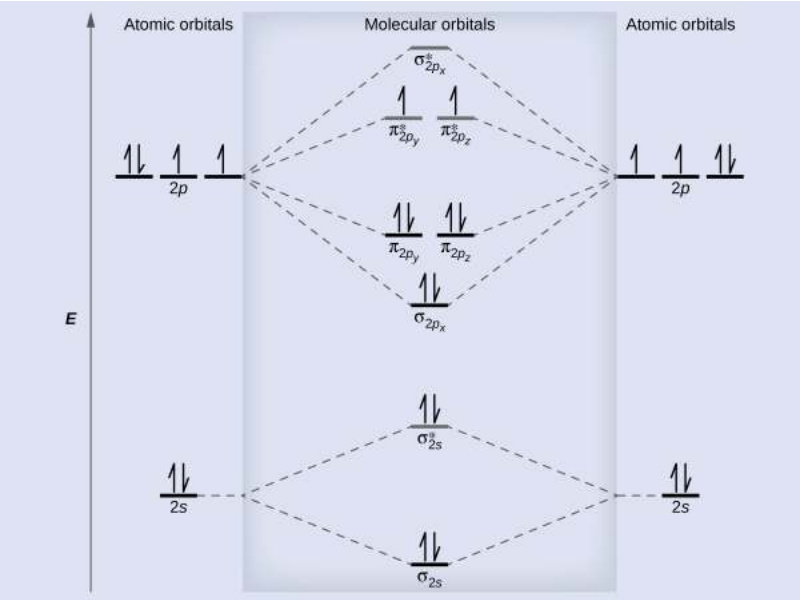


***Figure* 2.4.13**: *The molecular orbital energy diagram for O_2 predicts two unpaired electrons.*

We calculate the bond order as

$$\mathrm{O_2} = \frac{(8-4)}{2} = 2 \tag{2.4.4}$$

Oxygen's paramagnetism is explained by the presence of two unpaired electrons in the (π_{2py}, π_{2pz})* molecular orbitals.

Exercise 2.4.2

The main component of air is N_2. From the molecular orbital diagram of N_2, predict its bond order and whether it is diamagnetic or paramagnetic.

Answer

N_2 has a bond order of 3 and is diamagnetic.

Example 2.4.3: Ion Predictions with MO Diagrams

Give the molecular orbital configuration for the valence electrons in C_2^{2-}. Will this ion be stable?

Solution

Looking at the appropriate MO diagram, we see that the π orbitals are lower in energy than the σ_p orbital. The valence electron configuration for C_2 is

$$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2py},\ \pi_{2pz})^4.$$

Adding two more electrons to generate the C_2^{2-} anion will give a valence electron configuration of

$$(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2py},\ \pi_{2pz})^4(\sigma_{2px})^2$$

Since this has six more bonding electrons than antibonding, the bond order will be 3, and the ion should be stable.

Exercise 2.4.3

How many unpaired electrons would be present on a Be_2^{2-} ion? Would it be paramagnetic or diamagnetic?

Answer

two, paramagnetic

Key Concepts and Summary

Molecular orbital (MO) theory describes the behavior of electrons in a molecule in terms of combinations of the atomic wave functions. The resulting molecular orbitals may extend over all the atoms in the molecule. Bonding molecular orbitals are formed by in-phase combinations of atomic wave functions, and electrons in these orbitals stabilize a molecule. Antibonding molecular orbitals result from out-of-phase combinations of atomic wave functions and electrons in these orbitals make a molecule less stable. Molecular orbitals located along an internuclear axis are called σ MOs. They can be formed from *s* orbitals or from *p* orbitals oriented in an end-to-end fashion. Molecular orbitals formed from *p* orbitals oriented in a side-by-side fashion have electron density on opposite sides of the internuclear axis and are called π orbitals.

We can describe the electronic structure of diatomic molecules by applying molecular orbital theory to the valence electrons of the atoms. Electrons fill molecular orbitals following the same rules that apply to filling atomic orbitals; Hund's rule and the Aufbau principle tell us that lower-energy orbitals will fill first, electrons will spread out before they pair up, and each orbital can hold a maximum of two electrons with opposite spins. Materials with unpaired electrons are paramagnetic and attracted to a magnetic field, while those with all-paired electrons are diamagnetic and repelled by a magnetic field. Correctly predicting the magnetic properties of molecules is in advantage of molecular orbital theory over Lewis structures and valence bond theory.

Contributors

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2.5: Constructing Molecular Orbitals from Atomic Orbitals

Molecular orbital theory involves solving (approximately) the Schrödinger equation for the electrons in a molecule. To review from Chapter 1, this is a differential equation in which the first and second terms on the right represent the kinetic and potential energies:

$$E\psi = -\frac{\hbar^2}{2\mu}\nabla^2\psi + V\psi \tag{2.5.1}$$

While the Schrödinger equation can be solved analytically for the hydrogen atom, the potential energy function V becomes more complicated - and the equation can then only be solved numerically - when there are many (mutually repulsive) electrons in a molecule. So as a first approximation we will assume that the s, p, d, f, etc. orbitals of the atoms that make up the molecule are good solutions to the Schrödinger equation. We can then allow these wavefunctions to interfere constructively and destructively as we bring the atoms together to make bonds. In this way, we use the atomic orbitals (AO) as our basis for constructing MO's.

LCAO-MO = **linear combination of atomic orbitals.** In physics, this is called this the tight binding approximation.

We have actually seen linear combinations of atomic orbitals before when we constructed hybrid orbitals in Chapter 1. The basic rules we developed for hybridization also apply here: orbitals are added with scalar coefficients (c) in such a way that the resulting orbitals are **orthogonal** and **normalized**. The difference is that in the MO case, the atomic orbitals come from different atoms.

The linear combination of atomic orbitals always gives back the *same number of molecular orbitals.* So if we start with two atomic orbitals (e.g., an s and a p_z orbital as shown in Fig. 2.5.1), we end up with two molecular orbitals. When atomic orbitals add in phase, we get constructive interference and a lower energy orbital. When they add out of phase, we get a node and the resulting orbital has higher energy. The lower energy MOs are *bonding* and higher energy MOs are *antibonding.*

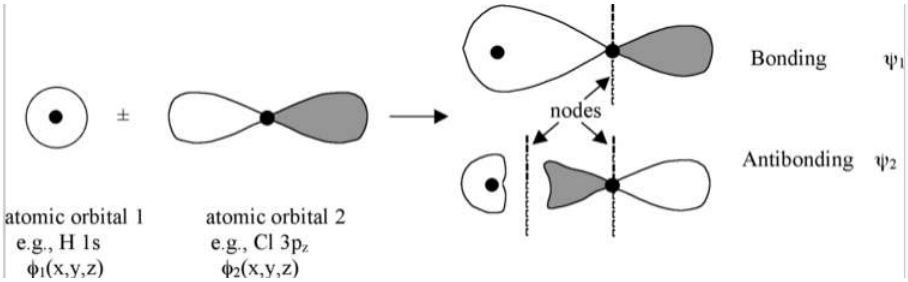


Figure 2.5.1: Sigma bonding and antibonding combinations of an s and p orbital

Molecular orbitals are also called **wavefunctions** (ψ), because they are solutions to the Schrödinger equation for the molecule. The atomic orbitals (also called basis functions) are labeled as φ's, for example, φ_{1s} and φ_{3pz} or simply as $\varphi_1$and φ_2.

In principle, we need to solve the Schrödinger equation for all the orbitals in a molecule, and then fill them up with pairs of electrons as we do for the orbitals in atoms. In practice we are really interested only in the MOs that derive from the valence orbitals of the constituent atoms, because these are the orbitals that are involved in bonding. We are especially interested in the **frontier orbitals**, i.e., the highest occupied molecular orbital (the **HOMO**) and the lowest unoccupied molecular orbital (the **LUMO**). Filled orbitals that are much lower in energy (i.e., core orbitals) do not contribute to bonding, and empty orbitals at higher energy likewise do not contribute. Those orbitals are however important in photochemistry and spectroscopy, which involve electronic transitions from occupied to empty orbitals. The fluorescent dyes that stain the cells shown in Fig. 2.5.2 absorb light by promoting electrons in the HOMO to empty MOs and give off light when the electrons drop back down to their original energy levels.

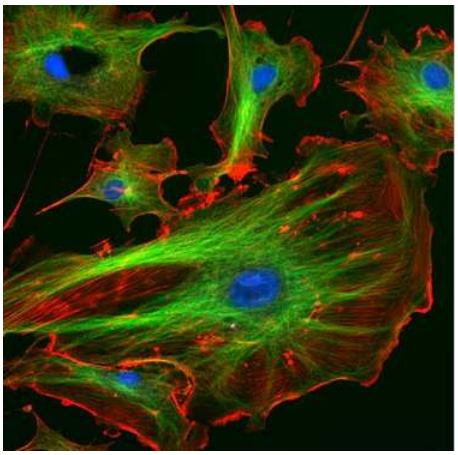


Figure 2.5.2: Different components of endothelial cells are stained by blue, green, and red fluorescent dyes. For each dye the color of emitted light corresponds to the energy given off when an electron drops from the LUMO to the HOMO of the molecule.

As an example of the LCAO-MO approach we can construct two MO's (ψ_1 and ψ_2) of the HCl molecule from two AO's $\varphi_1$and φ_2 (Fig. 2.1.1). To make these two linear combinations, we write:

$$\Psi_1 = c_1\varphi_1 + c_2\varphi_2 \tag{2.5.2}$$

and

$$\Psi_2 = c_1\varphi_1 - c_2\varphi_2 \tag{2.5.3}$$

The coefficients c_1 and c_2 will be equal (or nearly so) when the two AOs from which they are constructed are the same, e.g., when two hydrogen 1s orbitals combine to make bonding and antibonding MOs in H_2. They will be unequal when there is an energy difference between the AOs, for example when a hydrogen 1s orbital and a chlorine 3p orbital combine to make a polar H-Cl bond.

Nodes:

The wavefunctions φ and ψ are **amplitudes** that are related to the probability of finding the electron at some point in space. They have lobes with (+) or (-) signs, which we indicate by shading or color. Wherever the wavefunction changes sign we have a node. As you can see in Fig. 2.5.1, nodes in MOs result from destructive interference of (+) and (-) wavefunctions. Generally, the more nodes, the higher the energy of the orbital.

In the example above we have drawn a simplified picture of the Cl $3p_z$ orbital and the resulting MOs, leaving out the radial node. Recall that 2p orbitals have no radial nodes, 3p orbitals have one, as illustrated in Fig. 2.5.3. 4p orbitals have two radial nodes, and so on. The MOs we make by combining the AOs have these nodes too.



Figure 2.5.3: Nodal structure of 2p and 3p orbitals

Normalization:

We square the wave functions to get probabilities, which are always positve or zero. So if an electron is in orbital φ_1, the probability of finding it at point xyz is the square[1] of φ_1(x,y,z). The total probability does not change when we combine AOs to make MOs, so for the simple case of combining φ_1 and φ_2 to make $\psi_1$and ψ_2,

$$\Psi_1^2 + \Psi_2^2 = \varphi_1^2 + \varphi_2^2 \tag{2.5.4}$$

Overlap integral:

The spatial overlap between two atomic orbitals φ_1 and φ_2 is described by the overlap integral S,

$$S_{12} = \int \varphi_1 * \varphi_2 d\tau \tag{2.5.5}$$

where the integration is over all space $d\tau = dxdydz$.

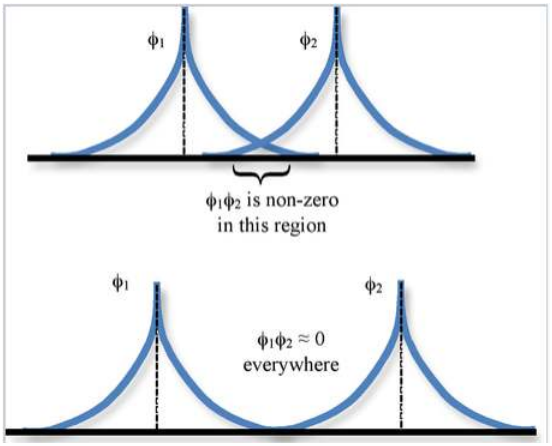


Figure 2.5.4: The wavefunctions of atomic orbitals decrease exponentially with distance. Orbital overlap is non-zero when two atoms are close together, as illustrated for 1s orbitals in the upper figure. The lower figure shows orbitals that are too far away to interact. In this case both S and β are close to zero.

Energies of bonding and antibonding MOs:

The energies of bonding and antibonding orbitals depend strongly on the distance between atoms. This is illustrated in Fig. 2.1.5 for the hydrogen molecule, H_2. At very long distances, there is essentially no difference in energy between the in-phase and out-of-phase combinations of H 1s orbitals. As they get closer, the in-phase (bonding) combination drops in energy because electrons are shared between the two positively charged nuclei. The energy reaches a minimum at the equilibrium bond distance (0.74 Å) and then rises again as the nuclei get closer together. The antibonding combination has a node between the nuclei so its energy rises continuously as the atoms are brought together.

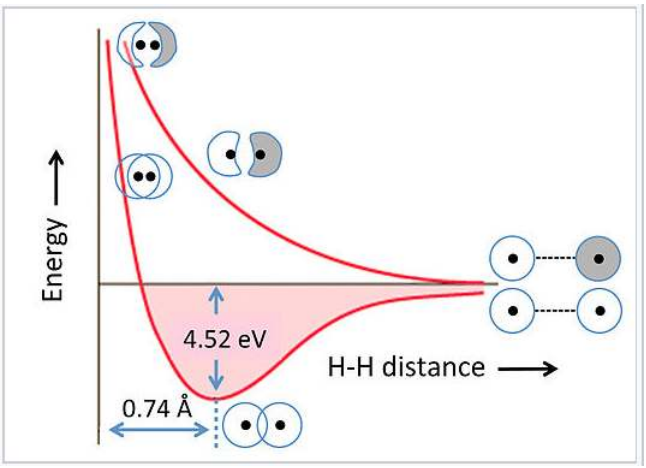


Figure 2.5.5: Energy as a function of distance for the bonding and antibonding orbitals of the H_2 molecule

At the equilibrium bond distance, the energies of the bonding and antibonding molecular orbitals (ψ_1, ψ_2) are lower and higher, respectively, than the energies of the atomic basis orbitals φ_1 and φ_2. This is shown in Fig. 2.5.6 for the MO's of the H_2 molecule.

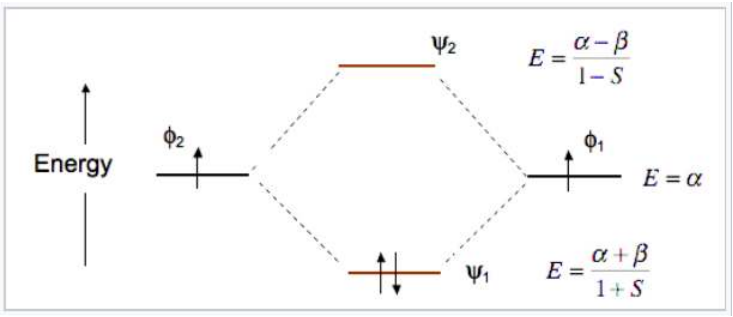


Figure 2.5.6: Molecular orbital energy diagram for the H_2 molecule

The energy of an electron in one of the atomic orbitals is α, the **Coulomb integral**.

$$\alpha = \int \varphi_1 H \varphi_1 d\tau \tag{2.5.6}$$

where **H** is the **Hamiltonian operator**. Essentially, α represents the *ionization energy* of an electron in atomic orbital φ_1 or φ_2.

The energy difference between an electron in the AO's and the MO's is determined by the **exchange integral β**,

$$\beta = \int \varphi_1 H \varphi_2 d\tau \tag{2.5.7}$$

β is an important quantity, because it tells us about the bonding energy of the molecule, and also the difference in energy between bonding and antibonding orbitals. Calculating β is not straightforward for multi-electron molecules because we cannot solve the Schrödinger equation analytically for the wavefunctions. We can however make some approximations to calculate the energies and wavefunctions numerically. In the Hückel approximation, which can be used to obtain approximate solutions for π molecular orbitals in organic molecules, we simplify the math by taking S=0 and setting H=0 for any p-orbitals that are not adjacent to each other. The extended Hückel method,[2] developed by Roald Hoffmann, and other semi-empirical methods can be used to rapidly obtain relative orbital energies, approximate wavefunctions, and degeneracies of molecular orbitals for a wide variety of molecules and extended solids. More sophisticated ab initio methods are now readily available in software packages and can be used to compute accurate orbital energies for molecules and solids.

We can get the coefficients c_1 and c_2 for the hydrogen molecule by applying the normalization criterion:

$$\Phi_1 = (\varphi_1 + \varphi_2)/(\sqrt{2(1+S)})(\text{bonding orbital}) \tag{2.5.8}$$

and

$$\Phi_2 = (\varphi_1 - \varphi_2)/(\sqrt{2(1-S)})(\text{antibonding orbital}) \tag{2.5.9}$$

In the case where S≈0, we can eliminate the 1-S terms and both coefficients become 1/√2

Note that the bonding orbital in the MO diagram of H_2 is stabilized by an energy β/1+S and the antibonding orbital is destabilized by β/1-S. That is, the antibonding orbital goes up in energy more than the bonding orbital goes down. This means that H_2 ($\psi_1^2\psi_2^0$) is energetically more stable than two H atoms, but He_2 with four electrons ($\psi_1^2\psi_2^2$) is *unstable* relative to two He atoms.

Bond order: In any MO diagram, the bond order can be calculated as ½ (# of bonding electrons - # of antibonding electrons). For H_2 the bond order is 1, and for $He_2$the bond order is zero.

Heteronuclear case (e.g., HCl) - Polar bonds

Here we introduce an electronegativity difference between the two atoms making the chemical bond. The energy of an electron in the H 1s orbital is higher (it is easier to ionize) than the electron in the chlorine $3p_z$ orbital. This results in a larger energy difference between the resulting molecular orbitals ψ_1 and ψ_2, as shown in Fig. 2.5.7. The bigger the electronegativity difference between atomic orbitals (the larger Δα is) the more "φ_2 character" the bonding orbital has, i.e., the more it resembles the Cl $3p_z$ orbital in this case. This is consistent with the idea that H-Cl has a polar single bond: the two electrons reside in a bonding molecular orbital that is primarily localized on the Cl atom.

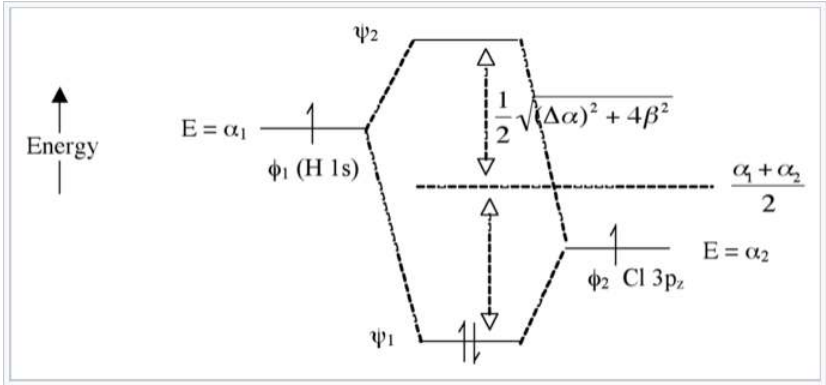


Figure 2.5.7: Molecular orbital energy diagram for the HCl molecule

The antibonding orbital (empty) has more H-character. The bond order is again 1 because there are two electrons in the bonding orbital and none in the antibonding orbital.

Extreme case - Ionic bonding (NaF): very large Δα

In this case, there is not much mixing between the AO's because their energies are far apart (Fig. 2.5.8). The two bonding electrons are localized on the F atom , so we can write the molecule as Na^+F^-. Note that if we were to excite an electron from ψ_1 to ψ_2 using light, the resulting electronic configuration would be $(\psi_1^1\psi_2^1)$ and we would have Na^0F^0. This is called a charge transfer transition.

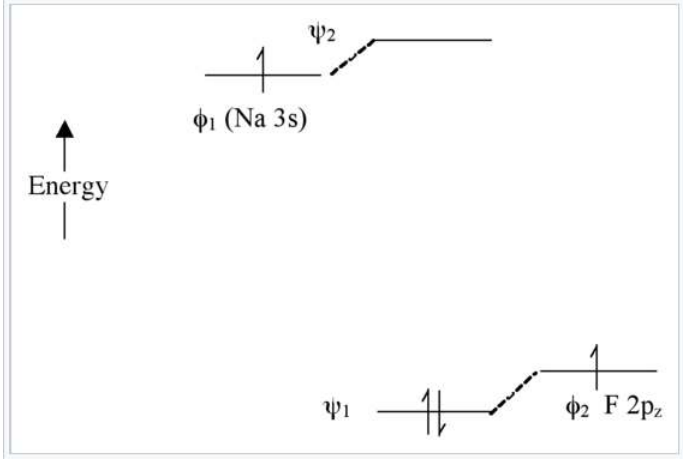


Figure 2.5.8: Molecular orbital energy diagram illustrating ionic bonding in the NaF molecule

Summary of molecular orbital theory so far:

• **Add and subtract** AO wavefunctions to make MOs. Two AOs → two MOs. More generally, the *total number of MOs equals the number of AO basis orbitals*.

• We showed the simplest case (only two basis orbitals). More accurate calculations use a much larger basis set (more AOs) and solve for the matrix of c's that gives the lowest total energy, using mathematically friendly approximations of the potential energy function that is part of the Hamiltonian operator H.

• **More nodes → higher energy** MO

• **Bond order** = ½ (# of bonding electrons - # of antibonding electrons)

• **Bond polarity** emerges in the MO picture as orbital "character."

• AOs that are **far apart in energy** do not interact much when they combine to make MOs.

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2.6: Orbital Symmetry

The MO picture for a molecule gets complicated when many valence AOs are involved. We can simplify the problem enormously by noting (without proof here) that orbitals of different symmetry with respect to the molecule do not interact. The symmetry operations of a molecule (which can include rotations, mirror planes, inversion centers, etc.), and the symmetry classes of bonds and orbitals in molecules, can be rigorously defined according to **group theory**. Here we will take a simple approach to this problem based on our intuitive understanding of the symmetry of three-dimensional objects as illustrated in Fig. 2.6.1.



Figure 2.6.1: Example of σ symmetry.

AO's must have the same **nodal symmetry** (as defined by the molecular symmetry operations), or their overlap is zero.

For example, in the HCl molecule, there is a unique symmetry axis →, which is typically defined as the Cartesian z-axis, as shown in Fig. 2.6.2.

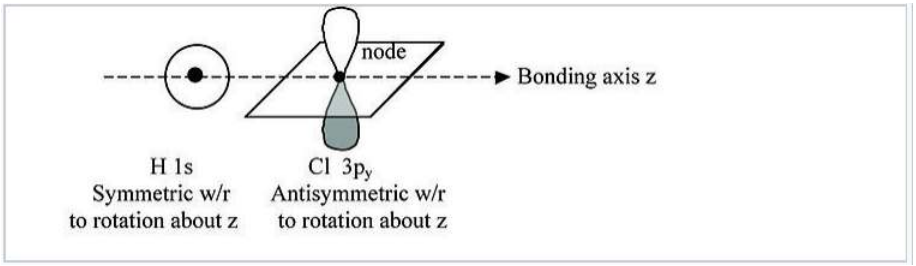


Figure 2.6.2: Orbitals of σ and π symmetry do not interact.

We can see from this figure that the H 1s orbital is unchanged by a 180° rotation about the bond axis. However, the same rotation inverts the sign of the Cl $3p_y$wavefunction. Because these two orbitals have different symmetries, the Cl $3p_y$ orbital is **nonbonding** and doesn't interact with the H 1s. The same is true of the Cl $3p_x$orbital. The p_x and p_y orbitals have π symmetry (nodal plane containing the bonding axis) and are labeled π_{nb} in the MO energy level diagram, Fig. 2.6.3. In contrast, the H 1s and Cl $3p_z$ orbitals both have σ symmetry, which is also the symmetry of the clay pot shown in Fig. 2.6.1. Because these orbitals have the same symmetry (in the point group of the molecule), they can make the bonding and antibonding combinations shown in Fig. **2.1.1**.

The MO diagram of HCl that includes all the valence orbitals of the Cl atom is shown in Fig. 2.6.3. Two of the Cl valence orbitals ($3p_x$ and $3p_y$) have the wrong symmetry to interact with the H 1s orbital. The Cl 3s orbital has the same (σ) symmetry as H 1s, but it is much lower in energy so there is little orbital interaction. The energy of the Cl 3s orbital is thus affected only slightly by forming the molecule. The pairs of electrons in the π_{nb} and σ_{nb} orbitals are therefore **non-bonding**.

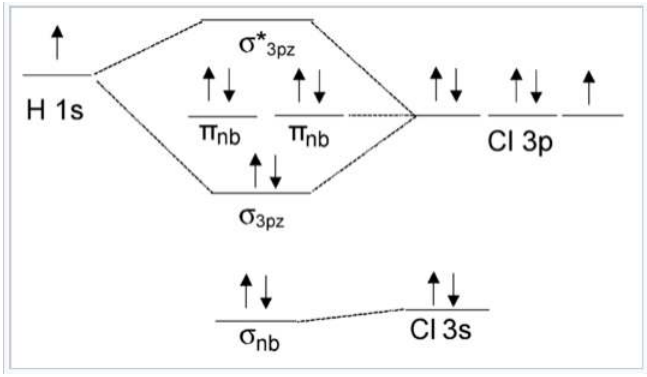


Figure 2.6.3: Energy level diagram of the HCl molecule showing MOs derived from the valence AOs.

Note that the MO result in Fig. 2.6.3 (1 bond and three pairs of nonbonding electrons) is the same as we would get from valence bond theory for HCl. The nonbonding orbitals are localized on the Cl atom, just as we would surmise from the valence bond picture.

In order to differentiate it from the σ bonding orbital, the σ antibonding orbital, which is empty in this case, is designated with an asterisk.

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2.7: σ, π, and δ orbitals

Inorganic compounds use s, p, and d orbitals (and more rarely f orbitals) to make bonding and antibonding combinations. These combinations result in **σ, π,** and **δ** bonds (and antibonds).

You are already familiar with σ and π bonding in organic compounds. In inorganic chemistry, π bonds can be made from p- and/or d-orbitals. δ bonds are more rare and occur by face-to-face overlap of d-orbitals, as in the ion $Re_2Cl_8^{2-}$. The fact that the Cl atoms are eclipsed in this anion is evidence of δ bonding.

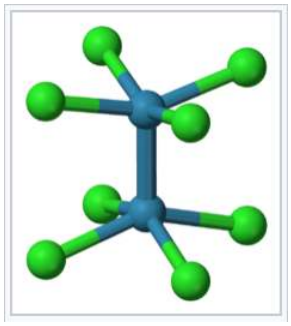
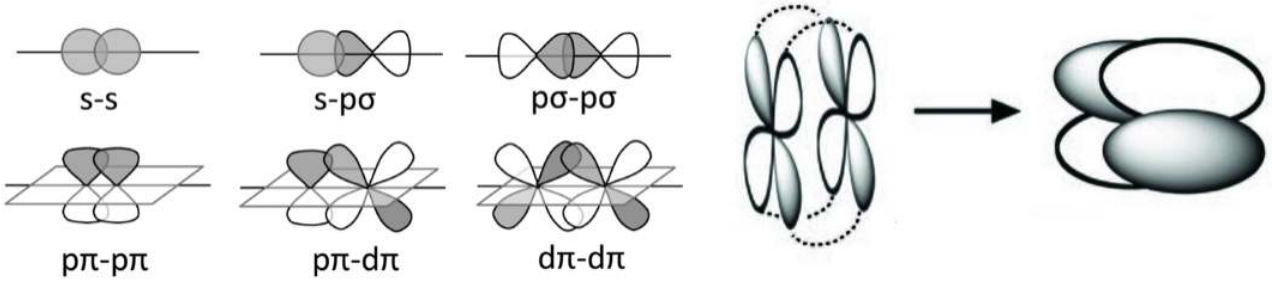
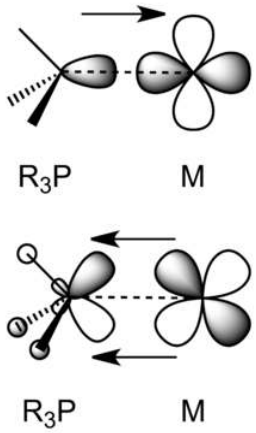


Figure 2.7.1: The octachlorodirhenate(III) anion, $[Re_2Cl_8]^{2-}$, which has a quadruple Re-Re bond.[3]

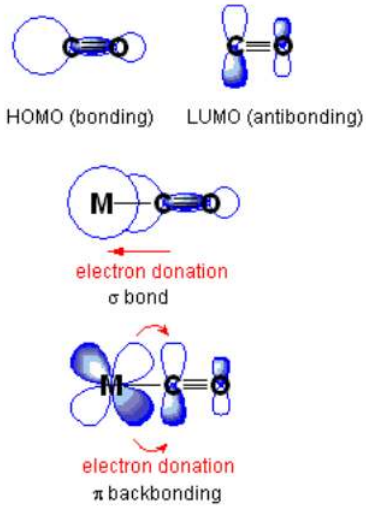
Some possible σ (top row), π (bottom row), and δ bonding combinations (right) of s, p, and d orbitals are sketched below. In each case, we can make bonding or antibonding combinations, depending on the signs of the AO wavefunctions. Because pπ-pπ bonding involves sideways overlap of p-orbitals, it is most commonly observed with second-row elements (C, N, O). π-bonded compounds of heavier elements are rare because the larger cores of the atoms prevent good π-overlap. For this reason, compounds containing C=C double bonds are very common, but those with Si=Si bonds are rare. δ bonds are generally quite weak compared to σ and π bonds. Compounds with metal-metal δ bonds occur in the middle of the transition series.



Transition metal d-orbitals can also form σ bonds, typically with s-p hybrid orbitals of appropriate symmetry on ligands. For example, phosphines (R_3P:) are good σ donors in complexes with transition metals, as shown below.



pπ-dπ bonding is also important in transition metal complexes. In metal carbonyl complexes such as $Ni(CO)_4$ and $Mo(CO)_6$, there is sideways overlap between filled metal d-orbitals and the empty π-antibonding orbitals (the LUMO) of the CO molecule, as shown in the figure below. This interaction strengthens the metal-carbon bond but weakens the carbon-oxygen bond. The C-O infrared stretching frequency is diagnostic of the strength of the bond and can be used to estimate the degree to which electrons are transferred from the metal d-orbital to the CO π-antibonding orbital.



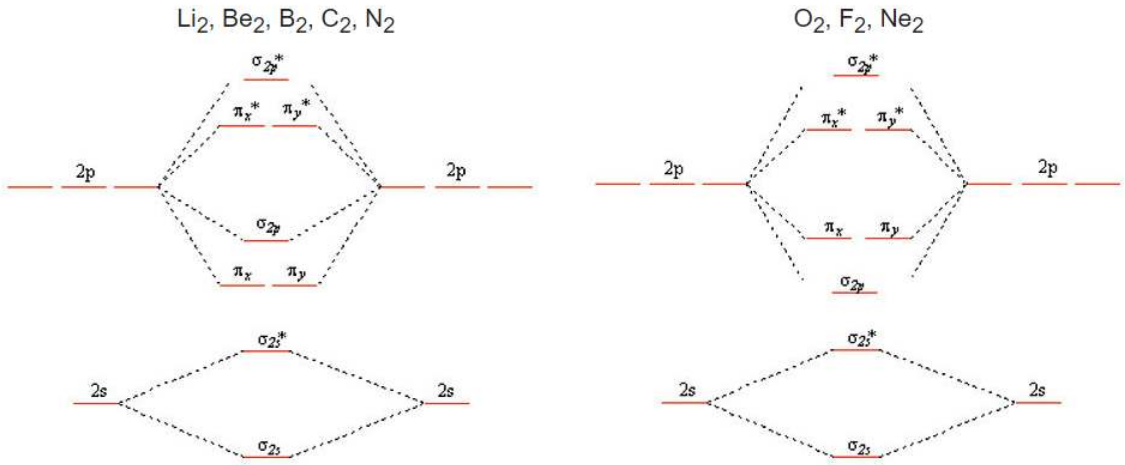
The same kind of backbonding occurs with phosphine complexes, which have empty π orbitals, as shown at the right. Transition metal complexes containing halide ligands can also have significant pπ-dπ bonding, in which a filled pπ orbital on the ligand donates electron density to an unfilled metal dπ orbital. We will encounter these bonding situations in Chapter 5.

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2.8: Diatomic Molecules

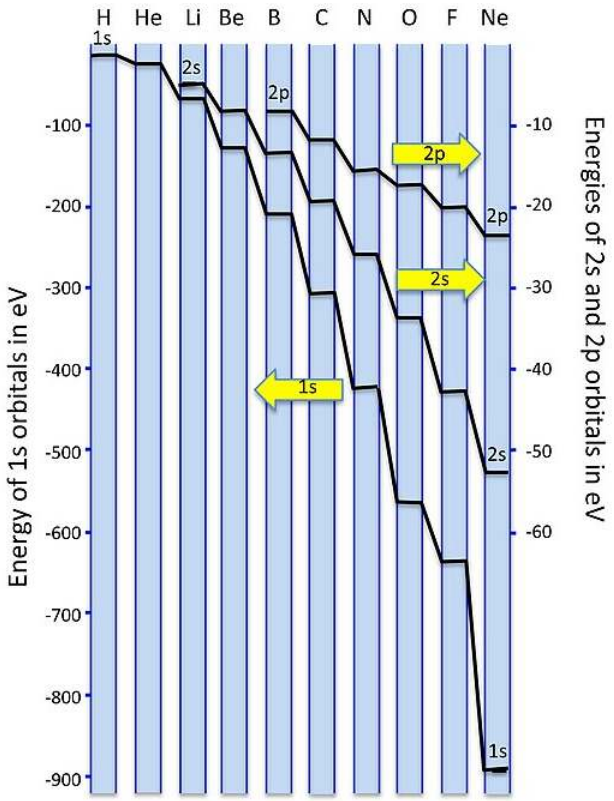
Valence bond theory fails for a number of the second row diatomics, most famously for O_2, where it predicts a diamagnetic, doubly bonded molecule with four lone pairs. O_2 does have a double bond, but it has two unpaired electrons in the ground state, a property that can be explained by the MO picture. We can construct the MO energy level diagrams for these molecules as follows



We get the simpler diatomic MO picture on the right when the 2s and 2p AOs are well separated in energy, as they are for O, F, and Ne. The picture on the left results from mixing of the σ_{2s} and σ_{2p} MO's, which are close in energy for Li_2, Be_2, B_2, C_2, and N_2. The effect of this mixing is to push the σ_{2s}* down in energy and the σ_{2p}up, to the point where the pπ orbitals are below the σ_{2p}. Asymmetric diatomic molecules and ions such as CO, NO, and NO^+ also have the ordering of energy levels shown on the left because of sp mixing. A good animation of the molecular orbitals in the CO molecule can be found on the University of Liverpool **Structure and Bonding** website.

Why don't we get sp-orbital mixing for O_2 and F_2? The reason has to do with the energies of the orbitals, which are not drawn to scale in the simple picture above. As we move across the second row of the periodic table from Li to F, we are progressively adding protons to the nucleus. The 2s orbital, which has finite amplitude at the nucleus, "feels" the increased nuclear charge more than the 2p orbital. This means that as we progress across the periodic table (and also, as we will see later, when we move down the periodic table), the **energy difference between the s and p orbitals increases**. As the 2s and 2p energies become farther apart in energy, there is less interaction between the orbitals (i.e., less mixing).

A plot of orbital energies is shown below. Because of the very large energy difference between the 1s and 2s/2p orbitals, we plot them on different energy scales, with the 1s to the left and the 2s/2p to the right. For elements at the left side of the 2nd period (Li, Be, B) the 2s and 2p energies are only a few eV apart. The energy difference becomes very large - more than 20 electron volts - for O and F. Since single bond energies are typically about 3-4 eV, this energy difference would be very large on the scale of our MO diagrams. For all the elements in the 2nd row of the periodic table, the 1s (core) orbitals are very low in energy compared to the 2s/2p (valence) orbitals, so we don't need to consider them in drawing our MO diagrams.



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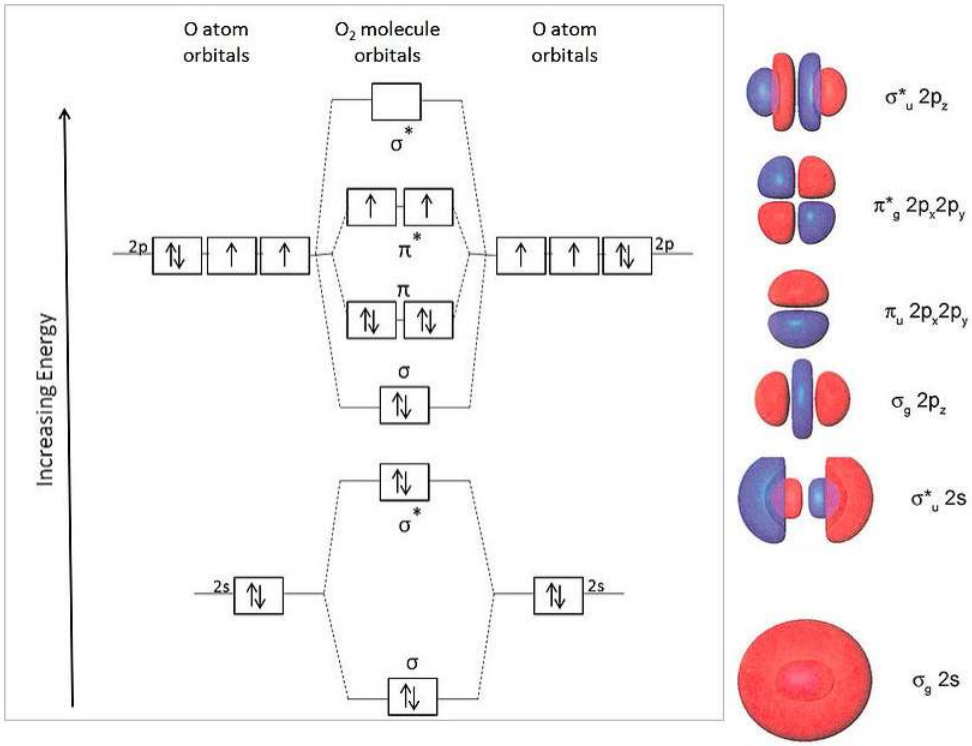
2.9: Orbital Filling

MO's are filled from the bottom according to the **Aufbau principle** and **Hund's rule**, as we learned for atomic orbitals.

Question: what is the quantum mechanical basis of Hund's rule?

> Consider the case of two degenerate orbitals, such as the π or π* orbitals in a second-row diatomic molecule. If these orbitals each contain one electron, their spins can be parallel (as preferred by Hund's rule) or antiparallel. The Pauli exclusion principle says that no two electrons in an orbital can have the same set of quantum numbers (n, l, m_l, m_s). That means that, in the parallel case, the Pauli principle prevents the electrons from ever visiting each other's orbitals. In the antiparallel case, they are free to come and go because they have different m_s quantum numbers. However, having two electrons in the same orbital is energetically unfavorable because like charges repel. Thus, the parallel arrangement, thanks to the Pauli principle, has lower energy.

For O_2 (12 valence electrons), we get the MO energy diagram below. The shapes of the molecular orbitals are shown at the right.



This energy ordering of MOs correctly predicts **two unpaired electrons** in the π* orbital and a net **bond order of two** (8 bonding electrons and 4 antibonding electrons). This is consistent with the experimentally observed paramagnetism of the oxygen molecule.

Other interesting predictions of the MO theory for second-row diatomics are that the C_2 molecule has a bond order of 2 and that the B_2 molecule has two unpaired electrons (both verified experimentally).

We can also predict (using the O_2, F_2, Ne_2 diagram above) that NO has a bond order of 2.5, and CO has a bond order of 3.

The symbols "g" and "u" in the orbital labels, which we only include in the case of centrosymmetric molecules, refer to their symmetry with respect to inversion. *Gerade* (g) orbitals are symmetric, meaning that inversion through the center leaves the orbital unchanged. *Ungerade* (u) means that the sign of the orbital is reversed by the inversion operation. Because g and u orbitals have different symmetries, they have zero overlap with each other. As we will see below, factoring orbitals according to g and u symmetry simplifies the task of constructing molecular orbitals in more complicated molecules, such as butadiene and benzene.

The orbital shapes shown above were computed using a *one-electron model* of the molecule, as we did for hydrogen-like AOs to get the shapes of s, p, and d-orbitals. To get accurate MO energies and diagrams for *multi-electron* molecules (i.e. all real molecules), we must include the fact that electrons are "correlated," i.e. that they avoid each other in molecules because of their negative charge. This problem cannot be solved analytically, and is solved approximately in numerical calculations by using

density functional theory (DFT). We will learn about the consequences of electron correlation in solids (such as superconductors) in Chapter 10.



Red giant stars are characterized by the presence of C_2 molecules in their atmospheres. Since C_2 has a net bond order of two, it reacts rapidly as it cools from the gas phase to make other forms of carbon such as **fullerenes**, **graphite**, and **diamond**, all of which have four bonds for every two carbon atoms.

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2.10: Second-Row Diatomic Molecules

Learning Objectives

- To apply Molecular Orbital Theory to the diatomic homonuclear molecule from the elements in the second period.

If we combine the splitting schemes for the 2s and 2p orbitals, we can predict bond order in all of the diatomic molecules and ions composed of elements in the first complete row of the periodic table. Remember that only the valence orbitals of the atoms need be considered; as we saw in the cases of lithium hydride and dilithium, the inner orbitals remain tightly bound and retain their localized atomic character. We now describe examples of systems involving period 2 homonuclear diatomic molecules, such as N_2, O_2, and F_2.

four key points to remember when drawing molecular orbital diagrams:

1. The number of molecular orbitals produced is the same as the number of atomic orbitals used to create them (the *"law of conservation of orbitals"*).
2. As the overlap between two atomic orbitals increases, the difference in energy between the resulting bonding and antibonding molecular orbitals increases.
3. When two atomic orbitals combine to form a pair of molecular orbitals, the bonding molecular orbital is stabilized about as much as the antibonding molecular orbital is destabilized.
4. The interaction between atomic orbitals is greatest when they have the same energy.

We illustrate how to use these points by constructing a molecular orbital energy-level diagram for F_2. We use the diagram in part (a) in Figure 2.10.1; the n = 1 orbitals (σ_{1s} and σ_{1s}*) are located well below those of the n = 2 level and are not shown. As illustrated in the diagram, the σ_{2s} and σ_{2s}* molecular orbitals are much lower in energy than the molecular orbitals derived from the 2p atomic orbitals because of the large difference in energy between the 2s and 2p atomic orbitals of fluorine. The lowest-energy molecular orbital derived from the three 2p orbitals on each F is σ_{2p_z} and the next most stable are the two degenerate orbitals, π_{2p_x} and π_{2p_y}. For each bonding orbital in the diagram, there is an antibonding orbital, and the antibonding orbital is destabilized by about as much as the corresponding bonding orbital is stabilized. As a result, the $\sigma^{\star}_{2p_z}$ orbital is higher in energy than either of the degenerate $\pi^{\star}_{2p_x}$ and $\pi^{\star}_{2p_y}$ orbitals. We can now fill the orbitals, beginning with the one that is lowest in energy.

Each fluorine has 7 valence electrons, so there are a total of 14 valence electrons in the F_2 molecule. Starting at the lowest energy level, the electrons are placed in the orbitals according to the Pauli principle and Hund's 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.

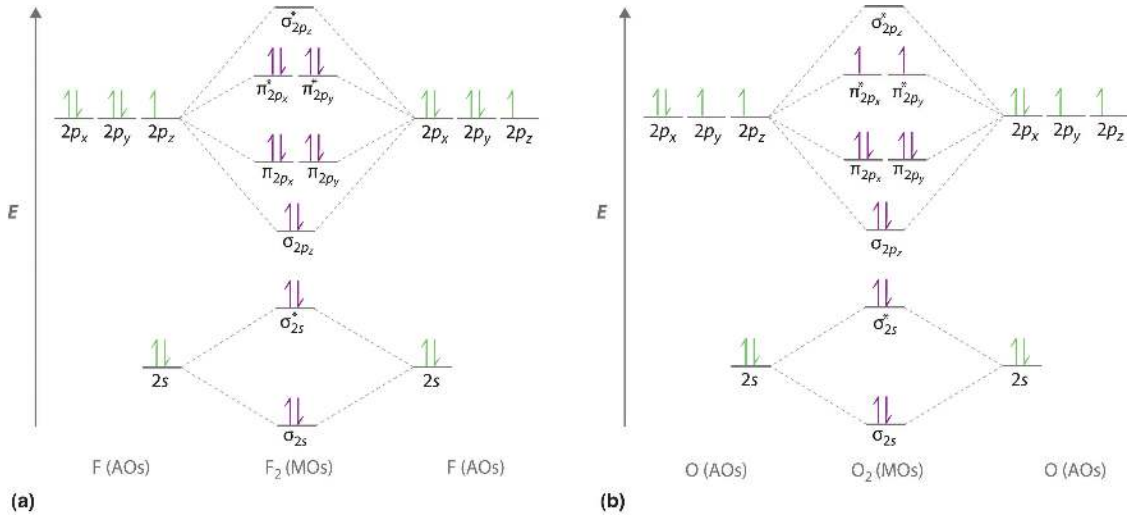


Figure 2.10.1: Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For F_2, with 14 valence electrons (7 from each F atom), all of the energy levels except the highest, $\sigma^{\star}_{2p_z}$ are filled. This diagram shows 8 electrons in bonding orbitals and 6 in antibonding 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 $\left(\pi^{\star}_{np_x}, \pi^{\star}_{np_y}\right)$ pair of orbitals. Hund's rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2.

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 2.10.1. We again fill the orbitals according to Hund's rule and the Pauli principle, beginning with the orbital that is lowest in energy. Two electrons each are needed to fill the σ_{2s} and σ_{2s}* orbitals, 2 more to fill the σ_{2p_z} orbital, and 4 to fill the degenerate $\pi^{\star}_{2p_x}$ and $\pi^{\star}_{2p_y}$ 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 2.10.2, it actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for O_2 to have unpaired electrons, making it paramagnetic, exactly as predicted by molecular orbital theory. This result was one of the earliest triumphs of molecular orbital theory over the other bonding approaches we have discussed.



Figure 2.10.2: Liquid O_2 Suspended between the Poles of a Magnet.Because the O_2 molecule has two unpaired electrons, it is paramagnetic. Consequently, it is attracted into a magnetic field, which allows it to remain suspended between the poles of a powerful magnet until it evaporates. Full video can be found at www.youtube.com/watch?featur...&v=Lt4P6ctf06Q.

The magnetic properties of O_2 are not just a laboratory curiosity; they are absolutely crucial to the existence of life. Because Earth's atmosphere contains 20% oxygen, all organic compounds, including those that compose our body tissues, should react rapidly with air to form H_2O, CO_2, and N_2 in an exothermic reaction. Fortunately for us, however, this reaction is very, very slow. The reason for the unexpected stability of organic compounds in an oxygen atmosphere is that virtually all organic compounds, as well as H_2O, CO_2, and N_2, have only paired electrons, whereas oxygen has two unpaired electrons. Thus the reaction of O_2 with organic compounds to give H_2O, CO_2, and N_2 would require that at least one of the electrons on O_2 change its spin during the reaction. This would require a large input of energy, an obstacle that chemists call a *spin barrier*. Consequently, reactions of this type are usually exceedingly slow. If they were not so slow, all organic substances, including this book and you, would disappear in a puff of smoke!

For period 2 diatomic molecules to the left of N_2 in the periodic table, a slightly different molecular orbital energy-level diagram is needed because the σ_{2p_z} molecular orbital is slightly *higher* in energy than the degenerate $\pi^*_{np_x}$ 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 2.10.3 Experimentally, it is found that the energy gap between the *ns* and *np* atomic orbitals *increases* as the nuclear charge increases (Figure 2.10.3). Thus for example, the σ_{2p_z} molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ pair.

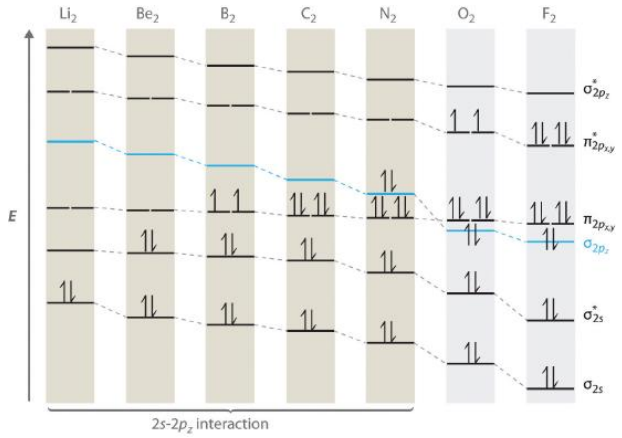


Figure 2.10.3: Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component *atoms* have been omitted. For Li_2 through N_2, the σ_{2p_z} orbital is higher in energy than the $\pi_{2p_{x,y}}$ orbitals. In contrast, the σ_{2p_z} orbital is *lower* in energy than the $\pi_{2p_{x,y}}$ orbitals for O_2 and F_2 due to the increase in the energy difference between the 2*s* and 2*p* atomic orbitals as the nuclear charge increases across the row.

Completing the diagram for N_2 in the same manner as demonstrated previously, we find that the 10 valence electrons result in 8 bonding electrons and 2 antibonding electrons, for a predicted bond order of 3, a triple bond. Experimental data show that the N–N bond is significantly shorter than the F–F bond (109.8 pm in N_2 versus 141.2 pm in F_2), and the bond energy is much greater for N_2 than for F_2 (945.3 kJ/mol versus 158.8 kJ/mol, respectively). Thus the N_2 bond is much shorter and stronger than the F_2 bond, consistent with what we would expect when comparing a triple bond with a single bond.

Example 2.10.3: Diatomic Sulfur

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in S_2, a bright blue gas at high temperatures.

Given: chemical species

Asked for: molecular orbital energy-level diagram, bond order, and number of unpaired electrons

Strategy:

A. Write the valence electron configuration of sulfur and determine the type of molecular orbitals formed in S_2. Predict the relative energies of the molecular orbitals based on how close in energy the valence atomic orbitals are to one another.

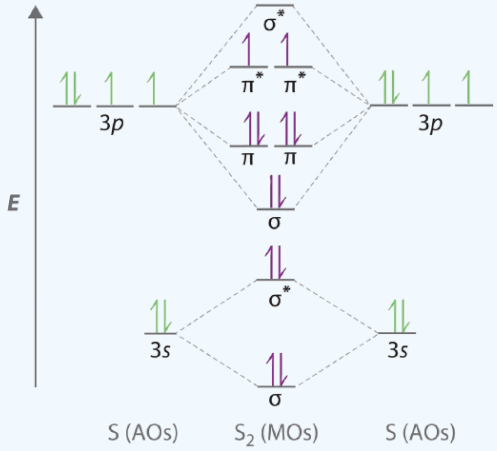
B. Draw the molecular orbital energy-level diagram for this system and determine the total number of valence electrons in S_2.

C. Fill the molecular orbitals in order of increasing energy, being sure to obey the Pauli principle and Hund's rule.
D. Calculate the bond order and describe the bonding.

Solution:

A Sulfur has a [Ne]$3s^2 3p^4$ valence electron configuration. To create a molecular orbital energy-level diagram similar to those in Figure 2.10.1 and Figure 2.10.3, we need to know how close in energy the 3*s* and 3*p* atomic orbitals are because their energy separation will determine whether the $\pi_{3p_{x,y}}$ or the σ_{3p_z}> molecular orbital is higher in energy. Because the *ns*–*np* energy gap *increases* as the nuclear charge increases (Figure 2.10.3), 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:



Two filled sigma orbitals, one filled sigma * orbital, two filled pi orbitals, and two pi * orbitals with one unpaired electron.

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

C Ten valence electrons are used to fill the orbitals through π_{3p_x} and π_{3p_y}, leaving 2 electrons to occupy the degenerate $\pi^{\star}_{3p_x}$ and $\pi^{\star}_{3p_y}$ pair. From Hund's rule, the remaining 2 electrons must occupy these orbitals separately with their spins aligned. With the numbers of electrons written as superscripts, the electron configuration of S_2 is $(\sigma_{3s})^2(\sigma^{\star}_{3s})^2(\sigma_{3p_z})^2(\pi_{3p_{x,y}})^4(\pi_{3p^{\star}_{x,y}})^2$ with 2 unpaired electrons. The bond order is (8 − 4) ÷ 2 = 2, so we predict an S=S double bond.

? Exercise 2.10.3: The Peroxide Ion

Use a qualitative molecular orbital energy-level diagram to predict the electron configuration, the bond order, and the number of unpaired electrons in the peroxide ion (O_2^{2-}).

Answer

$(\sigma_{2s})^2(\sigma^{\star}_{2s})^2(\sigma_{2p_z})^2(\pi_{2p_{x,y}})^4(\pi_{2p^{\star}_{x,y}})^4$ 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 2.10.4. The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B. The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B. Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

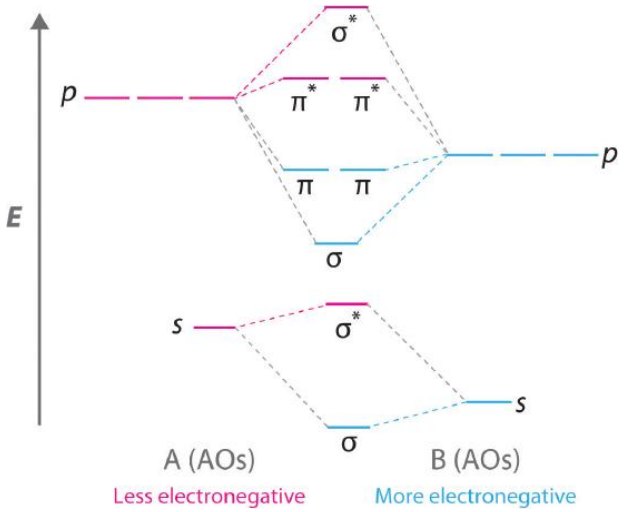


Figure 2.10.4: Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$. The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. On average, they are closer to the B atom, resulting in a polar covalent bond.

> *A molecular orbital energy-level diagram is always skewed toward the more electronegative atom.*

An Odd Number of Valence Electrons: NO

Nitric oxide (NO) is an example of a heteronuclear diatomic molecule. The reaction of O_2 with N_2 at high temperatures in internal combustion engines forms nitric oxide, which undergoes a complex reaction with O_2 to produce NO_2, which in turn is responsible for the brown color we associate with air pollution. Recently, however, nitric oxide has also been recognized to be a vital biological messenger involved in regulating blood pressure and long-term memory in mammals.

Because NO has an odd number of valence electrons (5 from nitrogen and 6 from oxygen, for a total of 11), its bonding and properties cannot be successfully explained by either the Lewis electron-pair approach or valence bond theory. The molecular orbital energy-level diagram for NO (Figure 2.10.13) shows that the general pattern is similar to that for the O_2 molecule (Figure 2.10.11). 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.

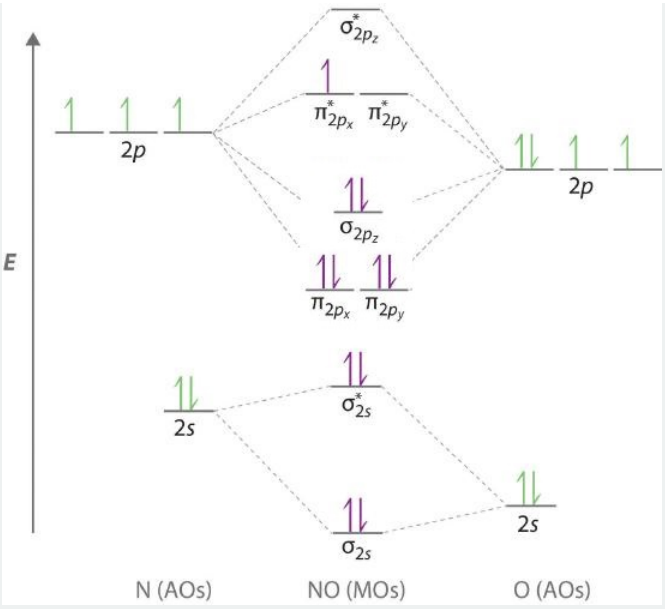


Figure 2.10.13: Molecular Orbital Energy-Level Diagram for NO. Because NO has 11 valence electrons, it is paramagnetic, with a single electron occupying the $\left(\pi^{\star}_{2p_x},\ \pi^{\star}_{2p_y}\right)$ pair of orbitals.

Note that electronic structure studies show the ground state configuration of NO to be $(\sigma_{2s})^2\left(\sigma^{\star}_{2s}\right)^2\left(\pi_{2p_{x,y}}\right)^4\left(\sigma_{2p_z}\right)^2\left(\pi_{2p^{\star}_{x,y}}\right)^1$ in order of increasing energy. Hence, the $\pi_{2p_{x,y}}$ orbitals are lower in energy than the σ_{2p_z} orbital. This is because the NO molecule is near the transition of flipping energies levels observed in homonuclear diatomics where the sigma bond drops below the pi bond (Figure 2.10.11).

Molecular orbital theory can also tell us something about the *chemistry* of NO. As indicated in the energy-level diagram in Figure 2.10.13, 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.

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 2.10.6 that the 1*s* orbital of atomic hydrogen is closest in energy to the 3*p* orbitals of chlorine. Consequently, the filled Cl 3*s* atomic orbital is not involved in bonding to any appreciable extent, and the only important interactions are those between the H 1*s* and Cl 3*p* orbitals. Of the three *p* orbitals, only one, designated as $3p_z$, can interact with the H 1*s* orbital. The $3p_x$ and $3p_y$ atomic orbitals have no net overlap with the 1*s* orbital on hydrogen, so they are not involved in bonding. Because the energies of the Cl 3*s*, $3p_x$, and $3p_y$ orbitals do not change when HCl forms, they are called **nonbonding molecular orbitals**. A nonbonding molecular orbital occupied by a pair of electrons is the molecular orbital equivalent of a lone pair of electrons. By definition, electrons in nonbonding orbitals have no effect on bond order, so they are not counted in the calculation of bond order. Thus the predicted bond order of HCl is (2 − 0) ÷ 2 = 1. Because the σ bonding molecular orbital is closer in energy to the Cl $3p_z$ than to the H 1*s* atomic orbital, the electrons in the σ orbital are concentrated closer to the chlorine atom than to hydrogen. A molecular orbital approach to bonding can therefore be used to describe the polarization of the H–Cl bond to give $H^{\delta+}--Cl^{\delta-}$.

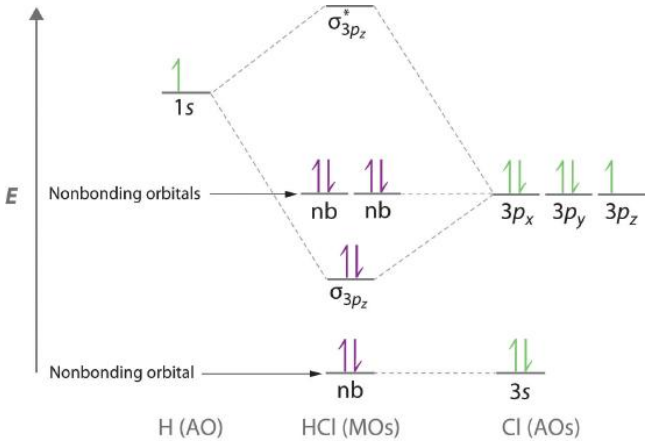


Figure 2.10.6: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1*s* atomic orbital interacts most strongly with the 3p_z orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.

> *Electrons in nonbonding molecular orbitals have no effect on bond order.*

Example 2.10.4: The Cyanide Ion

Use a "skewed" molecular orbital energy-level diagram like the one in Figure 2.10.4 to describe the bonding in the cyanide ion (CN^-). What is the bond order?

Given: chemical species

Asked for: "skewed" molecular orbital energy-level diagram, bonding description, and bond order

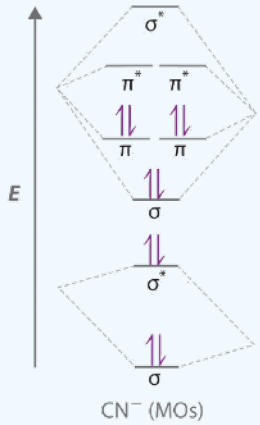
Strategy:

A. Calculate the total number of valence electrons in CN^-. Then place these electrons in a molecular orbital energy-level diagram like Figure 2.10.4 in order of increasing energy. Be sure to obey the Pauli principle and Hund's rule while doing so.

B. Calculate the bond order and describe the bonding in CN^-.

Solution:

A The CN^- ion has a total of 10 valence electrons: 4 from C, 5 from N, and 1 for the −1 charge. Placing these electrons in an energy-level diagram like Figure 2.10.4 fills the five lowest-energy orbitals, as shown here:



Because $\chi_N > \chi_C$, the atomic orbitals of N (on the right) are lower in energy than those of C.

B The resulting valence electron configuration gives a predicted bond order of (8 − 2) ÷ 2 = 3, indicating that the CN^- ion has a triple bond, analogous to that in N_2.

? Exercise 2.10.4: The Hypochlorite Ion

Use a qualitative molecular orbital energy-level diagram to describe the bonding in the hypochlorite ion (OCl^-). What is the bond order?

Answer

All molecular orbitals except the highest-energy σ* are filled, giving a bond order of 1.

Although the molecular orbital approach reveals a great deal about the bonding in a given molecule, the procedure quickly becomes computationally intensive for molecules of even moderate complexity. Furthermore, because the computed molecular orbitals extend over the entire molecule, they are often difficult to represent in a way that is easy to visualize. Therefore we do not use a pure molecular orbital approach to describe the bonding in molecules or ions with more than two atoms. Instead, we use a valence bond approach and a molecular orbital approach to explain, among other things, the concept of resonance, which cannot adequately be explained using other methods.



Summary

Molecular orbital energy-level diagrams for diatomic molecules can be created if the electron configuration of the parent atoms is known, following a few simple rules. Most important, the number of molecular orbitals in a molecule is the same as the number of atomic orbitals that interact. The difference between bonding and antibonding molecular orbital combinations is proportional to the overlap of the parent orbitals and decreases as the energy difference between the parent atomic orbitals increases. With such an approach, the electronic structures of virtually all commonly encountered **homonuclear diatomic molecules**, molecules with two identical atoms, can be understood. The molecular orbital approach correctly predicts that the O_2 molecule has two unpaired electrons and hence is attracted into a magnetic field. In contrast, most substances have only paired electrons. A similar procedure can be applied to molecules with two dissimilar atoms, called **heteronuclear diatomic molecules**, using a molecular orbital energy-level diagram that is skewed or tilted toward the more electronegative element. Molecular orbital theory is able to describe the bonding in a molecule with an odd number of electrons such as NO and even to predict something about its chemistry.

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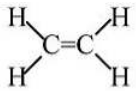
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2.11: Periodic Trends in π Bonding

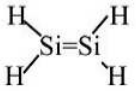
As we noted in Section 2.3, *pπ-bonding almost always involves a second-row element.*

We encounter π-bonding from the sideways overlap of p-orbitals in the MO diagrams of second-row diatomics (B_2…O_2). It is important to remember that π-bonds are weaker than σ bonds made from the same AOs, and are especially weak if they involve elements beyond the second row.

Example:



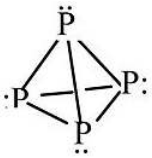
Ethylene: Stable molecule, doesn't polymerize without a catalyst.



Silylene: Never isolated, spontaneously polymerizes. Calculations indicate 117 kJ/mol stability in the gas phase relative to singly-bonded (triplet) $H_2Si\text{-}SiH_2$.

The large Ne core of Si atoms inhibits sideways overlap of 3p orbitals → weak π-bond.

Other examples: **P_4 vs. N_2**



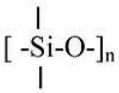
P cannot make π-bonds with itself, so it forms a tetrahedral molecule with substantial ring strain. This allotrope of P undergoes spontaneous combustion in air. Solid white phosphorus very slowly converts to red phosphorus, a more stable allotrope that contains sheets of pyramidal P atoms, each with bonds to three neighboring atoms and one lone pair.

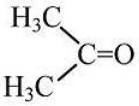


White phosphorus (P_4) is a soft, waxy solid that ignites spontaneously in air, burning with a bright flame and generating copious white P_4O_{10} smoke. The sample shown here is photographed under water to prevent the oxidation reaction

N can make π-bonds, so N_2 has a very strong triple bond and is a relatively inert diatomic gas.

$(CH_3)_2SiO$ vs. $(CH_3)_2CO$





"RTV" silicone polymer (4 single bonds to Si) vs. acetone (C=O double bond). Silicones are soft, flexible polymers that can be heated to high temperatures (>300 °C) without decomposing. Acetone is a flammable molecular liquid that boils at 56 °C.



Silicone polymers $(R_2SiO)_n$ are used in non-stick cookware like these muffin cups, in Silly Putty, soft robotics, and many other applications.



Exceptions:

2nd row elements can form reasonably strong π-bonds with the *smallest* of the 3rd row elements, P, S, and Cl. Thus we find S=N bonds in sulfur-nitrogen compounds such as S_2N_2 and $S_3N_3^-$, P=O bonds in phosphoric acid and P_4O_{10} (shown above), and a delocalized π-molecular orbital in SO_2 (as in ozone).

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2.12: References

1. More precisely, in the case of a complex wavefunction φ, the probability is the product of φ and its complex conjugate φ*
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CHAPTER OVERVIEW

3: Coordination Chemistry

Coordination compounds are molecules that poses one or multiple metal centers 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. A complex ion has a metal ion at its center with a number of other molecules or ions surrounding it. These can be considered to be attached to the central ion by coordinate (dative covalent) bonds and in some cases, the bonding is actually more complicated than that. The molecules or ions surrounding the central metal ion are called ligands.

3.1: History of Coordination Compounds
3.2: Metal Complexes
3.3: Ligands with more than one Donor Atom
3.4: Nomenclature of Coordination Chemistry
3.5: Isomerization
3.6: Enantiomers in Octahedral Complexes with Bidentate Ligands
3.7: Structural Isomers- Coordination Isomerism in Transition Metal Complexes
3.8: Structural Isomers- Ionization Isomerism in Transition Metal Complexes
3.9: Structural Isomers- Linkage Isomerism in Transition Metal Complexes
3.10: Color and Magnetism

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3.1: History of Coordination Compounds

Learning Objectives

- To know the most common structures observed for metal complexes.
- To predict the relative stabilities of metal complexes with different ligands

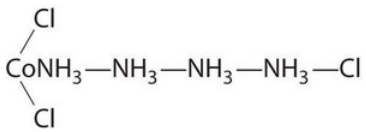
One of the most important properties of metallic elements is their ability to act as Lewis acids that form complexes with a variety of Lewis bases. A metal complex consists of a central metal atom or ion that is bonded to one or more ligands (from the Latin ligare, meaning “to bind”), which are ions or molecules that contain one or more pairs of electrons that can be shared with the metal. Metal complexes can be neutral, such as $Co(NH_3)_3Cl_3$; positively charged, such as $[Nd(H_2O)_9]^{3+}$; or negatively charged, such as $[UF_8]^{4-}$. Electrically charged metal complexes are sometimes called *complex ions*. A *coordination compound* contains one or more metal complexes.

Coordination compounds are important for at least three reasons. First, most of the elements in the periodic table are metals, and almost all metals form complexes, so metal complexes are a feature of the chemistry of more than half the elements. Second, many industrial catalysts are metal complexes, and such catalysts are steadily becoming more important as a way to control reactivity. For example, a mixture of a titanium complex and an organometallic compound of aluminum is the catalyst used to produce most of the polyethylene and polypropylene “plastic” items we use every day. Finally, transition-metal complexes are essential in biochemistry. Examples include hemoglobin, an iron complex that transports oxygen in our blood; cytochromes, iron complexes that transfer electrons in our cells; and complexes of Fe, Zn, Cu, and Mo that are crucial components of certain enzymes, the catalysts for all biological reactions.

History of the Coordination Compounds

Coordination compounds have been known and used since antiquity; probably the oldest is the deep blue pigment called Prussian blue: $KFe_2(CN)_6$. The chemical nature of these substances, however, was unclear for a number of reasons. For example, many compounds called “double salts” were known, such as $AlF_3 \cdot 3\,KF$, $Fe(CN)_2 \cdot 4\,KCN$, and $ZnCl_2 \cdot 2\,CsCl$, which were combinations of simple salts in fixed and apparently arbitrary ratios. Why should $AlF_3 \cdot 3\,KF$ exist but not $AlF_3 \cdot 4\,KF$ or $AlF_3 \cdot 2\,KF$? And why should a 3:1 KF:AlF3 mixture have different chemical and physical properties than either of its components? Similarly, adducts of metal salts with neutral molecules such as ammonia were also known—for example, $CoCl_3 \cdot 6\,NH_3$, which was first prepared sometime before 1798. Like the double salts, the compositions of these adducts exhibited fixed and apparently arbitrary ratios of the components. For example, $CoCl_3 \cdot 6\,NH_3$, $CoCl_3 \cdot 5\,NH_3$, $CoCl_3 \cdot 4\,NH_3$, and $CoCl_3 \cdot 3\,NH_3$ were all known and had very different properties, but despite all attempts, chemists could not prepare $CoCl_3 \cdot 2\,NH_3$ or $CoCl_3 \cdot NH_3$.

Although the chemical composition of such compounds was readily established by existing analytical methods, their chemical nature was puzzling and highly controversial. The major problem was that what we now call valence (i.e., the oxidation state) and coordination number were thought to be identical. As a result, highly implausible (to modern eyes at least) structures were proposed for such compounds, including the “Chattanooga choo-choo” model for $CoCl_3{\cdot}4NH_3$ shown here.



$CoCl_3 \cdot 4NH_3$

The modern theory of coordination chemistry is based largely on the work of Alfred Werner (1866–1919; Nobel Prize in Chemistry in 1913). In a series of careful experiments carried out in the late 1880s and early 1890s, he examined the properties of several series of metal halide complexes with ammonia. For example, five different “adducts” of ammonia with $PtCl_4$ were known at the time: $PtCl_4{\cdot}nNH_3$ (n = 2–6). Some of Werner’s original data on these compounds are shown in Table 3.1.1. The electrical conductivity of aqueous solutions of these compounds was roughly proportional to the number of ions formed per mole, while the number of chloride ions that could be precipitated as AgCl after adding $Ag^+(aq)$ was a measure of the number of “free” chloride ions present. For example, Werner’s data on $PtCl_4{\cdot}6NH_3$ in Table 3.1.1 showed that all the chloride ions were present as free chloride. In contrast, $PtCl_4{\cdot}2NH_3$ was a neutral molecule that contained no free chloride ions.

Alfred Werner (1866–1919)

Werner, the son of a factory worker, was born in Alsace. He developed an interest in chemistry at an early age, and he did his first independent research experiments at age 18. While doing his military service in southern Germany, he attended a series of chemistry lectures, and he subsequently received his PhD at the University of Zurich in Switzerland, where he was appointed professor of chemistry at age 29. He won the Nobel Prize in Chemistry in 1913 for his work on coordination compounds, which he performed as a graduate student and first presented at age 26. Apparently, Werner was so obsessed with solving the riddle of the structure of coordination compounds that his brain continued to work on the problem even while he was asleep. In 1891, when he was only 25, he woke up in the middle of the night and, in only a few hours, had laid the foundation for modern coordination chemistry.

Table 3.1.1: Werner's Data on Complexes of Ammonia with $PtCl_4$

Complex	Conductivity (ohm^{-1})	Number of Ions per Formula Unit	Number of Cl^- Ions Precipitated by Ag^+
$PtCl_4 \cdot 6NH_3$	523	5	4
$PtCl_4 \cdot 5NH_3$	404	4	3
$PtCl_4 \cdot 4NH_3$	299	3	2
$PtCl_4 \cdot 3NH_3$	97	2	1
$PtCl_4 \cdot 2NH_3$	0	0	0

These data led Werner to postulate that metal ions have two different kinds of valence: (1) a primary valence (**oxidation state**) that corresponds to the positive charge on the metal ion and (2) a secondary valence (**coordination number**) that is the total number of ligand-metal bonds bound to the metal ion. If Pt had a primary valence of 4 and a secondary valence of 6, Werner could explain the properties of the $PtCl_4 \cdot NH_3$ adducts by the following reactions, where the metal complex is enclosed in square brackets:

$$[Pt(NH_3)_6]Cl_4 \rightarrow [Pt(NH_3)_6]^{4+}(aq) + 4Cl^-(aq)$$
$$[Pt(NH_3)_5Cl]Cl_3 \rightarrow [Pt(NH_3)_5Cl]^{3+}(aq) + 3Cl^-(aq)$$
$$[Pt(NH_3)_4Cl_2]Cl_2 \rightarrow [Pt(NH_3)_4Cl_2]^{2+}(aq) + 2Cl^-(aq)$$
$$[Pt(NH_3)_3Cl_3]Cl \rightarrow [Pt(NH_3)_3Cl_3]^{+}(aq) + Cl^-(aq)$$
$$[Pt(NH_3)_2Cl_4] \rightarrow [Pt(NH_3)_2Cl_4]^{0}(aq)$$

Further work showed that the two missing members of the series—$[Pt(NH_3)Cl_5]^-$ and $[PtCl_6]^{2-}$—could be prepared as their mono- and dipotassium salts, respectively. Similar studies established coordination numbers of 6 for Co^{3+} and Cr^{3+} and 4 for Pt^{2+} and Pd^{2+}.

Werner's studies on the analogous Co^{3+} complexes also allowed him to propose a structural model for metal complexes with a coordination number of 6. Thus he found that $[Co(NH_3)_6]Cl_3$ (yellow) and $[Co(NH_3)_5Cl]Cl_2$ (purple) were 1:3 and 1:2 electrolytes. Unexpectedly, however, two different $[Co(NH_3)_4Cl_2]Cl$ compounds were known: one was red, and the other was green (Figure 3.1.1*a*). Because both compounds had the same chemical composition and the same number of groups of the same kind attached to the same metal, there had to be something different about the arrangement of the ligands around the metal ion. Werner's key insight was that the six ligands in $[Co(NH_3)_4Cl_2]Cl$ had to be arranged at the vertices of an octahedron because that was the only structure consistent with the existence of two, and only two, arrangements of ligands (Figure 3.1.1*b*. His conclusion was corroborated by the existence of only two different forms of the next compound in the series: $Co(NH_3)_3Cl_3$.

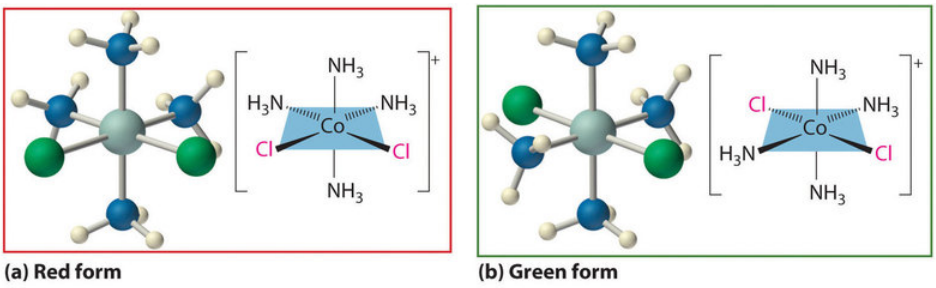


Figure 3.1.1: Complexes with Different Arrangements of the Same Ligands Have Different Properties. The $[Co(NH_3)_4Cl_2]^+$ ion can have two different arrangements of the ligands, which results in different colors: if the two Cl^- ligands are next to each other, the complex is red (a), but if they are opposite each other, the complex is green (b).

Example 3.1.1

In Werner's time, many complexes of the general formula MA_4B_2 were known, but no more than two different compounds with the same composition had been prepared for any metal. To confirm Werner's reasoning, calculate the maximum number of different structures that are possible for six-coordinate MA_4B_2 complexes with each of the three most symmetrical possible structures: a hexagon, a trigonal prism, and an octahedron. What does the fact that no more than two forms of any MA_4B_2 complex were known tell you about the three-dimensional structures of these complexes?

Given: three possible structures and the number of different forms known for MA_4B_2 complexes

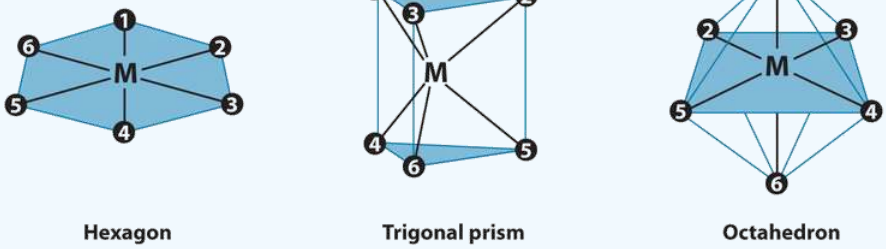
Asked for: number of different arrangements of ligands for MA_4B_2 complex for each structure

Strategy:

Sketch each structure, place a B ligand at one vertex, and see how many different positions are available for the second B ligand.

Solution

The three regular six-coordinate structures are shown here, with each coordination position numbered so that we can keep track of the different arrangements of ligands. For each structure, all vertices are equivalent. We begin with a symmetrical MA_6 complex and simply replace two of the A ligands in each structure to give an MA_4B_2 complex:



For the hexagon, we place the first B ligand at position 1. There are now three possible places for the second B ligand: at position 2 (or 6), position 3 (or 5), or position 4. These are the only possible arrangements. The (1, 2) and (1, 6) arrangements are chemically identical because the two B ligands are adjacent to each other. The (1, 3) and (1, 5) arrangements are also identical because in both cases the two B ligands are separated by an A ligand.

Turning to the trigonal prism, we place the first B ligand at position 1. Again, there are three possible choices for the second B ligand: at position 2 or 3 on the same triangular face, position 4 (on the other triangular face but adjacent to 1), or position 5 or 6 (on the other triangular face but not adjacent to 1). The (1, 2) and (1, 3) arrangements are chemically identical, as are the (1, 5) and (1, 6) arrangements.

In the octahedron, however, if we place the first B ligand at position 1, then we have only two choices for the second B ligand: at position 2 (or 3 or 4 or 5) or position 6. In the latter, the two B ligands are at opposite vertices of the octahedron, with the metal lying directly between them. Although there are four possible arrangements for the former, they are chemically identical because in all cases the two B ligands are adjacent to each other.

The number of possible MA_4B_2 arrangements for the three geometries is thus: hexagon, 3; trigonal prism, 3; and octahedron, 2. The fact that only two different forms were known for all MA_4B_2 complexes that had been prepared suggested that the correct structure was the octahedron but did not prove it. For some reason one of the three arrangements possible for the other two structures could have been less stable or harder to prepare and had simply not yet been synthesized. When combined with analogous results for other types of complexes (e.g., MA_3B_3), however, the data were best explained by an octahedral structure for six-coordinate metal complexes.

? Exercise 3.1.1

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

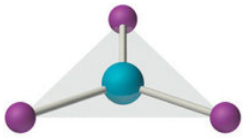
Although it is rare for most metals, this coordination number is surprisingly common for d^{10} metal ions, especially Cu^+, Ag^+, Au^+, and Hg^{2+}. An example is the $[Au(CN)_2]^-$ ion, which is used to extract gold from its ores. As expected based on VSEPR considerations, these complexes have the 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.

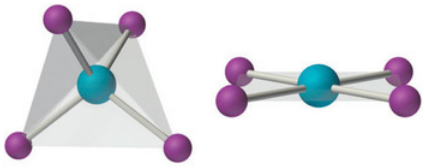


Trigonal planar ML_3

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

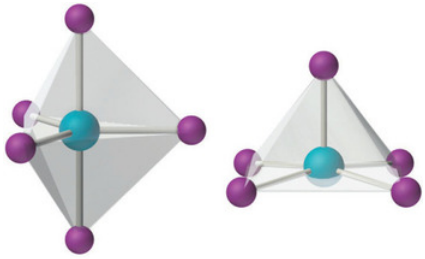
transition metals with d^8 electron configurations, such as Rh^+ and Pd^{2+}, and they are also encountered in some complexes of Ni^{2+} and Cu^{2+}.



Tetrahedral and square planar ML_4

Coordination Number 5

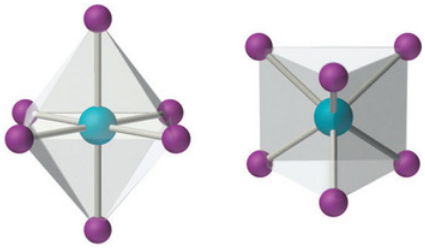
This coordination number is less common than 4 and 6, but it is still found frequently in two different structures: trigonal bipyramidal and square pyramidal. Because the energies of these structures are usually rather similar for most ligands, many five-coordinate complexes have distorted structures that lie somewhere between the two extremes.



Trigonal bipyramidal and square pyramidal ML_5

Coordination Number 6

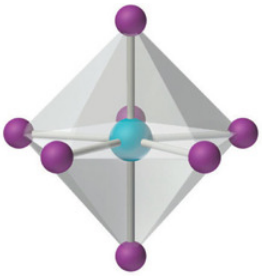
This coordination number is by far the most common. The six ligands are almost always at the vertices of an octahedron or a distorted octahedron. The only other six-coordinate structure is the trigonal prism, which is very uncommon in simple metal complexes.



Octahedral and trigonal prismatic ML_6

Coordination Number 7

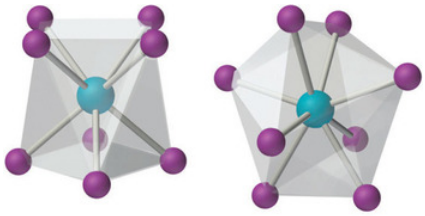
This relatively uncommon coordination number is generally encountered for only large metals (such as the second- and third-row transition metals, lanthanides, and actinides). At least three different structures are known, two of which are derived from an octahedron or a trigonal prism by adding a ligand 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

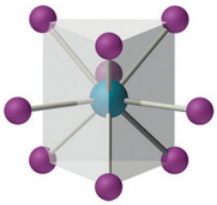
This coordination number is relatively common for larger metal ions. The simplest structure is the cube, which is rare because it does not minimize interligand repulsive interactions. Common structures are the square antiprism and the dodecahedron, both of which can be generated from the cube.



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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3.2: Metal Complexes

Learning Objectives

- To introduce complex ions and the basic principles of metal-ligand bonding

A complex ion has a metal ion at its center with a number of other molecules or ions surrounding it. These can be considered to be attached to the central ion by coordinate (dative covalent) bonds (in some cases, the bonding is actually more complicated than that. The molecules or ions surrounding the central metal ion are called ligands. Simple ligands include water, ammonia and chloride ions.

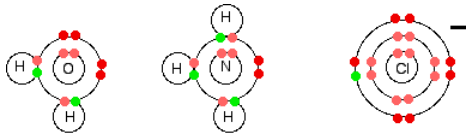


Figure 3.2.1: Simple Bohr diagram bonding in water, ammonia, and the chloride ion.

What all these have got in common is active lone pairs of electrons in the outer energy level. These are used to form co-ordinate bonds with the metal ion. All ligands are lone pair donors. In other words, all ligands function as Lewis bases.

Bonding in Simple Complex Ions

We are going to look in detail at the bonding in the complex ion formed when water molecules attach themselves to an aluminum ion to give $Al(H_2O)_6^{3+}$. Start by thinking about the structure of a naked aluminum ion before the water molecules bond to it.

Example 3.2.1: $Al(H_2O)_6^{3+}$

Aluminum has the electronic structure

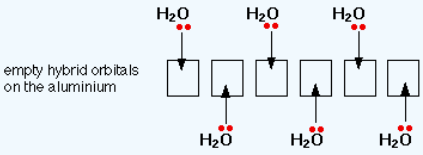
$$1s^2 2s^2 2p^6 3s^2 3p_x^1$$

When it forms an Al^{3+} ion it loses the 3-level electrons to leave

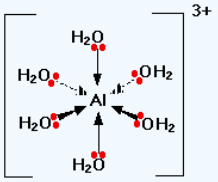
$$1s^2 2s^2 2p^6$$

That means that all the 3-level orbitals are now empty. The aluminium uses all six of these empty 3-level orbitals to accept lone pairs from six water molecules. It re-organizes (hybridizes) the 3s, the three 3p, and two of the 3d orbitals to produce six new orbitals all with the same energy.

You might wonder why it chooses to use six orbitals rather than four or eight or whatever. Six is the maximum number of water molecules that will fit around an aluminum ion (and most other metal ions) due to steric constraints. By making the maximum number of bonds, it releases most energy and so becomes most energetically stable.



Only one lone pair is shown on each water molecule. The other lone pair is pointing away from the aluminum and so isn't involved in the bonding. The resulting ion looks like this:



Because of the movement of electrons towards the center of the ion, the 3+ charge is no longer located entirely on the aluminum, but is now spread over the whole of the ion. Because the aluminum is forming 6 bonds, the co-ordination number of

the aluminum is said to be 6. The co-ordination number of a complex ion counts the number of co-ordinate bonds being formed by the metal ion at its center.

In a simple case like this, that obviously also counts the number of ligands - but that is not necessarily so, as you will see later. Some ligands can form more than one co-ordinate bond with the metal ion.

Example 3.2.2: $Fe(H_2O)_6^{3+}$

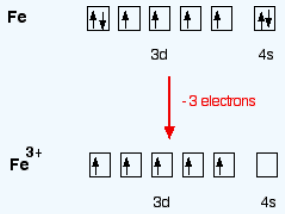
Iron has the electronic structure

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

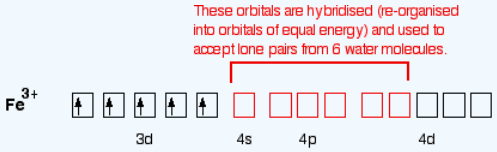
When it forms an Fe^{3+} ion it loses the 4s electrons and one of the 3d electrons to leave

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

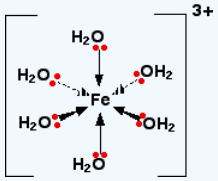
Looking at this as electrons-in-boxes, at the bonding level:



The single electrons in the 3d level are NOT involved in the bonding in any way. Instead, the ion uses 6 orbitals from the 4s, 4p and 4d levels to accept lone pairs from the water molecules. Before they are used, the orbitals are re-organized (hybridized) to produce 6 orbitals of equal energy.



Once the co-ordinate bonds have been formed, the ion looks exactly the same as the equivalent aluminium ion.



Because the iron is forming 6 bonds, the co-ordination number of the iron is 6.

Example 3.2.3: $CuCl_4^{2-}$

This is a simple example of the formation of a complex ion with a negative charge.

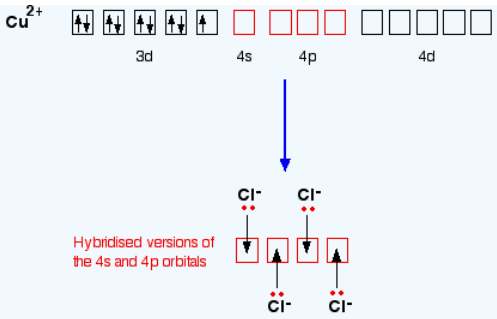
Copper has the electronic structure

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

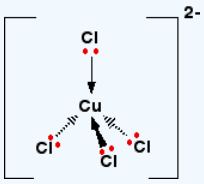
When it forms a Cu^{2+} ion it loses the 4s electron and one of the 3d electrons to leave

$$1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$$

To bond the four chloride ions as ligands, the empty 4s and 4p orbitals are used (in a hybridized form) to accept a lone pair of electrons from each chloride ion. Because chloride ions are bigger than water molecules, you can't fit 6 of them around the central ion - that's why you only use 4.



Only one of the 4 lone pairs on each chloride ion is shown. The other three are pointing away from the copper ion, and aren't involved in the bonding. That gives you the complex ion:



The ion carries 2 negative charges overall. That comes from a combination of the 2 positive charges on the copper ion and the 4 negative charges from the 4 chloride ions. In this case, the co-ordination number of the copper is 4.

Contributors and Attributions

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3.3: Ligands with more than one Donor Atom

Ligands can be further characterized as monodentate, bidentate, tridentate etc. where the concept of teeth **(dent)** is introduced. Monodentate ligands bind through only one donor atom. Monodentate means "one-toothed." The halides, phosphines, ammonia and amines seen previously are monodentate ligands. Bidentate ligands bind through two donor sites. Bidentate means "two-toothed." An example of a bidentate ligand is ethylenediamine. It can bind to a metal via two donor atoms at once.



Figure 3.3.1: The hypothetical "lobster ligand" binds to the Ni^{2+} via two donor sites.

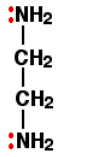
Bidentate binding allows a ligand to bind more tightly. Tridentate ligands, which bind through three donors, can bind even more tightly, and so on. This phenomenon is generally called the "**chelate effect**." This term comes from the Greek chelos, meaning "crab." A crab does not have any teeth at all, but it does have two claws for tightly holding onto something for a couple of reasons. A very simple analogy is that, if you are holding something with two hands rather than one, you are not as likely to drop it.

Complex metal ions containing more complicated ligands

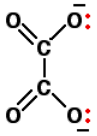
In the examples previously disccussed, each ligand only forms one bond with the central metal ion to give the complex ion. Such a ligand is said to be unidentate. That means literally that it only has one tooth! It only has one pair of electrons that it can use to bond to the metal - any other lone pairs are pointing in the wrong direction. Some ligands, however, have rather more teeth! These are known generally as multidentate or polydentate ligands, but can be broken down into a number of different types.

Bidentate ligands

Bidentate ligands have two lone pairs, both of which can bond to the central metal ion. The two commonly used examples are 1,2-diaminoethane (old name: ethylenediamine - often given the abbreviation "en"), and the ethanedioate ion (old name: oxalate).

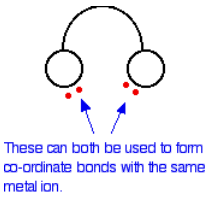


1,2-diaminoethane



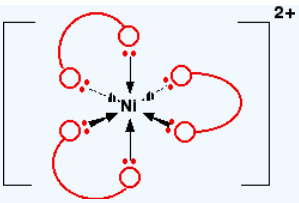
ethanedioate ion

In the ethanedioate ion, there are lots more lone pairs than the two shown, but these are the only ones we are interested in. You can think of these bidentate ligands rather as if they were a pair of headphones, carrying lone pairs on each of the "ear pieces". These will then fit snuggly around a metal ion.



Example 3.3.1: $Ni(NH_2CH_2CH_2NH_2)_3^{2+}$

You might find this abbreviated to $[Ni(en)_3]^{2+}$. The structure of the ion looks like this:



In this case, the "ear pieces" are the nitrogen atoms of the NH2 groups - and the "bit that goes over your head " is the $-CH_2CH_2-$ group. If you were going to draw this in an exam, you would obviously want to draw it properly - but for learning purposes, drawing all the atoms makes the diagram look unduly complicated!

Notice that the arrangement of the bonds around the central metal ion is exactly the same as it was with the ions with 6 water molecules attached. The only difference is that this time each ligand uses up two of the positions - at right angles to each other.

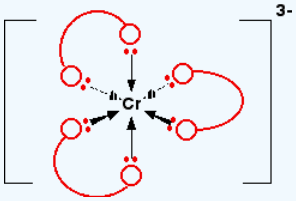
Because the nickel is forming 6 co-ordinate bonds, the coordination number of this ion is 6, despite the fact that it is only joined to 3 ligands. Coordination number counts the number of bonds, not the number of ligands.

Example 5: $Cr(C_2O_4)_3^{3-}$

This is the complex ion formed by attaching 3 ethanedioate (oxalate) ions to a chromium(III) ion. The shape is exactly the same as the previous nickel complex. The only real difference is the number of charges. The original chromium ion carried 3+ charges, and each ethanedioate ion carried -2, i.e.,

$$(+3) + (3 \times -2) = -3.$$

The structure of the ion looks like this:

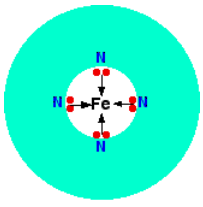


Again, if you drew this in an exam, you would want to show all the atoms properly. If you need to be able to do this, practice drawing it so that it looks clear and tidy! Refer back to the diagram of the ethanedioate ion further up the page to help you.

A Quadridentate Ligand

A quadridentate ligand has four lone pairs, all of which can bond to the central metal ion. An example of this occurs in haemoglobin (American: hemoglobin). The functional part of this is an iron(II) ion surrounded by a complicated molecule called heme. This is a sort of hollow ring of carbon and hydrogen atoms, at the center of which are 4 nitrogen atoms with lone pairs on them. Heme is one of a group of similar compounds called porphyrins. They all have the same sort of ring system, but with different groups attached to the outside of the ring. You aren't going to need to know the exact structure of the haem at this level.

We could simplify the heme with the trapped iron ion as:



Each of the lone pairs on the nitrogen can form a co-ordinate bond with the iron(II) ion - holding it at the center of the complicated ring of atoms. The iron forms 4 co-ordinate bonds with the heme, but still has space to form two more - one above and one below the plane of the ring. The protein globin attaches to one of these positions using a lone pair on one of the nitrogens in one of its amino acids. The interesting bit is the other position.

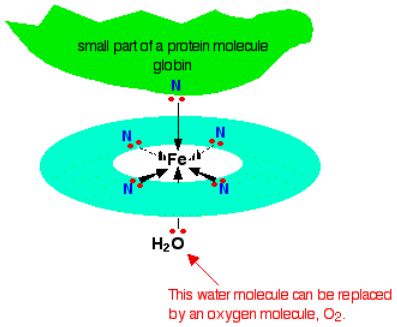


Figure 3.3.2: Overall, the complex ion has a co-ordination number of 6 because the central metal ion is forming 6 co-ordinate bonds.

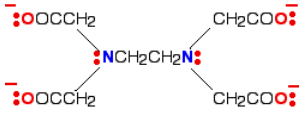
The water molecule which is bonded to the bottom position in the diagram is easily replaced by an oxygen molecule (again via a lone pair on one of the oxygens in O_2) - and this is how oxygen gets carried around the blood by the haemoglobin. When the oxygen gets to where it is needed, it breaks away from the haemoglobin which returns to the lungs to get some more.

Carbon Monoxide Poisoning

You probably know that carbon monoxide is poisonous because it reacts with hemeoglobin. It bonds to the same site that would otherwise be used by the oxygen - but it forms a very stable complex. The carbon monoxide doesn't break away again, and that makes that hemeoglobin molecule useless for any further oxygen transfer.

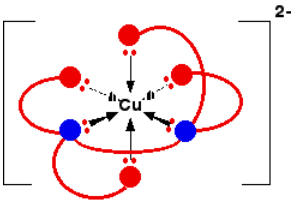
A Hexadentate Ligand

A hexadentate ligand has 6 lone pairs of electrons - all of which can form co-ordinate bonds with the same metal ion. The best example is EDTA. The diagram shows the structure of the ion with the important atoms and lone pairs picked out.



the $EDTA^{4-}$ ion

The EDTA ion entirely wraps up a metal ion using all 6 of the positions that we have seen before. The co-ordination number is again 6 because of the 6 co-ordinate bonds being formed by the central metal ion. The diagram below shows this happening with a copper(II) ion. Here is a simplified version. Make sure that you can see how this relates to the full structure above.



the $[Cu(EDTA)]^{2-}$ ion

The overall charge, of course, comes from the 2+ on the original copper(II) ion and the 4- on the $EDTA^{4-}$ ion.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

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3.4: Nomenclature of Coordination Chemistry

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 3.4.1: 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 3.4.2: 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 3.4.3: 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 3.4.4: 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 3.4.1

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 3.4.1

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 3.4.5: 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 3.4.3). Here are some examples with determining oxidation states, naming a metal in an anion complex, and naming coordination compounds.

Example 3.4.2

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 3.4.2

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 3.4.3

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 3.4.3: 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 3.4.4

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 3.4.4

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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3.5: Isomerization

Learning Objectives

- To understand that there may be more than one way to arrange the same groups around the same atom with the same geometry (stereochemistry).

Two compounds that have the same formula and the same connectivity do not always have the same shape. There are two reasons why this may happen. In one case, the molecule may be flexible, so that it can twist into different shapes via rotation around individual sigma bonds. This phenomenon is called conformation, and it is covered in a different chapter. The second case occurs when two molecules appear to be connected the same way on paper, but are connected in two different ways in three dimensional space. These two, different molecules are called **stereoisomers**.

One simple example of stereoisomers from inorganic chemistry is diammine platinum dichloride, $(NH_3)_2PtCl_2$. This important compound is sometimes called "platin" for short. As the formula implies, it contains a platinum ion that is coordinated to two ammonia ligands and two chloride ligands (remember, a ligand in inorganic chemistry is an electron donor that is attached to a metal atom, donating a pair of electrons to form a bond).

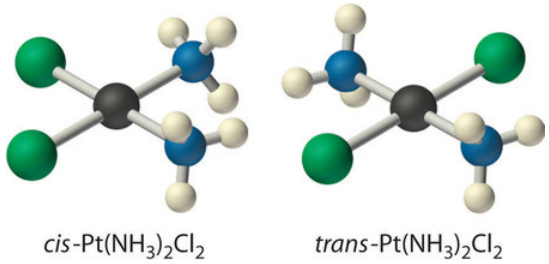


Figure 3.5.1: Two stereoisomers. The atoms are connected to each other in the same order, but differ in their three-dimensional relationships. (left) The cis-Platin compound is square planar at platinum and is flat when viewed from the edge, and square when viewed from the face. (right) The trans-Platin compound is connected in the same way as in cis-platin, and is still square planar, but there is a different 3-dimensional arrangement

Platin is an example of a coordination compound. The way the different pieces of coordination compounds bond together is discussed in the chapter of Lewis acids and bases. For reasons arising from molecular orbital interactions, platin has a square planar geometry at the platinum atom. That arrangement results in two possible ways the ligands could be connected. The two sets of like ligands could be connected on the same side of the square or on opposite corners.

These two arrangements result in two different compounds; they are isomers that differ only in three-dimensional space.

- The one with the two amines beside each other is called cis-platin.
- These two ligands are 90 degrees from each other.
- The one with the amines across from each other is trans-platin.
- These two ligands are 180 degrees from each other.

CIS/TRANS isomers have different physical properties

Although these two compounds are very similar, they have slightly different physical properties. Both are yellow compounds that decompose when heated to 270 degrees C, but trans-platin forms pale yellow crystals and is more soluble than cis-platin in water.

CIS/TRANS isomers have different biological properties

Cis-platin has clinical importance in the treatment of ovarian and testicular cancers. The biological mechanism of the drug's action was long suspected to involve binding of the platinum by DNA. Further details were worked out by MIT chemist Steve Lippard and graduate student Amy Rosenzweig in the 1990's. Inside the cell nucleus, the two ammines in cis-platin can be replaced by nitrogen donors from a DNA strand. To donate to the Lewis acidic platinum, the DNA molecule must bend slightly. Normally that bend is detected and repaired by proteins in the cell. However, ovarian and testicular cells happen to contain a protein that is just the right shape to fit around this slightly bent DNA strand. The DNA strand becomes lodged in the protein and can't be displaced, and so it is unable to bind with other proteins used in DNA replication. The cell becomes unable to replicate, and so cancerous growth is stopped.

? Exercise 3.5.1

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 3.5.2

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.

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:

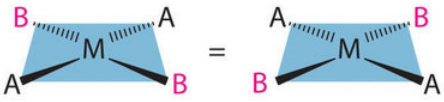


MA_3B square planar complex

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



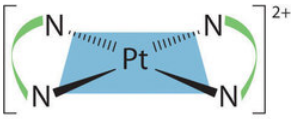
MA_2B_2 square planar complex, *trans* isomer

Figure 3.5.1).

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.

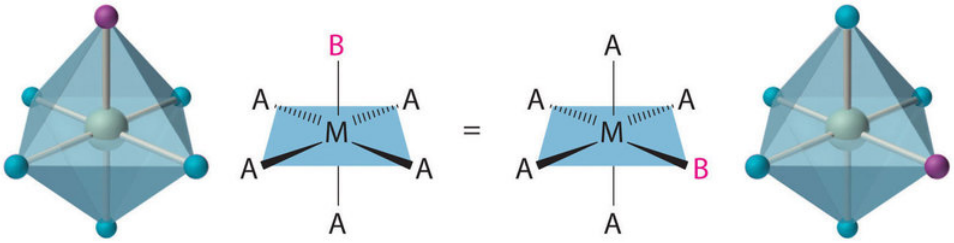
Square planar complexes that contain symmetrical bidentate ligands, such as $[Pt(en)_2]^{2+}$, have only one possible structure, in which curved lines linking the two N atoms indicate the ethylenediamine ligands:



$[Pt(en)_2]^{2+}$

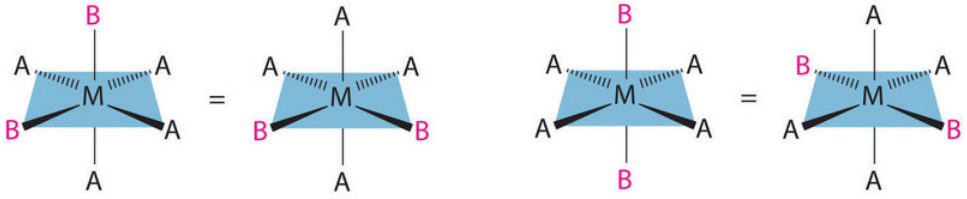
Octahedral Isomers

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:



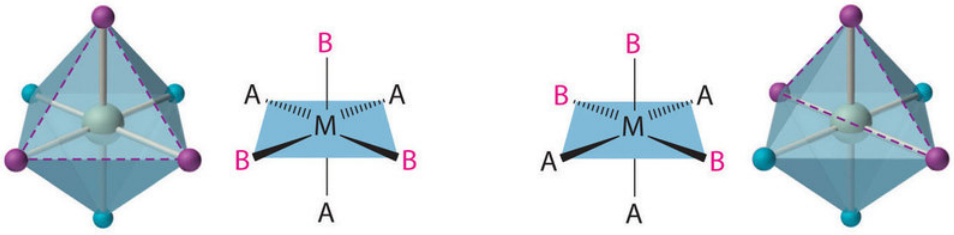
MA_5B octahedral complex

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 3.5.1

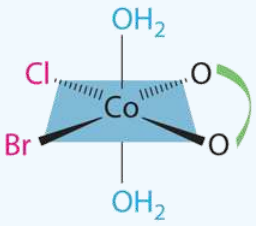
Draw all the possible geometrical isomers for the complex $[Co(H_2O)_2(ox)BrCl]^-$, where ox is $^-O_2CCO_2^-$, which stands for oxalate.

Given: formula of complex

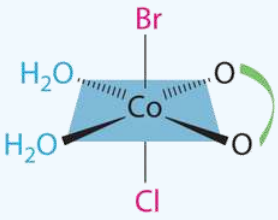
Asked for: structures of geometrical isomers

Solution

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:

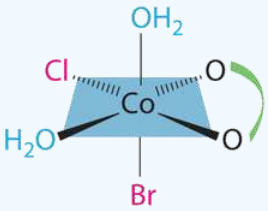


H_2O's *trans*

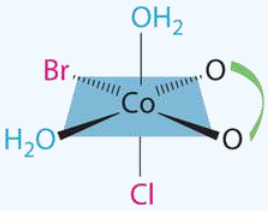


Br, Cl *trans*

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:



H_2O's *cis*; Br, Cl *cis*; Cl *trans* to O



H_2O's *cis*; Br, Cl *cis*; Br *trans* to O

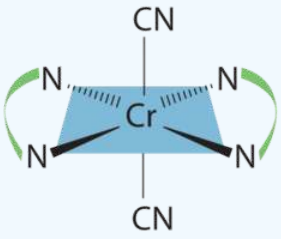
This complex can therefore exist as four different geometrical isomers.

Exercise 3.5.1

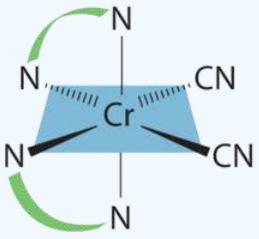
Draw all the possible geometrical isomers for the complex $[Cr(en)_2(CN)_2]^+$.

Answer

Two geometrical isomers are possible: trans and cis.



trans



cis

Summary

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.

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3.6: Enantiomers in Octahedral Complexes with Bidentate Ligands

Enantiomers are another kind of isomer that occur in octahedral metal complexes. Like the square planar platinum complexes seen before, these compounds consist of metal ions with other atoms or groups bound to them. More information about the binding of ligands to metals is found in the section on Lewis acids and bases. These groups that bind to metal ions are called ligands. One example of a type of octahedral compounds that can form enantiomers is bidentate complexes. In bidentate complexes (from the Greek two teeth) or chelating complexes (from the Greek crab), 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 SC18a: Ethylenediamine (sometimes abbreviated en).

Bidentate ligands bind very tightly to a metal because they form two bonds with it, rather than just one.

> *In an octahedral complex, the two donor atoms in a bidentate ligand bind **cis** to each other. They **cannot** reach all the way around the molecule to bind trans to each other.*

The spatial relationship between the metal and the two atoms connected to it from the same ligand forms a plane. If more than one bidentate ligand is connected to the metal, the relative orientation of one plane to another creates the possibility of mirror images. A complex containing three bidentate ligands can take on the shape of a left-handed propeller or a right-handed propeller.



Figure SC18b. A left-handed propeller shape (left) is seen in Λ isomers of octahedral enantiomers. A right-handed propeller (right) is seen in Δ isomers of octahedral enantiomers.

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.

What do we know about enantiomers?

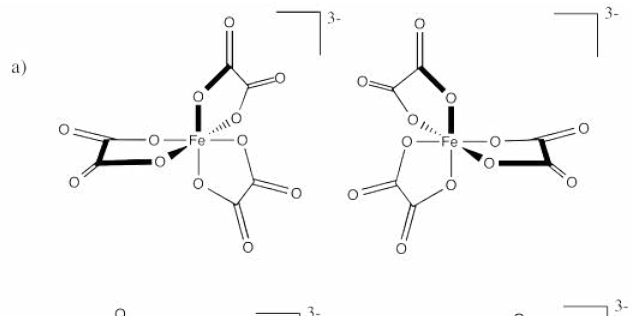
- enantiomers have identical physical properties, except...
- enantiomers have opposite optical rotation.

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.

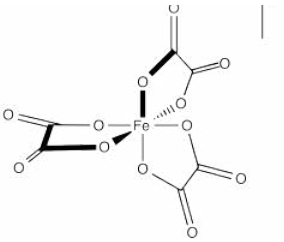
In addition, stereochemistry in metal complexes became very important in the late 20th century, especially as pharmaceutical companies looked for catalysts that could aid in the production of one enantiomer of a drug, and not the other, in order to maximize pharmaceutical effectiveness and minimize side effects.

Problem SC18.1.

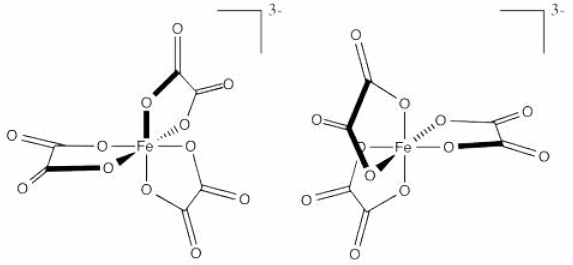
Identify the relationships between the following pairs of iron(III) oxalate ions.



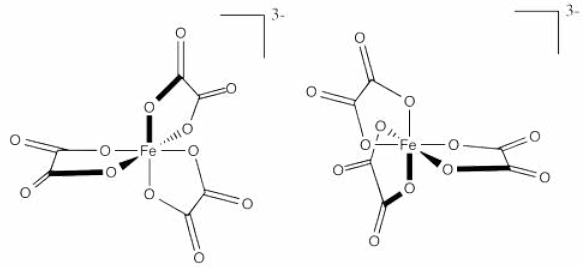
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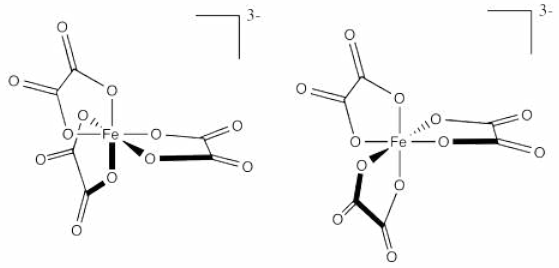
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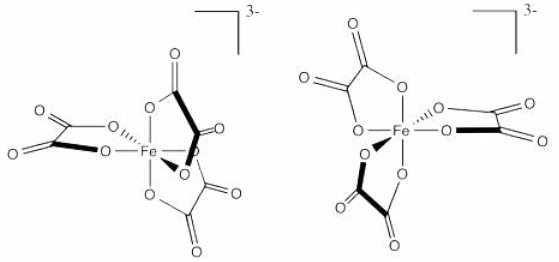
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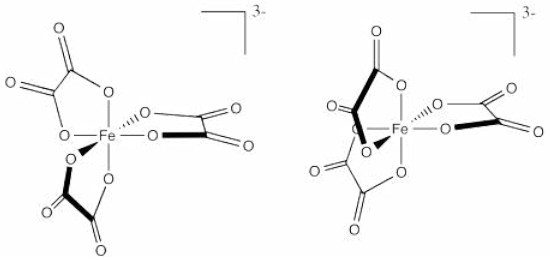
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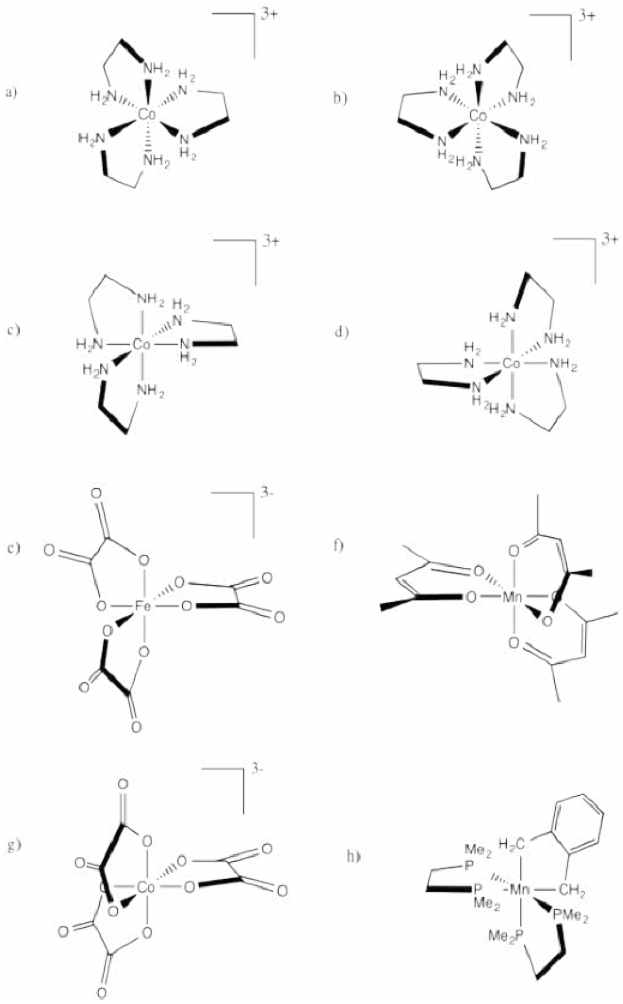
g)



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Problem SC18.2.

Indicate whether each of the following compounds is the Δ or Λ isomer and draw its enantiomer.



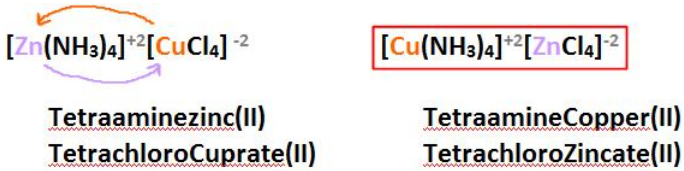
Exercise: How many stereoisomers does an octahedral complex have? (contribution from B.J. Johnson)

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3.7: Structural Isomers- Coordination Isomerism in Transition Metal Complexes

Coordination isomerism occurs in compounds containing complex anionic and cationic parts and can be viewed as the interchange of one or more ligands between the cationic complex ion and the anionic complex ion. For example, $[Co(NH_3)_6][Cr(CN)_6]$ is a coordination isomer with $[Cr(NH_3)_6][Co(CN)_6]$. Alternatively, coordination isomers may be formed by switching the metals between the two complex ions like $[Zn(NH_3)_4][CuCl_4]$ and $[Cu(NH_3)_4][ZnCl_4]$.



? Exercise 3.7.1

Are $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$ coordination isomers?

Solution

Here, both the cation and anion are complex ions. In the first isomer, NH_3 is attached to the copper and the Cl^- are attached to the platinum. In the second isomer, they have swapped.

Yes, they are coordination isomers.

? Exercise 3.7.2

What is one coordination isomer of $[Co(NH_3)_6][Cr(C_2O_4)_3]$?

Solution

Coordination isomers involve swapping the species from the inner coordination sphere to one metal (e.g, cation) to inner coordination sphere of a different metal (e.g., the anion) in the compound. One isomer is completely swapping the ligand sphere, e.g, $[Co(C_2O_4)_3][Cr(NH_3)_6]$.

Alternative coordination isomers are $[Co(NH_3)_4(C_2O_4)][Cr(NH_3)_2(C_2O_4)_2]$ and $[Co(NH_3)_2(C_2O_4)_2][Cr(NH_3)_4(C_2O_4)]$.

Contributors and Attributions

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3.8: Structural Isomers- Ionization Isomerism in Transition Metal Complexes

Coordination isomerism is a form of structural isomerism in which the composition of the complex ion varies. In a coordination isomer the total ratio of ligand to metal remains the same, but the ligands attached to a specific metal ion change. Ionization isomers can be thought of as occurring because of the formation of different ions in solution.

Introduction

Ionization isomers are identical except for a ligand has exchanged places with an anion or neutral molecule that was originally outside the coordination complex. The central ion and the 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.

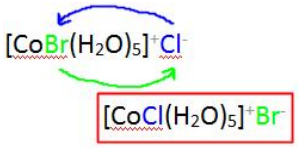


Figure 3.8.1: Two Ionization isomers. The two isomers differ only which ligands are actually bound to the center metal. These two isomers are called pentaaqua**bromo**cobaltate(II) **chloride** and pentaaqua**chloro**cobaltate(II) **bromide**.

The difference between the ionization isomers can be viewed within the context of the ions generated when each are dissolved in solution.

For example, when pentaaquabromocobaltate(II)chloride is dissolved in water, Cl^- ions are generated:

$$CoBr(H_2O)_5Cl(s) \rightarrow CoBr(H_2O)_5^+(aq) + Cl^+(aq)$$

whereas when pentaaquachlorocobaltate(II)bromide is dissolved, Br^- ions are generated:

$$CoCl(H_2O)_5Br(s) \rightarrow CoCl(H_2O)_5^+(aq) + Br^+(aq).$$

Note

If one dissolved $[PtBr(NH_3)_3]NO_2$ and $[Pt(NO_2)(NH_3)_3]Br$ into solution, then two different set of ions will be general.

- Dissolving $[Pt(NO_2)(NH_3)_3]Br$ in aqueous solution would have the following reaction

$$[PtBr(NH_3)_3]NO_2(s) \rightarrow [PtBr(NH_3)_3]^+(aq) + NO_2^-(aq) \tag{3.8.1}$$

- Dissolving of $[Pt(NO_2)(NH_3)_3]Br$ in aqueous solution would be

$$[Pt(NO_2)(NH_3)_3]Br(s) \rightarrow [Pt(NO_2)(NH_3)_3]^+(aq) + Br^-(aq) \tag{3.8.2}$$

Notice that these two ionization isomers differ in that one ion is directly attached to the central metal, but the other is not.

Equations 3.8.1 and 3.8.2 are valid under the assumption that the platinum-ligand bonds of the complexes are stable (i.e., not labile). Otherwise, they may break and other ligands (e.g., water) may bind.

Example 3.8.1

Are $[Cr(NH_3)_5(OSO_3)]Br$ and $[Cr(NH_3)_5Br]SO_4$ coordination isomers?

Solution

First, we need confirm that each compound has the same number of atoms of the respective elements (this requires viewing both cations and anions of each compound).

Element	number of atoms in $[Cr(NH_3)_5(OSO_3)]Br$	number of atoms in $[Cr(NH_3)_5Br]SO_4$

Element	number of atoms in $[Cr(NH_3)_5(OSO_3)]Br$	number of atoms in $[Cr(NH_3)_5Br]SO_4$
Cr	1	1
N	5	5
H	15	15
O	4	4
S	1	1
Br	1	1

Now, let's look at what these two compounds look like (Figure 3.8.2). The sulfate group is a ligand with a dative bond to the chromium atom and the bromide counter ion ($[Cr(NH_3)_5(OSO_3)]Br$). For $[Cr(NH_3)_5Br]SO_4$, this is the the reverse.

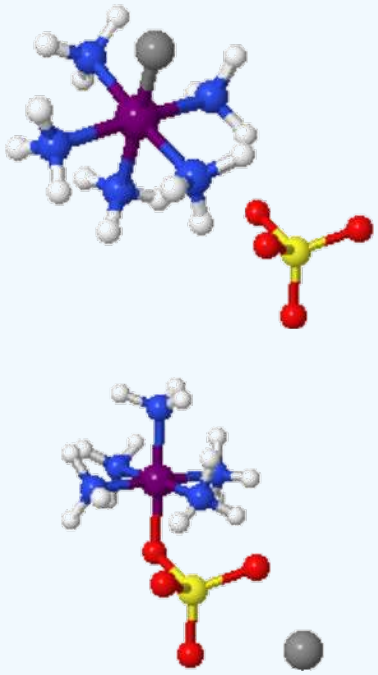


Figure 3.8.2: $[Cr(NH_3)_5(OSO_3)]Br$ (left) and $[Cr(NH_3)_5Br]SO_4$ (right) are coordination isomers.

Yes, $[Cr(NH_3)_5(OSO_3)]Br$ and $[Cr(NH_3)_5Br]SO_4$ are coordination isomers.

? Exercise 3.8.1

Are $[Co(NH_3)_5(SO_4)]Br$ and $[Co(NH_3)_5Br]SO_4$ ionization isomers?

Solution

In the first isomer, SO_4 is attached to the Cobalt and is part of the complex ion (the cation), with Br as the anion. In the second isomer, Br is attached to the cobalt as part of the complex and SO_4 is acting as the anion.

A hydrate isomer is a specific kind of ionization isomer where a water molecule is one of the molecules that exchanges places.

Solvate or Hydrate Isomerization: A Special kind of Ionization Isomer

A very similar type of isomerism results from replacement of a coordinated group by a solvent molecule (*Solvate Isomerism*). In the case of water, this is called *Hydrate isomerism*. The best known example of this occurs for chromium chloride "$CrCl_3.6H_2O$" which may contain 4, 5, or 6 coordinated water molecules.

- $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$: 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.

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3.9: Structural Isomers- Linkage Isomerism in Transition Metal Complexes

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 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* rather than an *ambidentate* ligand.

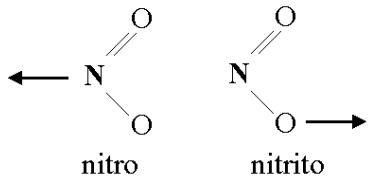
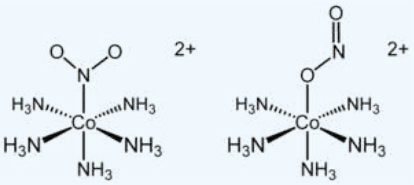


Figure 3.9.1: Linkage Isomerism in the NO_2 ligand. This occurs when a particular ligand is capable of coordinating to a metal in two different and distinct ways. from Angel C. de Dios.

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 3.9.1: Nitro- vs. Nitrito- Linkage Isomers

The cationic cobalt complex $[Co(NH_3)_5(NO_2)]Cl_2$ exists in two separable linkage isomers of the complex ion: $(NH_3)_5(NO_2)]^{2+}$.



(left) The nitro isomer (Co-NO_2) 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.

The formula of the complex is unchanged, but the properties of the complex may differ.

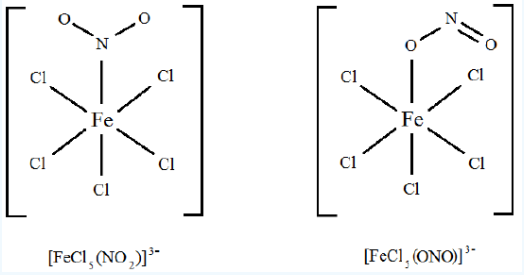
Another example of an ambidentate ligans is thiocyanate, SCN^-, which can attach at either the sulfur atom or the nitrogen atom. Such compounds give rise to linkage isomerism. Polyfunctional ligands can bond to a metal center through different ligand atoms to form various isomers. Other ligands that give rise to linkage isomers include selenocyanate, $SeCN^-$ – isoselenocyanate, $NCSe^-$ and sulfite, SO_3^{2-}.

Exercise 3.9.1

Are $[FeCl_5(NO_2)]^{3-}$ and $[FeCl_5(ONO)]^{3-}$ linkage isomers?

Solution

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:



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3.10: Color and Magnetism

Learning Objectives

- To get a simple overview of the origin of color and magnetism in complex ions.

Electromagnetic radiation is a form of energy that is produced by oscillating electric and magnetic disturbance, or by the movement of electrically charged particles traveling through a vacuum or matter. Electron radiation is released as photons, which are bundles of light energy that travel at the speed of light as quantized harmonic waves. This energy is then grouped into categories based on its wavelength into the electromagnetic spectrum and have certain characteristics, including amplitude, wavelength, and frequency (Figure 3.10.1).

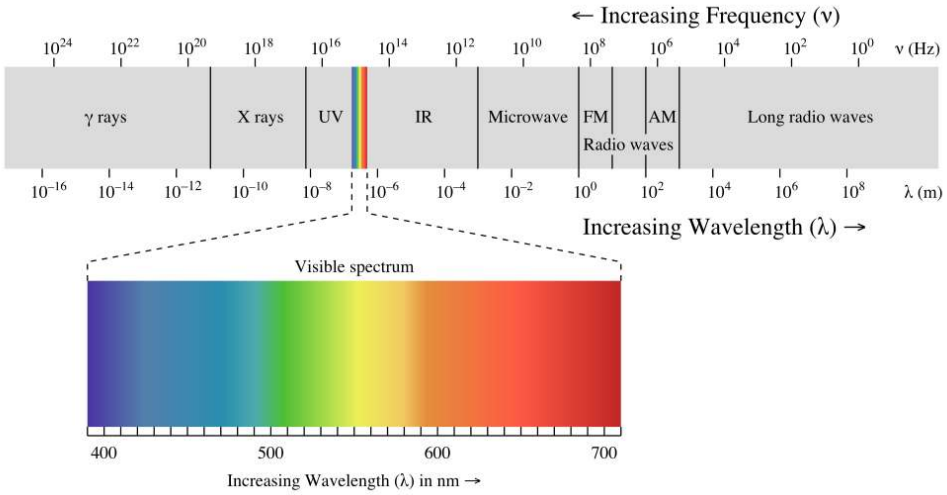


Figure 3.10.1: Electromagnetic spectrum with light highlighted. (CC -SA-BY 2.0 unported; Philip Ronan).

General properties of all electromagnetic radiation include:

1. Electromagnetic radiation can travel through empty space, while most other types of waves must travel through some sort of substance. For example, sound waves need either a gas, solid, or liquid to pass through to be heard.
2. The speed of light (c) is always a constant (2.99792458 x 10^8 m s^{-1}).
3. Wavelengths (λ) are measured between the distances of either crests or troughs.

The energy of a photon is expressed by Planck's law in terms of the frequency (u) of the photon

$$E = hu \tag{3.10.1}$$

since $\lambda u = c$ for all light Plancks law can be also expressed in terms of the wavelength of the photon

$$E = hu = \frac{hc}{\lambda} \tag{3.10.2}$$

If white light is passed through a prism, it splits into all the colors of the rainbow (Figure 3.10.2). Visible light is simply a small part of an electromagnetic spectrum most of which we cannot see - gamma rays, X-rays, infra-red, radio waves and so on. Each of these has a particular wavelength, ranging from 10^{-16} meters for gamma rays to several hundred meters for radio waves. Visible light has wavelengths from about 400 to 750 nm (1 nanometer = 10^{-9} meters).

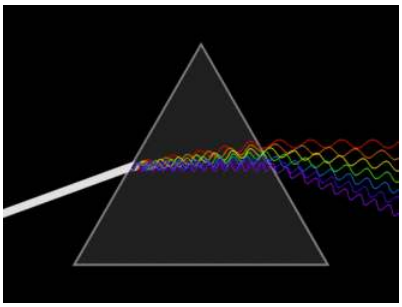
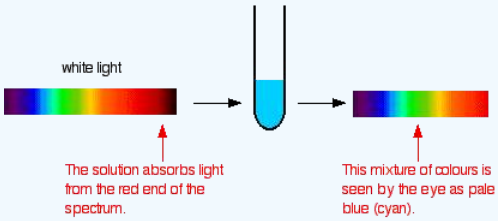


Figure 3.10.2: A triangular prism, dispersing light; waves shown to illustrate the differing wavelengths of light. (Public Domain; Lucas V. Barbosa).

Example 3.10.1: Blue Color of Copper (II) Sulfate in Solution

If white light (ordinary sunlight, for example) passes through copper(II) sulfate solution, some wavelengths in the light are absorbed by the solution. Copper(II) 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 copper(II) sulfate solution.



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.

Origin of Colors

The process of absorption involves the excitation of the valence electrons in the molecule typically from the low lying level called the Highest Occupied Molecular Orbital (HOMO) into a higher lying state called the the Lowest Unoccupied Molecular Orbital (**LUMO**). When this HOMO and LUMO transition (Figure 3.10.3) involves the absorption of visible light, the sample is colored.

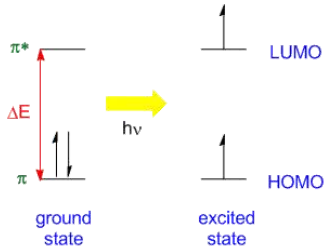


Figure 3.10.4: The general electron excitation process from a HOMO to a LUMO.

The HOMO-LUMO energy difference

$$\Delta E = E_{HOMO} - E_{LUMO} \tag{3.10.3}$$

depends on the nature of the molecule and can be connected to the wavelength of the light absorbed

$$\Delta E = hu = \frac{hc}{\lambda} \tag{3.10.4}$$

> *Equation 3.10.4 is the most important equation in the field of light-matter interactions (spectroscopy).*

As Example 3.10.1 demonstrated, when white light passes through or is reflected by a colored substance, a characteristic portion of the mixed wavelengths is absorbed. The remaining light will then assume the complementary color to the wavelength(s) absorbed. This relationship is demonstrated by the color wheel shown below. Here, complementary colors are diametrically opposite each other (Figure 3.10.5). Thus, absorption of 420-430 nm light renders a substance yellow, and absorption of 500-520 nm light makes it red. Green is unique in that it can be created by absorption close to 400 nm as well as absorption near 800 nm.

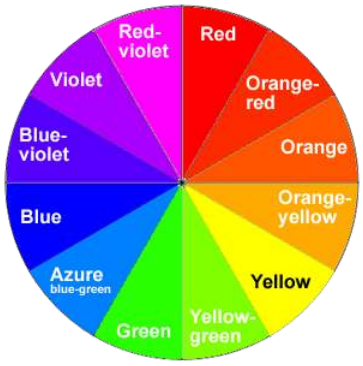


Figure 3.10.5: The color wheel used to identify the color of species.

Colors directly opposite each other on the color wheel are said to be complementary colors. Blue and yellow are complementary colors; red and cyan are complementary; and so are green and magenta. Mixing together two complementary colors of light will give you white light. What this all means is that if a particular color is absorbed from white light, what your eye detects by mixing up all the other wavelengths of light is its complementary color. Copper(II) sulfate solution is pale blue (cyan) because it absorbs light in the red region of the spectrum and cyan is the complementary color of red (Table 3.10.1).

Table 3.10.1: The Visible Spectrum

Color	Wavelength (nm)	ΔE HOMO - LUMO gap (eV)
UV	100 - 400	12.4 - 3.10
Violet	400 - 425	3.10 - 2.92
Blue	425 - 492	2.92 - 2.52
Green	492 - 575	2.52 - 2.15
Yellow	575 - 585	2.15 - 2.12
Orange	585 - 647	2.12 - 1.92
Red	647 - 700	1.92 - 1.77
Near IR	700 - 10,000	1.77 - 0.12

If the compound absorbs in one region of the spectra, it appears with the opposite (complementary) color, since all of the absorbed color has been removed. For example:

- the material absorbs violet light ⇒ color is yellow
- the material absorbs blue light ⇒ color is orange
- the material absorbs yellow-green light ⇒ color is red-violet

The Origin of Color in Complex Ions

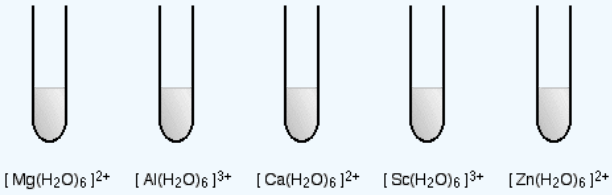
We often casually talk about the transition metals as being those in the middle of the Periodic Table where d orbitals are being filled, but these should really be called d block elements rather than transition elements (or metals). The definition of a transition metal is one which forms one or more stable ions which have incompletely filled d orbitals. Zinc with the electronic structure [Ar] $3d^{10}4s^2$ does not count as a transition metal whichever definition you use. In the metal, it has a full 3d level. When it forms an ion, the 4s electrons are lost - again leaving a completely full 3d level. At the other end of the row, scandium ([Ar] $3d^14s^2$) does not

really counts as a transition metal either. Although there is a partially filled d level in the metal, when it forms its ion, it loses all three outer electrons. The Sc^{3+} ion does not count as a transition metal ion because its 3d level is empty.

Example 3.10.3: Hexaaqua Metal Ions

The diagrams show the approximate colors of some typical hexaaqua metal ions, with the formula $[\ M(H_2O)_6\ ]^{n+}$. The charge on these ions is typically 2+ or 3+.

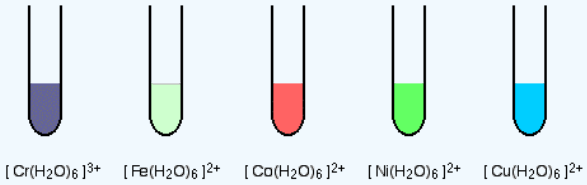
- Non-transition metal ions



These ions are all colorless.

Ions are [Mg(H2O)6] two plus, [Al(H2O)6] three plus, [Ca(H2O)6] two plus, [Sc(H2O)6] three plus, and [Zn(H2O)6] two plus

- Transition metal ions



Ions are [Cr(h2O)6] three plus, [Fe(H20)6] two plus, [Co(H2O)6] two plus, [Ni(H2O)6] two plus, and [Cu[H2O)6] two plus.

The corresponding transition metal ions are colored. Some, like the hexaaquamanganese(II) ion (not shown) and the hexaaquairon(II) ion, are quite faintly colored - but they are colored.

So, what causes transition metal ions to absorb wavelengths from visible light (causing color) whereas non-transition metal ions do not? And why does the color vary so much from ion to ion? This is discussed in the next sections.

Magnetism

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 the first two are introduced below.

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 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:



A chemical demonstration of the paramagnetism of oxygen, as shown by the attraction of liquid oxygen to a magnet. Carleton University, Ottawa, Canada.

As shown in the video, molecular oxygen (O_2 is paramagnetic and is attracted to the magnet. Incontrast, Molecular nitrogen, N_2, however, has no unpaired electrons and it is diamagnetic (this concept is discussed below); it is therefore unaffected by the magnet.

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. In fact, diamagnetic substances are weakly ***repelled*** by a magnetic field as demonstrated with the pyrolytic carbon sheet in Figure 3.10.6

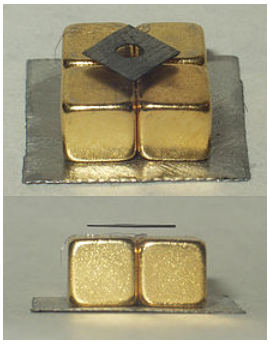


Figure 3.10.6 Levitating pyrolytic carbon: A small (~6 mm) piece of pyrolytic graphite levitating over a permanent neodymium magnet array (5 mm cubes on a piece of steel). Note that the poles of the magnets are aligned vertically and alternate (two with north facing up, and two with south facing up, diagonally). from Wikipedia.

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 unpaired electrons) or diamagnetic (all electrons paired)

Example 3.10.4: Chlorine atoms

Are chlorine atoms paramagnetic or diamagnetic?

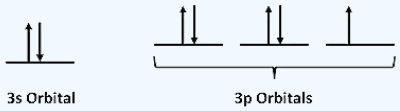
Solution

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

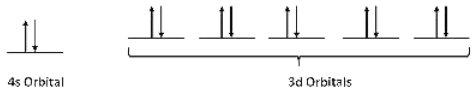
Since there is an unpaired electron, Cl atoms are paramagnetic (but is quite weak).

Example 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.

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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CHAPTER OVERVIEW

4: Coordination Chemistry and Crystal Field Theory

Learning Objectives

- Determine oxidation states and assign d-electron counts for transition metals in complexes.
- Derive the d-orbital splitting patterns for octahedral, elongated octahedral, square pyramidal, square planar, and tetrahedral complexes.
- For octahedral and tetrahedral complexes, determine the number of unpaired electrons and calculate the crystal field stabilization energy.
- Know the spectrochemical series, rationalize why different classes of ligands impact the crystal field splitting energy as they do, and use it to predict high vs. low spin complexes, and the colors of transition metal complexes.
- Use the magnetic moment of transition metal complexes to determine their spin state.
- Understand the origin of the Jahn-Teller effect and its consequences for complex shape, color, and reactivity.
- Understand the extra stability of complexes formed by chelating and macrocyclic ligands.

Coordination compounds (or complexes) are molecules and extended solids that contain bonds between a transition metal ion and one or more ligands. In forming these coordinate covalent bonds, the metal ions act as Lewis acids and the ligands act as Lewis bases. Typically, the ligand has a lone pair of electrons, and the bond is formed by overlap of the molecular orbital containing this electron pair with the d-orbitals of the metal ion.

4.1: Prelude to Coordination Chemistry and Crystal Field Theory
4.2: Chelate and Macrocyclic Effects
4.3: Ligand Substitution Reactions
4.4: Counting Electrons in Transition Metal Complexes
4.5: Crystal Field Theory
4.6: Spectrochemical Series
4.7: π-Bonding between Metals and Ligands
4.8: Crystal Field Stabilization Energy, Pairing, and Hund's Rule
4.9: Magnetic Susceptibility and the Spin-only Formula
4.10: Jahn-Teller Distortions
4.11: Non-octahedral Complexes
4.12: Tetrahedral Complexes
4.13: Stability of Transition Metal Complexes
4.14: Ligand Field Theory
4.15: The 18-electron Rule
4.16: References

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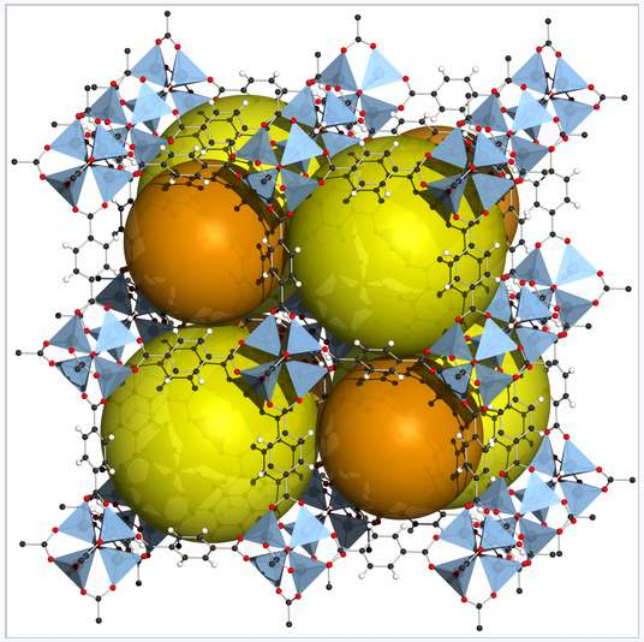
4.1: Prelude to Coordination Chemistry and Crystal Field Theory

Coordination compounds (or **complexes**) are molecules and extended solids that contain bonds between a **transition metal** ion and one or more **ligands**. In forming these **coordinate covalent bonds**, the metal ions act as Lewis acids and the ligands act as Lewis bases. Typically, the ligand has a lone pair of electrons, and the bond is formed by overlap of the molecular orbital containing this electron pair with the d-orbitals of the metal ion. Ligands that are commonly found in coordination complexes are neutral molecules (H_2O, NH_3, organic bases such as pyridine, CO, NO, H_2, ethylene, and phosphines PR_3) and anions (halides, CN^-, SCN^-, cyclopentadienide ($C_5H_5^-$), H^-, etc.). The resulting complexes can be cationic (e.g., $[Cu(NH_3)_4]^{2+}$), neutral ($[Pt(NH_3)_2Cl_2]$) or anionic ($[Fe(CN)_6]^{4-}$). As we will see below, ligands that have weak or negligible strength as Brønsted bases (for example, CO, CN^-, H_2O, and Cl^-) can still be potent Lewis bases in forming transition metal complexes.

With ligands that are Lewis bases, coordinate covalent bonds (also called dative bonds) are typically drawn as lines, or sometimes as arrows to indicate that the electron pair "belongs" to the ligand X:

$M \leftarrow\!: X$

In counting electrons on the metal (described below), the convention is to assign both electrons in the dative bond to the ligand, although in reality the bonds are typically polar covalent and electrons are shared between the metal and the ligand.



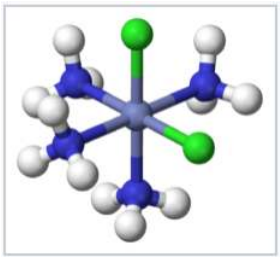
$Zn_4O(BDC)_3$, also called MOF-5, is a metal-organic framework in which 1,4-benzenedicarboxylate (BDC) anions bridge between cationic Zn_4O clusters.[1] The rigid framework contains large voids, represented by orange spheres. MOFs can be made from many different transition metal ions and bridging ligands, and are being developed for practical applications in storing gases, especially H_2 and CO_2. MOF-5 has a volumetric storage density of 66 g H_2/L, close to that of liquid H_2.

When writing out the formulas of coordination compounds, we use square brackets [···] around the metal ions and ligands that are directly bonded to each other. Thus the compound $[Co(NH_3)_5Cl]Cl_2$ contains octahedral $[Co(NH_3)_5Cl]^{2+}$ ions, in which five ammonia molecules and one chloride ion are directly bonded to the metal, and two Cl^- anions that are not coordinated to the metal.

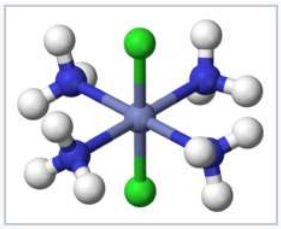
History

Coordination compounds have been known for centuries, but their structures were initially not understood. For example, Prussian Blue, which has an empirical formula $Fe_7(CN)_{18}•xH_2O$, is an insoluble, deep blue solid that has been used as a pigment since its accidental discovery by Diesbach in 1704. Prussian Blue actually contains Fe^{3+} cations and $[Fe(CN)_6]^{4-}$ anions, and a more descriptive formulation is $(Fe^{3+})_4([Fe(CN)_6]^{4-})_3•xH_2O$. Simpler compounds such as the ammonia complex of Co^{3+} were known to chemists but did not fit the expected behavior of ionic solids. For example, cobalt(III)hexammine chloride, $[Co(NH_3)_6]Cl_3$ was formulated as $CoCl_3•6NH_3$. It had mysterious properties, in that it dissolved in water like an ionic solid, but it retained its six

ammonia molecules when recrystallized. Even more intriguing was the observation that chemically different forms (isomers) of transition metal complexes such as $[Co(NH_3)_4Cl_2]Cl$ could be made. The puzzle was solved by Alfred Werner, who proposed in 1893 that these Co complexes contained octahedrally coordinated metal ions that made primary (covalent) bonds to six ligands. Werner showed through conductivity measurements that solutions of $CoCl_3 \cdot 6NH_3$ contained three free Cl^- anions and one $[Co(NH_3)_6]^{3+}$ cation per formula unit. Magnetic susceptibility measurements later confirmed the presence of diamagnetic Co^{3+} in both the salt and its solutions. Werner's theory also explained the existence of two (and only two) structural isomers for $[Co(NH_3)_4Cl_2]^+$.



cis-$[Co(NH_3)_4\ Cl_2]^+$



trans-$[Co(NH_3)_4\ Cl_2]^+$

Like organic compounds, transition metal complexes can vary widely in size, shape, charge and stability. We will see that bonds formed from the d-orbitals of the metal largely control these properties.



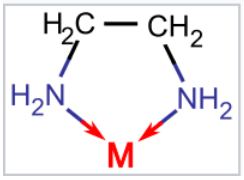
Alfred Werner was a Swiss chemist who received the Nobel prize in 1913 for elucidating the bonding in coordination compounds.

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4.2: Chelate and Macrocyclic Effects

Ligands that contain more than one binding site for a metal ion are called **chelating** ligands (from the Greek word χηλή, chēlē, meaning "claw"). 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.



Ethylenediamine (en) is a bidentate ligand that forms a five-membered ring in coordinating to a metal ion M

Consider the two complexation equilibria in aqueous solution, between the cobalt (II) ion, Co^{2+}(aq) and ethylenediamine (en) on the one hand and ammonia, NH_3, on the other.

$$[Co(H_2O)_6]^{2+} + 6\,NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 6\,H_2O \quad (1)$$

$$[Co(H_2O)_6]^{2+} + 3\,en \rightleftharpoons [Co(en)_3]^{2+} + 6\,H_2O \quad (2)$$

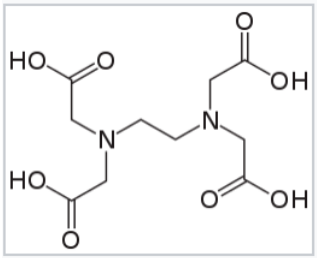
Electronically, the ammonia and en ligands are very similar, since both bind through N and since the Lewis base strengths of their nitrogen atoms are similar. This means that ΔH° must be very similar for the two reactions, since six Co-N bonds are formed in each case. Interestingly however, we observe that the equilibrium constant is *100,000 times larger* for the second reaction than it is for the first.

The big difference between these two reactions is that the second one involves "condensation" of *fewer particles* to make the complex. This means that the **entropy changes** for the two reactions are different. The first reaction has a ΔS° value close to zero, because there are the same number of molecules on both sides of the equation. The second one has a positive ΔS° because four molecules come together but seven molecules are produced. The difference between them (ΔΔS°) is about +100 J/mol-K. We can translate this into a ratio of equilibrium constants using:

$K_f(en)/K_f(NH_3) = e^{-\Delta\Delta G°/RT} \approx e^{+\Delta\Delta S°/R} \approx e^{12} \approx 10^5$

$$\frac{K_f(en)}{K_f(NH_3)} = e^{\frac{-\Delta\Delta G^o}{RT}} \approx e^{\frac{+\Delta\Delta S^o}{R}} \approx e^{12} \approx 10^5 \qquad (4.2.1)$$

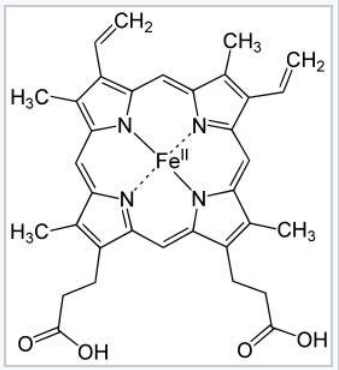
The bottom line is that the chelate effect is **entropy-driven**. It follows that the more binding groups a ligand contains, the more positive the ΔS° and the higher the K_f will be for complex formation. In this regard, the hexadentate ligand ethylenediamine tetraacetic acid (EDTA) is an optimal ligand for making octahedral complexes because it has six binding groups. In basic solutions where all four of the COOH groups are deprotonated, the **chelate effect** of the $EDTA^{4-}$ ligand is approximately 10^{15}. This means, for a given metal ion, K_f is 10^{15} times larger for $EDTA^{4-}$ than it would be for the relevant monodentate ligands at the same concentration. $EDTA^{4-}$tightly binds essentially any 2+, 3+, or 4+ ion in the periodic table, and is a very useful ligand for both analytical applications and separations.



Ethylenediaminetetraaceticacid acid (EDTA), a hexadentate ligand

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

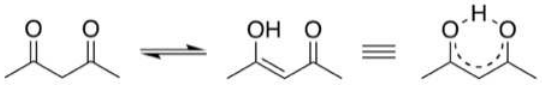
cyclic form, they allow less conformational freedom. The ligand is said to be "**pre-organized**" for binding, and there is little entropy penalty for wrapping it around the metal ion. For example heme b is a tetradentate cyclic ligand which is strongly complexes transition metal ions, including (in biological systems) Fe^{+2}.



Heme b

Some other common chelating and cyclic ligands are shown below:

Acetylacetonate ($acac^-$, right) 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.



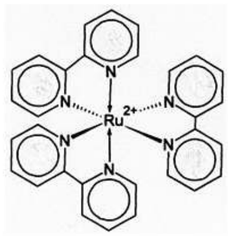
2,2'-Bipyridine and related bidentate ligands such as 1,10-phenanthroline (below, center left) form propeller-shaped complexes with metals such as Ru^{2+}. The $[Ru(bpy)_3]^{2+}$ complex (below left) is photoluminescent and can also undergo photoredox reactions, making it an interesting compound for both photocatalysis and artificial photosynthesis. The chiral propellor shapes of metal polypyridyl complexes such as $[Ru(bpy)_3]^{2+}$ coincidentally match the size and helicity of the major groove of DNA. This has led to a number of interesting studies of electron transfer reactions along the DNA backbone, initiated by photoexcitation of the metal complex.

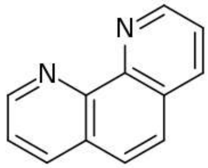


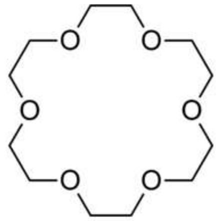
Prof. Jacqueline Barton (Caltech) has used metal polypyridyl complexes to study electron transfer reactions that are implicated in the biological sensing and repair of damage in DNA molecules.

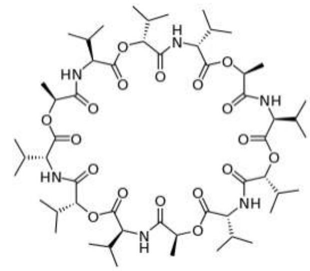
Crown ethers such as 18-crown-6 (below, center right) are cyclic hard bases that can complex alkali metal cations. Crowns can selectively bind Li^+, Na^+, or K^+ depending on the number of ethylene oxide units in the ring.

The chelating properties of crown ethers are mimetic of the natural antibiotic **valinomycin** (below 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.









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4.3: Ligand Substitution Reactions

Transition metal complexes can exchange one ligand for another, and these reactions are important in their synthesis, stereochemistry, and catalytic chemistry. The mechanisms of chemical reactions are intimately connected to reaction kinetics. As in organic chemistry, the mechanisms of transition metal reactions are typically inferred from experiments that examine the concentration dependence of the incoming and outgoing ligands on the reaction rate, the detection of intermediates, and the stereochemistry of the reactants and products.

Thermodynamic vs. kinetics. When we think about the reactions of transition metal complexes, it is important to recall the distinction between their *thermodynamics* and *kinetics*. Take for example the formation of the square planar tetracyanonickelate complex:

$$\mathrm{Ni^{2+}_{(aq)} + 4\,CN^{-}_{(aq)} = [Ni(CN)_4]^{2-}_{(aq)}} \quad K_{(eq)} \approx 10^{30} M^{-4} \tag{4.3.1}$$

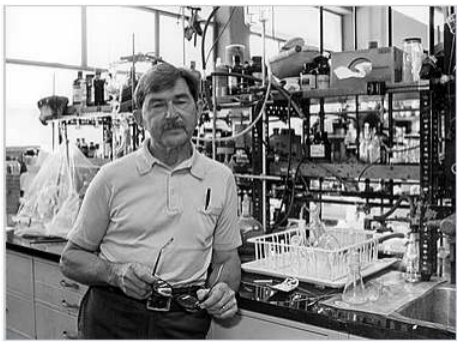
Thermodynamically, $[Ni(CN)_4]^{2-}$ is very **stable**, meaning that the equilibrium above lies very far to the right. Kinetically, however, the complex is **labile**, meaning that it can exchange its ligands rapidly. For example the exchange between a ^{13}C labeled CN^- ion and a bound CN^- ligand occurs on the timescale of tens of milliseconds:

$$\mathrm{[Ni(CN)_4]^{2-}_{(aq)} + {\cdot}CN^{-}_{(aq)} \longrightarrow [Ni(CN)_3({\cdot}CN)]^{2-} + CN^{-}_{(aq)}} \quad k_{exchange} \approx 10^2 M^{-1} s^{-1} \tag{4.3.2}$$

Conversely, a compound can be thermodynamically **unstable** but kinetically **inert**, meaning that it takes a relatively long time to react. For example, the $[Co(NH_3)_6]^{3+}$ ion is unstable in acid, but its hydrolysis reaction with concentrated HCl takes about one week to go to completion at room temperature:

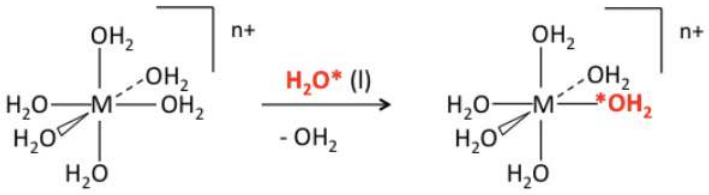
$$\mathrm{[Co(NH_3)_6]^{3+}_{(aq)} + 6\,H_3O^{+}_{(aq)} \longrightarrow [Co(H_2O)_6]^{3+}_{(aq)} + 6\,NH^{+}_{4(aq)}} \quad K_{eq} \approx 10^{30} \tag{4.3.3}$$

Henry Taube, who studied the mechanisms of ligand exchange reactions in simple test tube experiments, classified transition metal complexes as **labile** if their reaction half-life was one minute or less, and **inert** if they took longer to react. The dynamic range of ligand substitution rates is enormous, spanning at least 15 orders of magnitude. On the timescale of most laboratory experiments, the Taube definition of lability is a useful one for classifying reactions into those that have low and high activation energies. As we will see, the **crystal field stabilization energy (CFSE)** plays a key role in determining the activation energy and therefore the rate of ligand substitution.



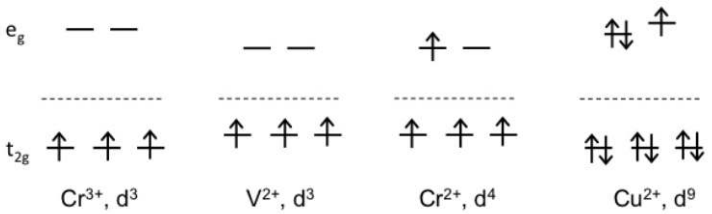
Henry Taube (Stanford University) received the 1983 Nobel Prize for his work on the electron transfer and ligand exchange reactions of transition metal complexes

Crystal field stabilization energy and ligand exchange rates. Let's consider a very commmon and simple ligand exchange reaction, which is the substitution of one water molecule for another in an octahedral $[M(H_2O)_6]^{n+}$ complex. Since the products (except for the label) are the same as the reactants, we know that $\Delta G° = 0$ and $K_{eq} = 1$ for this reaction. The progress of the reaction can be monitored by NMR by using isotopically labeled water (typically containing ^{17}O or ^{18}O):



The most striking thing about this (otherwise boring) reaction is the vast difference in rate constants - about 14 orders of magnitude - for different metal ions and oxidation states:

M^{n+}	log k (sec^{-1})
Cr^{3+}	-6
V^{2+}	-2
Cr^{2+}	8
Cu^{2+}	8



While at first it may seem strange that the same ion in two different oxidation states (Cr^{3+} vs. Cr^{2+}) would be inert or labile, respectively, we can begin to rationalize the difference by drawing d-orbital splitting diagrams for the complexes. What we find is that octahedral complexes that have **high CFSE** (Cr^{3+}, V^{2+}) tend to be **inert**. Conversely, ions with electrons in high energy e_g orbitals (Cr^{2+}, Cu^{2+}) tend to be labile. In the case of Cr^{3+} and V^{2+}, the energy penalty for distorting the complex away from octahedral symmetry - to make, for example, a 5- or 7-coordinate intermediate - is particularly high. This activation energy for ligand substitution is lower for Cr^{2+} and Cu^{2+}, which already have electrons in antibonding e_g orbitals.

Based on the rules we developed for calculating the CFSE of transition metal complexes, we can now predict the trends in ligand substitution rates:

- Octahedral complexes with **d^3** and **d^6(low spin)** configurations, such as Cr^{3+} (d^3), Co^{3+} (d^6), Rh^{3+} (d^6), Ru^{2+} (d^6), and Os^{2+} (d^6) tend to be **substitution-inert** because of their high CFSE.
- **Square planar d^8** complexes, especially those in the 4d and 5d series, are also s**ubstitution-inert**. Examples are complexes of Pd^{2+}, Pt^{2+}, and Au^{3+}.
- Intermediate cases are complexes of Fe^{3+}, V^{3+}, V^{2+}, Ni^{2+}, and of main group ions (Be^{2+}, Al^{3+}) that are hard Lewis acids. These complexes make strong metal-oxygen bonds and have water exchange rates in the range of 10^1-10^6 s^{-1}.
- **Ions with zero CFSE** exchange water molecules on a timescale of nanoseconds ($k \approx 10^8$-10^9 s^{-1}). These include ions with d^0, d^5 (high spin), and d^{10} electron counts, including alkali metal (Li^+, Na^+, K^+, Rb^+, Cs^+) and alkali earth (Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}) cations, Zn^{2+}, Cd^{2+}, Hg^{2+}, and Mn^{2+}. In these cases the CFSE is zero and the energetic cost of breaking octahedral symmetry is relatively low.
- For p-block elements, faster exchange occurs with larger ions (e.g., $Ba^{2+} > Ca^{2+}$ and $Ga^{3+} > Al^{3+}$), because Lewis acid strength decreases with increasing ion size.
- The Cu^{2+} ion (d^9), as a **Jahn-Teller ion**, is already distorted away from octahedral symmetry and is therefore quite **labile**, exchanging water ligands at a rate of about 10^8 s^{-1}.

Ligand Substitution Mechanisms. For an ML_n complex undergoing ligand substitution, there are essentially three different reaction mechanisms:

- In the **dissociative mechanism**, a ML_n complex first **loses a ligand** to form an ML_{n-1} intermediate, and the incoming ligand Y reacts with the ML_{n-1} fragment:

$$\mathrm{L_{n-1}M{-}L} \underset{+L,k_{-1}}{\overset{-L,k_1}{\rightleftharpoons}} \mathrm{L_{n-1}M{-}\square} \xrightarrow{+Y,k_2} \mathrm{L_{n-1}M{-}Y} \tag{4.3.4}$$

This mechanism is illustrated below for ligand substitution on an octahedral ML_6 complex. The intermediate state in this example involves a trigonal bipyramidal ML_5 fragment as well as free L and Y ligands.

If the rate determining step is the dissociation of L from the complex, then the concentration of Y does not affect the rate of reaction, leading to the first-order rate law:

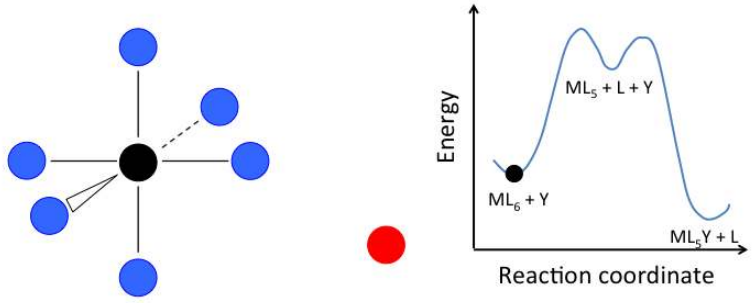


Illustration of the dissociative ligand substitution mechanism for an ML_6 complex. The reaction energy profile is shown at the right.

$$Rate = k_1[ML_n] \tag{4.3.5}$$

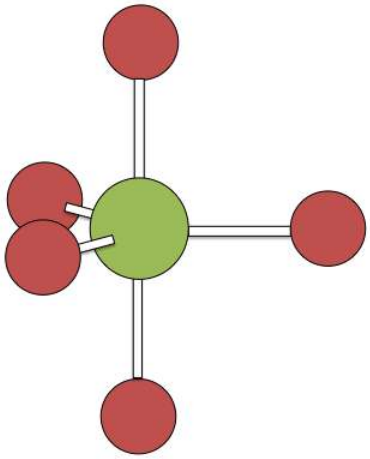
In the case of an octahedral complex, this reaction would be first order in ML_6 and zero order in Y, but only if the highest energy transition state is the one that precedes the formation of the ML_5 intermediate. If the two transition states are close in energy (as in the case of the animation at the right), then the rate law becomes more complicated. In this case, we can simplify the problem by assuming a low steady-state concentration of the ML_n intermediate. The resulting rate law is:

$$Rate = \frac{k_1 k_2[Y][ML_n]}{k_{-1}[L] + k_2[Y]} \tag{4.3.6}$$

which reduces to the simpler first-order rate law when $k_2[Y] >> k_{-1}[L]$. Because the formation of the transition state involves dissociation of a ligand, the entropy of activation is always positive in the dissociative mechanism.

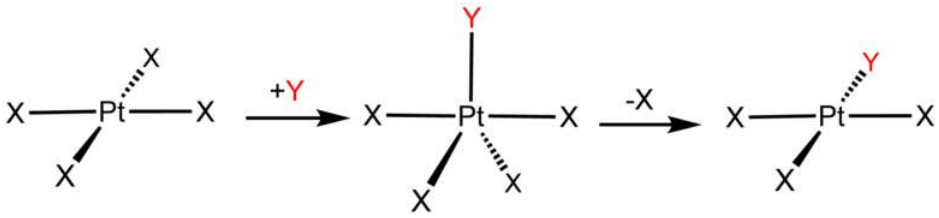
- In the **associative mechanism**, the incoming ligand Y attacks the ML_n complex, transiently forming an ML_nY intermediate, and the intermediate then loses a ligand L forming the $ML_{n-1}Y$ product

Complexes that undergo associative substitution are typically either coordinatively unsaturated or contain a ligand that can change its bonding to the metal, e.g. a change in the hapticity or bending of a nitric oxide ligand (NO). In homogeneous catalysis, the associative pathway is desirable because the binding event, and hence the selectivity of the reaction, depends not only on the nature of the metal catalyst but also on the molecule that is involved in the catalytic cycle.



Berry pseudorotation mechanism

Examples of associative mechanisms are commonly found in the chemistry of d^8 square planar metal complexes, e.g. Vaska's complex ($IrCl(CO)[P(C_6H_5)_3]_2$) and tetrachloroplatinate(II). These compounds (ML_4) bind the incoming (substituting) ligand Y to form pentacoordinate intermediates ML_4Y, which in a subsequent step dissociate one of their ligands. Although the incoming ligand is initially bound at an equatorial site, the **Berry pseudorotation** provides a low energy pathway for all ligands to sample both the equatorial and axial sites. Ligand dissociation must occur from an equatorial site according to the principle of microscopic reversibility. Dissociation of Y results in no reaction, but dissociation of L results in net substitution, yielding the d^8 complex ML_3Y. The first step is typically rate determining. Thus, the entropy of activation is negative, which indicates an increase in order in the transition state. Associative reactions follow second order kinetics: the rate of the appearance of product depends on the concentration of both ML_4 and Y.



The Trans Effect, which is connected with the associative mechanism, controls the stereochemistry of certain ligand substitution reactions.

The trans effect refers to the labilization (making more reactive) of ligands that are **trans** to certain other ligands, the latter being referred to as **trans-directing ligands**. The labilization of trans ligands is attributed to electronic effects and is most notable in square planar complexes, but it can also be observed with octahedral complexes.[18] The cis effect is most often observed in octahedral complexes.

In addition to the *kinetic trans effect*, trans ligands also have an influence on the ground state of the molecule, the most notable ones being bond lengths and stability. Some authors prefer the term **trans influence** to distinguish this from the kinetic effect,[19] while others use more specific terms such as **structural trans effect** or **thermodynamic trans effect**.[18]

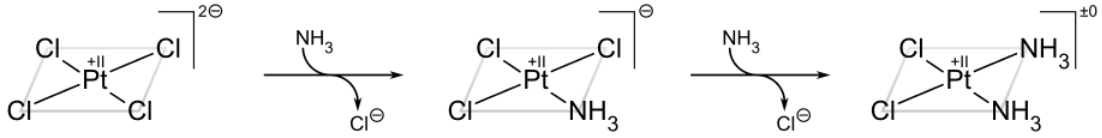
The discovery of the trans effect is attributed to Ilya Ilich Chernyaev,[20] who recognized it and gave it a name in 1926.[21]

The intensity of the trans effect (as measured by the increase in the rate of substitution of the trans ligand) follows this sequence:

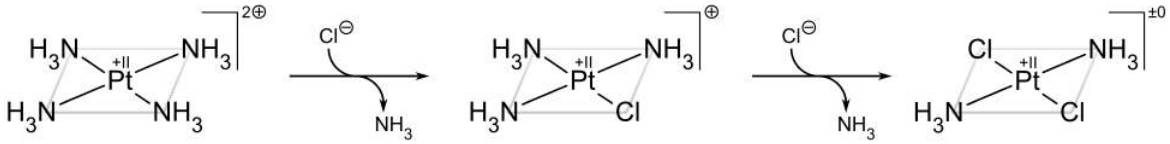
F^-, H_2O, OH^- < NH_3 < py < Cl^- < Br^- < I^-, SCN^-, NO_2^-, $SC(NH_2)_2$, Ph^- < SO_3^{2-} < PR_3, AsR_3, SR_2, CH_3^- < H^-, NO, CO, CN^-, C_2H_4

Note that weak field ligands tend to be poor trans-directing ligands, whereas strong field ligands are strongly trans-directing.

The classic example of the trans effect is the synthesis of cisplatin and its trans isomer.[22] Starting from $PtCl_4^{2-}$, the first NH_3 ligand is added to any of the four equivalent positions at random. However, since Cl^- has a greater trans effect than NH_3, the second NH_3 is added trans to a Cl^- and therefore cis to the first NH_3.



If, on the other hand, one starts from $Pt(NH_3)_4^{2+}$, the *trans* product is obtained instead:



The trans effect in square complexes can be explained in terms of the associative mechanism, described above, which goes through a trigonal bipyramidal intermediate. Ligands with a high kinetic trans effect are in general those with high π acidity (as in the case of phosphines) or low-ligand lone-pair–d_π repulsions (as in the case of hydride), which prefer the more π-basic equatorial sites in the intermediate. The second equatorial position is occupied by the incoming ligand. The third and final equatorial site is occupied by the departing trans ligand, so the net result is that the kinetically favored product is the one in which the ligand trans to the one with the largest trans effect is eliminated.[19]

- The **interchange mechanism** is similar to the associative and dissociative pathways, except that no distinct ML_nY or ML_{n-1} intermediate is formed. This concerted mechanism can be thought of as analogous to nucleophilic substitution via the S_N2 pathway at a tetrahedral carbon atom in organic chemistry. The interchange mechanism is further classified as associative (I_a) or dissociative (I_d) depending on the relative importance of M-Y and M-L bonding in the transition state. If the transition state is characterized by the formation of a strong M-Y bond, then the mechanism is I_a. Conversely, if weakening of the M-L bond is more important in reaching the transition state, then the mechanism is I_d.

An example of the I_a mechanism is the interchange of bulk and coordinated water in $[V(H_2O)_6]^{2+}$. In contrast, the slightly more compact ion $[Ni(H_2O)_6]^{2+}$ ion exchanges water via the I_d mechanism.[23]

Effects of ion pairing. Highly charged cationic complexes tend to form ion pairs with anionic ligands, and these ion pairs often undergo reactions via the I_a pathway. The electrostatically held nucleophilic incoming ligand can exchange positions with a ligand in the first coordination sphere, resulting in net substitution. An illustrative process is the "anation" (reaction with an anion) of the chromium(III) hexaaquo complex:

$$[Cr(H_2O)_6]^{3+} + SCN^- \longleftrightarrow [Cr(H_2O)_6], NCS^{2+}$$

$$[Cr(H_2O)_6], NCS^{2+} \longleftrightarrow [Cr(H_2O)_5NCS]^{2+} + H_2O$$

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4.4: Counting Electrons in Transition Metal Complexes

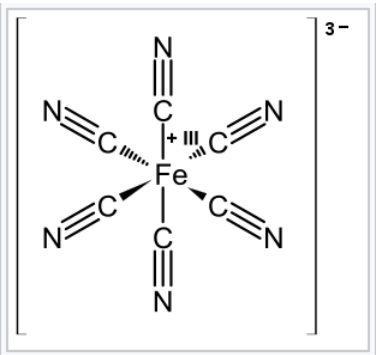
The d-orbitals are the frontier orbitals (the HOMO and LUMO) of transition metal complexes. Many of the important properties of complexes - their shape, color, magnetism, and reactivity - depend on the electron occupancy of the metal's d-orbitals. To understand and rationalize these properties it is important to know how to count the d-electrons.

Because transition metals are generally less electronegative than the atoms on the ligands (C, N, O, Cl, P...) that form the metal-ligand bond, our convention is to assign **both electrons** in the bond to the **ligand**. For example, in the ferricyanide complex $[Fe(CN)_6]^{3-}$, if the cyanide ligand keeps both of its electrons it is formulated as CN^-. By difference, iron must be Fe^{3+} because the charges ($3^+ + 6(1^-)$) must add up to the overall -3 charge on the complex.

The next step is to determine how many d-electrons the Fe^{3+} ion has. The rule is to count **all** of iron's valence electrons as **d-electrons**. Iron is in group 8, so

group 8 - 3+ charge = d^5 (or $3d^5$)

8 - 3 = 5

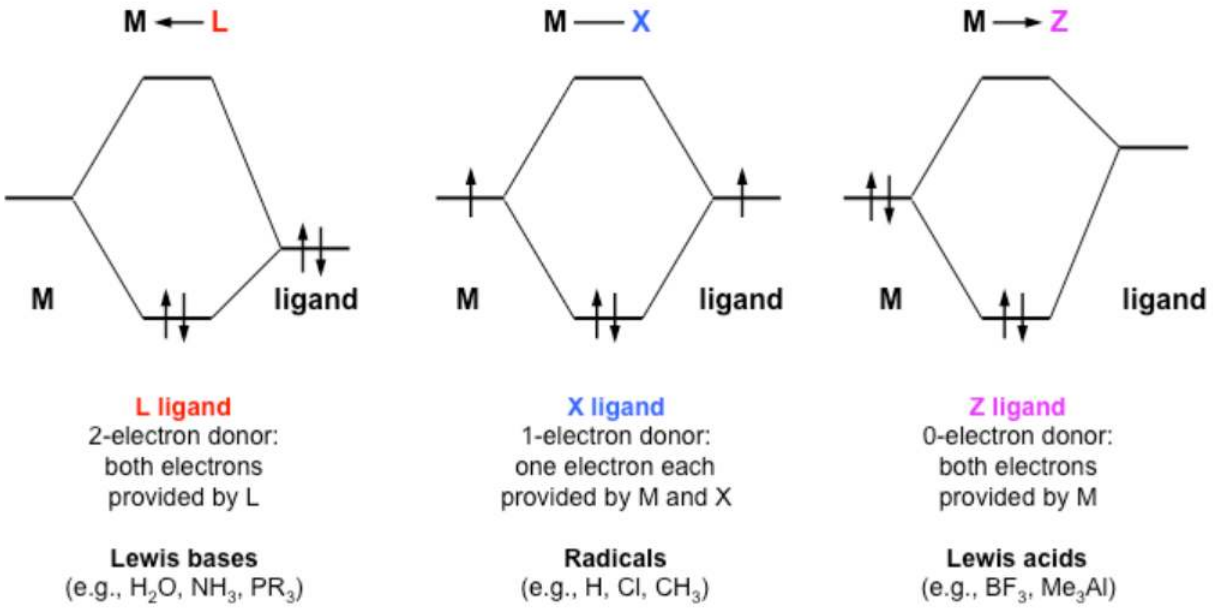


Structure of the octahedral ferricyanide anion. Because the overall charge of the complex is 3-, Fe is in the +3 oxidation state and its electron count is $3d^5$.

The same procedure can be applied to any transition metal complex. For example, consider the complex $[Cu(NH_3)_4]^{2+}$. Because ammonia is a neutral ligand, Cu is in the 2+ oxidation state. Copper (II), in group 11 of the periodic table has 11 electrons in its valence shell, minus two, leaving it with 9 d-electrons ($3d^9$). In the neutral complex $[Rh(OH)_3(H_2O)_3]$, Rh is in the +3 oxidation state and is in group 9, so the electron count is $4d^6$. Zinc(II) in group 12 would have 10 d-electrons in $[Zn(NH_3)_4]^{2+}$, a full shell, and manganese (VII) has zero d-electrons in MnO_4^-. Nickel carbonyl, $Ni(CO)_4$, contains the neutral CO ligand and Ni in the zero oxidation state. Since Ni is in group 10, we count the electrons on Ni as $3d^{10}$.

A frequent source of confusion about electron counting is the fate of the s-electrons on the metal. For example, our electron counting rules predict that Ti is $3d^1$ in the octahedral complex $[Ti(H_2O)_6]^{3+}$. But the electronic configuration of a free Ti atom, according to the Aufbau principle, is $4s^23d^2$. Why is the Ti^{3+} ion $3d^1$ and not $4s^1$? Similarly, why do we assign Mn^{2+} as $3d^5$ rather than $4s^23d^3$? The short answer is that the metal s orbitals are higher in energy in a metal complex than they are in the free atom because they have antibonding character. We will justify this statement with a MO diagram in Section 5.2.

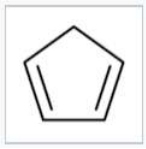
Covalent Bond Classification (CBC) Method. Although the electron counting rule we have developed above is useful and works reliably for all kinds of complexes, the assignment of all the shared electrons in the complex to the ligands does not always represent the true bonding picture. This picture would be most accurate in the case of ligands that are much more electronegative than the metal. But in fact, there all all kinds of ligands, including those such as H, alkyl, cyclopentadienide, and others where the metal and ligand have comparable electronegativity. In those cases, especially with late transition metals that are relatively electropositive, we should regard the metal-ligand bond as covalent. The CBC method, also referred to as LXZ notation, was introduced in 1995 by M. L. H. Green[2] in order to better describe the different kinds of metal-ligand bonds. The molecular orbital pictures below summarize the difference between L, X, and Z ligands.[3] Of these, L and X are the most common types.



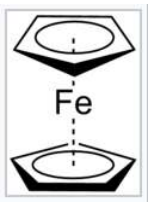
L-type ligands are Lewis bases that donate two electrons to the metal center regardless of the electron counting method being used. These electrons can come from lone pairs, pi or sigma donors. The bonds formed between these ligands and the metal are dative covalent bonds, which are also known as coordinate bonds. Examples of this type of ligand include CO, PR_3, NH_3, H_2O, carbenes (=CRR'), and alkenes.

X-type ligands are those that donate one electron to the metal and accept one electron from the metal when using the neutral ligand method of electron counting, or donate two electrons to the metal when using the donor pair method of electron counting.[4] Regardless of whether it is considered neutral or anionic, these ligands yield normal covalent bonds. A few examples of this type of ligand are H, CH_3, halogens, and NO (bent).

Z-type ligands are those that accept two electrons from the metal center as opposed to the donation occurring with the other two types of ligands. However, these ligands also form dative covalent bonds like the L-type. This type of ligand is not usually used, because in certain situations it can be written in terms of L and X. For example, if a Z ligand is accompanied by an L type, it can be written as X_2. Examples of these ligands are Lewis acids, such as BR_3.



Cp



Ferrocene

Some multidentate ligands can act as a combination of ligand types. A famous example is the cyclopentadienyl (or Cp) ligand, C_5H_5. We would classify this neutral ligand as [L_2X], with the two L functionalities corresponding to the two “olefinic” fragments while the X functionality corresponds to the CH “radical” carbon in the ring. The addition of one electron makes the Cp^- anion, which has six pi electrons and is thus planar and aromatic. In the ferrocene complex, Cp_2Fe, using the "standard" donor pair

counting method we can regard the two Cp^- ligands as each possessing six pi electrons, and by difference Fe is in the +2 oxidation state. The Fe^{2+} ion is d^6. Thus the iron atom in the complex (regardless of the counting method) has 6+6+6=18 electrons in its coordination environment, which is a particularly stable electron count for transition metal complexes.

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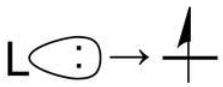
4.5: Crystal Field Theory

Crystal field theory is one of the simplest models for explaining the structures and properties of transition metal complexes. The theory is based on the electrostatics of the metal-ligand interaction, and so its results are only approximate in cases where the metal-ligand bond is substantially covalent. But because the model makes effective use of molecular symmetry, it can be surprisingly accurate in describing the magnetism, colors, structure, and relative stability of metal complexes.

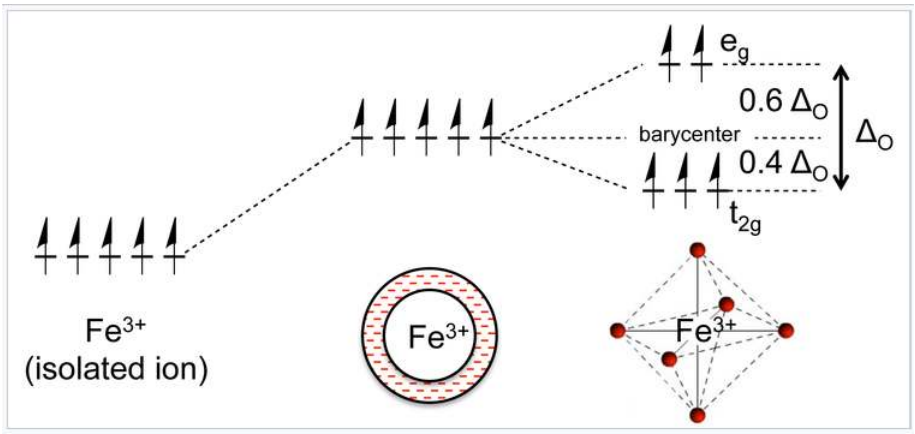
Consider a positively charged metal ion such as Fe^{3+} in the "field" of six negatively charged ligands, such as CN^-. There are two energetic terms we need to consider. The first is the **electrostatic attraction** between the metal and ligands, which is inversely proportional to the distance between them:

$$E_{elec} = \frac{1}{4\pi\varepsilon_0} \sum_{ligands} \frac{q_M q_L}{r_{ML}} \tag{4.5.1}$$

The second term is the **repulsion** that arises from the Pauli exclusion principle when a third electron is added to a filled orbital. There is no place for this third electron to go except to a higher energy antibonding orbital. This is the situation when a ligand lone pair approaches an occupied metal d-orbital:

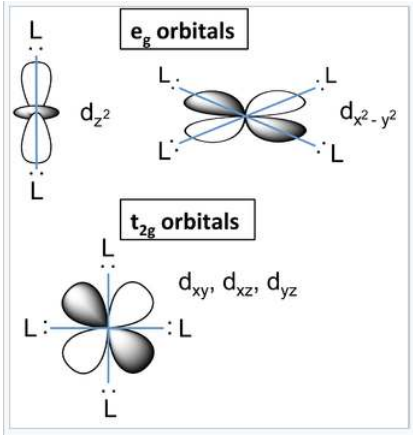


Now let us consider the effect of these attractive and repulsive terms as the metal ion and ligands are brought together. We do this in two steps, first forming a ligand "sphere" around the metal and then moving the six ligands to the vertices of an octahedron. Initially all five d-orbitals are degenerate, i.e., they have the same energy by symmetry. In the first step, the antibonding interaction drives up the energy of the orbitals, but they remain degenerate. In the second step, the d-orbitals split into two symmetry classes, a lower energy, triply-degenerate set (the t_{2g} orbitals) and a higher energy, doubly degenerate set (the e_g orbitals).



A Fe^{3+} ion has five d-electrons, one in each of the five d-orbitals. In a spherical ligand field, the energy of electrons in these orbitals rises because of the repulsive interaction with the ligand lone pairs. The orbitals split into two energy levels when the ligands occupy the vertices of an octahedron, but the average energy remains the same.

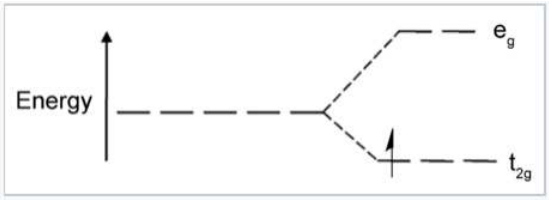
The **energy difference** between the e_g and t_{2g} orbitals is given the symbol $\mathbf{\Delta_O}$, where the "O" stands for "octahedral." We will see that this splitting energy is sensitive to the degree of orbital overlap and thus depends on both the metal and the ligand. Relative to the midpoint energy (the **barycenter**), the t_{2g} orbitals are stabilized by 2/5 Δ_O and the e_g orbitals are destabilized by 3/5 Δ_O in an octahedral complex.



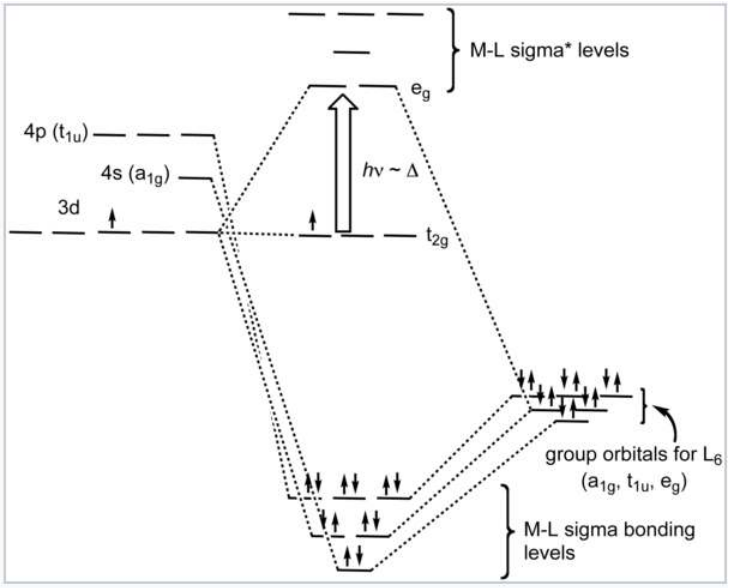
d-orbitals and their orientation with relation to ligands in an octahedral complex.

What causes the d-orbitals to split into two sets? Recall that the d-orbitals have a specific orientation with respect to the Cartesian axes. The lobes of the d_{xy}, d_{xz}, and d_{yz} orbitals (the **t_{2g} orbitals**) lie in the xy-, xz-, and yz-planes, respectively. These three d-orbitals have **nodes** along the x-, y-, and z-directions. The orbitals that contain the ligand lone pairs are oriented along these axes and therefore have **zero overlap with the metal t_{2g} orbitals**. It is easy to see that these three d-orbitals must be degenerate by symmetry. On the other hand, the lobes of the d_{z^2} and $d_{x^2-y^2}$ orbitals (the **e_g orbitals**) point directly along the bonding axes and have strong overlap with the ligand orbitals. While it is less intuitively obvious, these orbitals are also degenerate by symmetry and have antibonding character.

It is informative to compare the results of **crystal field theory** and **molecular orbital theory** (also called **ligand field theory** in this context) for an octahedral transition metal complex. The energy level diagrams below make this comparison for the d^1 octahedral ion $[Ti(H_2O)_6]^{3+}$. In the MO picture below, the frontier orbitals are derived from the metal d-orbitals. The lower t_{2g} set, which contains one electron, is non-bonding by symmetry, and the e_g orbitals are antibonding. The metal 4s orbital, which has a_{1g} symmetry, makes a low energy bonding combination that is ligand-centered, and an antibonding combination that is metal-centered and above the e_g levels. This is the reason that our d-electron counting rules do not need to consider the metal 4s orbital. The important take-home message is that crystal field theory and MO theory give **very similar results** for the frontier orbitals of transition metal complexes.



Crystal field energy diagram for the d^1 octahedral complex $[Ti(H_2O)_6]^{3+}$.



Ligand-field diagram for the octahedral complex $[Ti(H_2O)_6]^{3+}$.

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4.6: Spectrochemical Series

Strong and weak field ligands. The spectrochemical series ranks ligands according the **energy difference Δ_O** between the t_{2g} and e_g orbitals in their octahedral complexes. This energy difference is measured in the spectral transition between these levels, which often lies in the visible part of the spectrum and is responsible for the colors of complexes with partially filled d-orbitals. Ligands that produce a large splitting are called **strong field** ligands, and those that produce a small splitting are called **weak field** ligands.



An abbreviated spectrochemical series is:

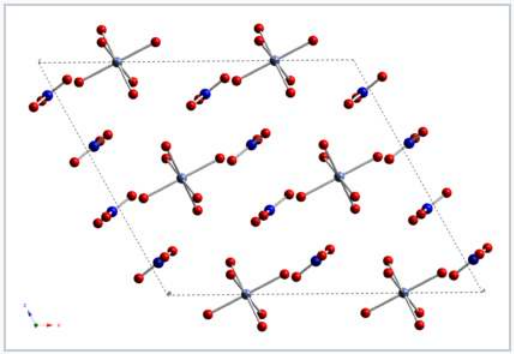
Weak field $I^- < Br^- < Cl^- < NO_3^- < F^- < OH^- < H_2O <$ Pyridine $< NH_3 < NO_2^- < CN^- <$ CO **Strong field**

Orbital overlap

Referring to the molecular orbital diagram above, we see that the splitting between d-electron levels reflects the antibonding interaction between the e_g metal orbitals and the ligands. Thus, we expect ligand field strength to correlate with metal-ligand orbital overlap. Ligands that bind through very electronegative atoms such as **O and halogens** are thus expected to be **weak field**, and ligands that bind through **C or P** are typically **strong field**. Ligands that bind through **N** are **intermediate** in strength. Another way to put this is that hard bases tend to be weak field ligands and soft bases are strong field ligands.



Water is a weak field ligand. The electronegative O atom is strongly electron-withdrawing, so there is poor orbital overlap between the electron pair on O and a metal d-orbital. The more electropositive C atom in the strong field ligand CN^- allows better orbital overlap and sharing of the electron pair. Note that CN^- typically coordinates metal ions through the C atom rather than the N atom.



Cobalt (II) complexes have different colors depending on the nature of the ligand. In crystals of the red compound cobalt(II) nitrate dihydrate, each cobalt ion is coordinated by six water molecules. The $[Co(H_2O)_6]^{2+}$ cations and NO_3^- anions crystallize to make a salt. When the complex is dissolved in water, Co(II) retains its coordination shell of six water molecules and the solution has the same red color as the crystal.

Energy units

Energy can be calculated in a number of ways and it is useful to try to relate the splitting energy Δ_O to more familiar quantities like bond energies.

$$E = h\nu = h\frac{c}{\lambda} = hc\tilde{\nu} \tag{4.6.1}$$

Here ν is the frequency of the electromagnetic radiation, h is Planck's constant (6.626×10^{-34} J*s), and c is the speed of light. $\tilde{\nu}$ is called the "wavenumber" and is the inverse of the wavelength, usually measured in cm^{-1}. Energy gaps are often expressed by spectroscopists in terms of wavenumbers.

For example, a red photon has a wavelength of about 620 nm and a wavenumber of about 16,000 cm^{-1}. In other energy units, the same red photon has an energy of 2.0 eV (1 eV = 1240 nm) or 193 kJ/mol (1 eV = 96.5 kJ/mol). If we compare this to the dissociation energy of a carbon-carbon single bond (350 kJ/mol), we see that the C-C bond has about twice the energy of a red photon. We would need an ultraviolet photon (E > 350 kJ/mol = 3.6 eV = 345 nm = 29,000cm^{-1}) to break a C-C bond.

We will see that Δ_O varies widely for transition metal complexes, from near-infrared to ultraviolet wavelengths. Thus the energy difference between the t_{2g} and e_g orbitals can range between the energy of a rather weak to a rather strong covalent bond.

Δ_O depends on both the metal and the ligand. We can learn something about trends in Δ_O by comparing a series of d^6 metal complexes

Complex	Δ_O (cm^{-1})
$[Co(H_2O)_6]^{2+}$	9,300
$[Co(H_2O)_6]^{3+}$	18,200
$[Co(CN)_6]^{3-}$	33,500
$[Rh(H_2O)_6]^{3+}$	27,000
$[Rh(CN)_6]^{3-}$	45,500

Important trends in Δ_O:

- **Co^{3+}** complexes have larger Δ_O than **Co^{2+}** complexes with the same ligand. This reflects the **electrostatic** nature of the crystal field splitting.
- **Rh^{3+}** complexes have larger Δ_O than **Co^{3+}** complexes. In general, elements in the 2nd and 3rd transition series (the **4d and 5d elements)** have **larger splitting** than those in the 3d series.

For a given metal in one oxidation state (e.g., Co^{3+}), the trend in Δ_O follows the **spectrochemical series**. Thus Δ_O is larger for $[Co(CN)_6]^{3-}$, which contains the strong field CN^- ligand, than it is for $[Co(H_2O)_6]^{3+}$ with the weak field ligand H_2O.

The 4d and 5d elements are similar in their size and their chemistry. In comparing Δ_O values for complexes in the 3d, 4d, and 5d series (e.g., comparing elements in the triads Co,Rh,Ir or Fe,Ru,Os), we always find 3d << 4d $\lesssim$ 5d. This trend reflects the spatial extent of the d-orbitals and thus their overlap with ligand orbitals. The 3d orbitals are smaller, and they are less effective in bonding than the 4d or 5d. The 4d and 5d orbitals are similar to each other because of the lanthanide contraction. At the beginning of the 5d series (between ^{56}Ba and ^{72}Hf) are the fourteen lanthanide elements (^{57}La - ^{71}Lu).

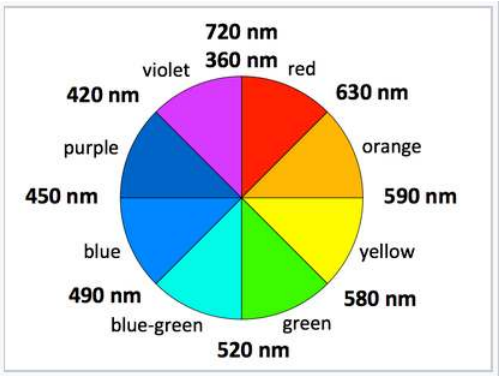
Although the valence orbitals of the 5d elements are in a higher principal quantum shell than those of the 4d elements, the addition of 14 protons to the nucleus in crossing the lanthanide series contracts the sizes of the atomic orbitals. The important result is that the **valence orbitals of the 4d and 5d elements have similar sizes** and thus the elements resemble each other in their chemistry much more than they resemble their cousins in the 3d series. For example, the chemistry of Ru is very similar to that of Os, as illustrated below, but quite different from that of Fe.



Both Os and Ru form volatile, molecular tetroxides MO_4. OsO_4 is used in epoxidation reactions and as a stain in electron microscopy. In contrast, the highest binary oxide of iron is Fe_2O_3.

Colors of transition metal complexes

A simple, qualitative way to see the relative crystal field splitting energy, Δ_O, is to observe the color of a transition metal complex. The higher the energy of the absorbed photon, the larger the energy gap. However, the color a complex absorbs is **complementary** to the color it appears (i.e., the color of light it reflects), which is **opposite** the absorbed color on the color wheel.



Complementary colors are across the color wheel from each other

Examples: (all d^7 Co^{2+} complexes)

$[Co(H_2O)_6]^{2+}$ looks purple in its salts and in concentrated solution because it absorbs in the green range.

$[Co(NH_3)_6]^{2+}$ is straw-colored because it absorbs in the blue range.

$[Co(CN)_6]^{4-}$, looks red, absorbs in the violet and ultra-violet part of the spectrum. This is consistent with the idea that CN^- is a stronger field ligand than NH_3, because the energy of a UV photon is higher than that of a red-orange photon.

This method is applicable to most transition metal complexes, as the majority of them absorb somewhere in the visible range (400-700 nm = 25,000 to 14,300 cm^{-1}), or have UV transitions that tail into the visible, making them appear yellow; however there are complexes such as $[Rh(CN)_6]^{3-}$ that appear colorless because their d-d transitions are in the ultraviolet. Other complexes such as $[Mn(H_2O)]_6^{2+}$ are weakly colored because their d-d transitions involve a change in the spin state of the complex.

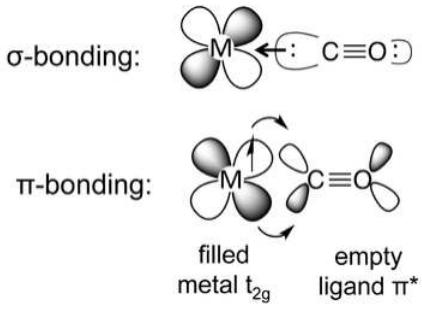
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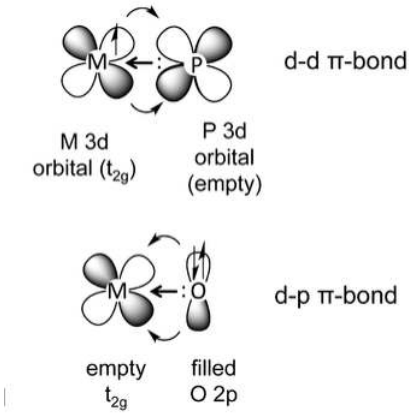
4.7: π-Bonding between Metals and Ligands

An important factor that contributes to the high ligand field strength of ligands such as CO, CN^-, and phosphines is **π-bonding** between the metal and the ligand. There are three types of pi-bonding in metal complexes:

The most common situation is when a ligand such as carbon monoxide or cyanide donates its sigma (nonbonding) electrons to the metal, while accepting electron density from the metal through overlap of a metal t_{2g} orbital and a ligand π* orbital. This situation is called "**back-bonding**" because the ligand donates σ-electron density to the metal and the metal donates π-electron density to the ligand. The ligand is thus acting as a **σ-donor and a π-acceptor.** In π-backbonding, the metal donates π electrons to the ligand π* orbital, adding electron density to an *antibonding* molecular orbital. This results in weakening of the C-O bond, which is experimentally observed as lengthening of the bond (relative to free CO in the gas phase) and lowering of the C-O infrared stretching frequency.



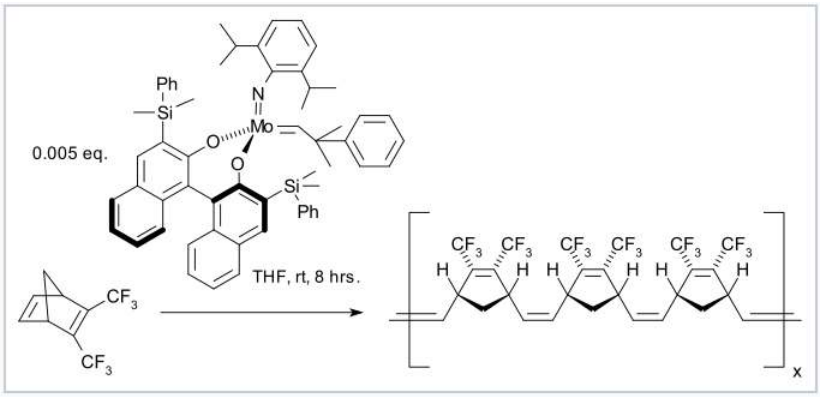
d-d π bonding occurs when an element such phosphorus, which has a σ-symmetry lone pair and an empty metal 3d orbital, binds to a metal that has electrons in a t_{2g} orbital. This is a common situation for phosphine complexes (e.g., triphenylphosphine) bound to low-valent, late transition metals. The backbonding in this case is analogous to the CO example, except that the acceptor orbital is a phosphorus 3d orbital rather than a ligand π* orbital. Here the phosphine ligand acts as a σ-donor and a π-acceptor, forming a dπ-dπ bond.



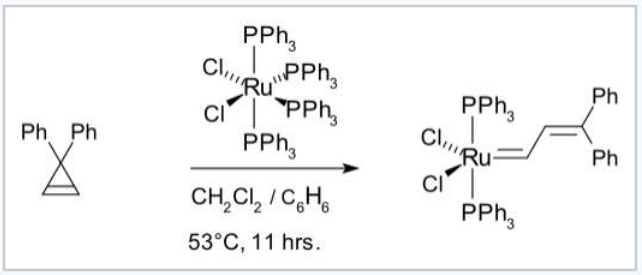
The third kind of metal-ligand π-bonding occurs when a **π-donor ligand** - an element with both a σ-symmetry electron pair and a filled orthogonal p-orbital - bonds to a metal, as shown above at the right for an O^{2-} ligand. This occurs in early transition metal complexes. In this example, $\mathbf{O^{2-}}$ is acting as both a **σ-donor and a π-donor**. This interaction is typically drawn as a metal-ligand multiple bond, e.g., the V=O bond in the vanadyl cation $[VO]^{2+}$. Typical π-donor ligands are oxide (O^{2-}), nitride (N^{3-}), imide (RN^{2-}), alkoxide (RO^-), amide (R_2N^-), and fluoride (F^-). For late transition metals, strong π-donors form anti-bonding interactions with the filled d-levels, with consequences for spin state, redox potentials, and ligand exchange rates. π-donor ligands are low in the spectrochemical series.[5]

Carbon-containing ligands that are π-donors and their complexes with transition metal ions are very important in **olefin metathesis**, a reaction in which carbon-carbon double bonds are interchanged. Using these catalysts, cyclic olefins can be transformed into linear polymers in high yield through ring-opening metathesis polymerization (ROMP). Catalysts of this kind were developed by the groups of Richard Schrock and Robert Grubbs, who shared the 2005 Nobel Prize in Chemistry with Yves Chauvin for their

discoveries. The Schrock catalysts are based on early transition metals such as Mo; they are more reactive but less tolerant of different organic functional groups and protic solvents than the Grubbs catalysts, which are based on Ru complexes.



A chiral Schrock catalyst polymerizes a norbornadiene derivative to a highly stereoregular isotactic polymer.[6]



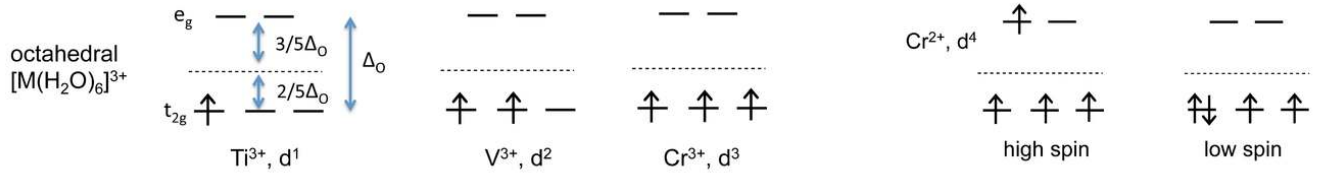
Synthesis of a Grubbs olefin metathesis catalyst.[7]

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4.8: Crystal Field Stabilization Energy, Pairing, and Hund's Rule

The splitting of the d-orbitals into different energy levels in transition metal complexes has important consequences for their stability, reactivity, and magnetic properties. Let us first consider the simple case of the octahedral complexes $[M(H_2O)_6]^{3+}$, where M = Ti, V, Cr. Because the complexes are octahedral, they all have the same energy level diagram:



The Ti^{3+}, V^{3+}, and Cr^{3+} complexes have one, two and three d-electrons respectively, which fill the degenerate t_{2g} orbitals singly. The spins align parallel according to Hund's rule, which states that the lowest energy state has the highest spin angular momentum.

For each of these complexes we can calculate a **crystal field stabilization energy, CFSE**, which is the energy difference between the complex in its ground state and in a hypothetical state in which all five d-orbitals are at the energy barycenter.

For Ti^{3+}, there is one electron stabilized by 2/5 Δ_O, so $CFSE = -(1)(\frac{2}{5})(\Delta_O) = \frac{-2}{5}\Delta_O$

Similarly, CFSE = -4/5 Δ_O and -6/5 Δ_O for V^{3+} and Cr^{3+}, respectively.

For Cr^{2+} complexes, which have four d-electrons, the situation is more complicated. Now we can have a high spin configuration $(t^{2g})^3(e_g)^1$, or a low spin configuration $(t_{2g})^4(e_g)^0$ in which two of the electrons are paired. What are the energies of these two states?

High spin: $CFSE = (-3)(\frac{2}{5})\Delta_O + (1)(\frac{3}{5})\Delta_O = -\frac{3}{5}\Delta_O$

Low spin: $CFSE = (-4)(\frac{2}{5})\Delta_O + P = -\frac{8}{5}\Delta_O + P$, where P is the **pairing energy**

Energy difference = $\mathbf{-\Delta_O + P}$

The **pairing energy P** is the energy penalty for putting two electrons in the same orbital, resulting from the electrostatic repulsion between electrons. For 3d elements, a typical value of P is about 15,000 cm^{-1}.

The important result here is that a complex will be **low spin** if $\mathbf{\Delta_O > P}$, and **high spin** if $\mathbf{\Delta_O < P}$.

Because Δ_O depends on both the metals and the ligands, it determines the spin state of the complex.

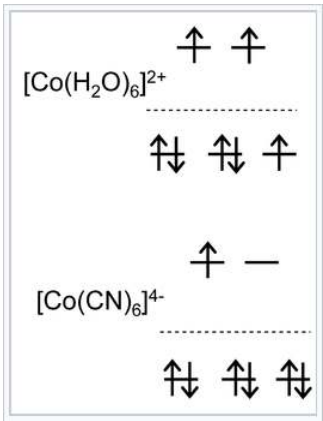
Rules of thumb:

3d complexes are **high spin** with **weak field** ligands and **low spin** with **strong field** ligands.

High valent 3d complexes (e.g., Co^{3+} complexes) tend to be **low spin** (large Δ_O)

4d and 5d complexes are **always low spin** (large Δ_O)

Note that high and low spin states occur only for 3d metal complexes with between 4 and 7 d-electrons. Complexes with 1 to 3 d-electrons can accommodate all electrons in individual orbitals in the t_{2g} set. Complexes with 8, 9, or 10 d-electrons will always have completely filled t_{2g} orbitals and 2-4 electrons in the e_g set.



d-orbital energy diagrams for high and low spin Co^{2+} complexes, d^7

Examples of high and low spin complexes:

$[Co(H_2O)_6{}^{2+}]$ contains a d^7 metal ion with a weak field ligand. This complex is known to be high spin from magnetic susceptibility measurements, which detect three unpaired electrons per molecule. Its orbital occupancy is $(t_{2g})^5(e_g)^2$.

We can calculate the CFSE as $-(5)(\frac{2}{5})\Delta_O + (2)(\frac{3}{5})\Delta_O = -\frac{4}{5}\Delta_O$

$[Co(CN)_6{}^{4-}]$ is also an octahedral d^7 complex but it contains CN^-, a strong field ligand. Its orbital occupancy is $(t_{2g})^6(e_g)^1$ and it therefore has one unpaired electron.

In this case the CFSE is $-(6)(\frac{2}{5})\Delta_O + (1)(\frac{3}{5})\Delta_O + P = -\frac{9}{5}\Delta_O + P$.

Magnetism of transition metal complexes

Compounds with **unpaired electrons** have an inherent magnetic moment that arises from the **electron spin**. Such compounds interact strongly with applied magnetic fields. Their **magnetic susceptibility** provides a simple way to measure the number of unpaired electrons in a transition metal complex.

If a transition metal complex has no unpaired electrons, it is **diamagnetic** and is weakly repelled from the high field region of an inhomogeneous magnetic field. Complexes with unpaired electrons are typically **paramagnetic**. The spins in paramagnets align independently in an applied magnetic field but do not align spontaneously in the absence of a field. Such compounds are attracted to a magnet, i.e., they are drawn into the high field region of an inhomogeneous field. The attractive force, which can be measured with a **Guoy balance** or a **SQUID magnetometer**, is proportional to the **magnetic susceptibility** (**χ**) of the complex.

The effective **magnetic moment** of an ion (μ_{eff}), in the absence of spin-orbit coupling, is given by the sum of its spin and orbital moments:

$$\mu_{\text{eff}} = \mu_{\text{spin}} + \mu_{\text{orbital}} = \mu_{\text{s}} + \mu_{\text{L}} \tag{4.8.1}$$

In octahedral 3d metal complexes, the orbital angular momentum is largely "quenched" by symmetry, so we can approximate:

$$\mu_{\text{eff}} \approx \mu_{\text{s}} \tag{4.8.2}$$

We can calculate μ_s from the number of unpaired electrons (n) using:

$$\mu_{eff} = \sqrt{n(n+2)}\,\mu_B \tag{4.8.3}$$

Here μ_B is the **Bohr magneton** (= $eh/4\pi m_e$) = 9.3 x 10^{-24} J/T. This spin-only formula is a good approximation for first-row transition metal complexes, especially high spin complexes. The table below compares calculated and experimentally measured values of μ_{eff} for octahedral complexes with 1-5 unpaired electrons.

Ion	Number of unpaired electrons	Spin-only moment /μ_B	observed moment /μ_B
Ti^{3+}	1	1.73	1.73
V^{4+}	1		1.68–1.78
Cu^{2+}	1		1.70–2.20
V^{3+}	2	2.83	2.75–2.85
Ni^{2+}	2		2.8–3.5
V^{2+}	3	3.87	3.80–3.90
Cr^{3+}	3		3.70–3.90
Co^{2+}	3		4.3–5.0
Mn^{4+}	3		3.80–4.0
Cr^{2+}	4	4.90	4.75–4.90
Fe^{2+}	4		5.1–5.7
Mn^{2+}	5	5.92	5.65–6.10
Fe^{3+}	5		5.7–6.0

The small deviations from the spin-only formula for these octahedral complexes can result from the neglect of orbital angular momentum or of spin-orbit coupling. Tetrahedral d^3, d^4, d^8 and d^9 complexes tend to show larger deviations from the spin-only formula than octahedral complexes of the same ion because quenching of the orbital contribution is less effective in the tetrahedral case.

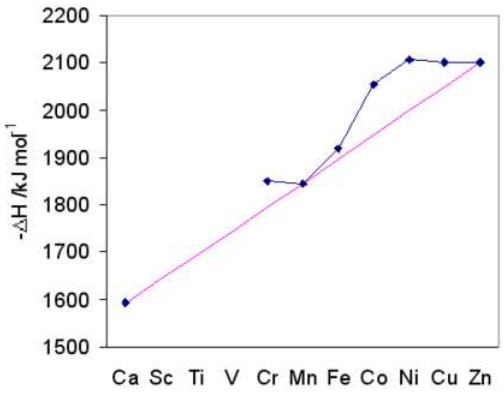
Summary of rules for high and low spin complexes:

3d complexes: Can be high or low spin, depending on the ligand (d^4, d^5, d^6, d^7)

4d and 5d complexes: Always low spin, because Δ_O is large

Maximum CFSE is for d^3 and d^8 cases (e.g., Cr^{3+}, Ni^{2+}) with weak field ligands (H_2O, O^{2-}, F^-,...) and for d^3-d^6 with strong field ligands (Fe^{2+}, Ru^{2+}, Os^{2+}, Co^{3+}, Rh^{3+}, Ir^{3+},...)

Irving-Williams series. For M^{2+} complexes, the stability of the complex follows the order $Mg^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$. This trend represents increasing Lewis acidity as the ions become smaller (going left to right in the periodic table) as well as the trend in CFSE. This same trend is reflected in the hydration enthalpy of gas-phase M^{2+} ions, as illustrated in the graph at the right. Note that Ca^{2+}, Mn^{2+}, and Zn^{2+}, which are d^0, d^5(high spin), and d^{10} aquo ions, respectively, all have zero CFSE and fall on the same line. Ions that deviate the most from the line such as Ni^{2+} (octahedral d^8) have the highest CFSE.



Colors and spectra of transition metal complexes

Transition metal complexes often have beautiful colors because, as noted above, their d-d transition energies can be in the visible part of the spectrum. With octahedral complexes these colors are faint (the transitions are weak) because they violate the Laporte selection rule. According to this rule, g -> g and u -> u transitions are forbidden in centrosymmetric complexes. d-orbitals have g (gerade) symmetry, so d-d transitions are Laporte-forbidden. However octahedral complexes can absorb light when they momentarily distort away from centrosymmetry as the molecule vibrates. Spin flips are also forbidden in optical transitions by the spin selection rule, so the excited state will always have the same spin multiplicity as the ground state.

The spectra of even the simplest transition metal complexes are rather complicated because of the many possible ways in which the d-electrons can fill the t_{2g} and e_g orbitals. For example, if we consider a d^2 complex such as $V^{3+}(aq)$, we know that the two electrons can reside in any of the five d-orbitals, and can either be spin-up or spin-down. There are actually 45 different such arrangements (called **microstates**) that do not violate the Pauli exclusion principle for a d^2 complex. Usually we are concerned only with the six of lowest energy, in which both electrons occupy individual orbitals in the t_{2g} set and all their spins are aligned either up or down.



From left: $[V(H_2O)_6]^{2+}$ (lilac), $[V(H_2O)_6]^{3+}$ (green), $[VO(H_2O)_5]^{2+}$ (blue) and $[VO(H_2O)_5]^{3+}$ (yellow).

We can see how these microstates play a role in electronic spectra when we consider the d-d transitions of the $[Cr(NH_3)_6]^{3+}$ ion. This ion is d^3, so each of the three t_{2g} orbitals contains one unpaired electron. We expect to see a transition when one of the three electrons in the t_{2g} orbitals is excited to an empty e_g orbital. Interestingly, we find not one but **two** transitions in the visible.

The reason that we see two transitions is that the electron can come from any one of the t_{2g} orbitals and end up in either of the e_g orbitals. Let us assume for the sake of argument that the electron is initially in the d_{xy} orbital. It can be excited to either the d_{z2} or the d_{x2-y2} orbital:

$d_{xy} \rightarrow d_{z^2}$ (higher energy)

$d_{xy} \rightarrow d_{x2-y2}$ (lower energy)

The first transition is at higher energy (shorter wavelength) because in the excited state the configuration is ($d_{yz}^1 d_{xz}^1 d_{z2}^1$). All three of the excited state orbitals have some z-component, so the d-electron density is "piled up" along the z-axis. The energy of this transition is thus increased by **electron-electron repulsion**. In the second case, the excited state configuration is ($d_{yz}^1 d_{xz}^1 d_{x2-y2}^1$), and the d-electrons are more symmetrically distributed around the metal. This effect is responsible for a splitting of the d-d bands by about 8,000 cm^{-1}. We can show that all other possible transitions are equivalent to one of these two by symmetry, and hence we see only two visible absorption bands for Cr^{3+} complexes.

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4.9: Magnetic Susceptibility and the Spin-only Formula

Complexes that contain unpaired electrons are paramagnetic and are attracted into magnetic fields. Diamagnetic compounds are those with no unpaired electrons are repelled by a magnetic field. All compounds, including transition metal complexes, posses some diamagnetic component which results from paired electrons moving in such a way that they generate a magnetic field that opposes an applied field. The magnitude of paramagnetism is measured in terms of the magnetic moment, μ, where the larger the magnitude of μ, greater the paramagnetism of the compound.

Magnetic Susceptibility

The magnetic susceptibility measures the strength of interaction on placing the substance in a magnetic field. For chemical applications the molar magnetic susceptibility (χ_{mol}) is the preferred quantity and is measured in $m^3 \cdot mol^{-1}$ (SI) or $cm^3 \cdot mol^{-1}$ (CGS) and is defined as

$$\chi_{\text{mol}} = M\chi_v/\rho \tag{4.9.1}$$

where ρ is the density in $kg \cdot m^{-3}$ (SI) or $g \cdot cm^{-3}$ (CGS) and M is molar mass in $kg \cdot mol^{-1}$ (SI) or $g \cdot mol^{-1}$ (CGS). There are multiple methods for measuring magnetic susceptibilities, including, the Gouy, Evans, and Faraday methods. These all depend on measuring the force exerted upon a sample when it is placed in a magnetic field. The more paramagnetic the sample, the more strongly it will be drawn toward the more intense part of the field.

Origin of Paramagnetism

Electrons in most atoms exist in pairs, with each electron spinning in an opposite direction. Each spinning electron causes a magnetic field to form around it. In most materials, the magnetic field of one electron is cancelled by an opposite magnetic field produced by the other electron in the pair. The atoms in materials materials such as iron, cobalt and nickel have unpaired electrons, so they don't cancel the electrons' magnetic fields. As result, each atom of these elements acts like very small magnets.

There are three origins of paramagnetism in complexes:

1. **Nuclear spin** (μ_n)**:** Some nuclei, such as a hydrogen atom, have a net spin, which creates a magnetic field.
2. **Electron spin** (μ_s)**:** An electron has two intrinsic spin states (similar to a top spinning) which we call up (α) and down (β).
3. **Electron orbital motion** (μ_l)**:** There is a magnetic field due to the electron moving around the nucleus.

Each of these magnetic moments interact with one another and/or with external magnetic fields to generate interesting physics. However, some of these interactions are stronger than others and can be (tentatively) ignored. For example, the nuclear spin magnetic moment (#1 above), which is central to NMR spectroscopy, is appreciably weaker than the other two moments and we can ignore it for this discussion and focus on the electronic moments.

The classical theory of magnetism was well developed before quantum mechanics with (see Lenz Law). From a quantum mechanical picture, for an individual electron in a molecule or atom, we can identify the orbital angular momentum l and spin angular momentum s. For multi-electron systems, the total orbital angular momentum (L) and total spin angular momentum (S) are sum of the constituent electron spins.

$$L = l_1 + l_2 + l_3 + \ldots \tag{4.9.2}$$

and

$$S = s_1 + s_2 + s_3 + \ldots \tag{4.9.3}$$

The total magnetic susceptibility from both orbital and spin angular momenta is

$$\mu_{L+S} = \sqrt{4S(S+1) + L(L+1)}\ \mu_B \tag{4.9.4}$$

where μ_B is the Bohr Magneton ($9.274 \times 10^{-24} J/T$).

nuclear magneton vs. Bohr magneton

The associated the nuclear magneton μ_N attributed to nuclear spin magnetic moments is ~2000 fold smaller than the Bohr magneton. This is why we can ignore the nuclear spin components for this discussion.

That is, the rotation of electrons about the nucleus is restricted which leads to

$$L = 0 \tag{4.9.5}$$

and

$$\mu_s = \sqrt{4S(S+1)}\,\mu_B \tag{4.9.6}$$

Equation 4.9.3 can be simplified to

$$S = n(1/2) = n/2 \tag{4.9.7}$$

where n is the number of unpaired electrons in the complex. Hence

$$\mu_s = \sqrt{4S(S+1)}\,\mu_B \tag{4.9.8}$$

$$= \sqrt{4(n/2)(n/2+1)}\,\mu_B \tag{4.9.9}$$

$$= \sqrt{n(n+2)}\,\mu_B \tag{4.9.10}$$

Equation 4.9.10 is called *Spin-Only Formula*. For transient metal complexes, the magnetic properties arise primarily from the exposed d-orbitals that are perturbed by ligands. Hence, experimentally measured magnetic moment can provide some important information about the compounds themselves including: (1) number of unpaired electrons present, (2) high-spin vs. low-spin states, (3). spectral behavior, and (4) even structure of the complexes (Table 4.9.1).

Table 4.9.1: Predicted Spin only Magnetic Moment

Ion	Number of unpaired electrons	μ_s	observed moment /μ_B
Ti^{3+}	1	$\sqrt{3} \approx 1.73\,\mu_B$	1.73
V^{4+}	1	$\sqrt{3} \approx 1.73\,\mu_B$	1.68–1.78
Cu^{2+}	1	$\sqrt{3} \approx 1.73\,\mu_B$	1.70–2.20
V^{3+}	2	$\sqrt{8} \approx 2.83\,\mu_B$	2.75–2.85
Ni^{2+}	2	$\sqrt{8} \approx 2.83\,\mu_B$	2.8–3.5
V^{2+}	3	$\sqrt{15} \approx 3.87\,\mu_B$	3.80–3.90
Cr^{3+}	3	$\sqrt{15} \approx 3.87\,\mu_B$	3.70–3.90
Co^{2+}	3	$\sqrt{15} \approx 3.87\,\mu_B$	4.3–5.0
Mn^{4+}	3	$\sqrt{15} \approx 3.87\,\mu_B$	3.80–4.0
Cr^{2+}	4	$\sqrt{24} \approx 4.90\,\mu_B$	4.75–4.90
Fe^{2+}	4	$\sqrt{24} \approx 4.90\,\mu_B$	5.1–5.7
Mn^{2+}	5	$\sqrt{35} \approx 5.92\mu_B$	5.65–6.10
Fe^{3+}	5	$\sqrt{35} \approx 5.92\mu_B$	5.7–6.0

The small deviations from the spin-only formula for these octahedral complexes can result from the neglect of orbital angular momentum or of spin-orbit coupling. Tetrahedral d^3, d^4, d^8 and d^9 complexes tend to show larger deviations from the spin-only formula than octahedral complexes of the same ion because quenching of the orbital contribution is less effective in the tetrahedral case.

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4.10: Jahn-Teller Distortions

The Jahn-Teller effect is a geometric distortion of a non-linear molecular system that reduces its symmetry and energy. This distortion is typically observed among octahedral complexes where the two axial bonds can be shorter or longer than those of the equatorial bonds. This effect can also be observed in tetrahedral compounds. This effect is dependent on the electronic state of the system.

Introduction

In 1937, Hermann Jahn and Edward Teller postulated a theorem stating that "stability and degeneracy are not possible simultaneously unless the molecule is a linear one," in regards to its electronic state.[1] This leads to a break in degeneracy which stabilizes the molecule and by consequence, reduces its symmetry. Since 1937, the theorem has been revised which Housecroft and Sharpe have eloquently phrased as "any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy, thereby removing the degeneracy."[2] This is most commonly observed with transition metal octahedral complexes, however, it can be observed in tetrahedral compounds as well.

For a given octahedral complex, the five d atomic orbitals are split into two degenerate sets when constructing a molecular orbital diagram. These are represented by the sets' symmetry labels: t_{2g} (d_{xz}, d_{yz}, d_{xy}) and e_g (d_{z^2} and $d_{x^2-y^2}$). When a molecule possesses a degenerate electronic ground state, it will distort to remove the degeneracy and form a lower energy (and by consequence, lower symmetry) system. The octahedral complex will either elongate or compress the z ligand bonds as shown in Figure 4.10.1below:

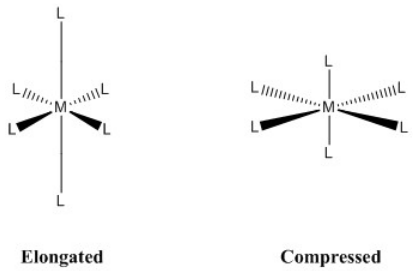


Figure 4.10.1: Jahn-Teller distortions for an octahedral complex.

When an octahedral complex exhibits elongation, the axial bonds are longer than the equatorial bonds. For a compression, it is the reverse; the equatorial bonds are longer than the axial bonds. Elongation and compression effects are dictated by the amount of overlap between the metal and ligand orbitals. Thus, this distortion varies greatly depending on the type of metal and ligands. In general, the stronger the metal-ligand orbital interactions are, the greater the chance for a Jahn-Teller effect to be observed.

Elongation

Elongation Jahn-Teller distortions occur when the degeneracy is broken by the stabilization (lowering in energy) of the d orbitals with a *z* component, while the orbitals without a *z* component are destabilized (higher in energy) as shown in Figure 4.10.2below:

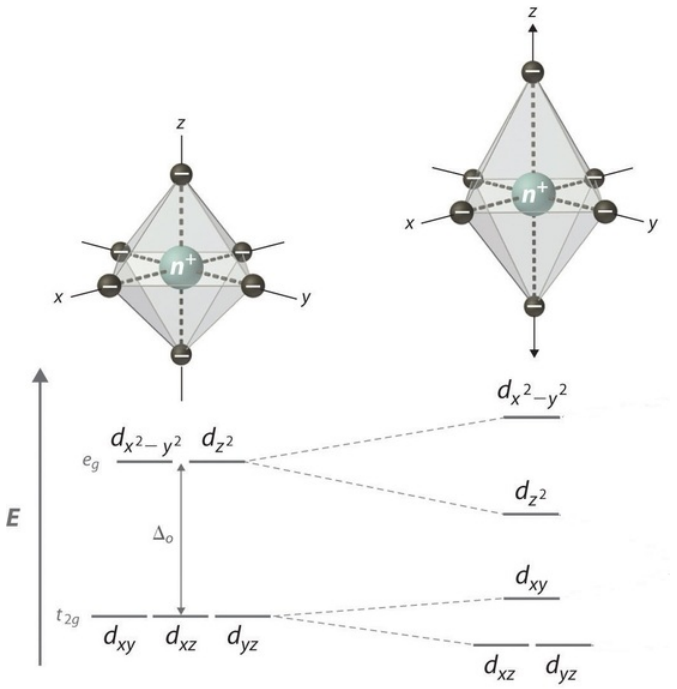


Figure 4.10.2: Illustration of tetragonal distortion (elongation) for an octahedral complex.

This is due to the d_{xy} and $d_{x^2-y^2}$ orbitals having greater overlap with the ligand orbitals, resulting in the orbitals being higher in energy. Since the $d_{x^2-y^2}$ orbital is antibonding, it is expected to increase in energy due to elongation. The d_{xy} orbital is still nonbonding, but is destabilized due to the interactions. Jahn-Teller elongations are well-documented for copper(II) octahedral compounds. A classic example is that of copper(II) fluoride as shown in Figure 4.10.3

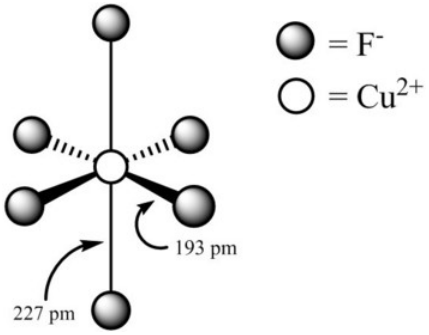


Figure 4.10.3: Structure of octahedral copper(II) fluoride.[3]

Notice that the two axial bonds are both elongated and the four shorter equatorial bonds are the same length as each other. According the theorem, the orbital degeneracy is eliminated by distortion, making the molecule more stable based on the model presented in Figure 4.10.2

Compression

Compression Jahn-Teller distortions occur when the degeneracy is broken by the stabilization (lowering in energy) of the d orbitals *without* a *z* component, while the orbitals with a *z* component are destabilized (higher in energy) as shown in Figure 4.10.4below:

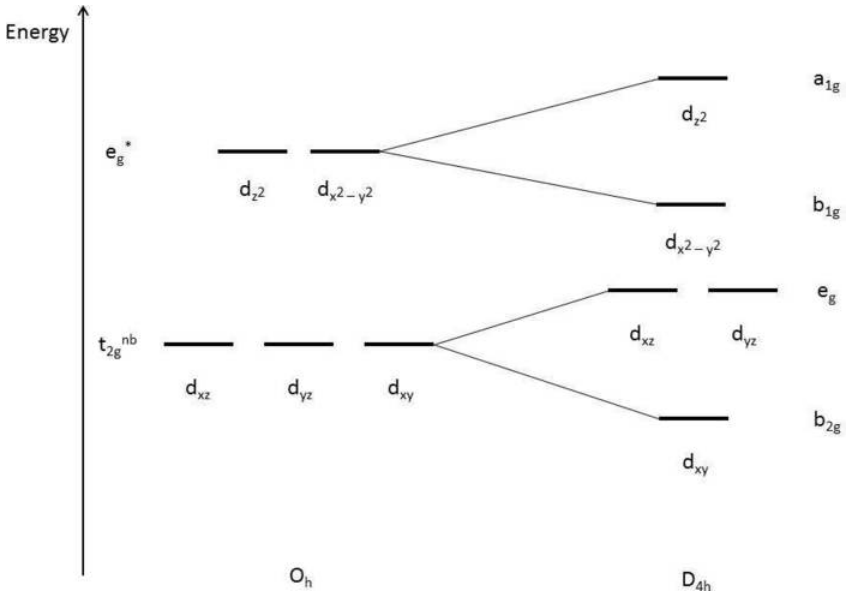


Figure 4.10.4: Illustration of tetragonal distortion (compression) for an octahedral complex.

This is due to the *z*-component d orbitals having greater overlap with the ligand orbitals, resulting in the orbitals being higher in energy. Since the d_{z^2} orbital is antibonding, it is expected to increase in energy due to compression. The d_{xz} and d_{yz} orbitals are still nonbonding, but are destabilized due to the interactions.

Electronic Configurations

For Jahn-Teller effects to occur in transition metals there must be degeneracy in either the t_{2g} or e_g orbitals. The electronic states of octahedral complexes depend on the number of d-electrons and the splitting energy, Δ. When Δ is large and is greater than the energy required to pair electrons, electrons pair in t_{2g} before occupying e_g. On the other hand, when $Delta$ small and is less than the pairing energy, electrons will occupy e_g before pairing in t_{2g}. The Δ of an octahedral complex is dictated by the chemical environment (ligand identity), and the identity and charge of the metal ion. If there electron configurations for any d-electron count is different depending on Δ, the configuration with more paired electrons is called low spin while the one with more unpaired electrons is called high spin.

The electron configurations diagrams for d1 through d10 with large and small δ are illustrated in the figures below. Notice that the electron configurations for d^1, d^2, d^3, d^8, d^9, and d^{10} are the same no matter what the magnitude of Δ. Low spin and high spin configurations exist only for the electron counts d^4, d^5, d^6, and d^7.

Large Δ

Figure 4.10.5 (below) shows the various electronic configurations for octahedral complexes with large Δ, including the low-spin configurations of d^4, d^5, d^6, and d^7:

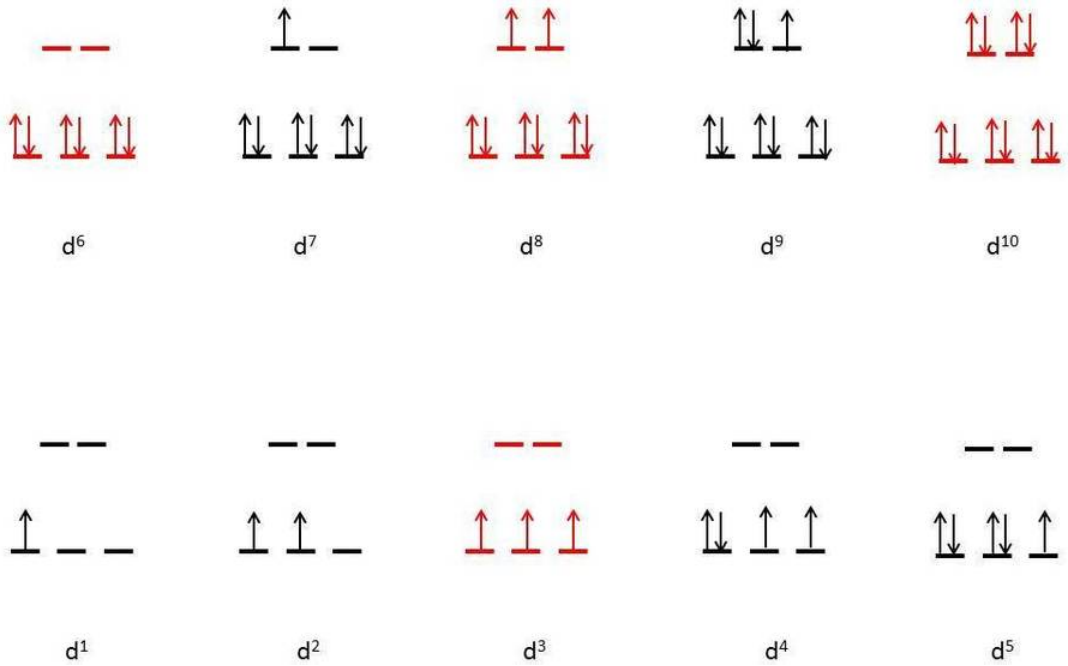


Figure 4.10.5: Electron configuration diagram of octahedral complexes (red indicates no degeneracies possible, thus no Jahn-Teller effects).

The figure illustrates the electron configurations in the case of large Δ. The electron configurations highlighted in red (d^3, low spin d^6, d^8, and d^{10}) **do not** exhibit Jahn-Teller distortions. On the other hand d^1, d^2, low spin d^4, low spin d^5, low spin d^7, and d^9, would be expected to exhibit Jhan-Teller distortion. These electronic configurations correspond to a variety of transition metals. Some common examples include Cr^{3+}, Co^{3+}, and Ni^{2+}.

Small Δ

Figure 4.10.6 (below) shows the various electronic configurations for octahedral complexes with small Δ, including the high-spin configurations of d^4, d^5, d^6, and d^7::

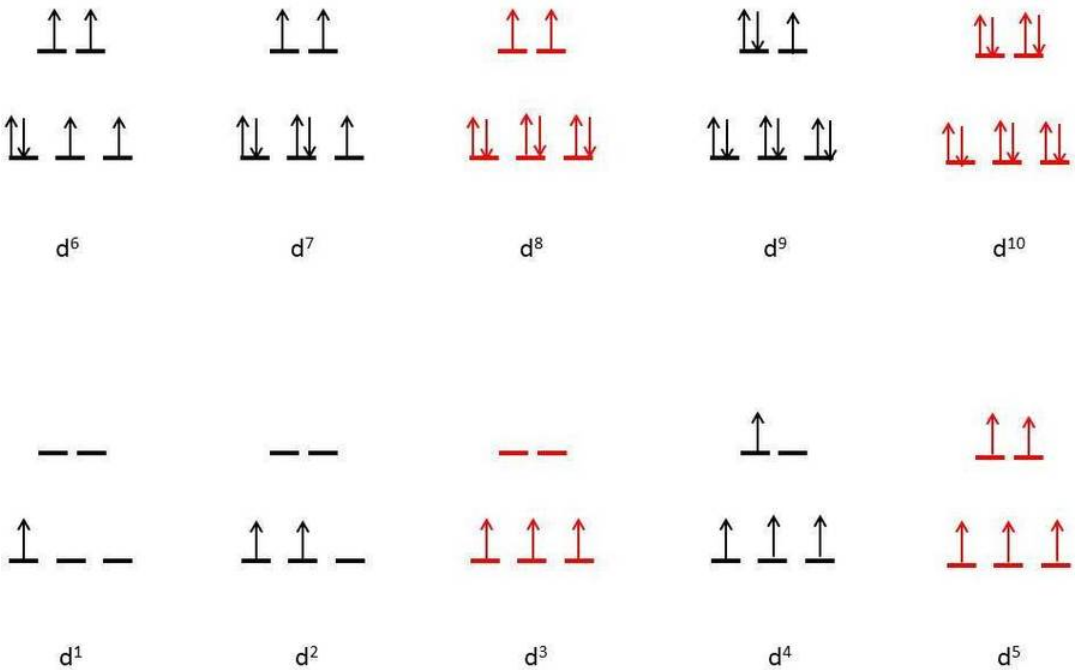


Figure 4.10.6: High spin octahedral coordination diagram (red indicates no degeneracies possible, thus no Jahn-Teller effects).

The figure illustrates the electron configurations in the case of small Δ. The electron configurations highlighted in red (d^3, high spin d^5, d^8, and d^{10}) **do not** exhibit Jahn-Teller distortions. In general, degenerate electronic states occupying the e_g orbital set tend to show stronger Jahn-Teller effects. This is primarily caused by the occupation of these high energy orbitals. Since the system is more stable with a lower energy configuration, the degeneracy of the e_g set is broken, the symmetry is reduced, and occupations at lower energy orbitals occur.

Spectroscopic Observation

Jahn-Teller distortions can be observed using a variety of spectroscopic techniques. In UV-VIS absorption spectroscopy, distortion causes splitting of bands in the spectrum due to a reduction in symmetry (O_h to D_{4h}). Consider a hypothetical molecule with octahedral symmetry showing a single absorption band. If the molecule were to undergo Jahn-Teller distortion, the number of bands would increase as shown in Figure 4.10.7below:

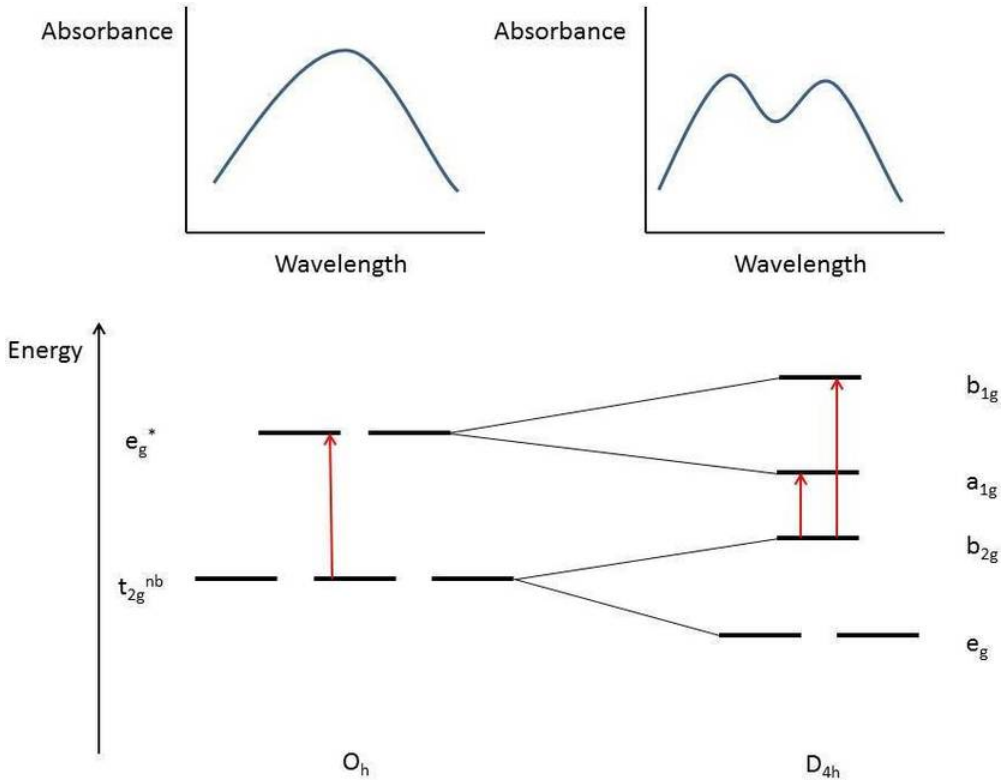


Figure 4.10.7: Hypothetical absorption spectra of an octahedral molecule (left) and the same molecule with Jahn-Teller elongation (right). The red arrows indicate electronic transitions.

A similar phenomenon can be seen with IR and Raman vibrational spectroscopy. The number of vibrational modes for a molecule can be calculated using the 3n - 6 rule (or 3n - 5 for linear geometry) rule. If a molecule exhibits an O_h symmetry point group, it will have fewer bands than that of a Jahn-Teller distorted molecule with D_{4h} symmetry. Thus, one could observe Jahn-Teller effects through either IR or Raman techniques. This effect can also be observed in EPR experiments as long as there is at least one unpaired electron.

Table 4.10.1: Examples of Jahn-Teller distorted complexes

$CuBr_2$	4 Br at 240 pm 2 Br at 318 pm
$CuCl_2$	4 Cl at 230 pm 2 Cl at 295 pm
$CuCl_2.2H_2O$	2 O at 193 pm 2 Cl at 228 pm 2 Cl at 295 pm
$CsCuCl_3$	4 Cl at 230 pm 2 Cl at 265 pm
CuF_2	4 F at 193 pm 2 F at 227 pm
$CuSO_4.4NH_3.H_2O$	4 N at 205 pm 1 O at 259 pm 1 O at 337 pm
K_2CuF_4	4 F at 191 pm 2 F at 237 pm

$KCuAlF_6$	2 F at 188 pm 4 F at 220 pm
CrF_2	4 F at 200 pm 2 F at 243 pm
$KCrF_3$	4 F at 214 pm 2 F at 200 pm
MnF_3	2 F at 209 pm 2 F at 191 pm 2 F at 179 pm

The Jahn-Teller Theorem predicts that distortions should occur for *any degenerate state*, including degeneracy of the t_{2g} level, however distortions in bond lengths are much more distinctive when the degenerate electrons are in the e_g level.

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Practice Questions

1. Why do d^3 complexes not show Jahn-Teller distortions?
2. Does the spin system (high spin v. low spin) of a molecule play a role in Jahn-Teller effects?
3. What spectroscopic method would one utilize in order to observe Jahn-Teller distortions in a diamagnetic molecule?
4. What spectroscopic method(s) would one utilize in order to observe Jahn-Teller distortions in a paramagnetic molecule?
5. Why are Jahn-Teller effects most prevalent in inorganic (transition metal) compounds?

Answers

1. Complexes with d^3 electron configurations do not show Jahn-Teller distortions because there is no ground state degeneracy.
2. Yes. Examining the d^5 electron configuration, one finds that the high spin scenario contains all singly occupied d orbitals (no degeneracy). However, the low spin d^5 electron configuration shows degeneracy, which then leads to possible Jahn-Teller effects.
3. UV-VIS absorption spectroscopy is one of the most common techniques for observing these effects. In general, it is independent of magnetism (diamagnetic v. paramagnetic). Thus, one would see the effect in the spectrum of UV-VIS absorption analysis. Note that EPR requires at least one unpaired electron, and therefore not EPR active.
4. Inorganic, specifically transition metal, complexes are most prevalent in showing Jahn-Teller distortions due to the availability of d orbitals. The most common geometry that the Jahn-Teller effect is observed is in octahedral complexes (see **Figures 2, 4, 5** and **6** above) due to the splitting of d orbitals into two degenerate sets. Due to stabilization, the degeneracies are removed, making a lower symmetry and lower energy molecule.
5. In addition to UV-VIS absorption, one can also employ EPR spectroscopy if a molecule possesses and unpaired electron.

Contributors and Attributions

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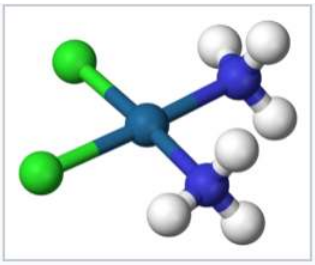
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4.11: Non-octahedral Complexes

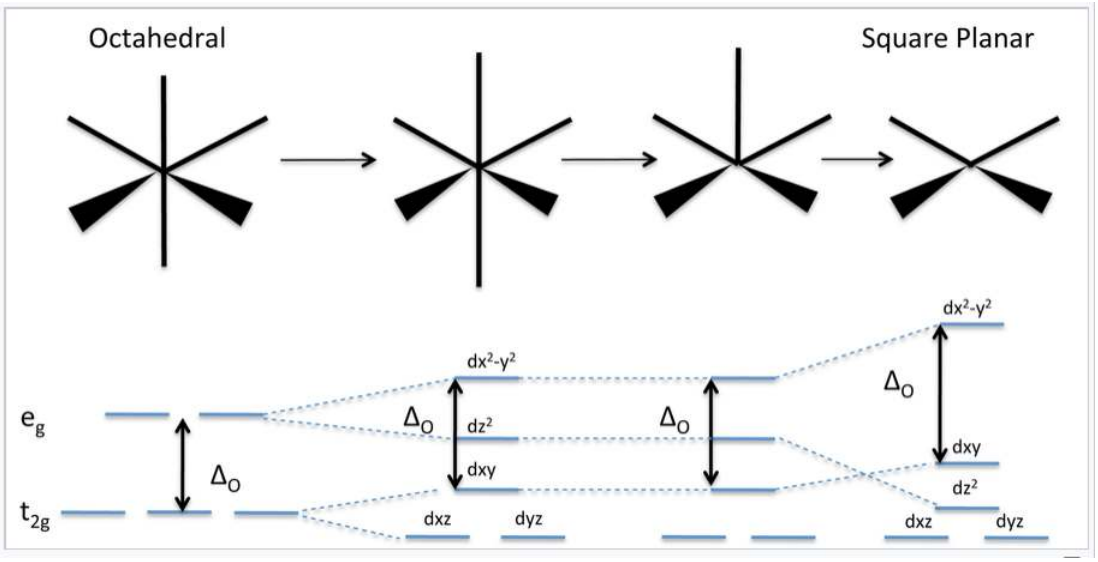
The most important non-octahedral geometries for transition metal complexes are:

4-coordinate: square planar and tetrahedral

5-coordinate: square pyramidal and trigonal bipyramidal



cis-$Pt(NH_3)_2Cl_2$, a $5d^8$ square planar complex



Crystal field energy diagram showing the transition from octahedral to square planar geometry

Energies of the d-orbitals in non-octahedral geometries

The figure above shows what happens to the d-orbital energy diagram as we progressively distort an octahedral complex by elongating it along the z-axis (a **tetragonal distortion**), by removing one of its ligands to make a **square pyramid**, or by removing both of the ligands along the z-axis to make a **square planar** complex. In all cases, we keep the total bond order the same by making the bonds in the xy plane shorter as the bonds in the z-direction are stretched and/or broken.



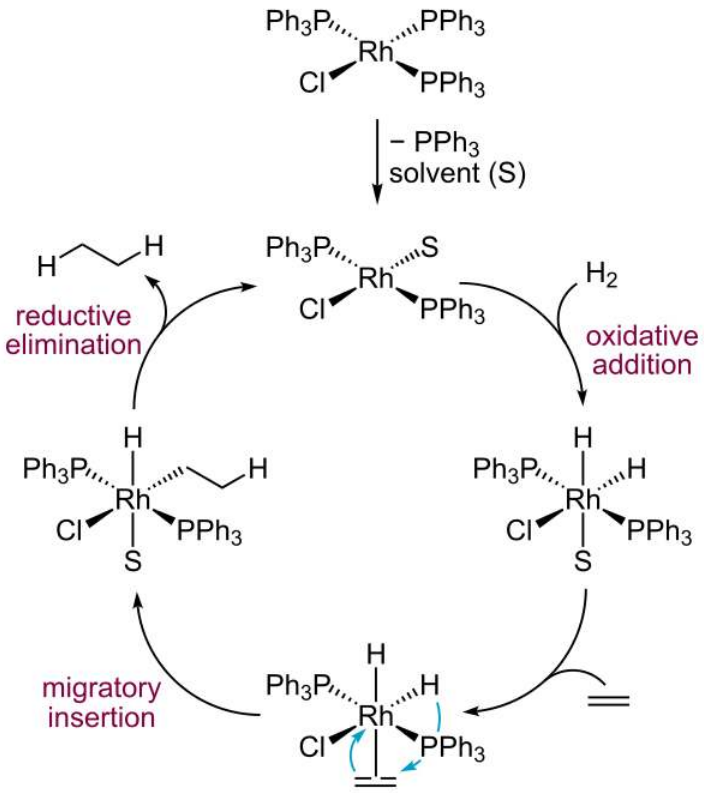
Barnett Rosenberg (Michigan State University) accidentally discovered the biological effects of square planar cis-$Pt(NH_3)_2Cl_2$ while researching bacterial growth in electric fields.[8] The Pt electrode he used reacted with chloride and ammonium ions in the electrolyte to produce the compound at 1-10 ppm concentration. Further experiments revealed that the cis-isomer (but not the trans-isomer) is a potent anti-cancer drug which is especially effective against testicular cancer. The drug works by cross-linking guanine-cytosine rich regions of DNA, thus inhibiting cell division.

The distortion away from octahedral symmetry breaks the degeneracy of the t_{2g} and e_g orbitals. d-orbitals with a z-component (d_{xz}, d_{yz}, d_{z2}) go down in energy as orbitals that reside in the xy plane (d_{xy}, d_{x2-y2}) rise in energy. The barycenter (the weighted average orbital energy) remains constant. Also, it is important to note that the splitting between the d_{xy} and d_{x2-y2} orbitals stays constant at Δ_O regardless of the nature of the distortion.

Why would a "happy" octahedral complex want to lose two of its ligands to make a **square planar** complex? This occurs frequently in d^8 and sometimes in d^9 complexes with large Δ_O, i.e., **$3d^8$ complexes with strong field ligands and $4d^8$, $5d^8$ complexes with any ligands**. Examples of such d^8 complexes are $[Ni(CN)_4]^{2-}$, the anti-cancer drug cisplatin (cis-$Pt(NH_3)_2Cl_2$), $[Pd(H_2O)_4]^{2+}$, and $[AuCl_4]^-$. At the d^8 electron count, the lowest four orbitals are filled and the highest orbital (the d_{x2-y2}) is empty, resulting in a large CFSE. These complexes are diamagnetic and tend to be quite stable. With weak field ligands, $3d^8$ complexes are octahedral and paramagnetic (e.g., $[Ni(H_2O)_6]^{2+}$, which has two unpaired electrons in the e_g orbitals.

Square planar complexes in catalysis:

Square planar d^8 complexes can be oxidized by two electrons to become octahedral (low spin) d^6 complexes, which also have a large CFSE. Because the loss of two electrons is accompanied by the gain of two ligands, this process is called **oxidative addition**. The reverse process is called **reductive elimination.** Both processes function together in catalytic cycles, such as the hydrogenation of olefins using **Wilkinson's catalyst**.[10][11] The catalytic cycle is shown below.



The catalyst cycles between 4-coordinate Rh(I) ($4d^8$) and 6-coordinate Rh(III) ($4d^6$). The complex first adds H_2 oxidatively, to give a six-coordinate complex in which the hydrogen is formally H^-. An olefin molecule displaces a solvent molecule, using its π-electrons to coordinate the metal. The complex rearranges by inserting the olefin into the metal-hydrogen bond, a process called **migratory insertion**. Finally, the complex returns to the square planar geometry by eliminating the hydrogenated olefin (reductive elimination). Wilkinson's catalyst is highly active and is widely used for homogeneous hydrogenation, hydroboration, and hydrosilation reactions.[12][13] With chiral phosphine ligands, the catalyst can hydrogenate prochiral olefins to give enantiomerically pure products.[14]



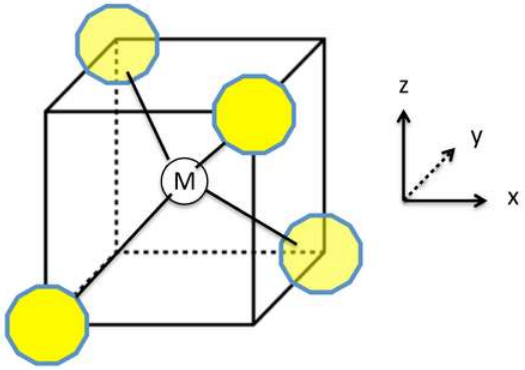
Sir Geoffrey Wilkinson, an inorganic chemist at Imperial College London, developed Wilkinson's catalyst in 1966. Earlier, as an Assistant Professor at Harvard University, he had elucidated the sandwich structure of ferrocene,[9] which had been discovered a few years before but not understood. Wilkinson was awarded the Nobel Prize in Chemistry in 1973 for his contributions to organometallic chemistry.

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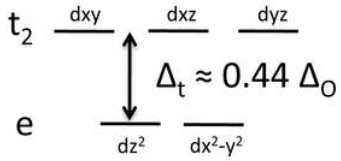
4.12: Tetrahedral Complexes

Tetrahedral complexes are formed with late transition metal ions (Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}) and some early transition metals (Ti^{4+}, Mn^{2+}), especially in situations where the ligands are large. In these cases the small metal ion cannot easily accommodate a coordination number higher than four. Examples of tetrahedal ions and molecules are $[CoCl_4]^{2-}$, $[MnCl_4]^{2-}$, and TiX_4 (X = halogen). Tetrahedral coordination is also observed in some oxo-anions such as $[FeO_4]^{4-}$, which exists as discrete anions in the salts Na_4FeO_4 and Sr_2FeO_4, and in the neutral oxides RuO_4 and OsO_4. The metal carbonyl complexes $Ni(CO)_4$ and $Co(CO)_4]^-$ are also tetrahedral.



The splitting of the d-orbitals in a tetrahedral crystal field can be understood by connecting the vertices of a tetrahedron to form a cube, as shown in the picture at the left. The tetrahedral M-L bonds lie along the body diagonals of the cube. The d_{z^2} and $d_{x^2-y^2}$ orbitals point along the cartesian axes, i.e., towards the faces of the cube, and have the least contact with the ligand lone pairs. Therefore these two orbitals form a low energy, doubly degenerate e set. The d_{xy}, d_{yz}, and d_{xz} orbitals point at the edges of the cube and form a triply degenerate t_2 set. While the t_2 orbitals have more overlap with the ligand orbitals than the e set, they are still weakly interacting compared to the e_g orbitals of an octahedral complex.

The resulting crystal field energy diagram is shown at the right. The splitting energy, Δ_t, is about 4/9 the splitting of an octahedral complex formed with the same ligands. For 3d elements, Δ_t is thus small compared to the pairing energy and their tetrahedral complexes are always high spin. Note that we have dropped the "g" subscript because the tetrahedron does not have a center of symmetry.

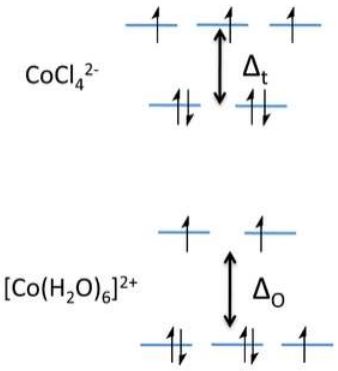


Tetrahedral complexes often have **vibrant colors** because they **lack the center of symmetry** that forbids a d-d* transition. Because the low energy transition is allowed, these complexes typically absorb in the visible range and have extinction coefficients that are 1-2 orders of magnitude higher than the those of the corresponding octahedral complexes. An illustration of this effect can be seen in Drierite, which contains particles of colorless, anhydrous calcium sulfate (gypsum) that absorbs moisture from gases. The indicator dye in Drierite is cobalt (II) chloride, which is is a light pink when wet (octahedral) and deep blue when dry (tetrahedral). The reversible hydration reaction is:

$$Co[CoCl_4] + 12\,H_2O \longrightarrow 2\,Co(H_2O)_6Cl_2 \tag{4.12.1}$$

(**deep blue**, tetrahedral $CoCl_4^{2-}$) (**light pink**, octahedral $[Co(H_2O)_6]^{2+}$)





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4.13: Stability of Transition Metal Complexes

The crystal field stabilization energy (**CFSE**) is an important factor in the stability of transition metal complexes. Complexes with high CFSE tend to be **thermodynamically** stable (i.e., they have high values of K_a, the equilibrium constant for metal-ligand association) and are also **kinetically** inert. They are kinetically inert because ligand substitution requires that they *dissociate* (lose a ligand), *associate* (gain a ligand), or *interchange* (gain and lose ligands at the same time) in the transition state. These distortions in coordination geometry lead to a large **activation energy** if the CFSE is large, even if the product of the ligand exchange reaction is also a stable complex. For this reason, complexes of Pt^{4+}, Ir^{3+} (both low spin $5d^6$), and Pt^{2+} (square planar $5d^8$) have very slow ligand exchange rates.

There are two other important factors that contribute to complex stability:

- **Hard-soft interactions** of metals and ligands (which relate to the **energy** of complex formation)
- The **chelate effect**, which is an **entropic** contributor to complex stability.

Hard-soft interactions

Hard acids are typically small, high charge density cations that are weakly polarizable such as H^+, Li^+, Na^+, Be^{2+}, Mg^{2+}, Al^{3+}, Ti^{4+}, and Cr^{6+}. *Electropositive metals* in *high oxidation states* are typically hard acids. These elements are predominantly found in oxide minerals, because O^{2-} is a hard base.
Some hard bases include H_2O, OH^-, O^{2-}, F^-, NO_3^-, Cl^-, and NH_3.
The hard acid-base interaction is primarily **electrostatic**. Complexes of hard acids with hard bases are stable because of the electrostatic component of the CFSE.

Soft acids are large, polarizable, *electronegative metal* ions in *low oxidation states* such as Ni^0, Hg^{2+}, Cd^{2+}, Cu^+, Ag^+, and Au^+.
Soft bases are anions/neutral bases such as H^-, C_2H_4, CO, PR_3, R_2S, and CN^-). Soft acids typically occur in nature as sulfide or arsenide minerals.

The bonding between soft acids and soft bases is predominantly **covalent**. For example, metal carbonyls bind through a covalent interaction between a zero- or low-valent metal and neutral CO to form $Ni(CO)_4$, $Fe(CO)_5$, $Co(CO)_4^-$, $Mn_2(CO)_{10}$, $W(CO)_6$, and related compounds.

The preference for hard-hard and soft-soft interactions ("like binds like") is nicely illustrated in the properties of the copper halides:

- CuF: unstable
- **CuI: stable**
- **CuF_2: stable**
- CuI_2: unstable

The compounds CuF and CuI_2 have never been isolated, and are thermodynamically unstable to disproportionation:

$$2\,CuF(s) \longrightarrow Cu(s) + CuF_2(s) \tag{4.13.1}$$

$$2\,CuI_2(s) \longrightarrow 2\,CuI(s) + I_2(s) \tag{4.13.2}$$

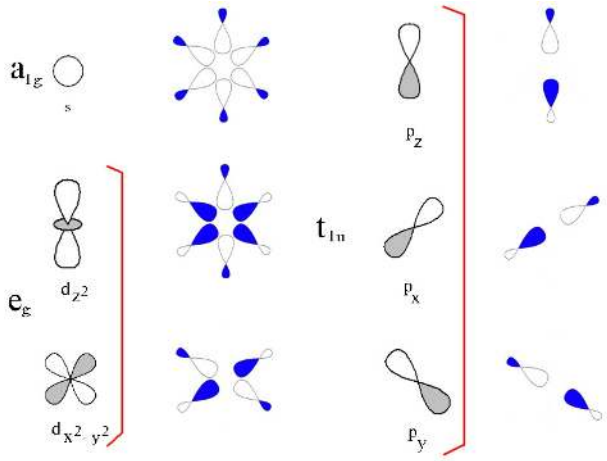
We will learn more about quantifying the energetics of these compounds in Chapter 9.

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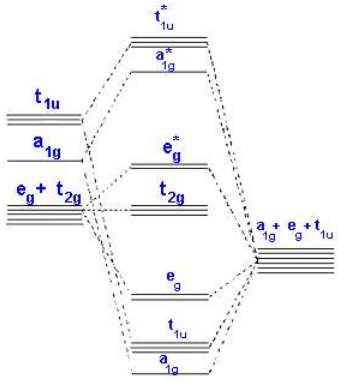
- **5.10: Stability of Transition Metal Complexes** by Chemistry 310 is licensed CC BY-SA 4.0. Original source: https://en.wikibooks.org/wiki/Introduction_to_Inorganic_Chemistry.

4.14: Ligand Field Theory

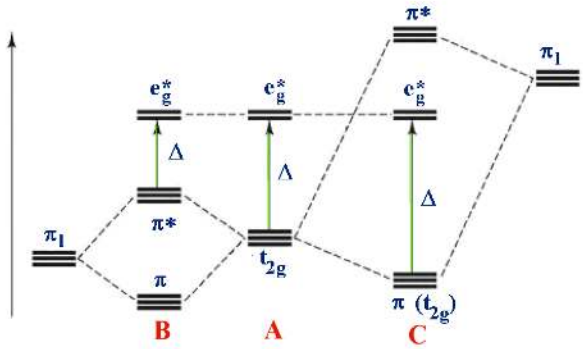
Ligand Field Theory can be considered an extension of Crystal Field Theory such that all levels of covalent interactions can be incorporated into the model. Treatment of the bonding in LFT is generally done using Molecular Orbital Theory. A qualitative approach that can be used for octahedral metal complexes is given in the following 3 diagrams.



In the first diagram, the 3d, 4s and 4p metal ion atomic orbitals are shown together with the ligand group orbitals that would have the correct symmetry to be able to overlap with them. The symmetry adapted linear comination of ligand orbitals are generated by taking 6 sigma orbitals from the ligands, designated as σ_x, σ_{-x}, σ_y, σ_{-y}, σ_z, σ_{-z} and then combining them to make 6 ligand group orbitals. (labelled e_g, a_{1g}, t_{1u})



In the second diagram only sigma bonding is considered and it shows the combination of the metal 3d, 4s and 4p orbitals with OCCUPIED ligand group orbitals (using 1 orbital from each ligand). The result is that that the metal electrons would be fed into t2g and eg* molecular orbitals which is similar to the CFT model except that the eg orbital is now eg*.



For example: B - $[M(II)I_6]^{4-}$ A - $[M(II)(H_2O)_6]^{2+}$ C - $[M(II)(CN)_6]^{4-}$

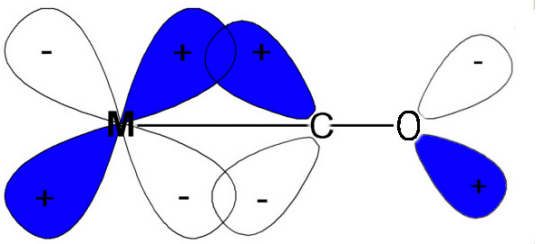
In the third diagram, π (pi) bonding is considered. In general π bonds are weaker than σ (sigma) bonds and so the effect is to modify rather than dramatically alter the description. 2 orbitals from each ligand are combined to give a total of 12 which are subdivided into four sets with three ligand group orbitals in each set. These are labelled t_{1g}, t_{1u}, t_{2g} and t_{2u}. The metal t_{2g} orbital is the most suitable for interaction and this is shown in the 2 cases above.
Case A is the same as above, ignoring π interactions.

- For case B, the ligand π orbitals are full and at lower energy than the metal t_{2g}. This causes a decrease in the size of Δ.
- For case C, the ligand π orbitals are empty and at higher energy than the metal t_{2g}. This causes an increase in the size of Δ.

Returning to the problem of correctly placing ligands in the Spectrochemical series, the halides are examples of case A and groups like CN- and CO are examples of case B. It is possible then to explain the Spectrochemical series once covalent effects are considered.

Some convincing arguments for covalency and effects on Δ come from a study of the IR spectra recorded for simple carbonyl compounds e.g. $M(CO)_6$.

- The CO molecule has a strong triple bond which in the IR gives rise to a strong absorption at ~2140 cm^{-1}. For the series $[Mn(CO)_6]^+$, $[Cr(CO)_6]$ and $[V(CO)_6]^-$, which are isoelectronic, the IR bands for the CO have shifted to 2090, 2000 and 1860 cm^{-1} respectively. Despite the fact that the metals have the same number of electrons (isoelectronic) the frequency of force constant of the CO bond is seen to vary $Mn^+ > Cr > V^-$.
- This can not be explained on an ionic basis but is consistent with the π bonding scheme since the greater the positive charge on the metal, the less readily the metal can delocalize electrons back into the π^* orbitals of the CO group.



Note that the IR values we are dealing with relate to the CO bond and not the M-C so when the CO frequency gets less then it is losing triple bond character and becoming more like a double bond. This is expected if electrons are pushed back from the metal into what were empty π^* antibonding orbitals.

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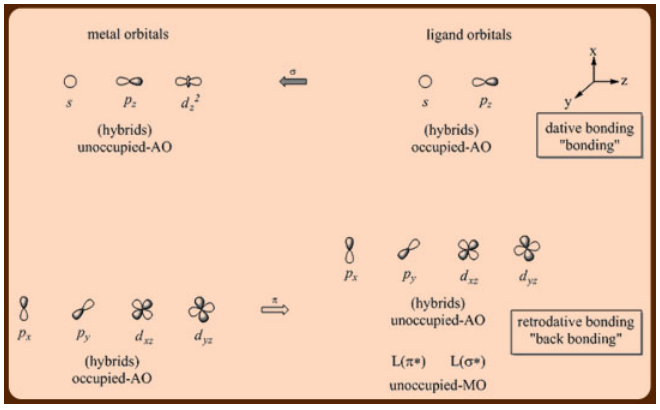
4.15: The 18-electron Rule

Learning Objectives

In this lecture you will learn the following

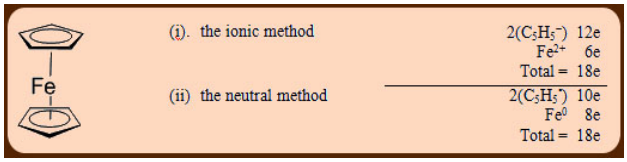
- Have an insight about the stability of the transition metal complexes with respect to their total valence electron count.
- Be aware of the transition metal complexes that obey or do not obey the 18 Valence Electron Rule.
- Have an appreciation of the valence electron count in the transition metal organometallic complexes that arise out of the metal-ligand orbital interactions.

The transition metal organometallic compounds exhibit diverse structural variations that manifest in different chemical properties. Many of these transition metal organometallic compounds are primarily of interest from the prospectives of chemical catalysis. Unlike the main group organometallic compounds, which use mainly *ns* and *np* orbitals in chemical bonding, the transition metal compounds regularly use the $(n-1)d$, *ns* and *np* orbitals for chemical bonding (Figure 1). Partial filling of these orbitals thus render these metal centers both electron donor and electron acceptor abilities, thus allowing them to participate in σ-donor/π-acceptor synergic interactions with donor-acceptor ligands like carbonyls, carbenes, arenes, isonitriles and etc,.

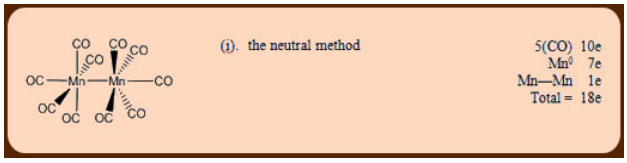


The 18 Valence Electron (18 VE) Rule or The Inert Gas Rule or The Effective Atomic Number (EAN) Rule: The 18-valence electron (VE) rule states that thermodynamically stable transition metal compounds contain 18 valence electrons comprising of the metal *d* electrons plus the electrons supplied by the metal bound ligands. The counting of the 18 valence electrons in transition metal complexes may be obtained by following either of the two methods of electron counting, (*i*). the ionic method and (*ii*). the neutral method. Please note that a metal-metal bond contributes one electron to the total electron count of the metal atom. A bridging ligand donates one electron towards bridging metal atom.

Example 1: Ferrocene $Fe(C_5H_5)_2$



Example 2. $Mn_2(CO)_{10}$



Transition metal organometallic compounds mainly belong to any of the three categories.

a. **Class I** complexes for which the number of valence electrons do not obey the 18 VE rule.
b. **Class II** complexes for which the number of valence electrons do not exceed 18.

c. **Class III** complexes for which the valence electrons exactly obey the 18 VE rule.

The guiding principle which governs the classification of transition metal organometallic compounds is based on the premise that the antibonding orbitals should not be occupied; the nonbonding orbitals may be occupied while the bonding orbitals should be occupied.

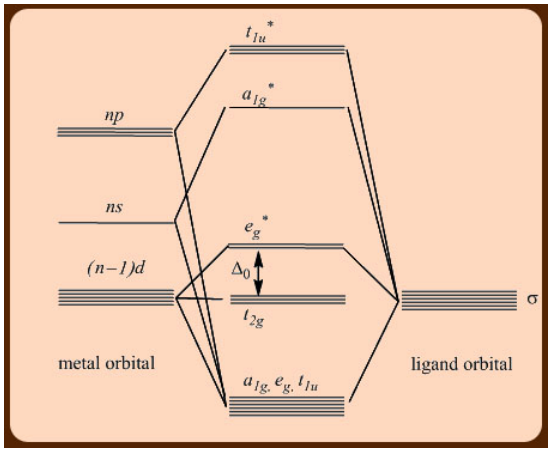


Figure 2. A simplified molecular orbital diagram for an octahedral transition metal complex showing σ−interactions only.

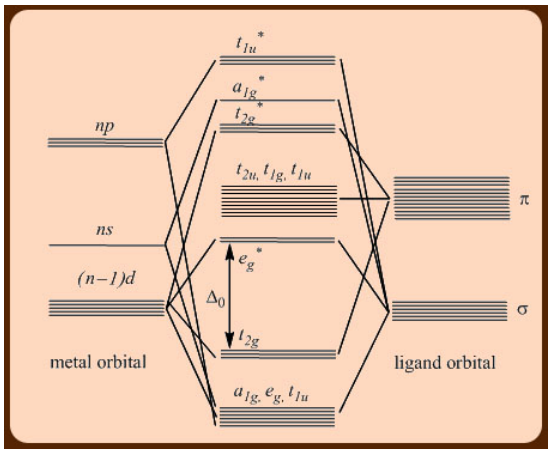


Figure 3. A simplified molecular orbital diagram for an octahedral transition metal complex showing σ−and π−interactions only.

Class I:

In **class I** complexes, the Δ_o splitting is small and often applies to *3d* metals and σ ligands at lower end of the spectrochemical series. In this case the t_{2g} orbital is nonbonding in nature and may be occupied by 0−6 electrons (Figure 2). The e_g* orbital is weakly antibonding and may be occupied by 0−4 electrons. As a consequence, 12−22 valence electron count may be obtained for this class of compounds. Owing to small Δ_{tetr} splitting energy, the tetrahedral transition metal complexes also belongs to this class.

Class II:

In **class II** complexes, the Δ_o splitting is relatively large and is applicable to *4d* and *5d* transition metals having high oxidation state and for σ ligands in the intermediate and upper range of the spectrochemical series. In this case, the t_{2g} orbital is essentially nonbonding in nature and can be filled by 0−6 electrons (Figure 3). The e_g* orbital is strongly antibonding and is not occupied at all. Consequently, the valence shell electron count of these type of complexes would thus be 18 electrons or less.

Class III:

In **class III** complexes, the Δ_o splitting is the largest and is applicable to good σ donor and π acceptor ligands like CO, PF_3, olefins and arenes located at the upper end of the spectrochemical series. The t_{2g}orbital becomes bonding owing to interactions with ligand orbitals and should be occupied by 6 electrons. The e_g* orbital is strongly antibonding and therefore remains unoccupied.

Problems

State the oxidation state of the metal and the total valence electron count of the following species.

1. $V(C_2O_4)_3^{3-}$

Ans: +3 and 14 2. $Mn(acac)_3$ Ans: +3 and 16 3. $W(CN)_8^{3-}$ Ans: +5 and 17 4. $CpMn(CO)_3$ Ans: 0 and 18 5. $Fe_2(CO)_9$ Ans: 0 and 18 Self Assessment test

State the oxidation state of the metal and the total valence electron count of the following species.

1. TiF_6^{2-}

Ans: +4 and 12 2. $Ni(en)_3^{2+}$ Ans: +2 and 20 3. $Cu(NH_3)_6^{2+}$ Ans: +2 and 21 4. $W(CN)_8^{4-}$ Ans: +4 and 18 5. $CH_3Co(CO)_4$ Ans: 0 and 18

Summary

The transition metal complexes may be classified into the following three types. (i). The ones that do not obey the 18 valence electron rule are of class I type (ii). the ones that do not exceed the 18 valence electron rule are of class II and (iii). the ones that strictly follow the 18 valence electron rule. Depending upon the interaction of the metal orbitals with the ligand orbitals and also upon the nature of the ligand position in spectrochemical series, the transition metal organometallic compounds can form into any of the three categories.

The 18-electron rule is used primarily for predicting and rationalizing formulae for stable metal complexes, especially organometallic compounds. The rule is based on the fact that the valence shells of transition metals consist of nine valence orbitals (one s orbital, three p orbitals and five d orbitals), which collectively can accommodate 18 electrons as either bonding or nonbonding electron pairs. This means that, the combination of these nine atomic orbitals with ligand orbitals creates nine molecular orbitals that are either metal-ligand bonding or non-bonding. When a metal complex has 18 valence electrons, it has achieved the same electron configuration as the noble gas in the period. The rule and its exceptions are similar to the application of the octet rule to main group elements.

This rule applies primarily to organometallic compounds, and the 18 electrons come from the 9 available orbitals in d orbital elements (1 s orbital, 3 p orbitals, and 5 d orbitals). The rule is not helpful for complexes of metals that are not transition metals, and interesting or useful transition metal complexes will violate the rule because of the consequences deviating from the rule bears on reactivity. If the molecular transition metal complex has an 18 electron count, it is called **saturated**. This means that additional ligands cannot bind to the transition metal because there are no empty low-energy orbitals for incoming ligands to coordinate. If the molecule has less than 18 electrons, then it is called **unsaturated** and can bind additional ligands.

Electron counting

Two methods are commonly employed for electron counting:

1. Neutral atom method: Metal is taken as in zero oxidation state for counting purpose
2. Oxidation state method: We first arrive at the oxidation state of the metal by considering the number of anionic ligands present and overall charge of the complex

To count electrons in a transition metal compound:

1. Determine the oxidation state of the transition metal and the resulting d-electron count.
    - Identify if there are any overall charges on the molecular complex.
    - Identify the charge of each ligand.
2. Determine the number of electrons from each ligand that are donated to the metal center.
3. Add up the electron counts for the metal and for each ligand.

Typically for most compounds, the electron count should add up to 18 electrons. However, there are many exceptions to the 18 electron rule, just like there are exceptions to the octet rule.

Reactivity

The 18 electron rule allows one to predict the reactivity of a certain compound. The associative mechanism means that there is an addition of a ligand while a dissociative mechanism means that there is a loss of a ligand. When the electron count is less than 18, a molecule will most likely undergo an associative reaction. For example: $(C_2H_4)PdCl_2$

- 16 electron count

- Would it more likely lose a C_2H_4 or gain a CO? Losing a C_2H_4 results in a 14 electron complex while gaining a CO gives an 18 electron complex. From the 18 electron rule, we will expect that the compound will more likely undergo an associative addition of CO.

Example 4.15.1:

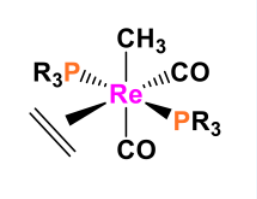


Figure 4.15.1: Saturated Re metal complex with 18 electron count. (CC SA-BY 4.0; Derrekli)

1. There is no overall charge on the molecule and there is one anionic ligand (CH_3^-)
   - The Re metal must have a positive charge that balances out the anionic ligand charge to equal the 0 overall molecular charge. Since there is a -1 charge contribution from the methyl ligand, the Re metal has a +1 charge.
   - Because the Re metal is in the +1 oxidation state, it is a d^6 electron count. It would have been its regular d^7 electron count if it had a neutral (0) oxidation state.
2. The CH_3^- ligand contributes 2 electrons. Each CO ligand contributes 2 electrons. Each PR_3 ligand contributes 2 electrons. The H2C=CH2 ligand contributes 2 electrons.
3. Adding up the electrons:
   - Re(1): 6 electrons
   - CH_3^-: 2 electrons
   - 2 x CO: 2 x 2 electrons = 4 electrons
   - 2 x PR_3: 2 x 2 electrons = 4 electrons
   - $H_2C=CH_2$: 2 electrons
   - Total: 18 electrons

In this example, the molecular compound has an 18 electron count, which means that all of its orbitals are filled and the compound is stable.

Example 4.15.2: $[M(CO)_7]^+$

The 18 electron rule can also be used to help identify an unknown transition metal in a compound. Take for example $[M(CO)_7]^+$. To find what the unknown transition metal M is, simply work backwards:

1. 18 electrons
2. Each (CO) ligand contributes 2 electrons
   - 7 x 2 electrons = 14 electrons
3. 18 - 14 = 4 electrons
4. d^4
5. M(I) oxidation state
6. The unknown metal M must be V, Vanadium

Example 4.15.3: $[Co(CO)_5]^z$

Similarly to Example 2, the 18 electron rule can also be applied to determine the overall expected charge of an molecule. Take for example $[Co(CO)_5]^z$. To find the unknown charge z:

1. 18 electrons
2. Each CO ligand contributes 2 electrons
   1. 5 x 2 electrons = 10 electrons
3. Co is typically d^9
4. 9 + 10 = 19 electrons

5. To satisfy the 18 electron rule, the $[Co(CO)_5]^z$ compound must have a charge of z = +1.

Ligand Contributions

Below is a list of common organometallic ligands and their respective electron contributions.

Neutral 2e donors	Anionic 2e donors	Anionic 4e donors	Anionic 6e donors
PR_3 (phosphines)	X^- (halide)	$C_3H_5^-$ (allyl)	Cp^- (cyclopentadienyl)
CO (carbonyl)	CH_3^- (methyl)	O^{2-} (oxide)	O^{2-} (oxide)
alkenes	CR_3^- (alkyl)	S^{2-} (sulfide)	
alkynes	Ph^- (phenyl)	NR^{2-} (imide)	
nitriles	H^- (hydride)	CR_2^{2-} (alkylidene)	
	R_nE^- (silyl, germyl, alkoxo, amido etc.)	OR^- (alkoxide, bridging ligand)	
		SR^- (thiolate, bridging ligand)	
		NR_2^- (inorganic amide, bridging ligand)	
		PR_2^- (phosphide, bridging ligand)	

Exceptions

Generally, the early transition metals (group 3 to 5) could have an electron count of 16 or less. Middle transition metals (group 6 to group 8) commonly have 18 electron count while late transition metals (group 9 to group 11) generally have 16 or lower electron count. When a structure has less than an 18 electron count, it is considered electron-deficient or coordinately unsaturated. This means that the compound has empty valence orbitals, making it electrophilic and extremely reactive. If a structure has "too many electrons," that means that not all of the bonds are covalent bonds, and thus some has to be ionic bonds. These bonds are weaker compared to covalent bonds. However, these organometallic compounds that have an electron count greater than 18 are fairly rare.

Summary

The 18-electron rule is similar to the octet rule for main group elements, something you might be more familiar with, and thus it may be useful to bear that in mind. So in a sense, there's not much more to it than "electron bookkeeping".

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CHAPTER OVERVIEW

5: Thermodynamics of Lattices

Lattice enthalpy is a measure of the strength of the forces between the ions in an ionic solid. The greater the lattice enthalpy, the stronger the forces. Those forces are only completely broken when the ions are present as gaseous ions, scattered so far apart that there is negligible attraction between them.

5.1: Lattice Energy

5.2: Lattice Energy- The Born-Haber cycle

5.3: Lattice Enthalpies and Born Haber Cycles

5.4: The Born-Lande' equation

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5.1: Lattice Energy

Discussion Questions

- How is lattice energy estimated using Born-Haber cycle?
- How is lattice energy related to crystal structure?

The Lattice energy, U, is the amount of energy required to separate a mole of the solid (s) into a gas (g) of its ions.

$$\mathrm{M_aL_b(s) \rightarrow aM^{b^+}(g) + bX^{a^-}(g)} \tag{5.1.1}$$

This quantity cannot be experimentally determined directly, but it can be estimated using a Hess Law approach in the form of *Born-Haber cycle*. It can also be calculated from the electrostatic consideration of its crystal structure. As defined in Equation 5.1.1, the lattice energy is positive, because energy is always required to separate the ions. For the reverse process of Equation 5.1.1:

$$\mathrm{aM^{b^+}(g) + bX^{a^-}(g) \rightarrow M_aL_b(s)}$$

the energy released is called **energy of crystallization** (E_{cryst}). Therefore,

$$U_{lattice} = -E_{cryst}$$

Values of lattice energies for various solids have been given in literature, especially for some common solids. Some are given here.

Table 5.1.1: Comparison of Lattice Energies (U in kJ/mol) of Some Salts

Solid	U	Solid	U	Solid	U	Solid	U
LiF	1036	LiCl	853	LiBr	807	LiI	757
NaF	923	NaCl	786	NaBr	747	NaI	704
KF	821	KCl	715	KBr	682	KI	649
MgF_2	2957	$MgCl_2$	2526	$MgBr_2$	2440	MgI_2	2327

The following trends are obvious at a glance of the data in Table 5.1.1:

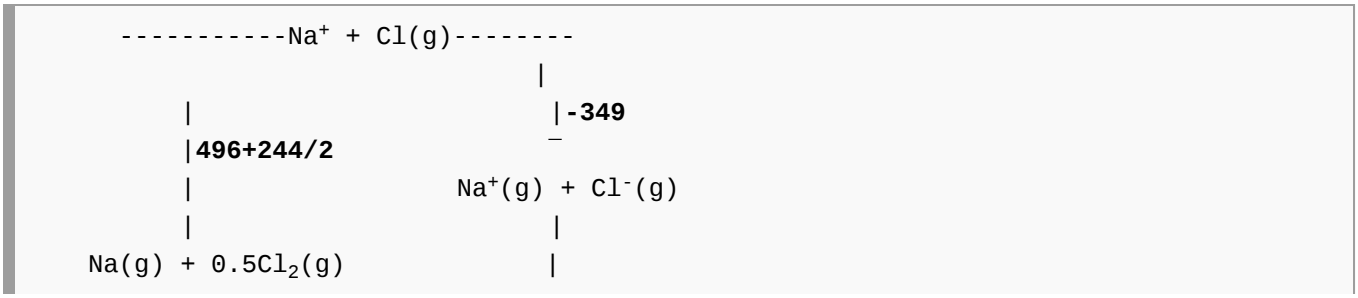
- As the ionic radii of either the cation or anion increase, the lattice energies decrease.
- The solids consists of divalent ions have much larger lattice energies than solids with monovalent ions.

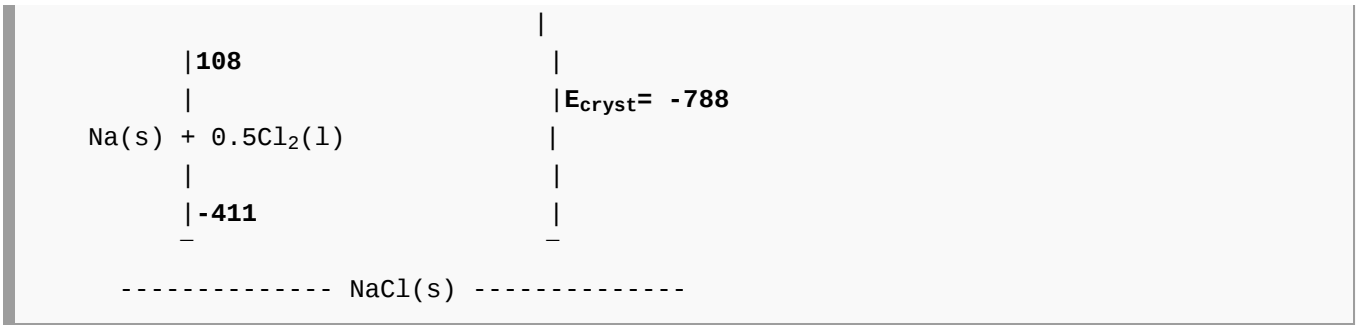
How is lattice energy estimated using Born-Haber cycle?

Estimating lattice energy using the Born-Haber cycle has been discussed in Ionic Solids. For a quick review, the following is an example that illustrate the estimate of the energy of crystallization of NaCl.

Hsub of Na = 108 kJ/mol (Heat of sublimation)
D of Cl2 = 244 (Bond dissociation energy)
IP of Na(g) = 496 (Ionization potential or energy)
EA of Cl(g) = -349 (Electron affinity of Cl)
Hf of NaCl = -411 (Enthalpy of formation)

The Born-Haber cycle to evaluate $E_{lattice}$ is shown below:





E_{cryst} = -411-(108+496+244/2)-(-349) kJ/mol
= -788 kJ/mol.

Discussion

The value calculated for U depends on the data used. Data from various sources differ slightly, and so is the result. The lattice energies for NaCl most often quoted in other texts is about 765 kJ/mol.

Compare with the method shown below

Na(s) + 0.5 Cl_2(l) ® NaCl(s)	- 411	H_f
Na(g) ® Na(s)	- 108	-H_{sub}
Na^+(g) + e ® Na(g)	- 496	-*IP*
Cl(g) ® 0.5 Cl_2(g)	- 0.5 * 244	-0.5*D
Cl^-(g) ® Cl(g) + 2 e	349	-*EA*
Add all the above equations leading to		
Na^+(g) + Cl^-(g) ® NaCl(s)	-788 kJ/mol = E_{cryst}	

Lattice Energy is Related to Crystal Structure

There are many other factors to be considered such as covalent character and electron-electron interactions in ionic solids. But for simplicity, let us consider the ionic solids as a collection of positive and negative ions. In this simple view, appropriate number of cations and anions come together to form a solid. The positive ions experience both attraction and repulson from ions of opposite charge and ions of the same charge.

As an example, let us consider the the NaCl crystal. In the following discussion, assume r be the distance between Na^+ and Cl^- ions. The nearest neighbors of Na^+ are 6 Cl^- ions at a distance 1r, 12 Na^+ ions at a distance 2r, 8 Cl^- at 3r, 6 Na^+ at 4r, 24 Na^+ at 5r, and so on. Thus, the energy due to one ion is

$$E = \frac{Z^2 e^2}{4\pi\epsilon_o r} M \tag{5.1.2}$$

The Madelung constant, M, is a poorly converging series of interaction energies:

$$M = \frac{6}{1} - \frac{12}{2} + \frac{8}{3} - \frac{6}{4} + \frac{24}{5} \ldots \tag{5.1.3}$$

with

- Z is the number of charges of the ions, (e.g., 1 for NaCl),
- e is the charge of an electron (1.6022×10^{-19} C),
- $4\pi\epsilon_o$ is 1.11265x10^{-10} C^2/(J m).

The above discussion is valid only for the sodium chloride (also called rock salt) structure type. This is a geometrical factor, depending on the arrangement of ions in the solid. The Madelung constant depends on the structure type, and its values for several structural types are given in Table 6.13.1.

A is the number of anions coordinated to cation and *C* is the numbers of cations coordinated to anion.

Table 5.1.2: Madelung Constants

Compound	Crystal Lattice	M	A : C	Type
NaCl	NaCl	1.74756	6 : 6	Rock salt
CsCl	CsCl	1.76267	6 : 6	CsCl type
CaF_2	Cubic	2.51939	8 : 4	Fluorite
$CdCl_2$	Hexagonal	2.244		
MgF_2	Tetragonal	2.381		
ZnS (wurtzite)	Hexagonal	1.64132		
TiO_2 (rutile)	Tetragonal	2.408	6 : 3	Rutile
$bSiO_2$	Hexagonal	2.2197		
Al_2O_3	Rhombohedral	4.1719	6 : 4	Corundum
A is the number of anions coordinated to cation and *C* is the numbers of cations coordinated to anion.				

Madelung constants for a few more types of crystal structures are available from the Handbook Menu. There are other factors to consider for the evaluation of energy of crystallization, and the treatment by *M. Born* led to the formula for the evaluation of crystallization energy E_{cryst}, for a mole of **crystalline solid**.

$$E_{cryst} = \frac{NZ^2e^2}{4\pi\epsilon_o r}\left(1 - \frac{1}{n}\right) \tag{5.1.4}$$

where *N* is the Avogadro's number (6.022x10^{-23}), and *n* is a number related to the electronic configurations of the ions involved. The *n* values and the electronic configurations (e.c.) of the corresponding inert gases are given below:

n =	5	7	9	10	12
e.c.	He	Ne	Ar	Kr	Xe

The following values of *n* have been suggested for some common solids:

n =	5.9	8.0	8.7	9.1	9.5
e.c.	LiF	LiCl	LiBr	NaCl	NaBr

Example 5.1.1

Estimate the energy of crystallization for NaCl.

Solution

Using the values giving in the discussion above, the estimation is given by Equation 5.1.4:

$$E_crust = \frac{(6.022\times10^{23}/mol(1.6022\times10^{-19})^2(1.747558)}{4\pi\,(8.854\times10^{-12}C^2/m)(282\times10^{-12}\ m}\left(1-\frac{1}{9.1}\right)$$

$$= -766kJ/mol$$

Discussion

Much more should be considered in order to evaluate the lattice energy accurately, but the above calculation leads you to a good start. When methods to evaluate the energy of crystallization or lattice energy lead to reliable values, these values can be used in the Born-Haber cycle to evaluate other chemical properties, for example the electron affinity, which is really difficult to determine directly by experiment.

Exercise 5.1.1

Which one of the following has the largest lattice energy? LiF, NaF, CaF_2, AlF_3

Answer

Skill: Explain the trend of lattice energy.

Exercise 5.1.2

Which one of the following has the largest lattice energy? LiCl, NaCl, $CaCl_2$, Al_2O_3

Answer

Corrundum Al_2O_3 has some covalent character in the solid as well as the higher charge of the ions.

Exercise 5.1.3

Lime, CaO, is know to have the same structure as NaCl and the edge length of the unit cell for CaO is 481 pm. Thus, Ca-O distance is 241 pm. Evaluate the energy of crystallization, E_{cryst} for CaO.

Answer

Energy of crystallization is -3527 kJ/mol

Skill: Evaluate the lattice energy and know what values are needed.

Exercise 5.1.4

Assume the interionic distance for $NaCl_2$ to be the same as those of NaCl (r = 282 pm), and assume the structure to be of the fluorite type (M = 2.512). Evaluate the energy of crystallization, E_{cryst} .

Answer

-515 kJ/mol

Discussion: This number has not been checked. If you get a different value, please let me know.

Contributors and Attributions

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5.2: Lattice Energy- The Born-Haber cycle

Ionic solids tend to be very stable compounds. The enthalpies of formation of the ionic molecules cannot alone account for this stability. These compounds have an additional stability due to the lattice energy of the solid structure. However, lattice energy cannot be directly measured. The Born-Haber cycle allows us to understand and determine the lattice energies of ionic solids.

Introduction

This module will introduce the idea of lattice energy, as well as one process that allows us to calculate it: the Born-Haber Cycle. In order to use the Born-Haber Cycle, there are several concepts that we must understand first.

Lattice Energy

Lattice Energy is a type of potential energy that may be defined in two ways. In one definition, the lattice energy is the energy required to break apart an ionic solid and convert its component atoms into gaseous ions. This definition causes the value for the lattice energy to always be positive, since this will always be an endothermic reaction. The other definition says that lattice energy is the reverse process, meaning it is the energy released when gaseous ions bind to form an ionic solid. As implied in the definition, this process will always be exothermic, and thus the value for lattice energy will be negative. Its values are usually expressed with the units kJ/mol.

Lattice Energy is used to explain the stability of ionic solids. Some might expect such an ordered structure to be less stable because the entropy of the system would be low. However, the crystalline structure allows each ion to interact with multiple oppositely charge ions, which causes a highly favorable change in the enthalpy of the system. A lot of energy is released as the oppositely charged ions interact. It is this that causes ionic solids to have such high melting and boiling points. Some require such high temperatures that they decompose before they can reach a melting and/or boiling point.

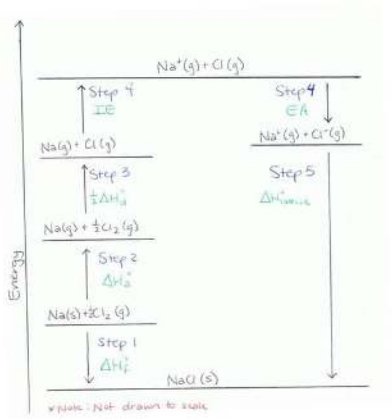
Born-Haber Cycle

There are several important concept to understand before the Born-Haber Cycle can be applied to determine the lattice energy of an ionic solid; ionization energy, electron affinity, dissociation energy, sublimation energy, heat of formation, and Hess's Law.

- **Ionization Energy** is the energy required to remove an electron from a neutral atom or an ion. This process always requires an input of energy, and thus will always have a positive value. In general, ionization energy increases across the periodic table from left to right, and decreases from top to bottom. There are some excepts, usually due to the stability of half-filled and completely filled orbitals.
- **Electron Affinity** is the energy released when an electron is added to a neutral atom or an ion. Usually, energy released would have a negative value, but due to the definition of electron affinity, it is written as a positive value in most tables. Therefore, when used in calculating the lattice energy, we must remember to subtract the electron affinity, not add it. In general, electron affinity increases from left to right across the periodic table and decreases from top to bottom.
- **Dissociation energy** is the energy required to break apart a compound. The dissociation of a compound is always an endothermic process, meaning it will always require an input of energy. Therefore, the change in energy is always positive. The magnitude of the dissociation energy depends on the electronegativity of the atoms involved.
- Sublimation energy is the energy required to cause a change of phase from solid to gas, bypassing the liquid phase. This is an input of energy, and thus has a positive value. It may also be referred to as the energy of atomization.
- **The heat of formation** is the change in energy when forming a compound from its elements. This may be positive or negative, depending on the atoms involved and how they interact.
- **Hess's Law** states that the overall change in energy of a process can be determined by breaking the process down into steps, then adding the changes in energy of each step. The Born-Haber Cycle is essentially Hess's Law applied to an ionic solid.

Using the Born-Haber Cycle

The values used in the Born-Haber Cycle are all predetermined changes in enthalpy for the processes described in the section above. Hess' Law allows us to add or subtract these values, which allows us to determine the lattice energy.



Step 1

Determine the energy of the metal and nonmetal in their elemental forms. (Elements in their natural state have an energy level of zero.) Subtract from this the heat of formation of the ionic solid that would be formed from combining these elements in the appropriate ration. This is the energy of the ionic solid, and will be used at the end of the process to determine the lattice energy.

Step 2

The Born-Haber Cycle requires that the elements involved in the reaction are in their gaseous forms. Add the changes in enthalpy to turn one of the elements into its gaseous state, and then do the same for the other element.

Step 3

Metals exist in nature as single atoms and thus no dissociation energy needs to be added for this element. However, many nonmetals will exist as polyatomic species. For example, Cl exists as Cl_2 in its elemental state. The energy required to change Cl_2 into 2Cl atoms must be added to the value obtained in Step 2.

Step 4

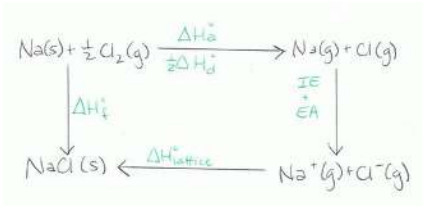
Both the metal and nonmetal now need to be changed into their ionic forms, as they would exist in the ionic solid. To do this, the ionization energy of the metal will be added to the value from Step 3. Next, the electron affinity of the nonmetal will be subtracted from the previous value. It is subtracted because it is a release of energy associated with the addition of an electron.

*This is a common error due to confusion caused by the definition of electron affinity, so be careful when doing this calculation.

Step 5

Now the metal and nonmetal will be combined to form the ionic solid. This will cause a release of energy, which is called the lattice energy. The value for the lattice energy is the difference between the value from Step 1 and the value from Step 4.

The diagram below is another representation of the Born-Haber Cycle.



Equation

The Born-Haber Cycle can be reduced to a single equation:

Heat of formation= Heat of atomization+ Dissociation energy+ (sum of Ionization energies)+ (sum of Electron affinities)+ Lattice energy

*Note: In this general equation, the electron affinity is added. However, when plugging in a value, determine whether energy is released (exothermic reaction) or absorbed (endothermic reaction) for each electron affinity. If energy is released, put a negative sign in front of the value; if energy is absorbed, the value should be positive.

Rearrangement to solve for lattice energy gives the equation:

Lattice energy= Heat of formation- Heat of atomization- Dissociation energy- (sum of Ionization energies)- (sum of Electron Affinities)

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Problems

1. Define lattice energy, ionization energy, and electron affinity.
2. What is Hess' Law?
3. Find the lattice energy of KF(s).
   Note: Values can be found in standard tables.
4. Find the lattice energy of $MgCl_2$(s).
5. Which one of the following has the greatest lattice energy?
   a. A) MgO
   b. B) NaC
   c. C) LiCl
   d. D) $MgCl_2$
6. Which one of the following has the greatest Lattice Energy?
   a. NaCl
   b. $CaCl_2$
   c. $AlCl_3$
   d. KCl

Solutions

1. Lattice energy: The difference in energy between the expected experimental value for the energy of the ionic solid and the actual value observed. More specifically, this is the energy gap between the energy of the separate gaseous ions and the energy of the ionic solid.
   Ionization energy: The energy change associated with the removal of an electron from a neutral atom or ion.
   Electron affinity: The release of energy associated with the addition of an electron to a neutral atom or ion.
2. Hess' Law states that the overall energy of a reaction may be determined by breaking down the process into several steps, then adding together the changes in energy of each step.
3. Lattice Energy= [-436.68-89-(0.5*158)-418.8-(-328)] kJ/mol= **-695.48 kJ/mol**
4. Lattice Energy= [-641.8-146-243-(737.7+1450.6)-(2*-349)] kJ/mol= **-2521.1 kJ/mol**
5. MgO. It has ions with the largest charge.
6. $AlCl_3$. According to the periodic trends, as the radius of the ion increases, lattice energy decreases.

References

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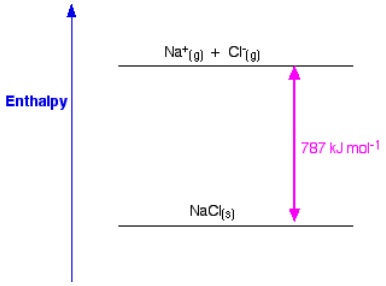
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5.3: Lattice Enthalpies and Born Haber Cycles

Lattice enthalpy is a measure of the strength of the forces between the ions in an ionic solid. The greater the **lattice enthalpy**, the stronger the forces. This page introduces lattice enthalpies (lattice energies) and Born-Haber cycles.

Defining Lattice Enthalpy

There are two different ways of defining lattice enthalpy which directly contradict each other, and you will find both in common use. In fact, there is a simple way of sorting this out, but many sources do not use it. Lattice enthalpy is a measure of the strength of the forces between the ions in an ionic solid. The greater the lattice enthalpy, the stronger the forces. Those forces are only completely broken when the ions are present as gaseous ions, scattered so far apart that there is negligible attraction between them. You can show this on a simple enthalpy diagram.



For sodium chloride, the solid is more stable than the gaseous ions by 787 kJ mol^{-1}, and that is a measure of the strength of the attractions between the ions in the solid. Remember that energy (in this case heat energy) is released when bonds are made, and is required to break bonds.

So lattice enthalpy could be described in either of two ways.

- It could be described as the enthalpy change when 1 mole of sodium chloride (or whatever) was formed from its scattered gaseous ions. In other words, you are looking at a downward arrow on the diagram.
- Or, it could be described as the enthalpy change when 1 mole of sodium chloride (or whatever) is broken up to form its scattered gaseous ions. In other words, you are looking at an upward arrow on the diagram.

Both refer to the same enthalpy diagram, but one looks at it from the point of view of making the lattice, and the other from the point of view of breaking it up. Unfortunately, both of these are often described as "lattice enthalpy".

Definitions

- The *lattice dissociation enthalpy* is the enthalpy change needed to convert 1 mole of solid crystal into its scattered gaseous ions. Lattice dissociation enthalpies are **always positive**.
- The *lattice formation enthalpy* is the enthalpy change when 1 mole of solid crystal is formed from its separated gaseous ions. Lattice formation enthalpies are **always negative**.

This is an absurdly confusing situation which is easily resolved by never using the term "lattice enthalpy" without qualifying it.

- You should talk about "lattice dissociation enthalpy" if you want to talk about the amount of energy needed to split up a lattice into its scattered gaseous ions. For NaCl, the lattice dissociation enthalpy is +787 kJ mol^{-1}.
- You should talk about "lattice formation enthalpy" if you want to talk about the amount of energy released when a lattice is formed from its scattered gaseous ions. For NaCl, the lattice formation enthalpy is -787 kJ mol^{-1}.

That immediately removes any possibility of confusion.

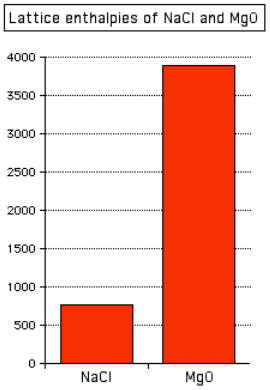
Factors affecting Lattice Enthalpy

The two main factors affecting lattice enthalpy are

- The charges on the ions and
- The ionic radii (which affects the distance between the ions).

The charges on the ions

Sodium chloride and magnesium oxide have exactly the same arrangements of ions in the crystal lattice, but the lattice enthalpies are very different.

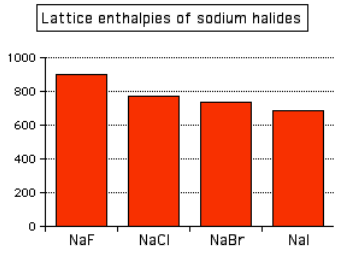


You can see that the lattice enthalpy of magnesium oxide is much greater than that of sodium chloride. That's because in magnesium oxide, 2+ ions are attracting 2- ions; in sodium chloride, the attraction is only between 1+ and 1- ions.

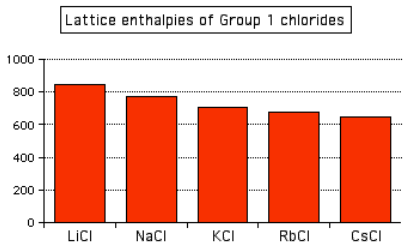
The Radius of the Ions

The lattice enthalpy of magnesium oxide is also increased relative to sodium chloride because magnesium ions are smaller than sodium ions, and oxide ions are smaller than chloride ions. That means that the ions are closer together in the lattice, and that increases the strength of the attractions.

This effect of ion size on lattice enthalpy is clearly observed as you go down a Group in the Periodic Table. For example, as you go down Group 7 of the Periodic Table from fluorine to iodine, you would expect the lattice enthalpies of their sodium salts to fall as the negative ions get bigger - and that is the case:



Attractions are governed by the distances between the centers of the oppositely charged ions, and that distance is obviously greater as the negative ion gets bigger. And you can see exactly the same effect if as you go down Group 1. The next bar chart shows the lattice enthalpies of the Group 1 chlorides.



Calculating Lattice Enthalpy

It is impossible to measure the enthalpy change starting from a solid crystal and converting it into its scattered gaseous ions. It is even more difficult to imagine how you could do the reverse - start with scattered gaseous ions and measure the enthalpy change

when these convert to a solid crystal. Instead, lattice enthalpies always have to be calculated, and there are two entirely different ways in which this can be done.

1. You can can use a Hess's Law cycle (in this case called a Born-Haber cycle) involving enthalpy changes which can be measured. Lattice enthalpies calculated in this way are described as experimental values.
2. Or you can do physics-style calculations working out how much energy would be released, for example, when ions considered as point charges come together to make a lattice. These are described as theoretical values. In fact, in this case, what you are actually calculating are properly described as lattice energies.

Born-Haber Cycles

Standard Atomization Enthalpies

Before we start talking about Born-Haber cycles, we need to define the **atomization enthalpy**, ΔH_a^o. The standard atomization enthalpy is the enthalpy change when 1 mole of gaseous atoms is formed from the element in its standard state. Enthalpy change of atomization is always positive. You are always going to have to supply energy to break an element into its separate gaseous atoms. All of the following equations represent changes involving atomization enthalpy:

$$\frac{1}{2}Cl_2(g) \rightarrow Cl(g) \quad \Delta H_a^o = +122\, kJ\, mol^{-1}$$

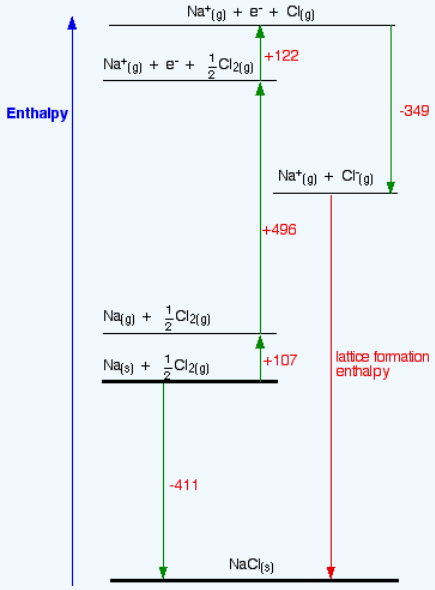
$$\frac{1}{2}Br_2(l) \rightarrow Br(g) \quad \Delta H_a^o = +122\, kJ\, mol^{-1}$$

$$Na(s) \rightarrow Na(g) \quad \Delta H_a^o = +107\, kJ\, mol^{-1}$$

Notice particularly that the "mol^{-1}" is per mole of atoms **formed** - NOT per mole of element that you start with. You will quite commonly have to write fractions into the left-hand side of the equation. Getting this wrong is a common mistake.

Example 5.3.1: Born-Haber Cycle for NaCl

Consider a Born-Haber cycle for sodium chloride, and then talk it through carefully afterwards. You will see that I have arbitrarily decided to draw this for lattice formation enthalpy. If you wanted to draw it for lattice dissociation enthalpy, the red arrow would be reversed - pointing upwards.



Focus to start with on the higher of the two thicker horizontal lines. We are starting here with the elements sodium and chlorine in their standard states. Notice that we only need half a mole of chlorine gas in order to end up with 1 mole of NaCl. The arrow pointing down from this to the lower thick line represents the enthalpy change of formation of sodium chloride.

The Born-Haber cycle now imagines this formation of sodium chloride as happening in a whole set of small changes, most of which we know the enthalpy changes for - except, of course, for the lattice enthalpy that we want to calculate.

- The +107 is the atomization enthalpy of sodium. We have to produce gaseous atoms so that we can use the next stage in the cycle.
- The +496 is the first ionization energy of sodium. Remember that first ionization energies go from gaseous atoms to gaseous singly charged positive ions.
- The +122 is the atomization enthalpy of chlorine. Again, we have to produce gaseous atoms so that we can use the next stage in the cycle.
- The -349 is the first electron affinity of chlorine. Remember that first electron affinities go from gaseous atoms to gaseous singly charged negative ions.
- And finally, we have the positive and negative gaseous ions that we can convert into the solid sodium chloride using the lattice formation enthalpy.

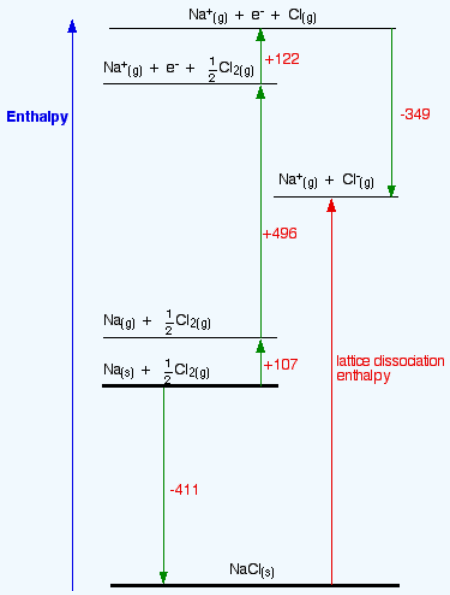
Now we can use Hess' Law and find two different routes around the diagram which we can equate. As drawn, the two routes are obvious. The diagram is set up to provide two different routes between the thick lines. So, from the cycle we get the calculations directly underneath it . . .

$$-411 = +107 + 496 + 122 - 349 + LE$$

$$LE = -411 - 107 - 496 - 122 + 349$$

$$LE = -787 \text{ kJ mol}^{-1}$$

How would this be different if you had drawn a lattice dissociation enthalpy in your diagram? Your diagram would now look like this:



The only difference in the diagram is the direction the lattice enthalpy arrow is pointing. It does, of course, mean that you have to find two new routes. You cannot use the original one, because that would go against the flow of the lattice enthalpy arrow. This time both routes would start from the elements in their standard states, and finish at the gaseous ions.

$$-411 + LE = +107 + 496 + 122 - 349$$

$$LE = +107 + 496 + 122 - 349 + 411$$

$$LE = +787 \text{ kJ mol}^{-1}$$

Once again, the cycle sorts out the sign of the lattice enthalpy.

Theoretical Estimates of Lattice Energies

Let's assume that a compound is fully ionic. Let's also assume that the ions are point charges - in other words that the charge is concentrated at the center of the ion. By doing physics-style calculations, it is possible to calculate a theoretical value for what you

would expect the lattice energy to be. Calculations of this sort end up with values of *lattice energy*, and not *lattice enthalpy*. If you know how to do it, you can then fairly easily convert between the two.

There are several different equations, of various degrees of complication, for calculating lattice energy in this way. There are two possibilities:

- There is reasonable agreement between the experimental value (calculated from a Born-Haber cycle) and the theoretical value. Sodium chloride is a case like this - the theoretical and experimental values agree to within a few percent. That means that for sodium chloride, the assumptions about the solid being ionic are fairly good.
- The experimental and theoretical values do not agree. A commonly quoted example of this is silver chloride, AgCl. Depending on where you get your data from, the theoretical value for lattice enthalpy for AgCl is anywhere from about 50 to 150 kJ mol^{-1} less than the value that comes from a Born-Haber cycle. In other words, treating the AgCl as 100% ionic underestimates its lattice enthalpy by quite a lot.

The explanation is that silver chloride actually has a significant amount of covalent bonding between the silver and the chlorine, because there is not enough electronegativity difference between the two to allow for complete transfer of an electron from the silver to the chlorine. Comparing experimental (Born-Haber cycle) and theoretical values for lattice enthalpy is a good way of judging how purely ionic a crystal is.

Example 5.3.2: Born-Haber Cycle for $MgCl_2$

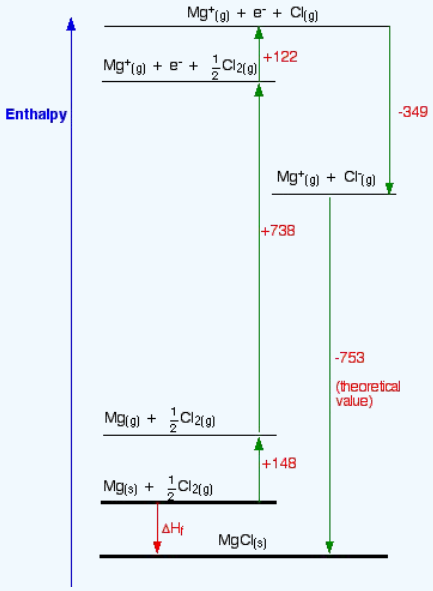
The question arises as to why, from an energetics point of view, magnesium chloride is $MgCl_2$ rather than MgCl or $MgCl_3$ (or any other formula you might like to choose). It turns out that $MgCl_2$ is the formula of the compound which has the most negative enthalpy change of formation - in other words, it is the most stable one relative to the elements magnesium and chlorine.

Let's look at this in terms of Born-Haber cycles of and contrast the enthalpy change of formation for the imaginary compounds MgCl and $MgCl_3$. That means that we will have to use theoretical values of their lattice enthalpies. We ca not use experimental ones, because these compounds obviously do not exist! I'm taking theoretical values for lattice enthalpies for these compounds that I found on the web. I can't confirm these, but all the other values used by that source were accurate. The exact values do not matter too much anyway, because the results are so dramatically clear-cut.

1. The Born-Haber cycle for MgCl

We will start with the compound MgCl, because that cycle is just like the NaCl one we have already looked at.

$$Mg(s) + \frac{1}{2}Cl_2(g) \rightarrow MgCl(s)$$



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Find two routes around this without going against the flow of any arrows. That's easy:

$$\Delta H_f = +148 + 738 + 122 - 349 - 753$$

$$\Delta H_f = -94 \text{ kJ mol}^{-1}$$

So the compound MgCl is definitely energetically **more stable** than its elements. I have drawn this cycle very roughly to scale, but that is going to become more and more difficult as we look at the other two possible formulae. So I am going to rewrite it as a table. You can see from the diagram that the enthalpy change of formation can be found just by adding up all the other numbers in the cycle, and we can do this just as well in a table.

	kJ
atomization enthalpy of Mg	+148
1st IE of Mg	+738
atomization enthalpy of Cl	+122
electron affinity of Cl	-349
lattice enthalpy	-753
calculated ΔH_f	-94

2. The Born-Haber cycle for $MgCl_2$

The equation for the enthalpy change of formation this time is

$$\mathrm{Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)}$$

So how does that change the numbers in the Born-Haber cycle?

- You need to add in the second ionization energy of magnesium, because you are making a 2+ ion.
- You need to multiply the atomization enthalpy of chlorine by 2, because you need 2 moles of gaseous chlorine atoms.
- You need to multiply the electron affinity of chlorine by 2, because you are making 2 moles of chloride ions.
- You obviously need a different value for lattice enthalpy.

	kJ
atomization enthalpy of Mg	+148
1st IE of Mg	+738
2nd IE of Mg	+1451
atomization enthalpy of Cl (x 2)	+244
electron affinity of Cl (x 2)	-698
lattice enthalpy	-2526
calculated ΔH_f	-643

You can see that much more energy is released when you make $MgCl_2$ than when you make MgCl. Why is that? You need to put in more energy to ionize the magnesium to give a 2+ ion, but a lot more energy is released as lattice enthalpy. That is because there are stronger ionic attractions between 1- ions and 2+ ions than between the 1- and 1+ ions in MgCl. So what about $MgCl_3$? The lattice energy here would be even greater.

3. The Born-Haber cycle for $MgCl_3$

The equation for the enthalpy change of formation this time is

$$Mg(s) + \frac{3}{2}Cl_2(g) \rightarrow MgCl_3(s)$$

So how does that change the numbers in the Born-Haber cycle this time?

- You need to add in the third ionization energy of magnesium, because you are making a 3+ ion.
- You need to multiply the atomization enthalpy of chlorine by 3, because you need 3 moles of gaseous chlorine atoms.
- You need to multiply the electron affinity of chlorine by 3, because you are making 3 moles of chloride ions.
- You again need a different value for lattice enthalpy.

	kJ
atomization enthalpy of Mg	+148
1st IE of Mg	+738
2nd IE of Mg	+1451
3rd IE of Mg	+7733
atomization enthalpy of Cl (x 3)	+366
electron affinity of Cl (x 3)	-1047
lattice enthalpy	-5440
calculated ΔH_f	+3949

This time, the compound is hugely energetically unstable, both with respect to its elements, and also to other compounds that could be formed. You would need to supply nearly 4000 kJ to get 1 mole of $MgCl_3$ to form!

Look carefully at the reason for this. The lattice enthalpy is the **highest** for all these possible compounds, but it is not high enough to make up for the very large third ionization energy of magnesium.

Why is the third ionization energy so big? The first two electrons to be removed from magnesium come from the 3s level. The third one comes from the 2p. That is closer to the nucleus, and lacks a layer of screening as well - and so much more energy is needed to remove it. The 3s electrons are screened from the nucleus by the 1 level and 2 level electrons. The 2p electrons are only screened by the 1 level (plus a bit of help from the 2s electrons).

Conclusion

Magnesium chloride is $MgCl_2$ because this is the combination of magnesium and chlorine which produces the most energetically stable compound - the one with the most negative enthalpy change of formation.

Contributors and Attributions

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5.4: The Born-Lande' equation

The Born-Landé equation is a concept originally formulated in 1918 by the scientists Born and Landé and is used to calculate the lattice energy (measure of the strength of bonds) of a compound. This expression takes into account both the Born interactions as well as the Coulomb attractions.

Introduction

Due to its high simplicity and ease, the Born-Landé equation is commonly used by chemists when solving for lattice energy. This equation proposed by Max Born and Alfred Landé states that lattice energy can be derived from ionic lattice based on electrostatic potential and the potential energy due to repulsion. To solve for the Born-Landé equation, you must have a basic understanding of lattice energy:

- Lattice energy decreases as you go down a group (as atomic radii goes up, lattice energy goes down).
- Going across the periodic table, atomic radii decreases, therefore lattice energy increases.

The Born-Landé equation was derived from these two following equations. the first is the electrostatic potential energy:

$$\Delta U = -\frac{N_A M \left|Z^+\right| \left|Z^-\right| e^2}{4\pi\epsilon_o r} \tag{5.4.1}$$

with

- M_A is Avogadro's constant (6.022×10^{23})
- M is the Madelung Constant (a constant that varies for different structures)
- e is the charge of an electron (1.6022×10^{-19} C)
- Z^+ is the cation charge
- Z^- is the anion charge
- ϵ_o is the permittivity of free space

The second equation is the repulsive interaction:

$$\Delta U = \frac{N_A B}{r^n} \tag{5.4.2}$$

with

- B is the repulsion coefficient and
- n is the Born Exponent (typically ranges between 5-12) that is used to measure how much a solid compresses

These equations combine to form:

$$\Delta U(0K) = \frac{N_A M \left|Z^+\right| \left|Z^-\right| e^2}{4\pi\epsilon_o r_o}\left(1 - \frac{1}{n}\right) \tag{5.4.3}$$

with

- r_0 is the closest ion distance

Calculate Lattice Energy

Lattice energy, based on the equation from above, is dependent on multiple factors. We see that the charge of ions is proportional to the increase in lattice energy. In addition, as ions come into closer contact, lattice energy also increases.

Example 5.4.1

Which compound has the greatest lattice energy?

- AlF_3
- NACl
- LiF
- $CaCl_2$

Solution

This question requires basic knowledge of lattice energy. Since F_3 gives the compound a +3 positive charge and the Al gives the compound a -1 negative charge, the compound has large electrostatic attraction. The bigger the electrostatic attraction, the greater the lattice energy.

Example 5.4.2

What is the lattice energy of NaCl? (Hint: you must look up the values for the constants for this compound)

Solution

-756 kJ/mol (again, this value is found in a table of constants)

Example 5.4.3

Calculate the lattice energy of NaCl.

Solution

$$Lattice\ Energy\ of\ NaCl = -\frac{\frac{6.022\,x\,10^{23}}{mole}(1.6022^{-19})\times 1.747}{4\pi \times 8.85\,x\,10^{-12}\frac{c^2}{m}\times 282\,x\,10^{-12}m}\left(1-\frac{1}{9}\right) \approx -756\ \frac{kJ}{mol}$$

References

1. Johnson, D. A. *Metals and Chemical Change*. Cambridge: Royal Society of Chemistry, 2002.
2. Cotton, F. Albert, and F. Albert Cotton. *Advanced Inorganic Chemistry.* New York: Wiley, 1999.

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CHAPTER OVERVIEW

6: Acid-Base Chemistry

Learning Objectives

- Understand the Brønsted and Lewis definitions of acids and bases.
- Identify conjugate acids and bases, and rules for strong & weak acids/bases, in both Brønsted and Lewis acid-base systems.
- Use Pauling's rules to predict the pK_as of oxoacids.
- Understand the periodic trends of acidic, basic, and amphoteric compounds
- Predict, describe, and rationalize acid/base chemistry in non-aqueous systems, including acidic and basic solvents, aprotic solvents, and molten salts.
- Apply the principles of acid-base chemistry to the design of molecules and Lewis acids with target functions.
- Understand the connection between acid-base chemistry and the stabilization of oxidation states.
- Predict favorable and stable compounds using hard-soft acid-base (HSAB) theory.
- Understand the applications of the ECW model.

Acid-base reactions form the basis of the most common kinds of equilibrium problems which you will encounter in almost any application of chemistry. There are three major classifications of acids and bases: (1) The Arrhenius definition states that an acid produces H^+ in solution and a base produces OH^- and the (2) Brønsted-Lowry and (3) Lewis definitions of acids and bases. Of particular importance in inorganic chemistry is the "hard and soft (Lewis) acids and bases" (HSAB) theory that is widely used for explaining stability of compounds, reaction mechanisms, and reaction pathways.

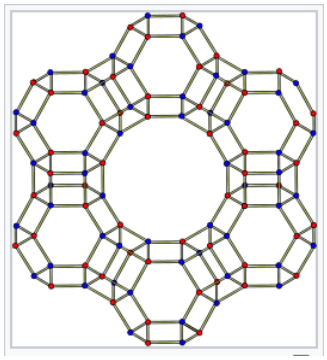
6.1: Prelude to Acid-Base Chemistry
6.2: Brønsted and Lewis Acids and Bases
6.3: Molecular Structure and Acid-Base Behavior
6.4: Oxides
6.5: Lewis Acids and Bases
6.6: Hard and Soft Acids and Bases
6.7: References

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6.1: Prelude to Acid-Base Chemistry

Acids and bases are important for a number reasons in inorganic chemistry.

- Many industrially useful catalytic reactions involve inorganic acids and superacids, such as zeolites, anhydrous hydrogen fluoride, and sulfated zirconia. These acids are sufficiently strong in anhydrous media that they can protonate olefins and alcohols to produce carbocations. Carbocations are key intermediates in the transformations of hydrocarbons.
- Inorganic compounds are sometimes synthesized in strongly acidic or basic media. For example, ternary metal oxides can be synthesized and crystallized in molten NaOH or KOH, which are strongly basic. Organic fluorination reactions are often done in strongly acidic media, such as anhydrous HF. Understanding the familiar chemistry of acids and bases in water helps us understand how these non-aqueous media work.
- The acidic or basic environment of metal ions affects the stability of their oxidation states. We will learn more about this in Chapter 4.
- Transition metal complexes (coordination compounds and organometallic compounds) are essentially Lewis acid-base complexes. We can understand a great deal about their stability and reactivity by considering the acid-base character of metals and ligands. We will learn about this in Chapter 5.



Solid acid catalysts, such as zeolite Y, are used to isomerize hydrocarbons in the processing of crude oil into gasoline. Edith Flanigen(below with President Barack Obama) received the 2014 National Medal of Technology for her research on the synthesis of zeolite Y.



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6.2: Brønsted and Lewis Acids and Bases

Three theories of acids and bases

There are three major classifications of substances known as acids or bases. The Arrhenius definition states that an acid produces H^+ in solution and a base produces OH^-. This theory was developed by Svante Arrhenius in 1883. Later, two more sophisticated and general theories were proposed. These are the Brønsted-Lowry and the Lewis definitions of acids and bases. The relationship between these theories is illustrated in the figure below.

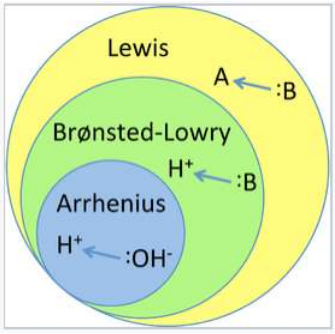


Illustration of the hierarchy of acid-base theories. Arrhenius acids and bases are a sub-class of Brønsted acids and bases, which are themselves a subclass of Lewis acids and bases.

The Arrhenius theory, which is the simplest and least general description of acids and bases, includes acids such as $HClO_4$ and bases such as NaOH or $Mg(OH)_2$. This theory successfully describes how acids and bases react with each other to make water and salts. However, it does not explain why some substances that do not contain hydroxide ions, for example F^- and NO_2^-, can make basic solutions in water. The Brønsted-Lowry definition of acids and bases addresses this problem. In this theory an **acid is a substance that can release a proton** (like in the Arrhenius theory) and a **base is a substance that can accept a proton**. A basic salt such as Na^+F^- generates OH^- ions in water by taking protons from water itself (to make HF):

$$\mathrm{F^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HF_{(aq)} + OH^-} \tag{6.2.1}$$

When a Brønsted acid dissociates, it increases the concentration of hydrogen ions in the solution, $[H^+]$; conversely, Brønsted bases dissociate by taking a proton from the solvent (water) to generate $[OH^-]$.

Acid Dissociation: $\mathrm{HA_{(aq)} \rightleftharpoons A^-_{(aq)} + H^+_{(aq)}}$

$$K_a = \frac{[A^-][H^+]}{[HA]} \tag{6.2.2}$$

Base dissociation: $\mathrm{B^+_{(aq)} H_2O_{(l)} \rightleftharpoons HB^+_{(aq)} + OH^{-+}(aq)}$

$$K_b = \frac{[HB^+][OH^-]}{[B]} \tag{6.2.3}$$

Conjugate acids and bases

One important consequence of these equilibria is that every **acid** (HA) has a **conjugate base** (A-), and vice-versa. In the base dissociation equilibrium above the conjugate acid of base B is HB^+.

For a given acid or base, these equilibria are linked by the water dissociation equilibrium:

$$\mathrm{H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}} \tag{6.2.4}$$

$$K_w = [H^+][OH^-] \tag{6.2.5}$$

for which the equilibrium constant K_w is 1.00 x 10^{-14} at 25°C. It can be easily shown that the product of the acid and base dissociation constants K_a and K_b is K_w.

Strong and weak acids and bases

Acids and bases that dissociate completely are said to be strong:

$$\mathrm{HClO_{4(aq)} \longrightarrow H^+_{(aq)} + ClO^-_{4(aq)}} \tag{6.2.6}$$

$$\mathrm{HBr_{(aq)} \longrightarrow H^+_{(aq)} + Br^-_{(aq)}} \tag{6.2.7}$$

$$\mathrm{CH_3O^-_{(aq)} + H_2O_{(l)} \longrightarrow CH_3OH_{(aq)} + OH^-_{(aq)}} \tag{6.2.8}$$

$$\mathrm{NH^-_{2(aq)} + H_2O_{(l)} \longrightarrow NH_{3(aq)} + OH^-_{(aq)}} \tag{6.2.9}$$

Here the right-handed arrow (→) implies that the reaction goes to completion. That is, a 1.0 M solution of $HClO_4$ in water actually contains 1.0 M H^+(aq) and 1.0 M ClO_4^-(aq), and very little undissociated $HClO_4$.

Conversely, weak acids such as acetic acid (CH_3COOH) and weak bases such as ammonia (NH_3) dissociate only slightly in water - typically a few percent, depending on their concentration and the values of K_a and K_b - and exist mostly as the undissociated molecules.



Antacid tablets typically contain calcium salts of the bicarbonate ion (HCO_3^-), a weak base. Its conjugate acid, carbonic acid (H_2CO_3) is a weak acid. The acid-base equilibrium between carbonic acid and bicarbonate is important in maintaining blood pH.

Example

Household ammonia is a solution of NH_3 in water that ranges from about 5-10% by weight. Let's calculate the percent ionization and the pH of the solution.

Solution

For a solution that is 8% ammonia by weight, assuming that the density is about the same as that of liquid water, the analytical concentration of ammonia is (80 g/L) / (17 g/mol) = 4.7 M.

The other thing we need to know to solve this problem is the base dissociation constant, K_b.

$$\mathrm{NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-} \quad K_b = 1.8 \times 10^{-5}$$

We can solve this problem rigorously by invoking both charge balance ($[H^+] + [NH_4^+] = [OH^-]$) and mass balance ($4.7\ M = [NH_3] + [NH_4^+]$) and using $K_W = [H^+][OH^-]$. But because the algebra becomes complicated with that method - leading to a cubic equation that is hard to solve - we'll invoke two simplifying assumptions:

$[NH_4^+] \approx [OH^-] \gg [H^+]$ (which is a reasonable assumption for a basic solution)

and

$[NH_3] \gg [NH_4^+]$ (also reasonable if the percent ionization is small)

Now we can write:

$$[NH_4^+][OH^-] \approx [OH^-]^2 = (4.7M)(K_b) = 8.4 \times 10^{-5}$$

$$[OH^-] = 9.2 \times 10^{-3} M\ (\approx [NH_4^+]),\ [H^+] = \frac{K_w}{[OH^-]} = 1.1 \times 10^{-12} M,\ \mathbf{pH = 11.97}$$

The percent ionization is:

$$100\% \times 9.2 \times 10^{-3} M / 4.7 M = \mathbf{0.19\%}$$

This example illustrates that it is technically incorrect to label a bottle of aqueous ammonia as “ammonium hydroxide,” since only about 2/10 of one percent of the weak base exists in that form.

Conjugate acids and bases

A common misconception is that strong acids have weak conjugate bases, and that weak acids have strong conjugate bases. It is easy to see that this is incorrect by remembering that $K_aK_b = K_w$. Our definition of a strong acid or base is that K >> 1, i.e., that the substance dissociates completely. Our definition of a weak acid or base is 1 > K > K_w. It follows that if K_a >> 1 (strong) then K_b cannot be > K_w (weak).

In fact, **strong acids** such as HCl dissociate to produce **spectator ions** such as Cl^- as conjugate bases, whereas **weak acids** produce **weak conjugate bases**. This is illustrated below for acetic acid and its conjugate base, the acetate anion. Acetic acid is a weak acid ($K_a = 1.8 \times 10^{-5}$) and acetate is a weak base ($K_b = \frac{K_w}{K_a} = 5.6 \times 10^{10}$)



The strength of a conjugate acid/base varies inversely with the strength or weakness of its parent acid or base. Any acid or base is technically a conjugate acid or conjugate base also; these terms are simply used to identify species in solution (i.e acetic acid is the conjugate acid of the acetate anion, a base, while acetate is the conjugate base of acetic acid, an acid).

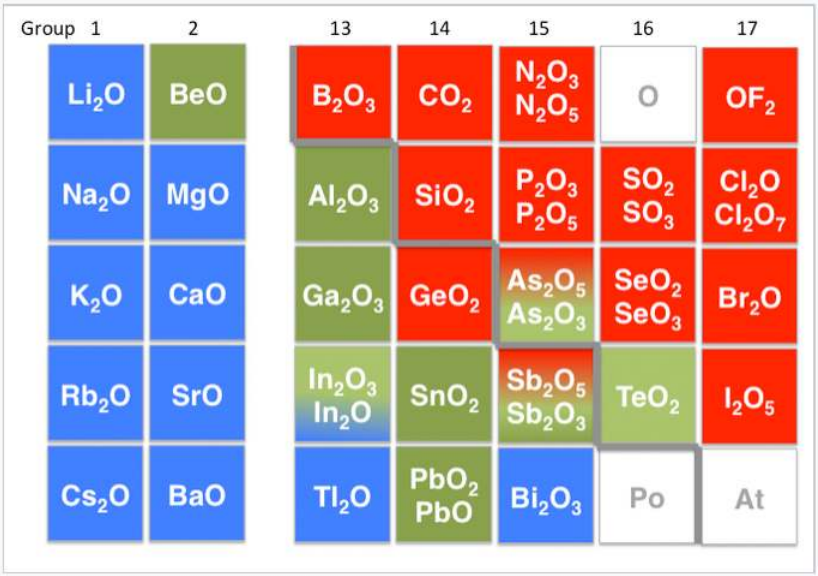
Neutral oxyacids (H_2SO_4, H_3PO_4, HNO_3, $HClO_2$, etc.) can be classified as strong or weak following a simple rule first noted by Linus Pauling. If the number of oxygen atoms exceeds the number of hydrogen atoms by two or more, then the acid is strong; otherwise it is weak. For example $HClO_4$ and $HClO_3$, where the difference is 3 and 2, respectively, are both strong acids. HNO_2 and $HClO_2$ are both weak because the difference is 1 in both cases. For weak acids, the relative strength depends on this difference (i.e., $HClO_2$ is a stronger weak acid than HOCl) and on the electronegativity of the central atom (HOCl is stronger than HOI).

Acids that can donate more than one proton are called **polyprotic acids**. For example, sulfuric acid, H_2SO_4, is a strong acid that has a conjugate base that actually happens to be a weak acid itself. This means that every mole of H_2SO_4 in aqueous solution donates more than 1 mole of protons. Carbonic acid (H_2CO_3) and phosphoric acid (H_3PO_4) are weak polyprotic acids. Typically, the sequential pK_a's of polyprotic acid are separated by about 5 pH units, because it becomes progressively more difficult to remove protons as the ion becomes more negatively charged. For example, the three pK_a's of phosphoric acid are 2.15, 7.20, and 12.35.

Amphoteric compounds

Some substances can act either as an acid and as a base. An example is water. H_2O molecules may either donate a hydrogen ion or accept one. This property makes water an **amphoteric** solvent. In the situation where an acid dissociates in solution, water is acting as a base. Conversely, water acts as an acid when bases dissociate. The strongest acid we can make in H_2O is H^+ (aq), and the strongest base we can make in H_2O is OH^- (aq).

Other examples of amphoteric compounds are oxides and hydroxides of elements that lie on the border between the metallic and non-metallic elements in the periodic table. For example, aluminum hydroxide ($Al(OH)_3$) is insoluble at neutral pH, but can accept protons in acid to make $[Al(H_2O)_6]^{3+}$ or accept an OH^- ion in base to form $Al(OH)_4^-$ ions. Consequently, aluminum oxide is soluble in acid and in base, but not neutral water. Other examples of amphoteric oxides are BeO, ZnO, Ga_2O_3, Sb_2O_3, and PbO. Increasing the oxidation state of a metal increases the acidity of its oxide by withdrawing electron density from the oxygen atoms. Thus, Sb_2O_5 is acidic, but Sb_2O_3 is amphoteric.



Periodic table showing basic (blue), amphoteric (green) and acidic (red) oxides. The metal-nonmetal boundary is indicated by the gray staircase line.

Solvent leveling

Solvent leveling is an effect that occurs when a strong acid is placed in a solvent such as (but not limited to) H_2O. Because strong acids donate their protons to the solvent, the strongest possible acid that can exist is the conjugate acid of the solvent. In aqueous solution, this is H_3O^+. This means that the strength of acids such as HCl and HBr cannot be differentiated in water as they both are dissociated 100% to H_3O^+. In the context of our discussion of conjugate bases above, we would say that both Cl^- and Br^- are spectator ions in water: neither one is a strong enough base to accept a proton from H_3O^+. In order to differentiate the acidities of strong acids such as $HClO_4$ and HCl, or the basicities of strong bases such as CH_3O^- and NH_2^-, we must typically work in non-aqueous solvents, as explained below.

Nonaqueous solutions

The Brønsted theory encompasses any type of solvent that can donate and accept H^+ ions, not just aqueous solutions. The strength of an acid or a base varies depending on the solvent. Non-aqueous acid-base chemistry follows similar rules to those developed for acids and bases in water. For example in liquid ammonia, the solvent autodissociates in the reaction:

$$2\,\mathrm{NH}_{3(l)} \rightleftharpoons \mathrm{NH}_4^+ + \mathrm{NH}_2^- \tag{6.2.10}$$

This equilibrium is analogous to the autodissociation of water, but has a smaller equilibrium constant ($K \approx 10^{-30}$). It follows by analogy to water that NH_4^+ is the strongest acid and NH_2^- is the strongest base that can exist in liquid ammonia. Because ammonia is a basic solvent, it enhances the acidity and suppresses the basicity of substances dissolved in it. For example, the ammonium ion (NH_4^+) is a weak acid in water ($K_a = 6 \times 10^{-10}$), but it is a strong acid in ammonia. Similarly, acetic acid is weak in water but strong in ammonia. Solvent leveling in fact makes HCl, CH_3COOH, and NH_4Cl all strong acids in ammonia, where they have equivalent acid strength.

Strong acids that are leveled in water have different acid strengths in acidic solvents such as HF or anhydrous acetic acid. For example, acid dissociation of HX in acetic acid (CH_3COOH) involves protonating the solvent to make its conjugate acid ($CH_3COOH_2^+$) and the X^- anion. Because $CH_3COOH_2^+$ is a stronger acid that H_3O^+, the anion X^- (which is a spectator in water) can become a weak base in CH_3COOH:

$$\mathrm{HX} + \mathrm{CH_3COOH} \rightleftharpoons \mathrm{CH_3COOH_2^+} + \mathrm{X^-} \tag{6.2.11}$$

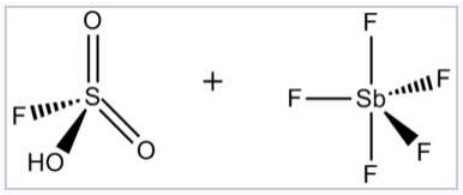
It follows that acidic solvents magnify the Brønsted basicities of substances that cannot accept protons in water. Conversely, basic solvents magnify the acidity of substances that cannot donate a proton to OH^-.

The acidity and basicity of non-aqueous solvents is difficult to quantify precisely, but one good relative measure is the Hammett acidity function, H_o. H_o is defined analogously to pH according to the Henderson-Hasselbach equation:

$$H_o = pK_a + \log(\frac{[base]}{[conjugate\ acid]}) \tag{6.2.12}$$

For non-aqueous solvents, or for acidic or basic compounds in dissolved in solvents that do not themselves dissociate, H_o is a rough measure of the pH of the solvent or compound in question. Anhydrous HF and H_2SO_4 have H_o values of approximately -10 and -12 respectively.

Superacids and superbases. The term *superacid* was originally coined by James Bryant Conant in 1927 to describe acids that were stronger than conventional mineral acids.[1] George A. Olah prepared the so-called magic acid, so-named for its ability to attack hydrocarbons, by mixing antimony pentafluoride (SbF_5) and fluorosulfonic acid (FSO_3H). The name was coined after a candle was placed in a sample of magic acid. The candle dissolved, showing the ability of the acid to protonate hydrocarbons, which under aqueous acidic conditions cannot be protonated.



Magic acid is made by mixing FSO_3H and SbF_5. Their reaction generates the $H_2SO_3F^+$ cation, which can protonate hydrocarbons.

At 140 °C , FSO_3H–SbF_5 converts methane into the tertiary-butyl carbocation, a reaction that begins with the protonation of methane:[2]

$$\mathrm{CH_4 + H^+ \longrightarrow CH_5^+} \tag{6.2.13}$$

$$\mathrm{CH_5^+ \longrightarrow CH_3^+ + H_2} \tag{6.2.14}$$

$$\mathrm{CH_3^+ + 3\,CH_4 \longrightarrow (CH_3)_3C^+ + 3\,H_2} \tag{6.2.15}$$

Fluoroantimonic acid, $HSbF_6$, can produce solutions with H_0 down to –28.[3] Fluoroantimonic acid is made by combining HF and SbF_5. In this system, HF releases its proton (H^+) concomitant with the binding of F^- by antimony pentafluoride, which (as described below) is a Lewis acid. The resulting anion (SbF_6-) is both a weak nucleophile and an extraordinarily weak base.

Superacids are useful in reactions such as the isomerization of alkanes. Industrially, anhydrous acid-exchanged zeolites, which are superacid catalysts, are used on a massive scale to isomerize hydrocarbons in the processing of crude oil to gasoline. Superbases such as lithium diethylamide ($LiNEt_2$), alkyllithium compounds (RLi), and Grignard reagents (RMgX) useful in a broad range of organic reactions. $LiNEt_2$ deprotonates C-H bonds to generate reactive carbanions. RLi and RMgX are powerful nucleophiles.

The use of superbases in nonaqueous media allows us to rank the acidities (and measure the pKa's) of different classes of molecules. This ranking is particularly important in understanding the reactions of organic molecules. Note that the order of acidities for hydrocarbons is alkynes >> alkenes, aromatics >> alkanes. This ordering has to do with the hybridization of the carbon atom that forms the carbanion. The negatively charged lone pair of the carbanion is stabilized in orbitals that have high s character (e.g., sp vs. sp^2 or sp^3). This is because s orbitals have finite probability density at the nucleus and "feel" the positive nuclear charge (thereby stabilizing the extra negative charge on carbon) more than p orbitals. Resonance effects also stabilize carbanions. Thus, cyclopentadiene is more acidic than even an alkyne because the negative charge is delocalized over the entire (aromatic) $C_5H_5^-$ ring when the C_5H_6 is deprotonated.

name	formula	structural formula	pKa
Methane	CH_4	Methane-2D-dimensions.svg	56
Propene	C_3H_6	Propylene skeletal.svg	44
Benzene	C_6H_6	Benzol.svg	43

Acetylene	C_2H_2	Acetylene-CRC-IR-dimensions-2D.png	25
Cyclopentadiene	C_5H_6	Cyclopentadiene.png	18

Table 1. Carbon acid acidities in pKa in DMSO [4].

Acid-base equilibria in molten salts

When a solid salt melts, it forms a solution of the cations and anions. For example, KOH melts at temperatures above 400 °C and dissociates into K^+ and OH^- ions which can act as a solvent for chemical reactions. Because of the autodissociation of the OH^- solvent, water is always present in a molten KOH flux, according to the acid-base equilibrium:

$$2\,OH^- \rightleftharpoons H_2O + O^{2-} \tag{6.2.16}$$

It follows that in this very basic solvent, water (the conjugate acid of the solvent) is the strongest acid that can exist. The conjugate base of the solvent, O^{2-}, is the strongest base. This autodissociation equilibrium allows for the acidity of a flux to be easily tuned through the addition or boiling off of water. A "wet" flux is more acidic, and can dissolve metal oxides that contain the basic O^{2-} anion. Conversely a "dry" flux is more basic and will cause oxides to precipitate. Molten hydroxide fluxes can thus be used in the synthesis of oxide crystals, such as the perovskite superconductor ($K_{1-X}Ba_XBiO_3$).[5]. Eutectic mixtures of NaOH and KOH are relatively low melting (≈ 200 °C) and can be used as solvents for crystallizing a variety of basic oxides.

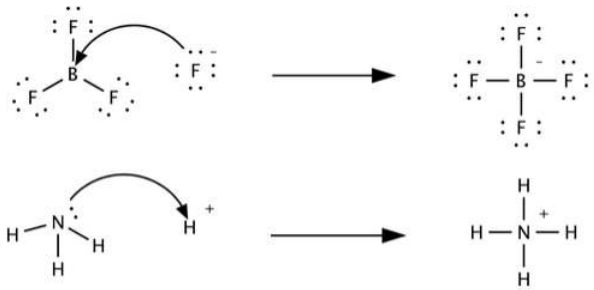
Lewis Acids and Bases

The Lewis classification of acids and bases is broader than the Brønsted-Lowry definition, and encompasses many more substances. Whereas the Brønsted-Lowry and the Arrhenius classifications are based on transfer of protons, Lewis acidity and basicity are based on the sharing of an electron pair. **Lewis acids** can accept an electron pair, while **Lewis bases** can donate an electron pair. This definition encompasses the Brønsted-Lowry definition, in that H^+ is an electron pair acceptor (when interacting with a base), and a base is an electron pair donor in its interaction with H^+. This is illustrated below for the protonation of ammonia.

Boron trifluoride, BF_3 acts as a Lewis acid when it combines with a basic ion or molecule that can donate an electron pair. Such a reaction is shown below.

\[\ce{BF3 + F^{-} <=> BF4^{-}}

Here, the acid is BF_3 and the base is F^-. This acid-base reaction allows boron (which is electron-deficient in BF_3) to complete its octet. Similarly, $AlCl_3$ is a Lewis acid that can react with Cl^- (a Lewis base) to make the Lewis "salt" $AlCl_4^-$. Note that in water Cl^- is a spectator ion (a weaker base than the solvent) in Brønsted acid-base reactions.



Additional examples of Lewis acid base reactions. In each, try to identify the acid, the base, and the salt, based on the concept that the base is the molecule or ion that donates an electron pair. In cases where you are not sure, it may help to draw the VSEPR structures of the molecules:

$I_2 + I^- \rightleftharpoons I_3^-$

$AuCl_3 + Cl^- \rightleftharpoons [AuCl_4]^-$

$Fe^{3+} + 6\,H_2O \rightleftharpoons [Fe(H_2O)_6]^{3+}$

$TiF_4 + 2\,F^- \rightleftharpoons [TiF_6]^{2-}$

$$SF_4 + SbF_5 \rightleftharpoons SSbF_9$$

In other Lewis acid base reactions both acid and base are molecules and the product is referred to as an adduct.

$$(CH_3)_3B + N(CH_3)_3 \longrightarrow (CH_3)_3B{-}N(CH_3)_3$$

$$I_2 + S(CH_3)_2 \longrightarrow I_2{-}S(CH_3)_2$$

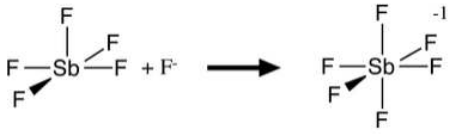
$$C_5N_5N + Cu(HFacac)_2 \longrightarrow C_5N_5N{-}Cu(HFacac)_2$$

Lewis acidity is the basis for coordination chemistry, a topic we will discuss in more detail in Chapter 5. This is because coordination chemistry involves **metal ions** that are Lewis acids, which bond to ligands that are Lewis bases.

Determining the strength of metal ion Lewis acids

There are three determining factors in the Lewis acid strength of a metal ion:
1. The higher positive charge on the metal, the more acidic it is. For example, Al^{3+} and Fe^{3+} are good Lewis acids and their salts make acidic solutions in water, but $K^+$and Na^+ are not.
2. The smaller the atomic radius of the metal ion, the more acidic it is. Going down the periodic table, the Lewis acidity of metal ions decreases (e.g., $Al^{3+} > Ga^{3+} > In^{3+}$) because the ionic radius increases.
3. For transition metal ions, more electronegative metals tend to make stronger Lewis acids. The electronegativity has maxima at W and Au in the 5d series, so metal ions near in that part of the periodic table are good Lewis acids.

Molecules with five coordinate geometries (e.g., PCl_5, AsF_5, SbF_5) are typically strong Lewis acids, because when accepting another pair of electrons from a base, they form an octahedral molecule or anion. Neither of the common five-coordinate geometries (trigonal bipyramidal or square pyramidal) is efficient in terms of packing. The Lewis acid-base reaction forms an additional bond with a relatively small energetic penalty of stretching the existing bonds:



Because F^- is a good Lewis base, and also a small anion, it can form stable octahedral anions with both main group elements and transition metals. For this reason, TiO_2 and SiO_2 dissolve in HF (but are unreactive with aqueous HCl and other strong acids):

$$TiO_2 + 4\,HF + 2\,F^- \rightleftharpoons TiF_6^{2-} + 2\,H_2O \tag{6.2.17}$$

$$SiO_2 + 4\,HF + 2\,F^- \rightleftharpoons SiF_6^{2-} + 2\,H_2O \tag{6.2.18}$$

Lewis bases stabilize high oxidation states.

An interesting example of using Lewis acid-base chemstry to drive reactions is the chemical synthesis of fluorine gas, which was devised by Karl O. Christe in 1986.[6] Christe at the time was organizing a symposium to commemorate the 100th anniversary of the isolation of elemental fluorine by Henri Moissan, which Moissan did in 1886 by electrolyzing a solution of anhydrous HF. 100 years later, there was still no direct (non-electrochemical) synthesis of F_2. Christe's reaction scheme followed two steps. The first was the known synthesis of K_2MnF_6 from $KMnO_4$:

$$4\,MnO^-_{4(aq)} + 10\,H_2O_{(l)} + 24\,F^-_{(aq)} \longrightarrow 4\,MnF^{2-}_{6(aq)} = 3\,O_{2(g)} + 20\,OH^-_{(aq)} \tag{6.2.19}$$

$$2\,K^+_{(aq)} + MnF^{2-}_{6(aq)} \longrightarrow K_2MnF_{6(s)} \tag{6.2.20}$$

The second step involved reacting K_2MnF_6 with the powerful Lewis acid SbF_5, to make metastable MnF_4, which decomposes spontaneously to MnF_3 and fluorine gas:

$$K_2MnF_{6(s)} + 2\,SbF_{5(l)} \longrightarrow 2\,KSbF_{6(s)} + MnF_{4(s)} \tag{6.2.21}$$

$$MnF_{4(s)} \longrightarrow MnF_{3(s)} + \frac{1}{2}F_{2(g)} \tag{6.2.22}$$

This reaction teaches us something interesting and important about the connection between acid-base and redox chemistry. Acids tend to stabilize low oxidation states, and bases stabilize high oxidation states (We will see this again soon in Chapter 4, in the

context of Pourbaix diagrams). Mn is stable in the +4 oxidation state in K_2MnF_6, where it is surrounded by six basic F^- anions. However, the highest stable neutral fluoride of Mn is MnF_3, and MnF_4 (transiently formed from K_2MnF_6) spontaneously decomposes to generate fluorine.

Oxide is a better base than fluoride. Interestingly, Mn can lose all its valence electrons to form Mn^{7+} in the permanganate ion, MnO_4^-. Here the 7+ oxidation state is stabilized electrostatically by coordination to four O^{2-} ions, and by the overall -1 charge on the MnO_4^- anion. Because of its 2- charge, O^{2-} is a stronger base and a better ion for stabilizing high oxidation states than F^-. This is a general trend among transition metals: the highest oxidation state is usually reached in the oxide, not in the fluoride, despite the fact that F is a more electronegative element than O. For example, Cr^{6+} is stable in the CrO_4^{2-} and $Cr_2O_7^{2-}$ anions, but not in any neutral fluoride or fluoroanion. The +8 oxidation state occurs in RuO_4 and OsO_4, but not in any fluoride of Ru or Os.

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6.3: 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 A– H or B– H^+ bond, the less likely the bond is to break to form H^+ ions and thus the less acidic the substance. This effect can be illustrated using the hydrogen halides:

Relative Acid Strength	HF	HCl	HBr	HI
H–X Bond Energy (kJ/mol)	570	432	366	298
pKa	3.20	−6.1	−8.9	−9.3

The trend in bond energies is due to a steady decrease in overlap between the 1s orbital of hydrogen and the valence orbital of the halogen atom as the size of the halogen increases. The larger the atom to which H is bonded, the weaker the bond. Thus the bond between H and a large atom in a given family, such as I or Te, is weaker than the bond between H and a smaller atom in the same family, such as F or O. As a result, acid strengths of binary hydrides increase as we go down a column of the periodic table. For example, the order of acidity for the binary hydrides of Group 16 elements is as follows, with pK_a values in parentheses:

$$H_2O(14.00 = pK_w) < H_2S(7.05) < H_2Se(3.89) < H_2Te(2.6) \tag{6.3.1}$$

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:

$$CH_4(\ 50) \ll NH_3(\ 36) < H_2O(14.00) < HF(3.20) \tag{6.3.2}$$

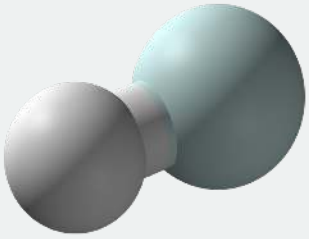
Consider, for example, the compounds at both ends of this series: methane and hydrogen fluoride. The conjugate base of CH_4 is CH_3^-, and the conjugate base of HF is F^-. Because fluorine is much more electronegative than carbon, fluorine can better stabilize the negative charge in the F^- ion than carbon can stabilize the negative charge in the CH3− ion. Consequently, HF has a greater tendency to dissociate to form H^+ and F^- than does methane to form H^+ and CH_3^-, making HF a much stronger acid than CH_4.

The same trend is predicted by analyzing the properties of the conjugate acids. For a series of compounds of the general formula HE, as the electronegativity of E increases, the E–H bond becomes more polar, favoring dissociation to form E^- and H^+. Due to both the increasing stability of the conjugate base and the increasing polarization of the E–H bond in the conjugate acid, acid strengths of binary hydrides increase as we go from left to right across a row of the periodic table.

Acid strengths of binary hydrides increase as we go down a column or from left to right across a row of the periodic table.

the strongest acid Known: The hydrohelium Cation

The storngest acid, the weaker the covalent bond to a hydrogen atom. So the strongest acid possible is the molecule with the weakest bond. That is the hydrohelium (1+) cation, HeH^+, which is a positively charged ion formed by the reaction of a proton with a helium atom in the gas phase. It was first produced in the laboratory in 1925 and is isoelectronic with molecular hydrogen (\ce{H2}). It is the strongest known acid, with a proton affinity of 177.8 kJ/mol.



Ball and stick model of the hydrohelium ion. (CC BY-SA 3.0; CCoil).

HeH^+ cannot be prepared in a condensed phase, as it would protonate any anion, molecule or atom with which it were associated. However it is possible to estimate a *hypothetical* aqueous acidity using Hess's law:

$HHe^+(g)$	→	$H^+(g)$	+ He(g)	+178 kJ/mol
$HHe^+(aq)$	→	$HHe^+(g)$		+973 kJ/mol
$H^+(g)$	→	$H^+(aq)$		−1530 kJ/mol
He(g)	→	He(aq)		+19 kJ/mol
$HHe^+(aq)$	→	$H^+(aq)$	+ He(aq)	−360 kJ/mol

A free energy change of dissociation of −360 kJ/mol is equivalent to a pK_a of −63.

It has been suggested that HeH^+ should occur naturally in the interstellar medium, but it has not yet been detected.

Inductive Effects

Atoms or groups of atoms in a molecule other than those to which H is bonded can induce a change in the distribution of electrons within the molecule. This is called an inductive effect, and, much like the coordination of water to a metal ion, it can have a major effect on the acidity or basicity of the molecule. For example, the hypohalous acids (general formula HOX, with X representing a halogen) all have a hydrogen atom bonded to an oxygen atom. In aqueous solution, they all produce the following equilibrium:

$$HOX_{(aq)} \rightleftharpoons H^+_{(aq)} + OX^-(aq) \tag{6.3.3}$$

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 6.3.1, 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 6.3.1 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 6.3.1 and Figure 6.3.2, 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.

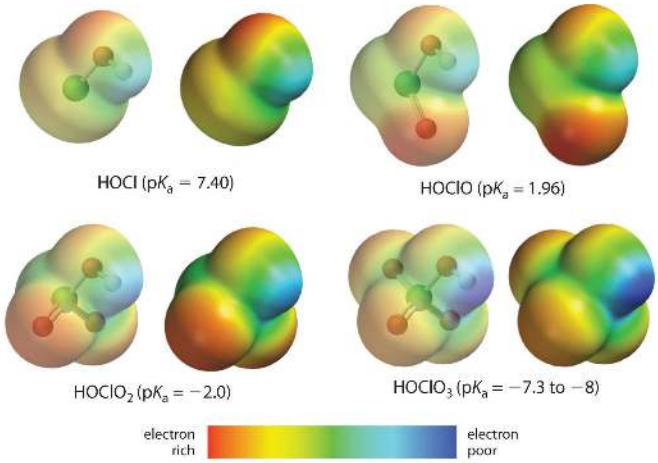
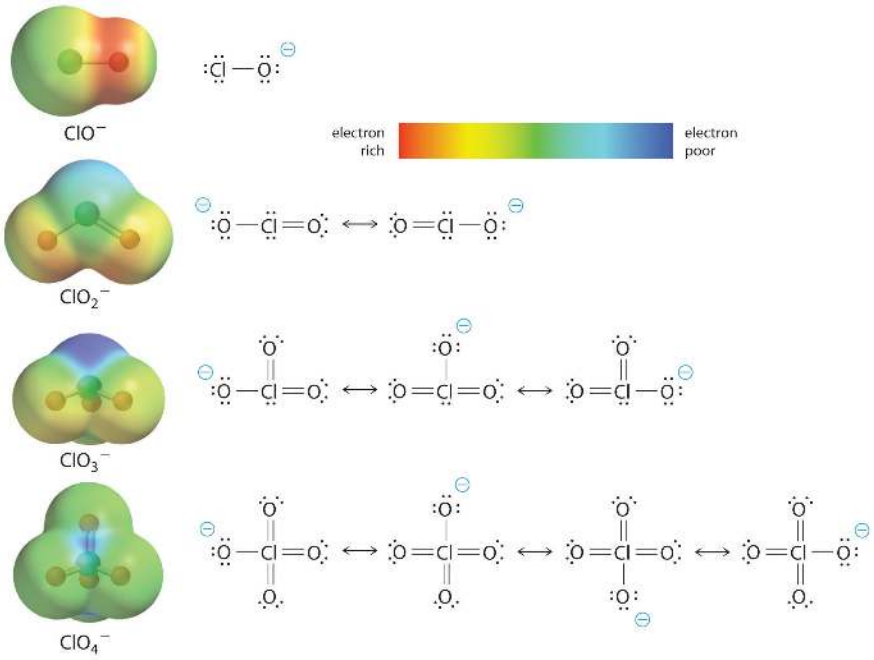


Figure 6.3.1: The Relationship between the Acid Strengths of the Oxoacids of Chlorine and the Electron Density on the O–H Unit. These electrostatic potential maps show how the electron density on the O–H unit decreases as the number of terminal oxygen atoms increases. Blue corresponds to low electron 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 6.3.2, 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.

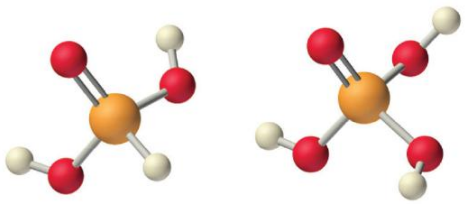
> *Electron delocalization in the conjugate base increases acid strength.*

The electrostatic potential plots in Figure 6.3.2 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 6.3.2). 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 6.3.1 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 6.3.1: Values of pKa for Selected Polyprotic Acids and Bases

Polyprotic Acids	Formula	pK_{a1}	pK_{a2}	pK_{a3}
carbonic acid*	"H_2CO_3"	6.35	10.33	
citric acid	$HO_2CCH-2C(OH)(CO_2H)CH_2CO_2H$	3.13	4.76	6.40
malonic acid	$HO-2CCH_2CO_2H$	2.85	5.70	
oxalic acid	HO_2CCO_2H	1.25	3.81	
phosphoric acid	H_3PO_4	2.16	7.21	12.32
phosphorous acid	H_3PO_3	1.3	6.70	
succinic acid	$HO_2CCH_2CH_2CO_2H$	4.21	5.64	
sulfuric acid	H_2SO_4	−2.0	1.99	
sulfurous acid*	"H_2SO_3"	1.85	7.21	
Polyprotic Bases	**Formula**	pK_{b1}	pK_{b2}	
ethylenediamine	$H_2N(CH_2)_2NH_2$	4.08	7.14	
piperazine	$HN(CH_2CH_2)_2NH$	4.27	8.67	
propylenediamine	$H_2N(CH_2)_3NH_2$	3.45	5.12	

*H_2CO_3 and H_2SO_3 are at best minor components of aqueous solutions of $CO_{2(g)}$ and $SO_{2(g)}$, respectively, but such solutions are commonly referred to as containing carbonic acid and sulfurous acid, respectively.

Inductive effects are also observed in organic molecules that contain electronegative substituents. The magnitude of the electron-withdrawing effect depends on both the nature and the number of halogen substituents, as shown by the pKa values for several acetic acid derivatives:

$$pK_aCH_3CO_2H4.76 < CH_2ClCO_2H2.87 < CHCl_2CO_2H1.35 < CCl_3CO_2H0.66 < CF_3CO_2H0.52$$

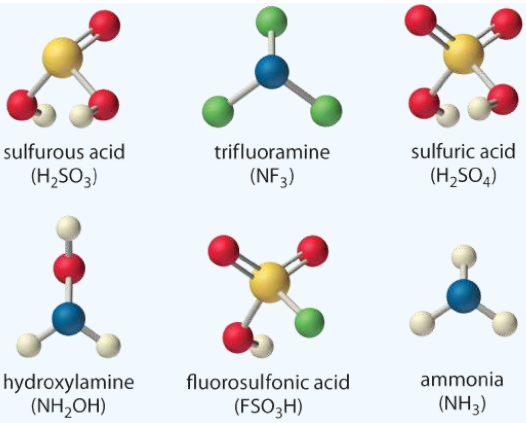
As you might expect, fluorine, which is more electronegative than chlorine, causes a larger effect than chlorine, and the effect of three halogens is greater than the effect of two or one. Notice from these data that inductive effects can be quite large. For instance, replacing the $-CH_3$ group of acetic acid by a $-CF_3$ group results in about a 10,000-fold increase in acidity!

Example 6.3.1

Arrange the compounds of each series in order of increasing acid or base strength.

a. sulfuric acid [H_2SO_4, or $(HO)_2SO_2$], fluorosulfonic acid (FSO_3H, or FSO_2OH), and sulfurous acid [H_2SO_3, or $(HO)_2SO$]
b. ammonia (NH_3), trifluoramine (NF_3), and hydroxylamine (NH_2OH)

The structures are shown here.



Given: series of compounds

Asked for: relative acid or base strengths

Strategy:

Use relative bond strengths, the stability of the conjugate base, and inductive effects to arrange the compounds in order of increasing tendency to ionize in aqueous solution.

Solution:

Although both sulfuric acid and sulfurous acid have two –OH groups, the sulfur atom in sulfuric acid is bonded to two terminal oxygen atoms versus one in sulfurous acid. Because oxygen is highly electronegative, sulfuric acid is the stronger acid because the negative charge on the anion is stabilized by the additional oxygen atom. In comparing sulfuric acid and fluorosulfonic acid, we note that fluorine is more electronegative than oxygen. Thus replacing an –OH by –F will remove more electron density from the central S atom, which will, in turn, remove electron density from the S–OH bond and the O–H bond. Because its O–H bond is weaker, FSO_3H is a stronger acid than sulfuric acid. The predicted order of acid strengths given here is confirmed by the measured pKa values for these acids:

$$pKaH_2SO_31.85 < H_2SO_4^{-2} < FSO_3H - 10$$

The structures of both trifluoramine and hydroxylamine are similar to that of ammonia. In trifluoramine, all of the hydrogen atoms in NH3 are replaced by fluorine atoms, whereas in hydroxylamine, one hydrogen atom is replaced by OH. Replacing the three hydrogen atoms by fluorine will withdraw electron density from N, making the lone electron pair on N less available to bond to an H^+ ion. Thus NF_3 is predicted to be a much weaker base than NH_3. Similarly, because oxygen is more electronegative than hydrogen, replacing one hydrogen atom in NH_3 by OH will make the amine less basic. Because oxygen is less electronegative than fluorine and only one hydrogen atom is replaced, however, the effect will be smaller. The predicted order of increasing base strength shown here is confirmed by the measured pK_b values:

$$pK_bNF_3 — << NH_2OH8.06 < NH_34.75$$

Trifluoramine is such a weak base that it does not react with aqueous solutions of strong acids. Hence its base ionization constant has never been measured.

? Exercise 6.3.1

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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6.4: Oxides

Oxides are chemical compounds with one or more oxygen atoms combined with another element (e.g. Li_2O). Oxides are binary compounds of oxygen with another element, e.g., CO_2, SO_2, CaO, CO, ZnO, BaO_2, H_2O, etc. These are termed as oxides because here, oxygen is in combination with only one element. Based on their acid-base characteristics oxides are classified as acidic, basic, amphoteric or neutral:

1. An oxide that combines with water to give an acid is termed as an acidic oxide.
2. The oxide that gives a base in water is known as a basic oxide.
3. An amphoteric solution is a substance that can chemically react as either acid or base.
4. However, it is also possible for an oxide to be neither acidic nor basic, but is a neutral oxide.

There are different properties which help distinguish between the three types of oxides. The term **anhydride** ("without water") refers to compounds that assimilate H_2O to form either an acid or a base upon the addition of water.

Acidic Oxides

Acidic oxides are the oxides of non-metals (Groups 14-17) and these **acid anhydrides** form acids with water:

- Sulfurous Acid

$$\mathrm{SO_2 + H_2O \rightarrow H_2SO_3} \tag{6.4.1}$$

- Sulfuric Acid

$$\mathrm{SO_3 + H_2O \rightarrow H_2SO_4} \tag{6.4.2}$$

- Carbonic Acid

$$\mathrm{CO_2 + H_2O \rightarrow H_2CO_3} \tag{6.4.3}$$

Acidic oxides are known as acid anhydrides (e.g., sulfur dioxide is sulfurous anhydride and sulfur trioxide is sulfuric anhydride) and when combined with bases, they produce salts, e.g.,

$$\mathrm{SO_2 + 2\,NaOH \rightarrow Na_2SO_3 + H_2O} \tag{6.4.4}$$

Basic Oxides

Generally Group 1 and Group 2 elements form bases called base anhydrides or basic oxides e.g.,

$$\mathrm{K_2O\ (s) + H_2O\ (l) \rightarrow 2\,KOH\ (aq)} \tag{6.4.5}$$

Basic oxides are the oxides of metals. If soluble in water, they react with water to produce hydroxides (alkalies) e.g.,

$$\mathrm{CaO + H_2O \rightarrow Ca(OH)_2} \tag{6.4.6}$$

$$\mathrm{MgO + H_2O \rightarrow Mg(OH)_2} \tag{6.4.7}$$

$$\mathrm{Na_2O + H_2O \rightarrow 2\,NaOH} \tag{6.4.8}$$

These metallic oxides are known as basic anhydrides. They react with acids to produce salts, e.g.,

$$\mathrm{MgO + 2\,HCl \rightarrow MgCl_2 + H_2O} \tag{6.4.9}$$

$$\mathrm{Na_2O + H_2SO_4 \rightarrow Na_2SO_4 + H_2O} \tag{6.4.10}$$

Amphoteric Oxides

An amphoteric solution is a substance that can chemically react as either acid or base. For example, when HSO_4^- reacts with water it will make both hydroxide and hydronium ions:

$$HSO_4^- + H_2O \rightarrow SO_4^{2^-} + H_3O^+ \tag{6.4.11}$$

$$HSO_4^- + H_2O \rightarrow H_2SO_4 + OH^- \tag{6.4.12}$$

Amphoteric oxides exhibit both basic as well as acidic properties. When they react with an acid, they produce salt and water, showing basic properties. While reacting with alkalies they form salt and water showing acidic properties.

- For example ZnO exhibits basic behavior with HCl

$$ZnO + 2HCl \rightarrow \underset{zinc\ chloride}{ZnCl_2} + H_2O\,(basic\ nature) \tag{6.4.13}$$

- and acidic behavior with $NaOH$

$$ZnO + 2NaOH \rightarrow \underset{sodium\ zincate}{Na_2ZnO_2} + H_2O\,(acidic\ nature) \tag{6.4.14}$$

- Similarly, Al_2O_3 exhibits basic behavior with H_2SO_4

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O\,(basic\ nature) \tag{6.4.15}$$

- and acidic behavior with $NaOH$

$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O\,(acidic\ nature) \tag{6.4.16}$$

Neutral Oxides

Neutral oxides show neither basic nor acidic properties and hence do not form salts when reacted with acids or bases, e.g., carbon monoxide (CO); nitrous oxide (N_2O); nitric oxide (NO), etc., are neutral oxides.

Peroxides and Dioxides

Oxides: Group 1 metals react rapidly with oxygen to produce several different ionic oxides, usually in the form of M_2O. With the oyxgen exhibiting an oxidation number of -2.

$$4Li + O_2 \rightarrow 2Li_2O \tag{6.4.17}$$

Peroxides: Often Lithium and Sodium reacts with **excess** oxygen to produce the peroxide, M_2O_2. with the oxidation number of the oxygen equal to -1.

$$H_2 + O_2 \rightarrow H_2O_2 \tag{6.4.18}$$

Superoxides: Often Potassium, Rubidium, and Cesium react with excess oxygen to produce the superoxide, MO_2. with the oxidation number of the oxygen equal to -1/2.

$$Cs + O_2 \rightarrow CsO_2 \tag{6.4.19}$$

A peroxide is a metallic oxide which gives hydrogen peroxide by the action of dilute acids. They contain more oxygen than the corresponding basic oxide, e.g., sodium, calcium and barium peroxides.

$$BaO_2 + H_2SO_4 \rightarrow BaSO_4 + H_2O_2 \tag{6.4.20}$$

$$Na_2O_2 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O_2 \tag{6.4.21}$$

Dioxides like PbO_2 and MnO_2 also contain higher percentage of oxygen like peroxides and have similar molecular formulae. These oxides, however, do not give hydrogen peroxide by action with dilute acids. Dioxides on reaction with concentrated HCl yield Cl_2 and on reacting with concentrated H_2SO_4 yield O_2.

$$PbO_2 + 4HCl \rightarrow PbCl_2 + Cl_2 + 2H_2O \tag{6.4.22}$$

$$2PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O + O_2 \tag{6.4.23}$$

Compound Oxides

Compound oxides are metallic oxides that behave as if they are made up of two oxides, one that has a lower oxidation and one with a higher oxidation of the same metal, e.g.,

$$\text{Red lead: } Pb_3O_4 = PbO_2 + 2PbO \tag{6.4.24}$$

$$\text{Ferro-ferric oxide: } Fe_3O_4 = Fe_2O_3 + FeO \tag{6.4.25}$$

On treatment with an acid, compound oxides give a mixture of salts.

$$\underset{\text{Ferro-ferric oxide}}{Fe_3O_4} + 8HCl \rightarrow \underset{\text{ferric chloride}}{2FeCl_3} + \underset{\text{ferrous chloride}}{FeCl_2} + 4H_2O \tag{6.4.26}$$

Preparation of Oxides

Oxides can be generated via multiple reactions. Below are a few.

By direct heating of an element with oxygen: Many metals and non-metals burn rapidly when heated in oxygen or air, producing their oxides, e.g.,

$$2Mg + O_2 \xrightarrow{Heat} 2MgO$$

$$2Ca + O_2 \xrightarrow{Heat} 2CaO$$

$$S + O_2 \xrightarrow{Heat} SO_2$$

$$P_4 + 5O_2 \xrightarrow{Heat} 2P_2O_5$$

By reaction of oxygen with compounds at higher temperatures: At higher temperatures, oxygen also reacts with many compounds forming oxides, e.g.,

- sulfides are usually oxidized when heated with oxygen.

$$2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2$$

$$2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2$$

- When heated with oxygen, compounds containing carbon and hydrogen are oxidized.

$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

- By thermal decomposition of certain compounds like hydroxides, carbonates, and nitrates

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

$$2Cu(NO_3)_2 \xrightarrow{\Delta} 2CuO + 4NO_2 + O_2$$

$$Cu(OH)_2 \xrightarrow{\Delta} CuO + H_2O$$

By oxidation of some metals with nitric acid

$$2Cu + 8HNO_3 \xrightarrow{Heat} 2CuO + 8NO_2 + 4H_2O + O_2$$

$$Sn + 4HNO_3 \xrightarrow{Heat} SnO_2 + 4NO_2 + 2H_2O$$

By oxidation of some non-metals with nitric acid

$$C + 4HNO_3 \rightarrow CO_2 + 4NO_2 + 2H_2O$$

Trends in Acid-Base Behavior

The oxides of elements in a period become progressively more acidic as one goes from left to right in a period of the periodic table. For example, in third period, the behavior of oxides changes as follows:

$$\underbrace{Na_2O,\ MgO}_{Basic} \quad \underbrace{Al_2O_3,\ SiO_2}_{Amphoteric} \quad \underbrace{P_4O_{10},\ SO_3,\ Cl_2O_7}_{Acidic}$$

If we take a closer look at a specific period, we may better understand the acid-base properties of oxides. It may also help to examine the physical properties of oxides, but it is not necessary. Metal oxides on the left side of the periodic table produce basic solutions in water (e.g. Na_2O and MgO). Non-metal oxides on the right side of the periodic table produce acidic solutions (e.g.

Cl_2O, SO_2, P_4O_{10}). There is a trend within acid-base behavior: basic oxides are present on the left side of the period and acidic oxides are found on the right side.

Aluminum oxide shows acid and basic properties of an oxide, it is amphoteric. Thus Al_2O_3 entails the marking point at which a change over from a basic oxide to acidic oxide occurs. It is important to remember that the trend only applies for oxides in their highest oxidation states. The individual element must be in its highest possible oxidation state because the trend does not follow if all oxidation states are included. Notice how the amphoteric oxides (shown in blue) of each period signify the change from basic to acidic oxides,

Groups

1	2	3	14	15	16	17
Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl
K	Ca	Ga	Ge	As	Se	Br
Rb	Sr	In	Sn	Sb	Te	I
Cs	Ba	Tl	Pb	Bi	Po	At

The figure above show oxides of the *s*- and *p-block* elements.
purple: basic oxides blue: amphoteric oxides pink: acidic oxides

Problems

1. Can an oxide be neither acidic nor basic?
2. $Rb + O_2\ (excess) \rightarrow ?$
3. $Na + O_2 \rightarrow ?$
4. BaO_2 is which of the following: hydroxide, peroxide, or superoxide?
5. What is an amphoteric solution?
6. Why is it difficult to obtain oxygen directly from water?

Solutions

1. Yes, an example is carbon monoxide (CO). CO doesn't produce a salt when reacted with an acid or a base.
2. $Rb + O_2\ (excess) \rightarrow RbO_2$
   With the presence of excess oxygen, Rubidium forms a superoxide. Please review section regarding basic oxides above for more detail.
3. $2Na + O_2 \rightarrow Na_2O$
   Note: The problem does not specify that the oxygen was in excess, so it cannot be a peroxide. Please review section regarding basic oxides for more detail.
4. BaO_2 is a peroxide. Barium has an oxidation state of +2 so the oxygen atoms have oxidation state of -1. As a result, the compound is a peroxide, but more specifically referred to as barium peroxide.
5. An amphoteric solution is a substance that can chemically react as either acid or base. See section above on Properties of Amphoteric Oxides for more detail.
6. Water as such is a neutral stable molecule. It is difficult to break the covalent O-H bonds easily. Hence, electrical energy through the electrolysis process is applied to separate dioxygen from water. When a small amount of acid is added to water ionization is initiated which helps in electrochemical reactions as follows.

$$[H_2O\ (acidulated) \rightleftharpoons H^+\ (aq) + OH]^- \times 4$$

At cathode:

$$[H^+\ (aq) + e^- \rightarrow \frac{1}{2} H_2(g)] \times 4$$

At anode:

$$4OH^-\ (aq) \rightarrow O_2 + 2H_2O + 4e^-$$

Net reaction:

$$2H_2O \xrightarrow{electrolysis} 2H_2\,(g) + O_2\,(g)$$

Oxygen can thus be obtained from acidified water by its electrolysis.

References

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2. http://www.wou.edu/las/physci/ch412/oxides.html
3. www.transtutors.com/chemistry...ts/oxides.aspx

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6.5: Lewis Acids and Bases

Learning Objectives

Make sure you thoroughly understand the following essential ideas which have been presented above. 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.

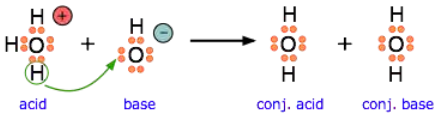
The Brønsted-Lowry proton donor-acceptor concept has been one of the most successful theories of Chemistry. But as with any such theory, it is fair to ask if this is not just a special case of a more general theory that could encompass an even broader range of chemical science. In 1916, G.N. Lewis of 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. According to Lewis,

- An *acid* is a substance that **accepts** a pair of electrons, and in doing so, forms a covalent bond with the entity that supplies the electrons.
- A *base* is a substance that **donates** an unshared pair of electrons to a recipient species with which the electrons can be shared.

> *In modern chemistry, electron donors are often referred to as nucleophiles, while acceptors are electrophiles.*

Proton-Transfer Reactions Involve Electron-Pair Transfer

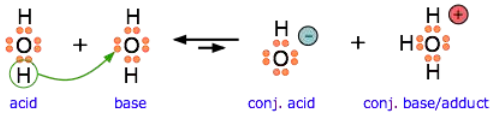
Just as any Arrhenius acid is also a Brønsted acid, any Brønsted acid is also a Lewis acid, so the various acid-base concepts are all "upward compatible". Although we do not really need to think about electron-pair transfers when we deal with ordinary aqueous-solution acid-base reactions, it is important to understand that it is the opportunity for electron-pair sharing that enables proton transfer to take place.



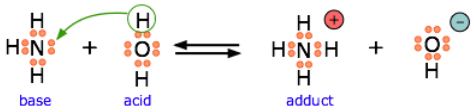
This equation for a simple acid-base neutralization shows how the Brønsted and Lewis definitions are really just different views of the same process. Take special note of the following points:

- The arrow shows the movement of a proton from the hydronium ion to the hydroxide ion.
- Note carefully 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.

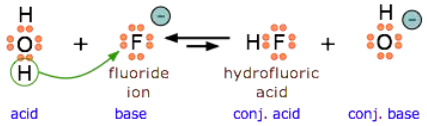
The point about the electron-pair remaining on the donor species is especially important to bear in mind. For one thing, it distinguishes a *Lewis acid-base reaction* from an *oxidation-reduction reaction*, in which a physical transfer of one or more electrons from donor to acceptor does occur. The product 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.



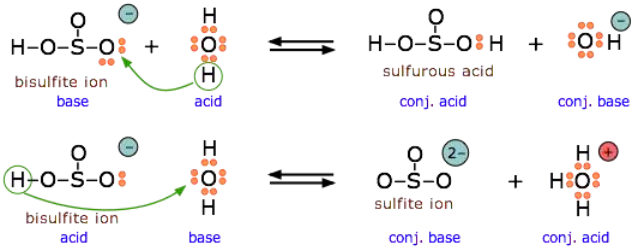
Another example, showing the autoprotolysis of water. Note that the conjugate base is also the adduct.



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.

Acid-base Reactions without Transferring Protons

The major utility of the Lewis definition is that it extends the concept of acids and bases beyond the realm of proton transfer reactions. The classic example is the reaction of boron trifluoride with ammonia to form an *adduct*:

$$BF_3 + NH_3 \rightarrow F_3B{-}NH_3 \tag{6.5.1}$$

One of the most commonly-encountered kinds of Lewis acid-base reactions occurs when electron-donating ligands form coordination complexes with transition-metal ions.

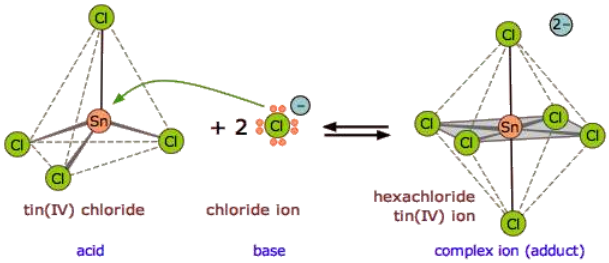


Figure 6.5.1: The tin atom in $SnCl_4$ can expand its valence shell by utilizing a pair of d-orbitals, changing its hybridization from sp^3 to sp^3d^2.

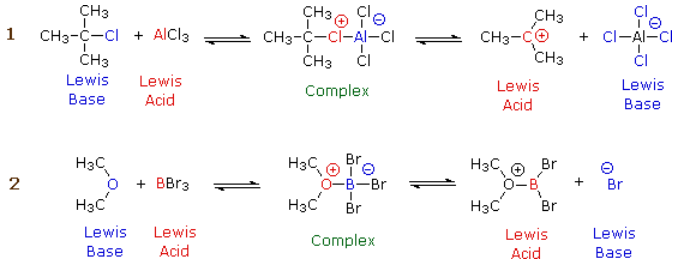
? Exercise 6.5.1

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. $Cd(CN)_2 + 2\,CN- \rightarrow Cd(CN)_4^{2+}$
d. $AgCl + 2\,NH_3 \rightarrow Ag(NH_3)_2^{+} + Cl-$
e. $Fe^{2+} + NO \rightarrow Fe(NO)^{2+}$
f. $Ni^{2+} + 6\,NH_3 \rightarrow Ni(NH_3)_5^{2+}$

Although organic chemistry is beyond the scope of these lessons, it is instructive to see how electron donors and acceptors play a role in chemical reactions. The following two diagrams show the mechanisms of two common types of reactions initiated by simple inorganic Lewis acids:



In each case, the species labeled "Complex" is an intermediate that decomposes into the products, which are conjugates of the original acid and base pairs. The electric charges indicated in the complexes are formal charges, but those in the products are "real".

In reaction 1, the incomplete octet of the aluminum atom in $AlCl_3$ serves as a better electron acceptor to the chlorine atom than does the isobutyl part of the base. In reaction 2, the pair of non-bonding electrons on the dimethyl ether coordinates with the electron-deficient boron atom, leading to a complex that breaks down by releasing a bromide ion.

Non-aqueous Protonic 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 6.5.1). Each of these has as its basis an amphiprotic solvent (one capable of undergoing autoprotolysis), in parallel with the familiar case of water.

The 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. However, many other familiar substances can also serve as the basis of protonic solvent systems as Table 6.5.1 indicates:

Table 6.5.1: Popular Solvent systems

solvent	autoprotolysis reaction	pK_{ap}
water	$2\,H_2O \rightarrow H_3O^+ + OH^-$	14
ammonia	$2\,NH_3 \rightarrow NH_4^+ + NH_2^-$	33
acetic acid	$2\,CH_3COOH \rightarrow CH_3COOH_2^+ + CH_3COO^-$	13
ethanol	$2\,C_2H_5OH \rightarrow C_2H_5OH_2^+ + C_2H_5O^-$	19
hydrogen peroxide	$2\,HO\text{-}OH \rightarrow HO\text{-}OH_2^+ + HO\text{-}O^-$	13
hydrofluoric acid	$2\,HF \rightarrow H_2F^+ + F^-$	10
sulfuric acid	$2\,H_2SO_4 \rightarrow H_3SO_4^+ + HSO_4^-$	3.5

One use of nonaqueous 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.

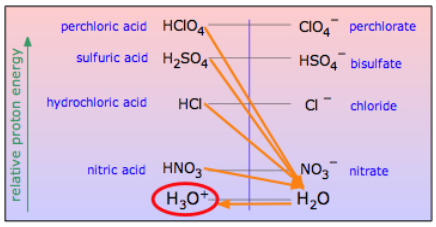


Figure 6.5.2: Use of non-aqueous solvents allows the study of strong acids that are hindered by the "leveling" of the solvent.

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6.6: Hard and Soft Acids and Bases

Lewis acids and bases can be classified by designating them as hard or soft.

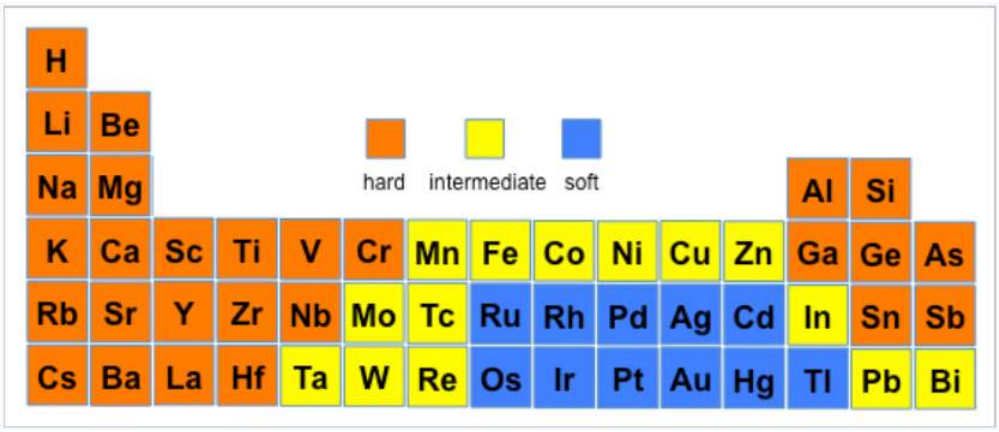
Hard Acids/Bases:

"Hard" acids and bases have a high charge (positive for acids, negative for bases) to ionic radius ratio along with higher oxidation states. Hard acids are not very polarizable and have high charge densities. Thus metal ions with high positive charges and smaller ionic sizes tend to be hard acids. Early transition metal ions in the 3d series tend to be hard Lewis acids. Hard bases are typically small anions and neutral molecules. Some examples of hard acids and bases include: H^+, O^{2-}, OH^-, F^-, Fe^{3+}, and Al^{3+}.

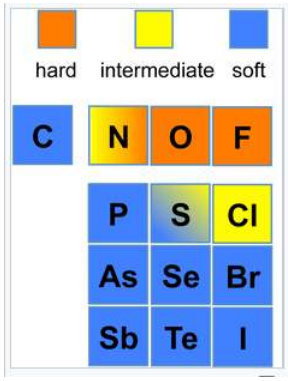
Soft Acids/Bases:

"Soft" acids or bases have a low charge to radius ratio, with low oxidation states. They are normally larger ions that are polarizable. For example, I^- and S^{2-} are soft bases and low charge density transition metals, such as Ag^+, are considered soft acids. Soft acids often include transition metals in the second and third row of the periodic table that have a +1 or +2 charge, as well as late transition metals (especially those in the 4d and 5d series) with filled or almost completely filled *d* orbitals.

Acids and bases are not strictly hard or soft, with many ions and compounds being classified as intermediate. For example, trimethylborane, Fe^{2+}, and Pb^{2+} cations are intermediate acids, and pyridine and aniline are examples of intermediate bases. An element can also change its hard/soft character depending on its oxidation state. The most extreme example is hydrogen, where H^+ is a hard acid and H^- is a soft base. Ni^{3+} (as in the layered compound NiOOH) is a hard acid, but Ni^0 (as in $Ni(CO)_4$) is a soft acid. The figures below show hard/soft trends for acids (left) and bases (right) in the periodic table. For bases, the major hard/soft discontinuity is between the 2nd row (N,O,F) and the rows below.



Hard-soft trends for acids



Hard-soft trends for bases

Like binds with Like

Hard acids interact more strongly with hard bases than they do with soft bases, and soft acids interact more strongly with soft bases than hard bases. Thus, the most stable complexes are those with hard-hard and soft-soft interactions. This tendency is illustrated in the table below, which shows the trend in formation constants for hard and soft acids. Hard acids bind halides in the order $F^- > Cl^- > Br^- > I^-$, whereas soft acids follow the opposite trend.

Log K_1	fluoride	chloride	bromide	iodide	acid classification
Fe^{3+}	6.0	1.4	0.5	-	Hard
Pb^{2+}	1.3	0.9	1.1	1.3	Intermediate
Ag^+	0.4	3.3	4.7	6.6	Soft
Hg^{2+}	1.0	6.7	8.9	12.9	Soft

The softest metal ion in the periodic table is $Au^+(aq)$. It forms stable complexes with soft bases such as phosphines and CN^-, but not with hard bases such as O^{2-} or F^-. The affinity of Au^+ for the soft base CN^- is high, and the resulting $[Au(CN)_2]^-$ complex is so stable that gold (which is normally very difficult to oxidize) can be oxidized by oxygen in the air:

$$4\,Au_{(s)} + 8\,CN^-_{(aq)} + O_{2(g)} + 2\,H_2O = 4\,[Au(CN)_2]^-_{(aq)} + 4\,OH^- \quad (6.6.1)$$

This reaction is used in gold mining to separate small flakes of Au from large volumes of sand and other oxides. Ag is similarly dissolved by air oxidation in cyanide solutions. The precious metals are then isolated from the solution using chemical reducing agents or by electroplating. The use of cyanide ion on a large scale in mining, however, creates a potentially serious environmental hazard. In 2000, a spill at Baia Mare, Romania resulted in the worst environmental disaster in Europe since Chernobyl. Cyanide, which is highly toxic, is gradually oxidized by air to the less toxic cyanate (OCN^-) ion. On the laboratory scale, cyanide plating solutions are typically disposed of by using bleach to oxidize CN^- to OCN^-, and the metal is recovered as an insoluble chloride salt.



Netted solution pond next to cyanide heap leaching of gold ore near Elko, Nevada (1992).

The Au^{3+} ion, because of its higher positive charge, is a harder acid than Au^+ and can form complexes with harder bases such as H_2O and amines. In keeping with the "like binds like" principle, the compound AuI (soft-soft) is stable, but AuI_3 (hard-soft) is unknown. Conversely, AuF has never been isolated but AuF_3 (hard-hard) is stable.

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CHAPTER OVERVIEW

7: Molecular Symmetry

Group Theory is a branch of the mathematical field of algebra. One important application, the theory of symmetry groups, is a powerful tool for the prediction of physical properties of molecules and crystals. It is for example possible to determine whether a molecule can have a dipole moment. Many important predictions of spectroscopic experiments (optical, IR or Raman) can be made purely by group theoretical considerations. The qualitative properties of molecular orbitals can be obtained from group theory (whereas their precise energetics and ordering have to be determined by a quantum chemical method). In quantum chemistry, group theory can applied to *ab initio* or semi-empirical calculations to significantly reduce the computational cost.

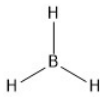
7.1: Introduction
7.2: Symmetry Operations and Elements
7.3: Symmetry Elements
7.4: Successive Operations
7.5: Point Groups
7.6: Character Tables - An Introduction

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7.1: Introduction

Symmetry is important in the study of chemistry. It can be studied on both the molecular level and the crystalline level, of which the former will be discussed in this book.

A molecule is symmetrical if it stays in an indistinguishable configuration after some movement. For example, the molecule BH_3 in **3.1** can be rotated about an axis perpendicular to the screen and passes through the boron atom. If the rotation angle is 120°, the new configuration is indistinguishable from the original form.



3.1

The study of symmetry has many applications, some of which will be introduced in this chapter. Also in this chapter, some of the terminology and definitions used in group theory, the mathematical representation of symmetry, will be introduced.

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7.2: Symmetry Operations and Elements

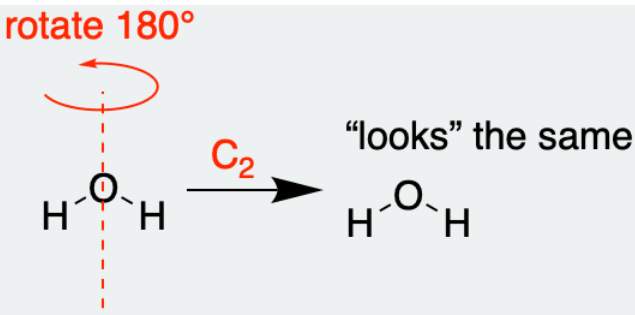


Figure 7.2.1: An example of a symmetry operation is a 180° rotation where the resulting position is indistinguishable from the original. A 180° rotation is called a C_2 operation; the axis of rotation is the symmetry element. (CC-BY-NC-SA; Kathryn Haas)

Introduction

The symmetry of a molecule consists of **symmetry operations** and **symmetry elements**. A symmetry operation is an operation that is performed to a molecule which leaves it indistinguishable and superimposable on the original position. Symmetry operations are performed with respect to symmetry elements (points, lines, or planes).

An example of a symmetry operation is a 180° rotation of a water molecule in which the resulting position of the molecule is indistinguishable from the original position (see Figure 7.2.1). In this example, the symmetry operation is the rotation and the symmetry element is the axis of rotation.

There are five types of symmetry operations including **identity**, **reflection**, **inversion**, **proper rotation**, and **improper rotation**. The improper rotation is the sum of a rotation followed by a reflection. The symmetry elements that correspond to the five types of symmetry operations are listed in Table 7.2.1.

Table 7.2.1: Table of elements and operations

Element	Operation	Symbol
Identity	identity	E
Proper axis	rotation by $(360/n)^o$	C_n
Symmetry plane	reflection in the plane	σ
Inversion center	inversion of a point at (x,y,z) to (-x,-y,-z)	*i*
Improper axis	rotation by $(360/n)^o$, followed by reflection in the plane perpendicular to the rotation axis	S_n

Symmetry Operations and Elements

Identity (E)

All molecules have the identity element. The identity operation is doing nothing to the molecule (it doesn't rotate, reflect, or invert...it just is).

Proper Rotation and Proper Axis (C_n)

A "proper" rotation is just a simple rotation operation about an axis. The symbol for any proper rotation or proper axis is $C_{(360/n)}$, where n is the degree of rotation. Thus, a 180° rotation is a C_2 rotation around a C_2 axis, and a 120° rotation is a C_3 rotation about a

C_3 axis.

PRINCIPLE AXIS: The principle axis of a molecule is the highest order proper rotation axis. For example, if a molecule had C_2 and C_4 axes, the C_4 is the principle axis.

Reflection and Symmetry Planes (σ)

Symmetry planes are mirror planes within the molecule. A reflection operation occurs with respect to a plane of symmetry. There are three classes of symmetry elements:

1. σ_h (horizontal): horizontal planes are perpendicular to principal axis
2. σ_v (vertical): vertical planes are parallel to the principal axis
3. σ_d (dihedral): dihedral planes are parallel to the principle axis and bisecting two C_2' axes

Inversion and Inversion Center (i)

The inversion operation requires a point of symmetry (a center of symmetry within a molecule). In other words, a point at the center of the molecule that can transform (x,y,z) into (-x,-y,-z) coordinate. Structures of tetrahedron, triangles, and pentagons lack an inversion center.

Improper rotation (S_n)

Improper rotation is a combination of a rotation with respect to an axis of rotation (C_n), followed by a reflection through a plane perpendicular to that C_n axis. In short, and S_n operation is equivalent to C_n followed by σ_h.

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Problems

1. Water molecule H_2O was used as an example and was mentioned that water was rotated 180 degree around an axis bisecting the oxygen, then the molecule was superimposable on the original water molecule, how about CO_2? Is it going to be like the water molecule since CO_2 also has 2 atoms of oxygen.

Of course not, because every molecule has different molecular shape. To recognize the symmetry of any molecule the structure and the molecular shape of that molecule should be defined. The water molecule is bent but CO_2 is not, and if CO_2 is rotated 360 degree around the axis bisecting the C atom then it can be superimposed on the original molecule. We then see the symmetry for the CO_2.

2. Why should all of the five symmetry elements be done on a molecule in order to find the point group the molecule belongs to, why is performing only one or two of the symmetry elements not enough for recognizing the point group?

One or two of the symmetry elements will not be able to tell us everything about the molecule's symmetry since those one or two properties do not tell us everything about the molecule. Also, while different molecules may have one or two symmetrical properties in common, the five properties will not be the same for all molecules.

3. What does the symbol C_n stand for and what does n represent? Why is it important to identify n?

C is the axis of rotation and n is the order of the axis.

4. How are the character tables helpful?

The character table tells us about all the operational elements performed on the molecule and indicates if we have forgotten to perform any of the symmetry elements. The tables serve as a checklist because all the operational elements should be done on the molecule in order to find the point group of the molecule.

5. Why is important to find symmetry in molecules?

Symmetry tells us about bounding for that molecular bonding.

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7.3: Symmetry Elements

A *symmetry operation* is an action that leaves an object looking the same after it has been carried out. For example, if we take a molecule of water and rotate it by 180° about an axis passing through the central O atom (between the two H atoms) it will look the same as before. Each symmetry operation has a corresponding *symmetry element*, which is the axis, plane, line or point with respect to which the symmetry operation is carried out. The symmetry element consists of all the points that stay in the same place when the symmetry operation is performed. In a rotation, the line of points that stay in the same place constitute a *symmetry axis*; in a reflection the points that remain unchanged make up a *plane of symmetry*. The symmetry elements that a molecule (and any other 3-D object) may possess are discussed below.

Symmetry Operations

A symmetry operation is a permutation of atoms such that the molecule is transformed into a state **indistinguishable** from the starting state.

E: The Identity Symmetry

The identity operation consists of doing nothing, and the corresponding symmetry element is the entire molecule. Every molecule has at least this element. For example, the $CHFClBr$ molecule in Figure 7.3.1. The identify symmetry is not indicated since all molecule exhibit this symmetry.

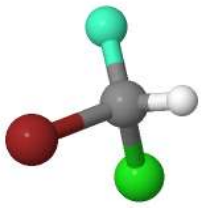


Figure 7.3.1: Example of Identify Symmetry: The $CHFClBr$ molecule contain no other symmetry other than identity. Image created via Symmetry @ Otterbein site by Dean Johnston et al.

C_n: an n-fold Axis of Rotation

Rotation by $360^\circ/n$ leaves the molecule unchanged. The H_2O molecule has a C_2 axis (Figure 7.3.2). Some molecules have more than one C_n axis, in which case the one with the highest value of n is called the *principal axis*. Note that by convention rotations are *counterclockwise* about the axis. C_n rotations are indicated via vectors with labels as indicated below.

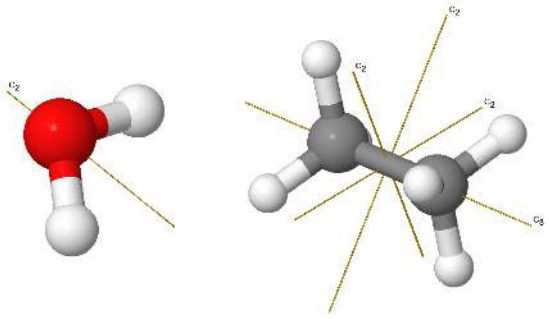


Figure 7.3.2: Examples of n-fold Axis of Rotation: (left) The water molecule contains a C_2 axis. (right) Ethane contains both C_2 and C_3 axes. Image created via Symmetry @ Otterbein site by Dean Johnston et al.

σ: a Plane of Symmetry

Reflection in the plane leaves the molecule looking the same. In a molecule that also has an axis of symmetry, a mirror plane that includes the axis is called a vertical mirror plane and is labeled σ_v, while one perpendicular to the axis is called a horizontal mirror plane and is labeled σ_h. A vertical mirror plane that bisects the angle between two C_2 axes is called a dihedral mirror plane, σ_d. σ symmetry is indicated as a plane on molecules; since they often bisect atoms, which should be clearly indicated.

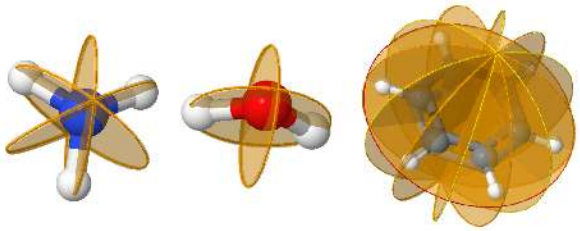


Figure 7.3.3: Examples of reflection symmetry. (left) The ammonia molecule contains three identical reflection planes. All are designated as vertical symmetry planes (σ_v) because they contain the principle rotation axis.(middle) The water molecule contains two different reflection planes. (right) benzene contains a total of seven reflection planes, one horizontal plane (σ_h) and six vertical planes (σ_v and σ_d). Image created via Symmetry @ Otterbein site by Dean Johnston et al.

i: a Center of Inversion Symmetry

Inversion through the center of symmetry leaves the molecule unchanged. Inversion consists of passing each point through the center of inversion and out to the same distance on the other side of the molecule. Examples of molecules with centers of inversion is shown in Figure 7.3.4. Centers of inversion are indicated via a point, which may or may not overlap with an atoms. The centers of inversion in the examples below do not overlap with atoms.

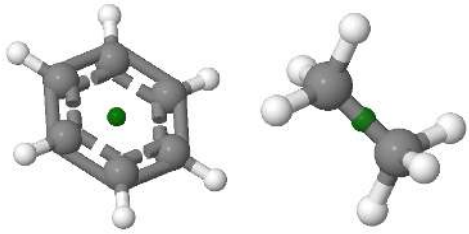


Figure 7.3.4: Examples of Center of Inversion Symmetry. (left) Benzene and (right) staggard ethane have centers of inversion (green balls). Image created via Symmetry @ Otterbein site by Dean Johnston et al.

S_n: an n-fold axis of improper rotation Symmetry

Improper rotations are also called a rotary-reflection axis. The rotary reflection operation consists of rotating through an angle $360^\circ/n$ about the axis, followed by reflecting in a plane perpendicular to the axis. Improper rotation symmetry is indicated with both an axis and a plan as demonstrated in the examples in Figure 7.3.5.

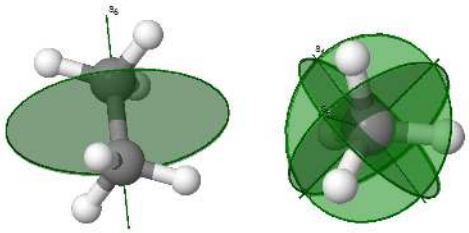


Figure 7.3.5: Examples of Improper axis of rotation. (left) Staggered ethane contains an S_6 axis of improper rotation. (right) Methane contains three S_4 axes of improper rotation. Image created via Symmetry @ Otterbein site by Dean Johnston et al.

Note

S_1 is the same as reflection and S_2 is the same as inversion.

The identity E and rotations C_n are symmetry operations that could actually be carried out on a molecule. For this reason they are called *proper symmetry operations*. Reflections, inversions and improper rotations can only be imagined (it is not actually possible to turn a molecule into its mirror image or to invert it without some fairly drastic rearrangement of chemical bonds) and as such, are termed *improper symmetry operations*. These five symmetry elements are tabulated in Table 7.3.1 with their corresponding operators.

Table 7.3.1: The five principal symmetry elements and their operators for 3D space

Symbol Elements	Description	Symbol Operator	Symbol
E	identity	$\hat{E}$	no change
C_n	n-fold axis of rotation	$\hat{C}_n$	Rotation by $360^\circ/n$ leaves the molecule unchanged
σ	plane of symmetry	$\hat{\sigma}$	Reflection in the plane leaves the molecule unchanged
i	center of symmetry.	$\hat{i}$	Inversion through the center of symmetry leaves the molecule unchanged.
S_n	n-fold improper rotation	$\hat{S}_n$	The rotary reflection operation consists of rotating through an angle $360^\circ/n$ about the axis, followed by reflecting in a plane perpendicular to the axis.

Axis Definitions

Conventionally, when imposing a set of Cartesian axes on a molecule (as we will need to do later on in the course), the z axis lies along the principal axis of the molecule, the x axis lies in the plane of the molecule (or in a plane containing the largest number of atoms if the molecule is non-planar), and the y axis makes up a right handed axis system.

Molecular Point Groups

It is only possible for certain combinations of symmetry elements to be present in a molecule (or any other object). As a result, we may group together molecules that possess the same symmetry elements and classify molecules according to their symmetry. These groups of symmetry elements are called *point groups* (due to the fact that there is at least one point in space that remains unchanged no matter which symmetry operation from the group is applied). There are two systems of notation for labeling symmetry groups, called the Schoenflies and Hermann-Mauguin (or International) systems. The symmetry of individual molecules is usually described using the **Schoenflies** notation, which is used below.

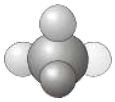
Table 7.3.2: Common Point Groups for Molecules

Nonaxial groups	C_1	C_s	C_i	-	-	-	-	-	-
C_n groups	C_2	C_3	C_4	C_5	C_6	C_7	C_8	-	-
D_n groups	D_2	D_3	D_4	D_5	D_6	D_7	D_8	-	-
C_{nv} groups	C_{2v}	C_{3v}	C_{4v}	C_{5v}	C_{6v}	C_{7v}	C_{8v}	-	-
C_{nh} groups	C_{2h}	C_{3h}	C_{4h}	C_{5h}	C_{6h}	-	-	-	-
D_{nh} groups	D_{2h}	D_{3h}	D_{4h}	D_{5h}	D_{6h}	D_{7h}	D_{8h}	-	-
D_{nd} groups	D_{2d}	D_{3d}	D_{4d}	D_{5d}	D_{6d}	D_{7d}	D_{8d}	-	-
S_n groups	S_2	-	S_4	-	S_6		S_8	S_{10}	S_{12}
Cubic groups	T	T_h	T_d	O	O_h	I	I_h	-	-
Linear groups	$C_{\infty v}$	$D_{\infty h}$	-	-	-	-	-	-	-

Shared Names

Some of the point groups share their names with symmetry operations, so be careful you do not mix up the two. It is usually clear from the context which one is being referred to.

1. C_1 - contains only the identity (a C_1 rotation is a rotation by 360° and is the same as the identity operation) e.g. CHDFCl.



2. C_i - contains the identity E and a center of inversion i.



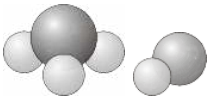
3. C_S - contains the identity E and a plane of reflection σ.



4. C_n - contains the identity and an n-fold axis of rotation.



5. C_{nv} - contains the identity, an n-fold axis of rotation, and n vertical mirror planes σ_v.



6. C_{nh} - contains the identity, an n-fold axis of rotation, and a horizontal reflection plane σ_h (note that in C_{2h} this combination of symmetry elements automatically implies a center of inversion).



7. D_n - contains the identity, an n-fold axis of rotation, and n 2-fold rotations about axes perpendicular to the principal axis.



8. D_{nh} - contains the same symmetry elements as D_n with the addition of a horizontal mirror plane.



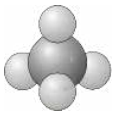
9. D_{nd} - contains the same symmetry elements as D_n with the addition of n dihedral mirror planes.



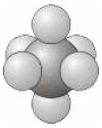
10. S_n - contains the identity and *one* S_n axis. Note that molecules only belong to S_n if they have not already been classified in terms of one of the preceding point groups (e.g. S_2 is the same as C_i, and a molecule with this symmetry would already have been classified).

The following groups are the cubic groups, which contain more than one principal axis. They separate into the tetrahedral groups (T_d, T_h and T) and the octahedral groups (O and O_h). The icosahedral group also exists, but is not included below.

11. T_d - contains all the symmetry elements of a regular tetrahedron, including the identity, 4 C_3 axes, 3 C_2 axes, 6 dihedral mirror planes, and 3 S_4 axes e.g. CH_4.



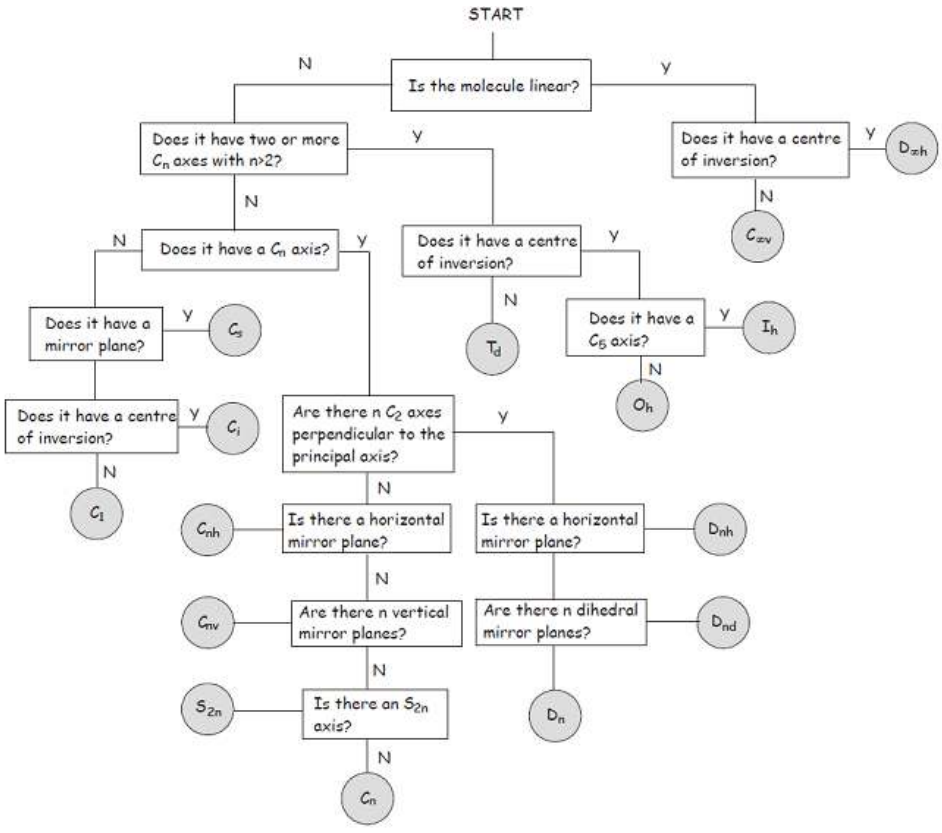
12. T - as for T_d but no planes of reflection.
13. T_h - as for T but contains a center of inversion.
14. O_h - the group of the regular octahedron e.g. SF_6.



15. O - as for O_h, but with no planes of reflection.

The final group is the full rotation group R_3, which consists of an infinite number of C_n axes with all possible values of n and describes the symmetry of a sphere. Atoms (but no molecules) belong to R_3, and the group has important applications in atomic quantum mechanics. However, we won't be treating it any further here.

Once you become more familiar with the symmetry elements and point groups described above, you will find it quite straightforward to classify a molecule in terms of its point group. In the meantime, the flowchart shown below provides a step-by-step approach to the problem.



[1]Though the Hermann-Mauguin system can be used to label point groups, it is usually used in the discussion of crystal symmetry. In crystals, in addition to the symmetry elements described above, translational symmetry elements are very important. Translational symmetry operations leave no point unchanged, with the consequence that crystal symmetry is described in terms of *space groups* rather than *point groups*.

Symmetry and physical properties

Carrying out a symmetry operation on a molecule must not change any of its physical properties. It turns out that this has some interesting consequences, allowing us to predict whether or not a molecule may be chiral or polar on the basis of its point group.

For a molecule to have a permanent dipole moment, it must have an asymmetric charge distribution. The point group of the molecule not only determines whether the molecule may have a dipole moment, but also in which direction(s) it may point. If a molecule has a C_n axis with $n > 1$, it **cannot** have a dipole moment perpendicular to the axis of rotation (for example, a C_2 rotation would interchange the ends of such a dipole moment and reverse the polarity, which is not allowed – rotations with higher values of n would also change the direction in which the dipole points). Any dipole must lie parallel to a C_n axis.

Also, if the point group of the molecule contains any symmetry operation that would interchange the two ends of the molecule, such as a σ_h mirror plane or a C_2 rotation perpendicular to the principal axis, then there cannot be a dipole moment along the axis. The only groups compatible with a dipole moment are C_n, C_{nv} and C_s. In molecules belonging to C_n or C_{nv} the dipole must lie along the axis of rotation.

One example of symmetry in chemistry that you will already have come across is found in the isomeric pairs of molecules called enantiomers. Enantiomers are non-superimposable mirror images of each other, and one consequence of this symmetrical relationship is that they rotate the plane of polarized light passing through them in opposite directions. Such molecules are said to be chiral,[2] meaning that they cannot be superimposed on their mirror image. Formally, the symmetry element that precludes a molecule from being chiral is a rotation-reflection axis S_n. Such an axis is often implied by other symmetry elements present in a group.

For example, a point group that has C_n and σ_h as elements will also have S_n. Similarly, a center of inversion is equivalent to S_2. As a rule of thumb, a molecule definitely cannot have be chiral if it has a center of inversion or a mirror plane of any type (σ_h, σ_v or σ_d), but if these symmetry elements are absent the molecule should be checked carefully for an S_n axis before it is assumed to be chiral.

Chirality

The word chiral has its origins in the Greek word for hand ($\chi\epsilon\rho\iota$, pronounced ‘cheri’ with a soft ch as in ‘loch’). A pair of hands is also a pair of non-superimposable mirror images, and you will often hear chirality referred to as ‘handedness’ for this reason.

Summary

All molecules can be described in terms of their symmetry or lack thereof, which may contain symmetry elements (point, line, plane). Reflection, rotation, and inversion are symmetry operations (movement of the molecules such that after the movement, all the atoms of the molecules is coincidental with equivalent atom of the molecule in original).

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7.4: Successive Operations

Sometimes, new symmetry operations form by carrying out two or more simpler operations successively to result in an indistinguishable configuration. For example, the improper rotation axis that was introduced in the last section results from rotation about an axis of rotation (C_n) followed by reflection about a plane perpendicular to that axis (σ_h).

$$S_n = C_n \times \sigma_h$$

Note also that C_n in this case need not be a symmetry element for the molecule. For example, staggered ethane has an S_6 symmetry element although it does not have a C_6. Another example of a symmetry element that results from a combination of two different elements is the inversion center (i), which results from a C_2 rotation followed by a reflection about a plane perpendicular to that axis (σ_h).

$$i = C_2 \times \sigma_h$$

Note that an inversion center is a special case of an improper rotation axis because it results when, in the first equation, $n = 2$. That is,

$$i = S_2$$

In fact, any symmetry operation can be carried out multiple time in a row. For example, when BH_3 is rotated twice by 120°, the two-step operation can be symboled by C_3^2. When the C_3 operation is performed a third time, the molecule returns to its original configuration; i.e,

$$C_3^3 = E$$

In general,

$$C_n^n = E$$

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7.5: Point Groups

Point groups are used to describe molecular symmetries and are a condensed representation of the symmetry elements a molecule may posses. This includes both bond and orbital symmetry. Knowing molecular symmetry allows for a greater understanding of molecular structure and can help to predict many molecular properties.

Introduction

Point groups are a quick and easy way to gain knowledge of a molecule. They not only contain a molecule's symmetry elements, but also give rise to a character table, which is a complete set of irreducible representations for a point group. A molecule's point group can be determined by either elucidating each symmetry element contained in a molecule or by properly using the Schreiber chart (see below).

Point groups usually consist of (but are not limited to) the following elements:

- E - The identity operator. This operation leaves a molecule completely unchanged and exists for mathematical purposes.
- C_n - The C_n proper axis of rotation is a 360/n° rotation that when performed leaves a molecule the same. A proper rotation with the highest value of n is known as the major axis of rotation.
- σ - The mirror plane. The mirror plane can be described as a plane which produces a reflection of part of a molecule that is unnoticeable and can be labeled as either σ_h , σ_v , σ_d.
- i - The inversion center. A molecule has a center of inversion if, when inverted, the molecule is unchanged.

See the section on symmetry elements for a more thorough explanation of each.

Each point group is associated with a specific combination of symmetry elements

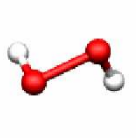
Each point group has it's own combination of symmetry elements. Listed below are some of the many point groups and their respective symmetry elements, according to category, followed by a representative example.

Non axial groups

C_1: E C_1: E, i

C_n groups

C_2: E, C_2 (notice the major axis of rotation is the point group) C_3: E, C_3, C_3^2



H_2O_2 C_2

D_n groups

D_2: E $C_2(z)$, $C_2(y)$, $C_2(x)$ D_3: E, $2C_3$, $3C_2$

C_{nv} groups

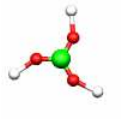
C_{2v}: E, C_2, $\sigma_v(xz)$, $\sigma_v'(yz)$ C_{3v}: E, $2C_3$, $3\sigma_v$



H_2O C_{2v}

C_{nh} groups

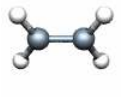
C_{2h}: E, C_2, i, σ_h C_{3h}: E, C_3, C_3^2, σ_h, S_3, S_3^3



$B(OH)_3$

D_{nh} groups

D_{2h}: E



C_2H_4 D_{2h}

How to determine a molecules point group

A molecule's point group can be determined by calculating all the symmetry elements of a molecule and matching them to a respective point group. This process, however, is greatly simplified when the Schreiber chart is used:

References

1. Housecroft, Catherine E.; Sharpe, Alan G., *Inorganic Chemistry*, 3rd Ed. Pearson Education Limited 2008, Chapter 4
2. Koster, George F.; Wheeler, Robert G.; Dimmock, John O., The Properties of Thirty-Two Point Groups, The MIT Press 1963
3. Bertolucci, Michael D.; Harris, Daniel C., Symmetry and Spectroscopy: An Introduction to Vibrational and Electronic Spectroscopy, Dover Publications 1989

Outside Links

- Point groups in 3-D

Problems

1. Determine the point group of BH_3 by calculating all it's symmetry elements then use the chart and determine which method is faster.
2. Determine the point groups of BH_3 and NH_3. Why is there a difference?
3. What is the point group of PPh_3?
4. Determine the point groups of CO_2 and H_2O and then compare them.
5. Propose a molecule with no symmetry. What is it's point group?

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7.6: Character Tables - An Introduction

Although the method of assigning a point group to a molecule depends on some knowledge of the symmetry elements the molecule has, it does not require the consideration of all elements. For example, the molecule CO_2 can be assigned the point group $D_{\infty h}$ using the scheme in section 3.4 by merely knowing that the molecule is linear and that it has the a center io inversion i. The point group assignment in this case did not require knowing that the molecule also has σ_h, for example. This type of knowledge is gained by examining character tables.

Definition

A character table is a table that contains the symmetry information of the molecule. This information can be used to analyze the molecule's behavior in many application, among which is spectroscopy. Each point group has its own character table. The following table is the character table of the point group C_{2v}:

Table 1: *The character table of the point group C_{2v}.*

C_{2v}	E	C_2 (z)	σ_v(xz)	σ_v(yz)	h = 4	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

Understanding Character Tables

Symbols under the first column of the character tables

A (Mulliken Symbol)	(singly degenerate or one dimensional) symmetric with respect to rotation of the principle axis
B (Mulliken Symbol)	(singly degenerate or one dimensional) anti-symmetric with respect to rotation of the principle axis
E (Mulliken Symbol)	(doubly degenerate or two dimensional)
T (Mulliken Symbol)	(thirdly degenerate or three dimensional)
Subscript 1	symmetric with respect to the $C_n$principle axis, if no perpendicular axis, then it is with respect to σ_V
Subscript 2	anti-symmetric with respect to the $C_n$principle axis, if no perpendicular axis, then it is with respect to σ_V
Subscript g	symmetric with respect to the inverse
subscript u	anti-symmetric with respect to the inverse
prime	symmetric with respect to $/* <![CDATA[*/\sigma_h/*]]> */$ (reflection in horizontal plane)
double prime	anti-symmetric with respect to $/* <![CDATA[*/\sigma_h/*]]> */$ (opposite reflection in horizontal pla

Symbols in the first row of the character tables

E	describes the degeneracy of the row (A and B= 1) (E=2) (T=3)
C_n	2pi/n= number of turns in one circle on the main axis without changing the look of a molecule (rotation of the molecule)
C_n'	2π/n= number of turns in one circle perpendicular to the main axis, without changing the structure of the molecule
C_n''	2π/n= number of turns in one circle perpendicular to the C_n' and the main axis, without changing the structure

σ'	reflection of the molecule perpendicular to the other sigma
σ_v (vertical)	reflection of the molecule vertically compared to the horizontal highest fold axis.
σ_h or σ_d (horizontal)	reflection of the molecule horizontally compared to the horizontal highest fold axis.
i	Inversion of the molecule from the center
S_n	rotation of $2\pi/n$ and then reflected in a plane perpendicular to rotation axis.
#C_n	the # stands for the number of irreducible representation for the C_n
#σ	the # stands for the number irreducible representations for the sigmas.
the number in superscript	in the same rotation there is another rotation, for instance O_h has $3C_2=C_4^2$
other useful definitions	
(R_x,R_y)	the (,) means they are the same and can be counted once.
x^2+y^2, z^2	without (,) means they are different and can be counted twice.

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CHAPTER OVERVIEW

8: Solids

8.1: The Solid State of Matter
8.2: Lattice Structures in Crystalline Solids
8.3: Simple Cubic
8.4: Body Centered Packing
8.5: Metal Structures
8.6: Solids
8.7: Sphere Packing
8.8: Tetrahedral and Octahedral Sites

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8.1: 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 8.1.1).

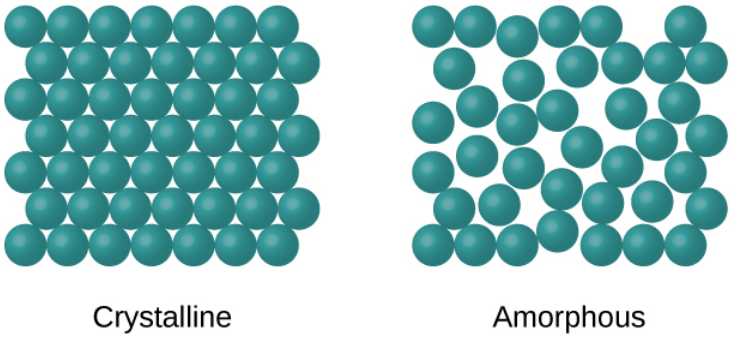


Figure 8.1.1: The entities of a solid phase may be arranged in a regular, repeating pattern (crystalline solids) or randomly (amorphous).

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 8.1.2), 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.

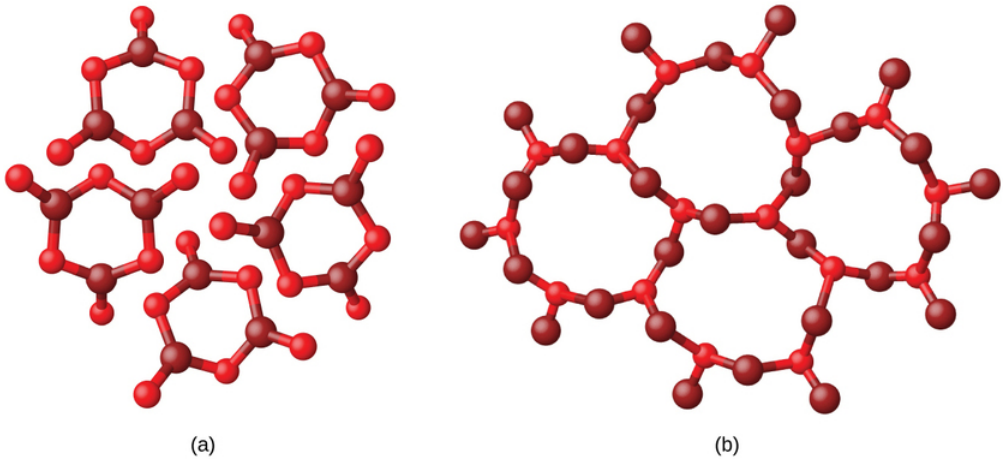


Figure 8.1.2: (a) Diboron trioxide, B_2O_3, is normally found as a white, amorphous solid (a glass), which has a high degree of disorder in its structure. (b) By careful, extended heating, it can be converted into a crystalline form of B_2O_3, which has a very ordered arrangement.

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.

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 8.1.3). 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.

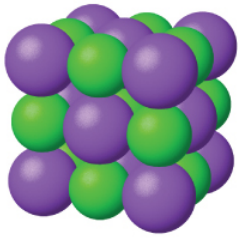


Figure 8.1.3: Sodium chloride is an ionic solid.

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.

Metallic Solids

Metallic solids such as crystals of copper, aluminum, and iron are formed by metal atoms Figure 8.1.4. 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.

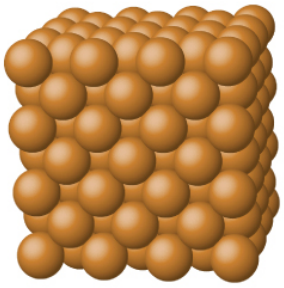


Figure 8.1.4: Copper is a metallic solid.

Covalent Network Solids

Covalent network solids include crystals of diamond, silicon, some other nonmetals, and some covalent compounds such as silicon dioxide (sand) and silicon carbide (carborundum, the abrasive on sandpaper). Many minerals have networks of covalent bonds. The atoms in these solids are held together by a network of covalent bonds, as shown in Figure 8.1.5. 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.

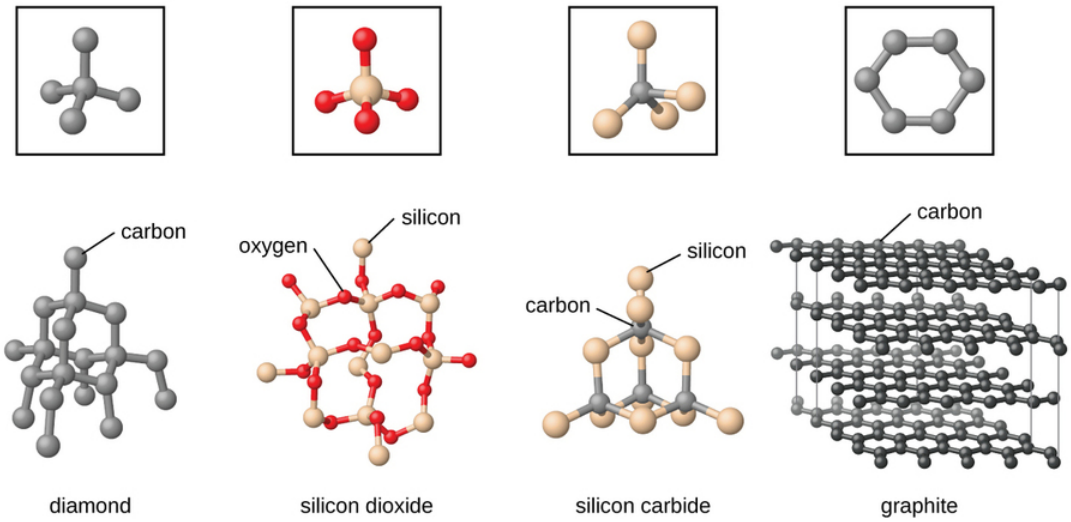


Figure 8.1.5. A covalent crystal contains a three-dimensional network of covalent bonds, as illustrated by the structures of diamond, silicon dioxide, silicon carbide, and graphite. Graphite is an exceptional example, composed of planar sheets of covalent crystals that are held together in layers by 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.

Molecular Solids

Molecular solids, such as ice, sucrose (table sugar), and iodine, as shown in Figure 8.1.6, 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).

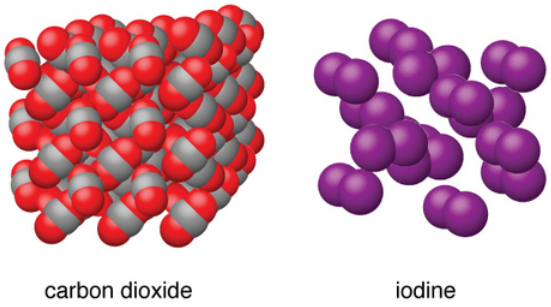


Figure 8.1.6: Carbon dioxide (CO_2) consists of small, nonpolar molecules and forms a molecular solid with a melting point of −78 °C. Iodine (I_2) consists of larger, nonpolar molecules and forms a molecular solid that melts at 114 °C.

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.

Properties of Solids

A crystalline solid, like those listed in Table 8.1.1 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 8.1.1: 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 8.1.7. 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.

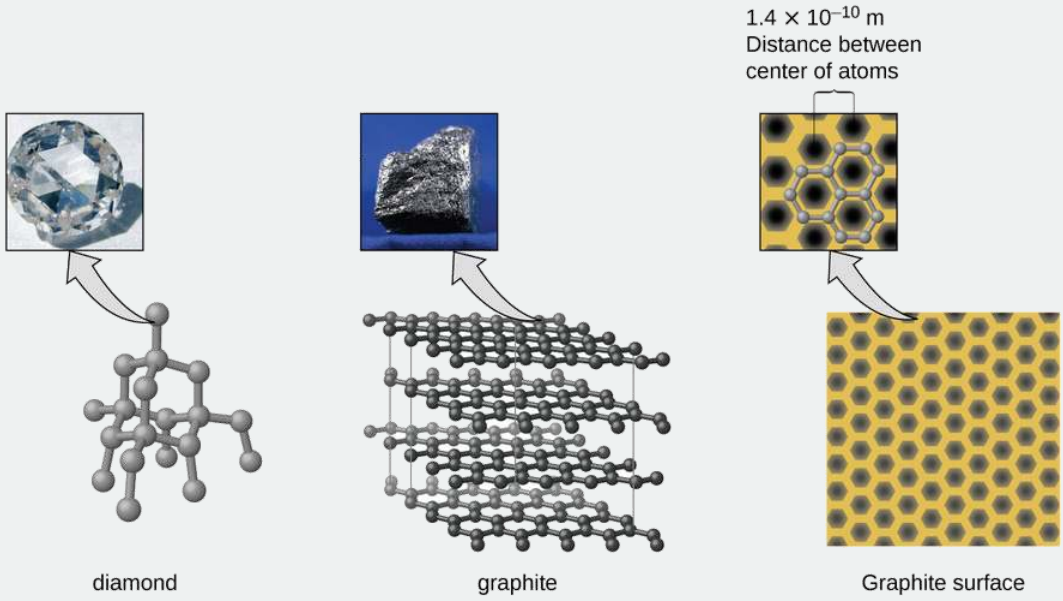


Figure 8.1.7: Diamond is extremely hard because of the strong bonding between carbon atoms in all directions. Graphite (in pencil lead) rubs off onto paper due to the weak attractions between the carbon layers. An image of a graphite surface shows the distance between the centers of adjacent carbon atoms. (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 8.1.8, 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.

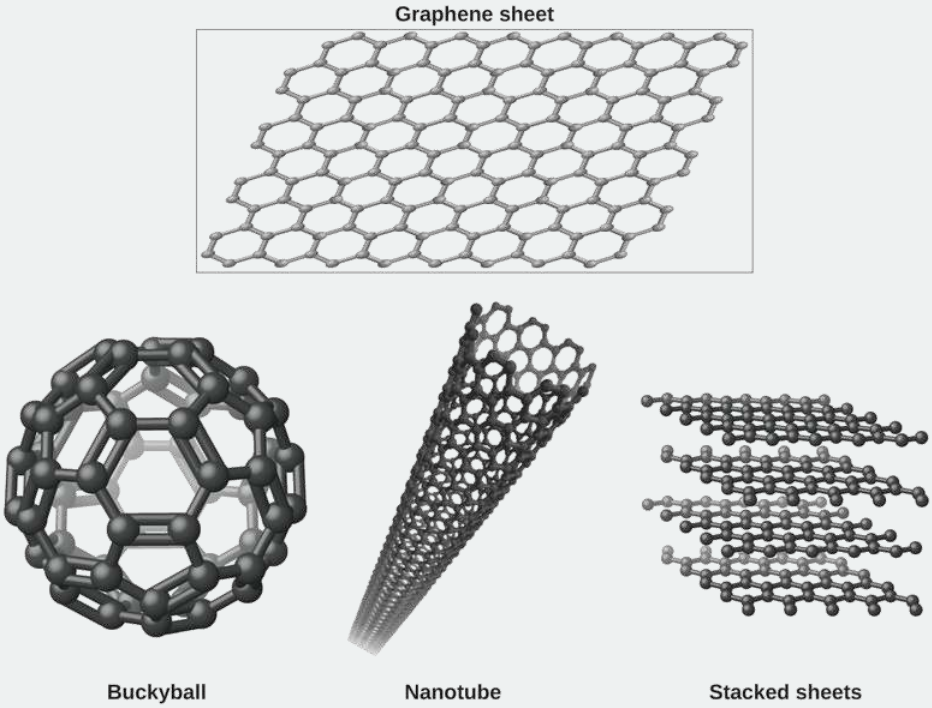


Figure 8.1.8: Graphene sheets can be formed into buckyballs, nanotubes, and stacked layers.
A sheet of interconnected hexagonal rings is shown at the top. Below it, a bukcyball is shown which is a sphere is composed of hexagonal rings. In the lower middle image, a nanotube is shown that is made by rolling 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.

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 8.1.9. 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.

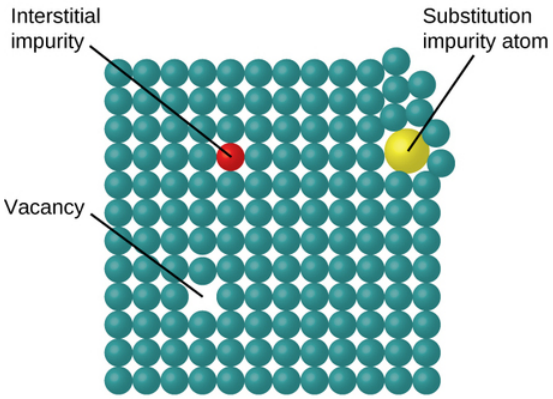


Figure 8.1.9: Types of crystal defects include vacancies, interstitial atoms, and substitutions impurities.

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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8.2: 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.

The Structures of Metals

We will begin our discussion of crystalline solids by considering elemental metals, which are relatively simple because each contains only one type of atom. A pure metal is a crystalline solid with metal atoms packed closely together in a repeating pattern. Some of the properties of metals in general, such as their malleability and ductility, are largely due to having identical atoms arranged in a regular pattern. The different properties of one metal compared to another partially depend on the sizes of their atoms and the specifics of their spatial arrangements. We will explore the similarities and differences of four of the most common metal crystal geometries in the sections that follow.

Unit Cells of Metals

The structure of a crystalline solid, whether a metal or not, is best described by considering its simplest repeating unit, which is referred to as its unit cell. The unit cell consists of lattice points that represent the locations of atoms or ions. The entire structure then consists of this unit cell repeating in three dimensions, as illustrated in Figure 8.2.1.

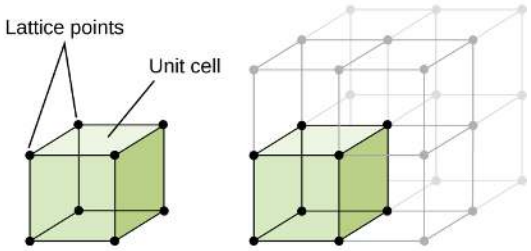


Figure 8.2.1: A unit cell shows the locations of lattice points repeating in all directions.

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 8.2.2. This arrangement is called simple cubic structure, and the unit cell is called the simple cubic unit cell or primitive cubic unit cell.

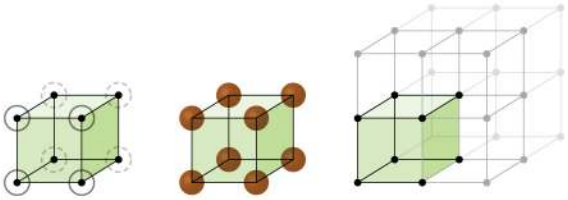


Figure 8.2.2: .When metal atoms are arranged with spheres in one layer directly above or below spheres in another layer, the lattice structure is called simple cubic. Note that the spheres are in contact.

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 8.2.3, 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.

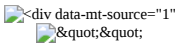


Figure 8.2.3: An atom in a simple cubic lattice structure contacts six other atoms, so it has a coordination number of six.

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 8.2.4. 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.

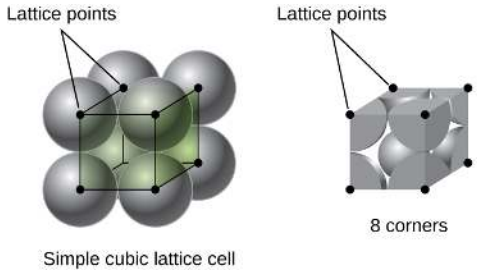


Figure 8.2.4: A simple cubic lattice unit cell contains one-eighth of an atom at each of its eight corners, so it contains one atom total.

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.

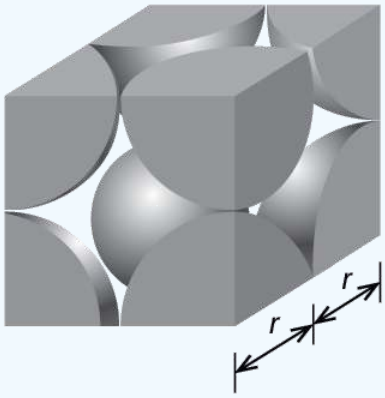
Example 8.2.1: Calculating Atomic Radius and Density for Metals (Part 1)

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 8.2.1

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 8.2.5. (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.)

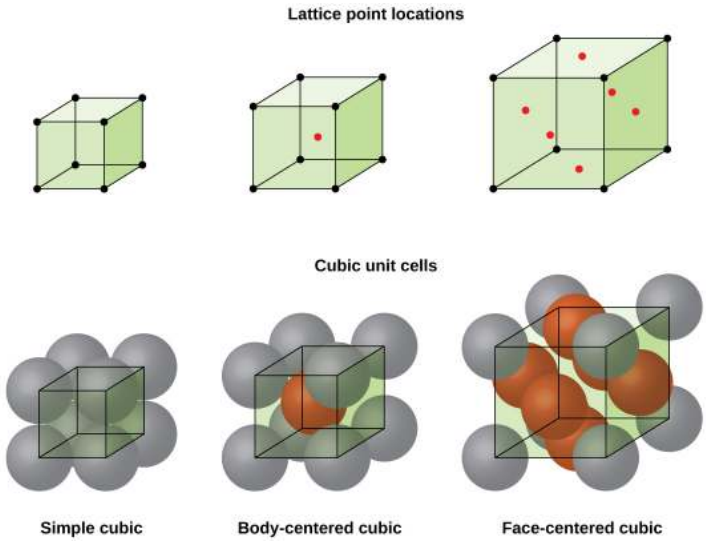


Figure 8.2.5: Cubic unit cells of metals show (in the upper figures) the locations of lattice points and (in the lower figures) metal atoms located in the unit cell.

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 8.2.6. 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.

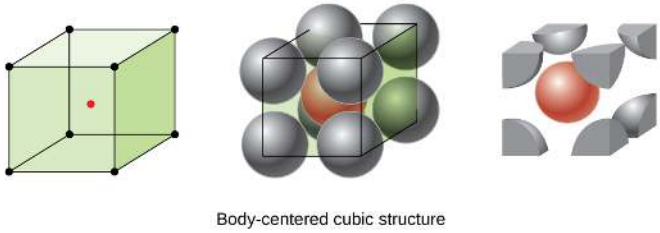


Figure 8.2.6: In a body-centered cubic structure, atoms in a specific layer do not touch each other. Each atom touches four atoms in the layer above it and four atoms in the layer below it.

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 8.2.7. 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.

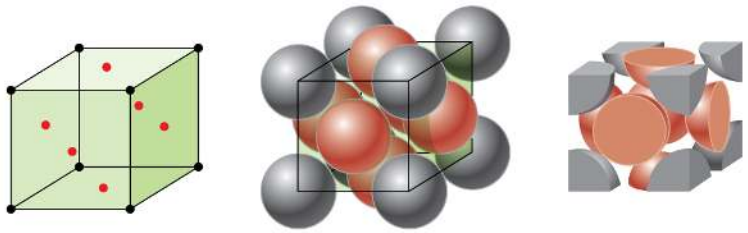


Figure 8.2.7:A face-centered cubic solid has atoms at the corners and, as the name implies, at the centers of the faces of its unit cells.

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 8.2.8.

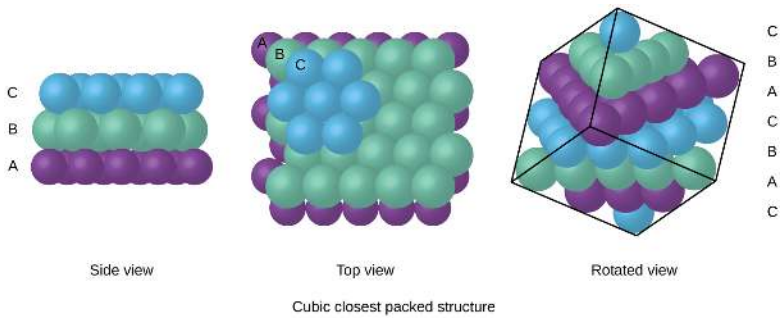


Figure 8.2.8: A CCP arrangement consists of three repeating layers (ABCABC…) of hexagonally arranged atoms. Atoms in a CCP structure have a coordination number of 12 because they contact six atoms in their layer, plus three atoms in the layer above and three atoms in the layer below. By rotating our 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 8.2.9. 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.

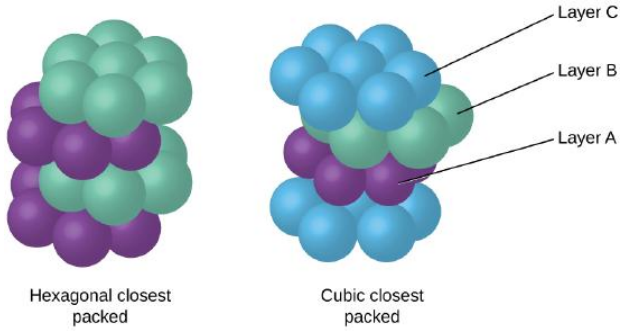


Figure 8.2.9: In both types of closest packing, atoms are packed as compactly as possible. Hexagonal closest packing consists of two alternating layers (ABABAB…). Cubic closest packing consists of three alternating layers (ABCABCABC…).

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.”

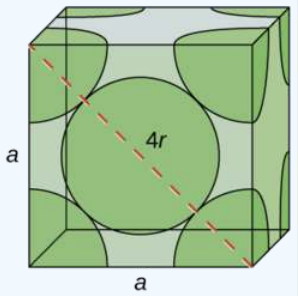
Example 8.2.2: Calculating Atomic Radius and Density for Metals (Part 2)

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 $\text{density} = \frac{\text{mass}}{\text{volume}}$. 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 8.2.2

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 8.2.10. The axes are defined as being the lengths between points in the space lattice. Consequently, unit cell axes join points with identical environments.

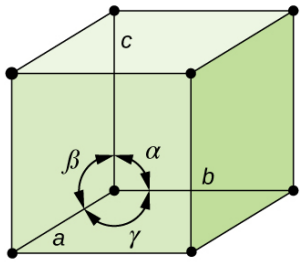


Figure 8.2.10: A unit cell is defined by the lengths of its three axes (a, b, and c) and the angles (α, β, and γ) between the axes.

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 8.2.11.

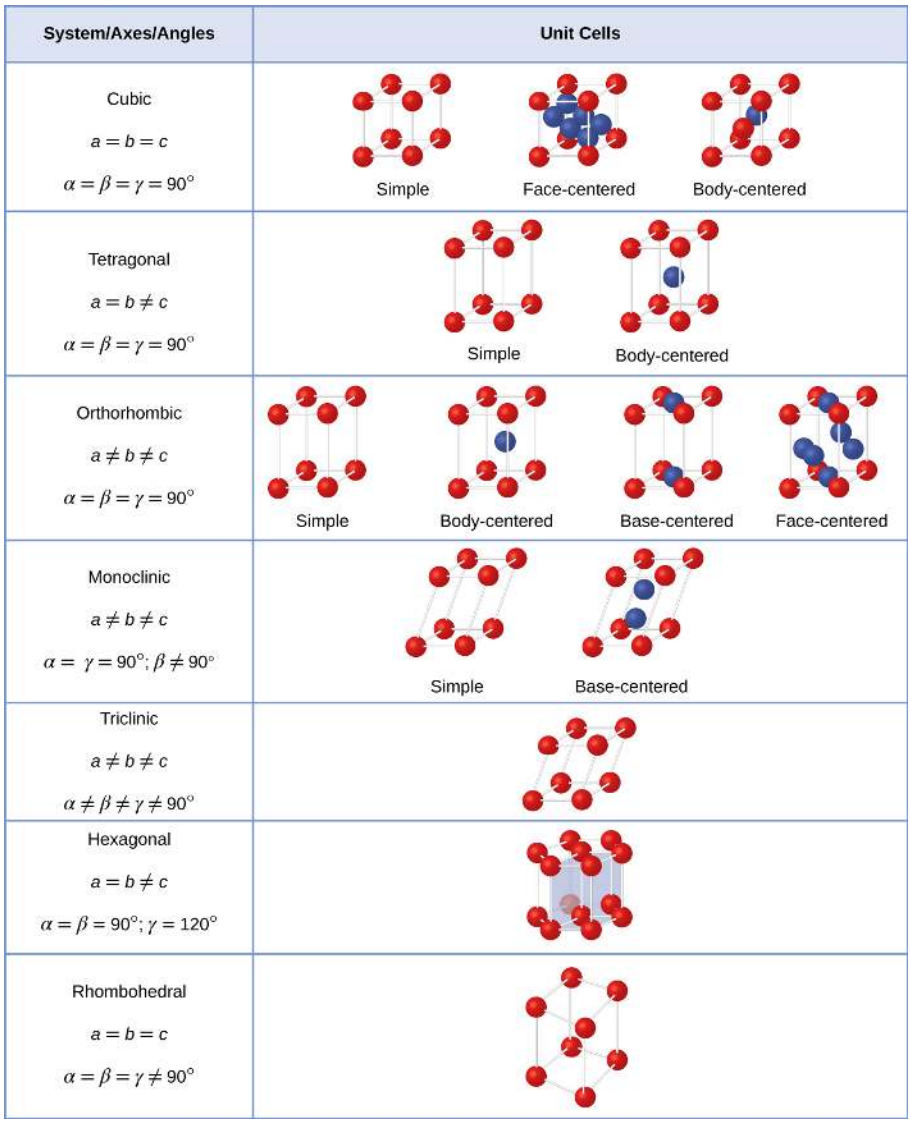


Figure 8.2.11:There are seven different lattice systems and 14 different unit cells.

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.

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 8.2.12 illustrates both of these types of holes.

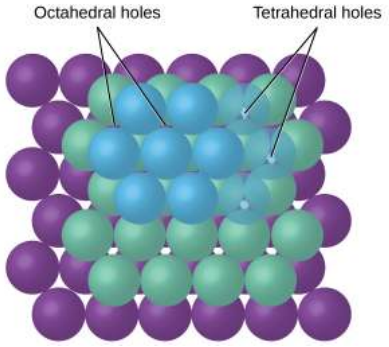


Figure 8.2.12: Cations may occupy two types of holes between anions: octahedral holes or tetrahedral holes.

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 8.2.13. 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.

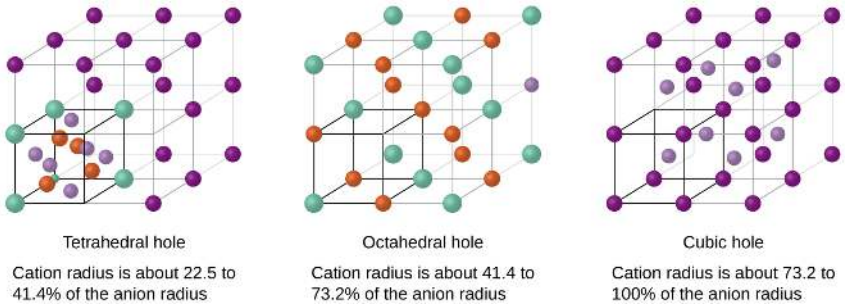


Figure 8.2.13:A cation’s size and the shape of the hole occupied by the compound are directly related.

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 8.2.3: 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 8.2.3: 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

$\mathrm{Li_2Se}$

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 8.2.4: 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 $\mathrm{Al_{2/3}O}$. The simplest whole number ratio is 2:3, so the formula is $\mathrm{Al_2O_3}$.

Exercise 8.2.4

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

$\mathrm{TiO_2}$

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 $\mathrm{SrH_2}$, $\mathrm{UO_2}$, $\mathrm{SrCl_2}$, and $\mathrm{CaF_2}$.

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.

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 8.2.14) is an example of this, with $\mathrm{Cs^+}$ and $\mathrm{Cl^-}$ 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 8.2.14: 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.

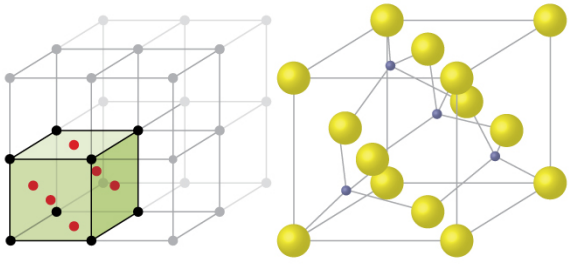
When an ionic compound is composed of a 1:1 ratio of cations and anions that differ significantly in size, it typically crystallizes with an FCC unit cell, like that shown in Figure 8.2.15. Sodium chloride, NaCl, is an example of this, with Na^+ and Cl^- having radii of 102 pm and 181 pm, respectively. 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 8.2.15: 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 8.2.16. 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.



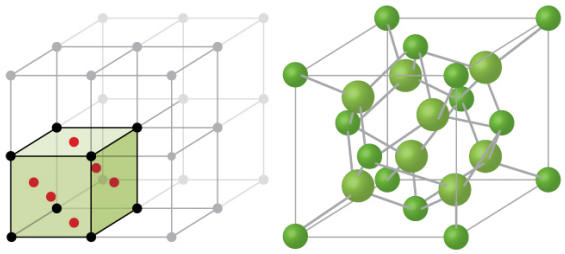
ZnS face-centered unit cell

Figure 8.2.16: 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 8.2.17, 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 8.2.17 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 8.2.17: 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.”

Calculation of Ionic Radii

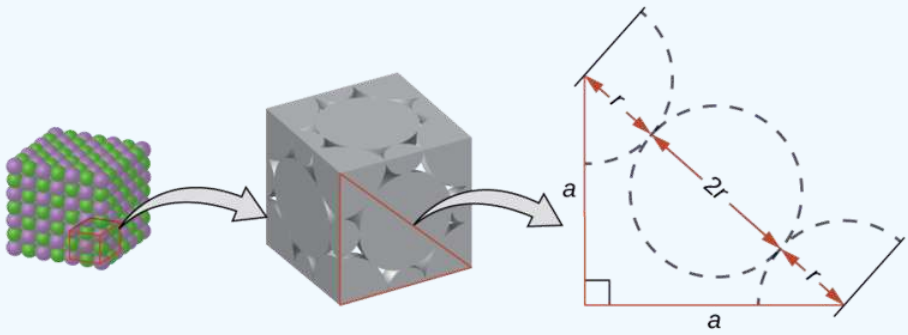
If we know the edge length of a unit cell of an ionic compound and the position of the ions in the cell, we can calculate ionic radii for the ions in the compound if we make assumptions about individual ionic shapes and contacts.

Example 8.2.5: 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:

$$r = \sqrt{\frac{(0.514\ \text{nm})^2 + (0.514\ \text{nm})^2}{16}} = 0.182\ \text{nm}\ (1.82\ \text{Å})\ \text{for a}\ \text{Cl}^-\ \text{radius.}$$

Exercise 8.2.6

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.

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 8.2.18).

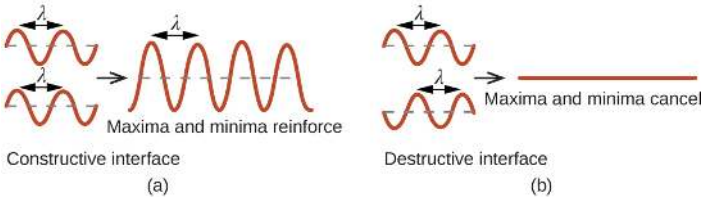


Figure 8.2.18: Light waves occupying the same space experience interference, combining to yield waves of greater (a) or lesser (b) intensity, depending upon the separation of their maxima and minima.

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:

$$n\lambda = 2d\sin\theta \tag{8.2.1}$$

This relation is known as the Bragg equation in honor of W. H. Bragg, the English physicist who first explained this phenomenon. Figure 8.2.18 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.

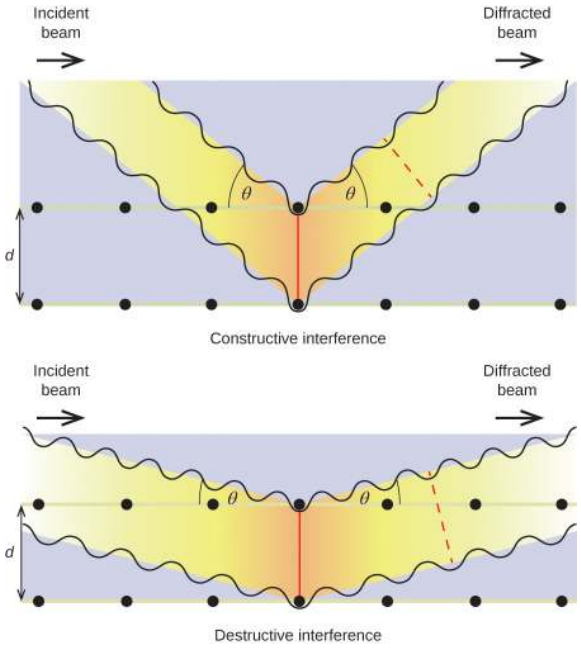


Figure 8.2.19: The diffraction of X-rays scattered by the atoms within a crystal permits the determination of the distance between the atoms. The top image depicts constructive interference between two scattered waves and a resultant diffracted wave of high intensity. The bottom image depicts destructive 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 8.2.20, 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.

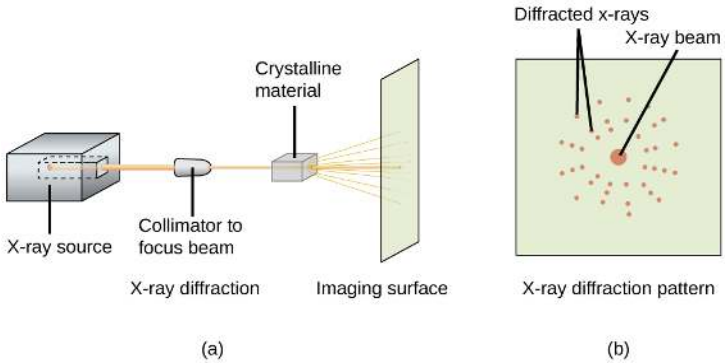


Figure 8.2.20: (a) In a diffractometer, a beam of X-rays strikes a crystalline material, producing (b) an X-ray diffraction pattern that can be analyzed to determine the crystal structure.

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 8.2.6: 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 8.2.1) for *d*.

This gives

$$d = \frac{n\lambda}{2\sin\theta} = \frac{1(0.1315\text{ nm})}{2\sin(25.25^\circ)} = 0.154\text{ nm}$$

Exercise 8.2.6

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.

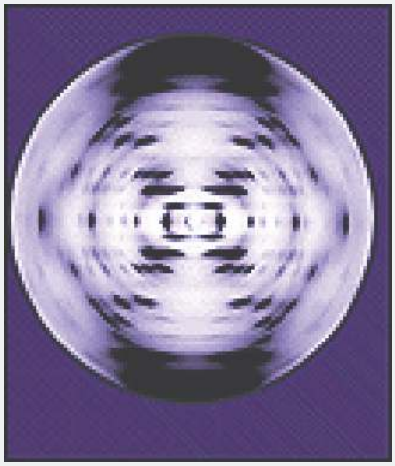


Figure 8.2.7.This illustration shows an X-ray diffraction image similar to the one Franklin found in her research. (credit: National Institutes of Health)

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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8.3: Simple Cubic

Learning Objectives

- Recognize a unit cell.
- Use geometry to correlate atomic radius with unit cell edge length.
- Calculate parameters relevant to crystal chemistry.

Contributors and Attributions

- Chung (Peter) Chieh (Professor Emeritus, Chemistry @ University of Waterloo)

Skills to Develop

- Recognize a unit cell.
- Use geometry to correlate atomic radius with unit cell edge length.
- Calculate parameters relevant to crystal chemistry.

The Model for Polonium Crystal Structure

If you always consider atoms to be spherical, you certainly will consider a simple cubic structure very unstable. The unit cell of such a structure is cubic, and the origin can be the center of an atom. One such sphere is placed in the diagram here, and you may complete the diagram by placing 7 more spheres at the 7 corners. We do not encounter simple cubic structures with one atom per unit cell often. However, one phase of polonium called alpha polonium has been reported to have such a structure by Beamer and Maxwell in 1946, and they re-affirm the result in 1949.

This so called **primitive** or **simple cubic** structure in the packing of spheres contains only one atom per cubic unit. do not take these words for granted, work it out yourself from the diagram shown here or one you have completed. Since correlating atomic radius with the unit cell edge of this structure is simple, we use it as a model of teaching. We ask you to calculate some relevant crystal parameters of this model.

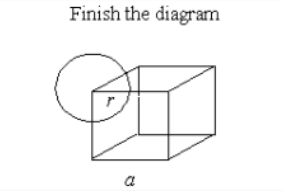
Example 1

The alpha polonium is primitive cubic with a cell edge of 335 pm. Show the following:

- **the six neighboring Po atoms form an octahedron around the central Po atom with Po−Po distances of 335 pm.**
- **the radius of the Po atom is 168 pm.**
- **the packing fraction = 0.52.**
- **the density of Po is 9.23 g/cc.**

SOLUTION

You are supposed to work on this problem. In case you have difficulty, some hints are given here to help you. These hints are given in such a way that you can work on them.



- Draw the unit cell as described in the problem. The diagram here is a good start, but complete it yourself.
- Mark R and and work out the cell edge length in R.
- You should remember the formula for volume of spheres of radius R:

$$V_{\text{sphere}} = \frac{4}{3}\pi R^3$$

- Since cell edge length $a = 2R$ $V_{\text{unit cell}} = (2R)^3 = 8R^3$
- Packing fraction $= \dfrac{V_{\text{sphere}}}{V_{\text{unit cell}}}$

$$= \frac{\pi}{6} = 0.52$$

  Derive the simplified formula above, do not let your calculator do unnecessary calculations.
- Density $= \dfrac{\left(\dfrac{209}{6.023 \times 10^{23}}\right)}{(2R)^3}$ and convert to proper units.

DISCUSSION

Packing fraction is the fraction of space occupied by the *spherical atoms* in the structure.

Confidence Building Questions

1. **Simple cubic packing is not common. The only example of this type of structure is polonium, Po. How many atoms per unit cell are there in this structure type?**

   Hint: Simple cubic structure has one atom per unit cell

   Discussion -
   The number of atoms per unit cell for structures resulting from packing are: 1 for simple cubic, 2 for bcc type, 4 for fcc type. The unit-cell edge = 2 r for this structure type.

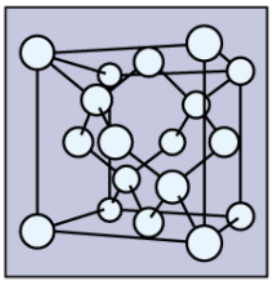
2. **Alpha polonium has a simple cubic packing, and its cell edge has been determined to be 336 pm. Its molar mass is 209. Calculate its density in g/cm^3.**
   Avogadro's number = 6.023e23 atoms/mol. (e23 means *10^{23})

   Hint: Density = 9.1 g/mL

   Discussion -
   Density = mass / volume. Use suitable formulas. Only about 52 % of the space is occupied by atoms in simple cubic packing. The density is thus not very high.

3. **Which of the following structures has the highest packing efficiency?**

   a. **primitive (simple) cubic packing**
   b. **fcc packing**
   c. **bcc packing**
   d. **diamond structure (see diagram here)**

   Hint: b.

   Discussion -
   The order of packing efficiency in the list is
   diamond < primitive cubic < bcc < hcp = fcc
   The packing efficiencies of fcc and hcp are the same, 74.05%.

4. **How many atoms are there in a body centered cubic packed structure?**

   Hint: two, 2

   Discussion -
   A more general way is to say that there are two lattice points in a body centered lattice. The point is an abstract atom or group of atoms. Generalization may be hard for you. If you find this confusing, do not worry about it.

5. **The NaCl structure belongs to a face centered lattice. How many Na^+ ions are there in a unit cell?**

   Hint: Four each of sodium and chloride ions.

   Discussion -
   The number of Na^+ or Cl^- is the same as the number of spheres in a fcc packing, $4\ Na^+$ and $4\ Cl^-$ ions, a total of 8 ions per unit cell.

Contributors

- Chung (Peter) Chieh (Professor Emeritus, Chemistry @ University of Waterloo)

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8.4: Body Centered Packing

The Model for Polonium Crystal Structure

Discussion -

```
O   O  |  If we cut the cube along a face diagonal, the arrangement of
  O    |  atoms look like the diagram on the left.
O   O  |     Thus, bd = 4 R
```

- **If the edge of the cube has a length represented by *a*, and if the radius of the atoms is *R*, express *a* as a function of *R*.**

  Hint: $a = \frac{4R}{\sqrt{3}}$

  Discussion -
  $a = {}^{4\,R}/_{\sqrt{3}}$

Contributors and Attributions

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8.4: Body Centered Packing

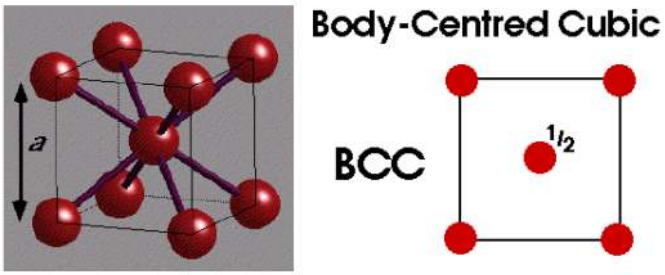
The Model for Polonium Crystal Structure

Skills to Develop

- Draw a diagram of body centred cubic (bcc) packing.
- Identify the bcc unit cell.
- Analyze the geometry of the bcc unit cell.
- Calculate geometric parameters of the bcc packing.

Body Centred Cubic Structure

At room temperatures, elements Li, Na, K, Rb, Ba, V, Cr and Fe have structures that can be described as body centre cubic (bcc) packing of spheres. The other two common ones are face centred cubic (fcc) and hexagonal closest (hcp) packing. This type of structure is shown by the diagram below.



In a crystal structure, the arrangement extends over millions and millions of atoms, and the above diagram shows the unit cell, the smallest unit that, when repeatedly stacked together, will generate the entire structure.

Actually, the unit we draw is more than a unit cell. We use the centre of the atoms (or spheres) to represent the corners of the unit cell, and each of these atoms are shared by 8 unit cells. There is a whole atom located in the centre of the unit cell.

Usually, the length of the cell edge is represented by a. The direction from a corner of a cube to the farthest corner is called body diagonal (bd). The face diagonal (fd) is a line drawn from one vertex to the opposite corner of the same face. If the edge is a, then we have:

$$fd^2 = a^2 + a^2 = 2a^2 \tag{8.4.1}$$
$$bd^2 = fd^2 + a^2 \tag{8.4.2}$$
$$= a^2 + a^2 + a^2 \tag{8.4.3}$$
$$= 3a^2 \tag{8.4.4}$$

Atoms along the body diagonal (bd) touch each other. Thus, the body diagonal has a length that is four times the radius of the atom, R.

$$bd = 4R$$

The relationship between a and R can be worked out by the Pythagorean theorem:

$$(4R)^2 = 3a^2$$

Thus,

$$4R = \sqrt{3}\, a$$

or

$$a = \frac{4}{\sqrt{3}} R$$

Recognizing these relationships enables you to calculate parameters for this type of crystal. For example, one of the parameters is the **packing fraction**, the fraction of volume occupied by the spheres in the structure

parameters is the **packing fraction**, the fraction of volume occupied by the spheres in the structure.

Example 1

What is the packing fraction for a body centred packed structure?

SOLUTION

Well, this means you should calculate the percentage of the volume occupied by the spheres in the packing.

$$\text{Packing fraction} = \frac{V_{\text{sphere}}}{V_{\text{unit cell}}} \tag{8.4.5}$$

$$\tag{8.4.6}$$

$$= \frac{2 \times \frac{4}{3}\pi R^3}{\left(\frac{4}{\sqrt{3}}R\right)^3} \tag{8.4.7}$$

$$\tag{8.4.8}$$

$$= \frac{\sqrt{3}\pi}{8} = 0.6802 \tag{8.4.9}$$

DISCUSSION

The packing fractions are

fcc and hcp	bcc	simple cubic
74.05%	68.01%	52%

Confidence Building Questions

1. **How many atoms are there per unit cell for the bcc structure model?**

   Hint: Two, 2

   Discussion -

   Recall the number of atoms per unit cell in a primitive cubic packing.
   Only 1/8 th of each atom in the corners belongs to the cell, and there are 8 such atoms. The one in the centre of the cell entirely belongs to the unit cell.

2. **If the radius of the atoms is *R*, how many times *R* is equal to the body diagonal *bd* of the unit cell?**

   Hint: $bd = 4R$

   Discussion -

   The atoms touch each other along the body diagonal directions.

3. **If the edge of the cube has a length represented by *a*, what is the face diagonal of the cube as a multiple of *a*?**

   Hint: $fd = \sqrt{2}\,a$

   Discussion -

   $fd^2 = a^2 + a^2 = 2a^2$

4. **If the edge of the cube has a length represented by *a*, what is the body diagonal of the cube as a multiple of *a*?**

   Hint: $bd = \sqrt{3}\,a$

   Discussion -

$$bd^2 = fd^2 + a^2 \tag{8.4.10}$$

$$= a^2 + a^2 + a^2 \tag{8.4.11}$$

$$= 3a^2 \tag{8.4.12}$$

5. **If the edge of the cube has a length represented by *a*, what is the volume of the cell in terms of *a*?**

Hint: Cubic of a

Discussion -
Area of face $= a^2$

6. **In the bcc packing, atoms along the body diagonal (*bd*) touch each other. If the atomic radius is *R*, express *bd* in terms of *R*.**

   Hint: $bd = 4R$

   Discussion -

```
O   O  |  If we cut the cube along a face diagonal, the arrangement of
  O    |  atoms look like the diagram on the left.
O   O  |     Thus, bd = 4 R
```

7. **If the edge of the cube has a length represented by *a*, and if the radius of the atoms is *R*, express *a* as a function of *R*.**

   Hint: $a = \dfrac{4R}{\sqrt{3}}$

   Discussion -
   $a = {}^{4\,R}/_{\sqrt{3}}$

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8.5: Metal Structures

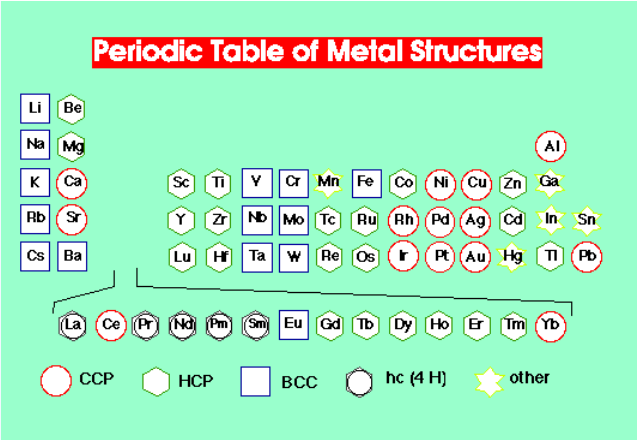


Figure 1: In the above diagram, the ccp (fcc) structures are represented by a red circle, whereas the hcp structures are represented by a black hexagon.

Copper is the most common mentioned metal that has the fcc structure. This element is one of the noble metals. It has been widely used for door knobs and other tools, and has been widely recognized. Yet, most noble metals (Cu, Ag, Au, Ni, Pd, Pt, Rh, and Ir) have fcc type structures. Among the group 2 elements, only Ca and Sr have the fcc structure, whereas Be and Mg have hcp structures. So do Zn, Cd, Sc, Y, Lu, Ti, Zr, Hf, Tc, Re, Ru, Os and most rare earth elements. These are mentioned to bring your attention to these two common types of structures, and you are encouraged to at least be able to give a few examples for each type.

Amazingly, the hcp and fcc structure are very similar in many aspects, but nature knows best. The structures adopted by various metals occur by their design. When crystallization takes place, the atoms arrange themselves according to their structure types.

Exercises 1

a. Copper has a *specific gravity* of 8.92; evaluate its atomic radius.
b. The atomic radius of silver Ag is listed as 145 pm. Evaluate its density.

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8.5: Metal Structures

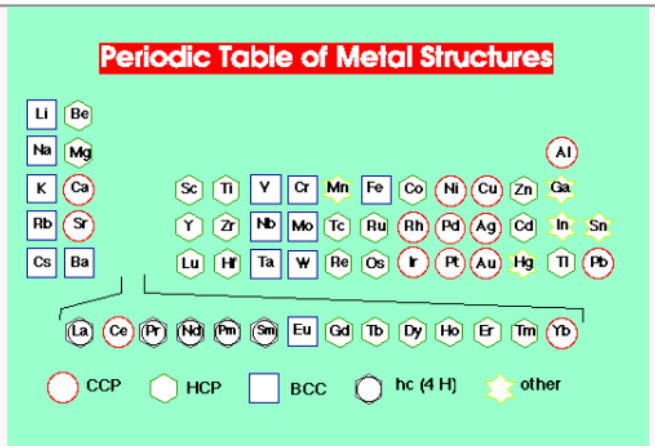


Figure 1: In the above diagram, the ccp (fcc) structures are represented by a red circle, whereas the hcp structures are represented by a black hexagon.

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Amazingly, the hcp and fcc structure are very similar in many aspects, but nature knows best. The structures adopted by various metals occur by their design. When crystallization takes place, the atoms arrange themselves according to their structure types.

Example 1

Gold has a very high density, ρ, of 19.3 g/mL, and it has the fcc structure. If the gold atoms were spheres as modeled by the fcc structure, what is the atomic radius?

SOLUTION

Assume the radius of gold *spheres* to be *r*, and the edge of the face centered unit cell to be *a*. There are four gold (atomic mass 197.0, Avogadro's number = 6.023×10^{23}) atoms per unit cell, thus

$$\rho = \frac{4 \times 197.0}{6.023 \times 10^{23} \times a^3} \tag{8.5.1}$$

$$= 19.3\ g/cm^3 \tag{8.5.2}$$

$$a = 4.0774 \times 10^{-8}\ cm \tag{8.5.3}$$

$$= 2 \times 2^{1/2}\ r \tag{8.5.4}$$

$$r = 1.442 \times 10^{-8}\ cm$$

Please work out these formulas and numbers yourself.

DISCUSSION

A handbook did give the radius of gold as 144 pm (1 pm = 10^{12}).

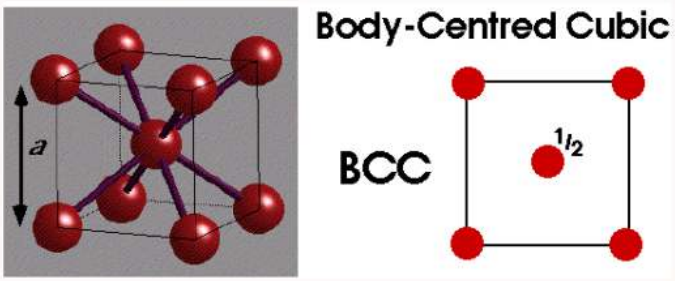
Exercises 1

a. Copper has a *specific gravity* of 8.92; evaluate its atomic radius.

b. The atomic radius of silver Ag is listed as 145 pm. Evaluate its density.

What metals have the body centered cubic structure?

Alkali metals (Li, Na, K, Rb, and Cs) all have the body centered cubic (bcc) structure. In addition, the vanadium and chromium groups also have the bcc structure. Furthermore, at room temperature, iron has a bcc structure.



This type of structure has two atoms per unit cell, and it is slightly less densely packed than the fcc or hcp types as shown by Example 1.

Example 2

What is the fraction of the volume occupied by spheres for a bcc type structure?

SOLUTION

Assume the radius of *spheres* be r, and the edge of the body centered unit cell to be a. There are two spheres per unit cell, thus

$$body\ diagonal = 4r \tag{8.5.5}$$

$$= 3^{1/2}a \tag{8.5.6}$$

$$a = \frac{4r}{3^{1/2}}$$

$$V_{sphere} = \frac{4}{3}\pi r^3$$

$$V_{cell} = a^3 = \frac{64 \times r^3}{3^{3/2}}$$

$$\text{Fraction of volume occupied by spheres} = \frac{2 \times V_{sphere}}{V_{cell}} \tag{8.5.7}$$

$$= \frac{3^{1/2}\pi}{8} \tag{8.5.8}$$

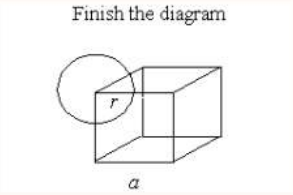
$$= 0.68 \text{ or } 68\% \tag{8.5.9}$$

DISCUSSION

The fraction of 0.68 is slightly less than those (0.74) of closest packed structures. Thus, the bcc structures are less densely packed according to the hardsphere model.

Does any metal adopt the simple cubic structure?

Polonium (Po) has been reported to have a simple cubic crystal structure. From a packing point of view, this type of arrangement is not stable, and this is not common. The cubic unit cell contains only one sphere, and the edge length is exactly equal to the diameter of the sphere. In the diagram, we choose the origin to be the center of an atom, but if you choose the origin to be the center among 8 spheres, your cube encloses a whole atom. You can work out the fraction of space occupied by spheres in such an arrangement to be $\pi/6$ (0.52), which is much less than the bcc structure type.



What are the features of rare earth metals?

If you go back to the periodic table of structure types, you will see that the rare earth elements have fcc (ccp), hcp, bcc, and another type marked by hc (4 H). In other words, these 14 elements exemplify many types of structures. We have covered the other types than the hc (4 H) type pretty well. Actually, the hc (4 H) type has a complicated packing sequence such as ABAC, ABCB, etc. That is why they are designated as (4 H). Actually, the structure of Sm (samarium) has a very complicated sequence of ACACBCBAB ACACBCBAB ....

Questions

1. **What is the volume of a sphere with a radius of 1.0 cm?**

   Hint: 4.19 cc

   Skill -
   Give the formula of volume for a sphere with radius r.

2. **What is the volume of a cube with an edge length of 2.0 cm?**

   Hint: 8.0 cc

   Discussion
   The fraction of space occupied by spheres in a simple cubic arrangement is 4.19/8.0 = 0.52.

3. **What is the number of nearest neighbours in a bcc structure?**

   Hint: 8

   Skill -
   Be prepared to answer simple "matter of fact" questions regarding structure types.

4. **From the previous question, you know that there are 8 nearest neighbours in a bcc structure. The next nearest neighbor is at a distance *a* (unit cell edge length). How many neighbours have a distance *a* from an atom of the bcc type structure?**

   Hint: 6

   Skill -
   Be prepared to answer simple "matter of fact" questions regarding structure types.

5. **Give three metals that have the bcc structure.**

   Hint: Any three of: Na, K, Fe (iron), Pb (lead) etc.

   Discussion
   Give some examples for the ccp (fcc) and hcp types.

Contributors

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8.6: Solids

Representation of 3-dimensional structures should usually be made using models, and their representation on a flat surface is difficult. For simplicity, we use a 2-dimensional pattern (plane) to illustrate a 2-dimensional (planar) crystal structure.

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This pattern or *crystal structure* is generated by using a unit marked by the centers of any four @ or # signs. The choice is up to you in this case. Such a unit is called a primitive unit. The pattern has a square (or rectangular on some screens) appearance, and to preserve the square, we may use a square unit of

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# @ #           @ # @
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as our **unit cell**. Such choices result in having two @ and # per unit cell, and these are called **centered cells**.

Thus, if we know the arrangement of a unit cell, we can use our imagination to build a crystal structure, or use symbols or models to represent a crystal structure. Since each pattern has features shared by many structures, often such a pattern is called a **lattice**. For example, the diamond, zinc blende, wurtzite, and NaCl structures have been called lattices; however, the word lattice has a more formal definition by crystal physics and chemists. The above site gives a gallery of lattices.

Definition: Crystals

Inorganic Chemistry by Swaddle defined crystals as packed regular arrays of atoms, ions, or molecules in a pattern repeated periodically *ad infinitum*.

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8.6: Solids

Discussion Questions

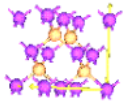
- What is a crystal and what is the meaning of crystal structure?
- What are X-rays and how do they help us investigate crystals?
- What are closest packed structures?

You all know that solid, liquid, and gas are the three states of matter. These states are also known as **phases**, and often a substance may exist in a few forms of solid, and each form is also a phase. As the temperature increases, a solid usually melts at some temperature. During the melting process, the temperature does not change as long as there are liquid and solid present. The energy absorbed by a solid during the melting process is called **enthalpy of fusion**. When all solid is melted, the liquid temperature will increase as it absorbs heat. Of course, vapour pressure of the liquid increases with temperature. When the vapour pressure is the same as the atmosphere, the liquid boils. The temperature at which the liquid and gas phases are in equilibrium is called the **boiling point**. A solid also sublimates into a vapour. The changes among vapour, liquid, and solid are called **phase transitions**.

A **glass state** is also seen as a solid, but from a structural point of view, a glass is really a frozen liquid, because the molecules do not have long range regular and periodic arrangement. On this web page, we concentrate on crystalline solids. We encounter solids all the time, and solids are used both in everyday life as well as technology. Metals, oxides, cement (concrete), diamond, minerals, and silicon devices are some of the important materials, and we must equip ourselves to deal with and understand them.

What is a crystal and what is the meaning of crystal structure?

At sufficiently low temperature, a material usually becomes a solid or crystal, in which the arrangement of atoms are periodic over a very large range. All solids occupy a volume, and the arrangement of atoms, chemical bonds, or molecules in them are in a 3-dimensional space. These arrangements are called their **crystal structures**. A portion of such an arrangement is animated here to show various orientations of this pattern.



Representation of 3-dimensional structures should usually be made using models, and their representation on a flat surface is difficult. For simplicity, we use a 2-dimensional pattern (plane) to illustrate a 2-dimensional (planar) crystal structure.

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```

This pattern or *crystal structure* is generated by using a unit marked by the centers of any four @ or # signs. The choice is up to you in this case. Such a unit is called a primitive unit. The pattern has a square (or rectangular on some screens) appearance, and to preserve the square, we may use a square unit of

```
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@ # @    or    # @ #
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```

as our **unit cell**. Such choices result in having two @ and # per unit cell, and these are called **centered cells**.

Thus, if we know the arrangement of a unit cell, we can use our imagination to build a crystal structure, or use symbols or models to represent a crystal structure. Since each pattern has features shared by many structures, often such a pattern is called a **lattice**. For example, the diamond, zinc blende, wurtzite, and NaCl structures have been called lattices; however, the word lattice has a more formal definition by crystal physics and chemists. The above site gives a gallery of lattices.

Definition: Crystals

Inorganic Chemistry by Swaddle defined crystals as packed regular arrays of atoms, ions, or molecules in a pattern repeated periodically *ad infinitum*.

What are X-rays and how do they help us investigate crystals?

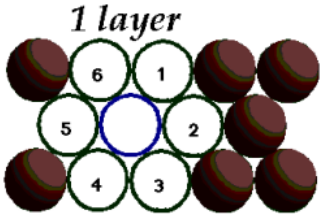
Like light, X-rays are electromagnetic radiation with wavelengths in the order of inter atomic distances. Thus X-rays are diffracted by crystals. The diffraction patterns of a crystal reveal the symmetry, geometry, and the measures of unit cell parameters. The details are rather complicated to learn, and we leave them out at this point.

However, it is important to understand what X-rays are by working on a problem related to X-rays. You are asked to calculate the frequencies and photon energies of X-rays of certain wavelengths. These are compared to photons of ordinary light. The equation required for this comes from Max Planck's postulates that lights are emitted one bundle of energy at a time. The energy E of the photon is proportional to the frequency v of the photon, and the proportional constant is h, now known as the Planck constant.

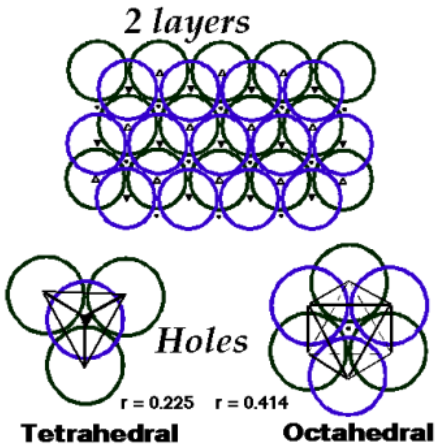
$$E = hv \tag{8.6.1}$$

What are closest packed structures?

We do not know what the shape of an atom is, but we often use a sphere to represent an atom. For example, the common crystal structures of metals can be represented by packing of spheres. These models illustrate not only the lattice types, but also explain the properties. When you put spheres on a flat surface, you have got a layer as shown on the right here. Note that an atom is surrounded by six atoms on the same layer.

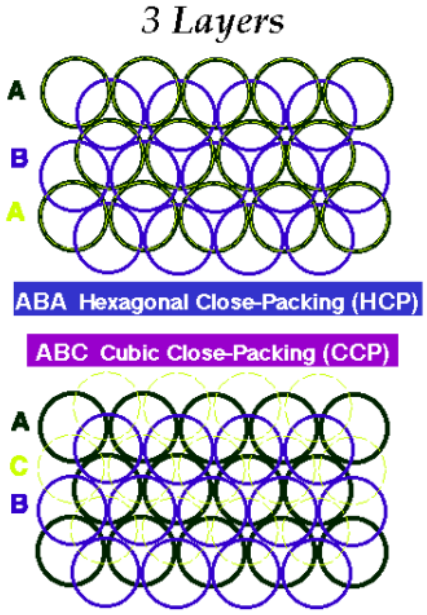


On top of this layer, you can pack a second layer. As you do so, please note that you have created two typical sites or holes called **octahedral** and **tetrahedral** sites. These sites accommodates spheres up to 0.414 and 0.225 times the radii of the sphere or atom, r_{atom}.



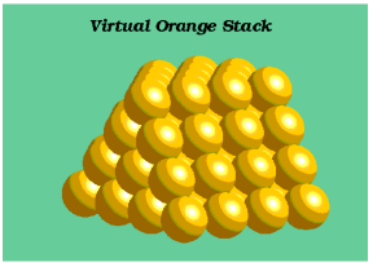
A side view showing the spheres (P), tetrahedral sites (T) and octahedral sites (O) is also shown here.

When you put the third layers on, there are two possible options. The 3rd layer can go directly on top of the first layer. In such an arrangement, you produce an ABAB... type of sequence. Such a sequence is called a **hexagonal closest packing (hcp)**. A second option is to place a layer that is not directly on top of A nor on top of B. We call such a location C. Thus, we produce an ABCABC... sequence. Such a sequence belongs to the cubic type, and is usually called **face-centered closest packing (fcc)**.



We demonstrated these types of packing in lectures, and asked you to evaluate the radii of the small balls that fit tightly in the octahedral and tetrahedral sites respectively in terms of r_{atom}.

If you do not have a set of models, take a good look at a pile of oranges in a super market on your next shopping trip. Dr. Heyes has an illustration shown here. This pile is the cubic arrangement.



The Crystal Lattice and Structures gives a dynamic view on these structures.

Example 1

Assume the radius of the ball used for closest packing as R and the radius of a small ball that just fits in the octahedral site as r. What is the relationship between R and r?

SOLUTION

If we assume the 6 balls forming the octahedral site to be located on the two directions of a set of Cartesian coordinates in such a manner that each ball touches four others, the coordinates will be (r+R, 0, 0), (-r-R, 0, 0), (0, r+R, 0), (0, -r-R, 0), (0, 0, r+R), and (0, 0, -r-R).

The ball touches along the edges. Therefore, we have

$$2(r+R)^2 = (2R)^2$$

DISCUSSION

Show that r = 0.414 R

Example 2

Assume the radius of the ball used for closest packing as R and the radius of a small ball that just fits in the tetrahedral site as r. What is the relationship between R and r?

SOLUTION

A tetrahedral site can be modeled by having the four balls of radius R located at alternate corners of a cube. The balls touch each other along the faces of the cube, whose edges have a length of a. Thus,

$$2a^2 = (2R)^2$$

The body diagonal of the cube $= 2(r+R)$. Thus, we have

$$3a^2 = (2(r+R))^2$$

and therefore

$$a = 2^{1/2}R = \frac{2(r+R)}{3^{1/2}}$$

DISCUSSION

Show that r = 0.215 R

Example 3

What fraction of the volume is occupied by spheres in an fcc type closest packing of spheres?

SOLUTION

Let the edge of a unit cell of the fcc closest packing be a, and the radius of the spheres be R. Then a = $8^{1/2}R$. There are four spheres per unit cell, and the volume occupied by each sphere is V_{sphere}. The volume of the unit cell is V_{cell}. We have these relationships

$$a = 8^{1/2}R$$

$$\mathrm{V_{sphere}} = \frac{4}{3}\pi R^3$$

$$\mathrm{V_{cell}} = \mathrm{a^3} = 16 \times 2^{1/2}\mathrm{R^3}$$

$$\text{Fraction of volume occupied by spheres} = \frac{4 \times \mathrm{V_{sphere}}}{\mathrm{V_{cell}}}$$
$$= \frac{\pi}{3 \times 2^{1/2}}$$
$$= 0.74 \text{ or } 74\%$$

Please work out these relationships with a diagram. There is no point remembering these formulas, except the formula for the volume of a sphere.

DISCUSSION

Show that the fraction of volume occupied by spheres in an hcp arrangement is 0.74.

Example 4

What is a unit cell of hcp structure? What are the relationships of the unit cell parameters and the atomic radii? What is the fraction of volume occupied by spheres?

SOLUTION

The hcp unit cell is outlined by the two top diagrams of the figure below.

A unit cell can be constructed in such a way that it has two base vectors of a = $2R$, extended by 120 degrees $(2\pi/3)$, R

being the radii of the spheres. The third c axis is perpendicular to both a's. It can be shown that for ideal *hcp* structures, $c = a\sqrt{\frac{8}{3}}$. The volume of the unit cell:

$$V_{cell} = a \times a \times \sin\left(\frac{2\pi}{3}\right) \times c \tag{8.6.2}$$

$$= (2R)^2 \times \frac{\sqrt{3}}{2} \times \sqrt{\frac{8}{3}} \times 2R \tag{8.6.3}$$

$$= 8\sqrt{2} \times R^3 \tag{8.6.4}$$

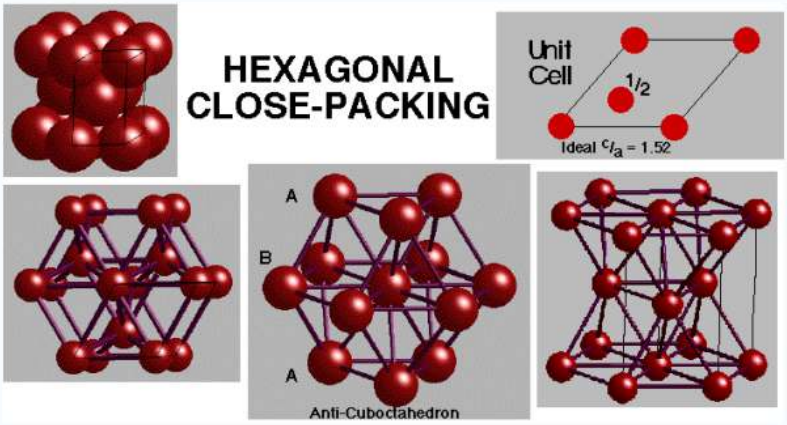
$$V_{sphere} = \frac{4}{3}\pi R^3$$

$$\text{Fraction of volume occupied by spheres} = \frac{2 \times V_{sphere}}{V_{cell}}$$

$$= \frac{\pi}{3 \times 2^{1/2}}$$

$$= 0.7405 \text{ or } 74\%$$

Note that there are two spheres per unit cell, and the volume occupied by the spheres is $\frac{8}{3}\pi R^3$.



Types of structures

One of the most common structure classifications is the Strukturbericht Types. Since the study of crystal began a long time ago, various notations have been used to represent types of crystal structures. This link provides a detailed index.

Questions

1. **How many spheres are in contact with a sphere deep in a pile of closest packed spheres?**

   Hint: 12

   Skill -
   Be able to construct a closest packed array of spheres and answer some specific questions. There are 12 neighbours in both the fcc and the hcp types of packing.

2. **What is the ratio *O***

$$O = \frac{\text{number of octahedral sites}}{\text{number of spheres}}$$

   in an infinite array of closest packed spheres?

   Hint: 1

   Skill -

Skill -

Realize that a structure with closest packed of anion $\mathbf{X}$ with all the octahedral sites occupied by $\mathbf{A}$ has a stoichiometry of $\mathbf{AX}$.

3. **What is the ratio *T***

$$T = \frac{\text{number of tetrahedral sites}}{\text{number of spheres}}$$

in an infinite array of closest packed spheres?

Hint: 2

Skill -

Realize that a structure with closest packed of anion $\mathbf{X}$ with all the tetrahedral sites occupied by $\mathbf{A}$ has a stoichiometry of $\mathbf{A_2X}$.

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8.7: Sphere Packing

Learning Objectives

- Use the packing of spheres to model the fcc crystal structure.
- Practice solving problems related to crystal structures.

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8.7: Sphere Packing

Skills to Develop

- Use the packing of spheres to model the fcc crystal structure.
- Practice solving problems related to crystal structures.

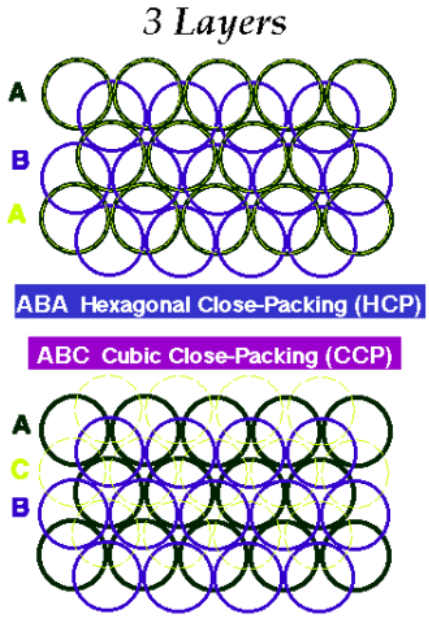
Closest Packing and Crystal Structures

We use models for sciences. Some models are mathematical formulas, some are theories, and some are physical representations.



The arrangements of molecules, atoms or ions are called **crystal structures** . The packing of spheres is often used to model metal crystal structures. Atoms, molecules, and ions are too small, so we use balls and sticks to represent them. These models enable us to *see* the invisible world of atoms and molecules.

There are two types of closest packing, the hexagonal and the face-centered closest packing, and they are called hcp and fcc (or ccp) respectively. The hcp packing has an ABABAB... two-layer sequence, where A and B represent the location of the layers. In other words, the third layer is exactly above the first layer in hcp. The fcc packing has a three-layer sequence, ABCABC... rather than the two-layer sequence of the hcp. The two types of packing are shown below:



Since these structures have been discussed in Solids, work on the questions below.

Confidence Building Questions

1. **There are two types of closest packing of spheres: face-centered-cubic (fcc with the ABCABC... sequence) and the hexagonal closest packing (hcp with the ABAB... sequence) How many neighbors are there for a sphere in these packings?**

   Hint: 12

   Skill -
   Draw diagrams of closest packing and draw the polyhedra of neighbouring atoms. One each for the fcc and hcp type.

2. **If the radii of the spheres are 1.5 Å, what will be the distance between centers of neighboring spheres?**

   Hint: The bond distance is 3.0 Å

Discussion -
The covalent radius is half the covalent bond length between two atoms of the same element.

3. **If the radius of an atom is 123 pm, calculate the volume of the atom. Assume the atom to be a sphere.**

   Hint: V = 7.79e6 cubic pm

   Discussion -
   The volume of a sphere with radius r is 4/3 π r^3. The chemical literature uses the unit Angstrom or Å (= 10^{-10} m). 1 Å = 100 pm.

4. **Nickel atoms pack in a fcc lattice in its crystal structure. Its density is 8.90 g/mL. The unit cell edge is 352 pm. Its molar mass is 58.7 g/mol. Calculate Avogadro's number from these data.**

   Hint: The calculated Avogadro's number is 6.023e23

   Discussion -
   You can almost guess Avogadro's number, but make sure you know how to calculate it from the given data.

5. **The crystal structure of calcium is face centered cubic. Its cell edge is 557 pm. Calculate the radius (in pm) of the calcium atoms, assuming they are spheres.**

   Hint: 197 pm

   Discussion -
   Find the relationship: $2 \times \sqrt{2} \times \text{radius of Ca} = \text{edge}$.

6. **The crystal structure of calcium is face centered cubic. Its cell edge is 557 pm. Calculate the density of Ca in g /cm^3 Atomic mass, Ca, 40.08; Avogadro's number 6.022e23**

   Hint: 1.54 g/mL

   Discussion -
   mass = 4 * 40.08 /6.023e23 g
   volume = (557e-10 cm)^3
   density = mass / volume.

7. **The density of silver (atomic mass: Ag, 107.9) is 10.6 g/cm^3, and it has a face centered cubic structure. Calculate the edge of the cubic unit cell in pm. (Avogadro's number 6.022e23)**

   Hint: a = 400 pm

   Discussion -
   Volume of cell = mass / density, and there are 4 atoms per unit cell.

   Calculate the number of atoms per unit cell from the density and a cell edge of 408 pm.

8. **Iron has a body-centered-cubic structure, with unit cell edge of 287 pm. Calculate its density in g / cm^3.**
   Atomic mass, Fe, 55.85; Avogadro's number 6.022e23

   Hint: density = 7.85 g/mL

   Discussion -
   Mass = 2 * 55.85/6.022e23 = 1.855e-22 gm
   Volume = 2.36e-23 cm^3
   Density = ?
   Iron transforms from a bcc structure to fcc structure at 910 C. The volume shrinks as the structure transforms from bcc to fcc; explain!

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8.8: Tetrahedral and Octahedral Sites

Learning Objectives

- To construct a model for the tetrahedral and octahedral holes of closest packing.
- To calculate geometric properties of the model.
- Apply these properties to interpret crystal chemistry.

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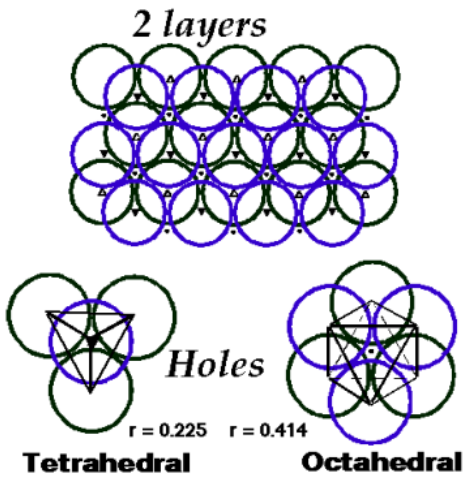
8.8: Tetrahedral and Octahedral Sites

Skills to Develop

- To construct a model for the tetrahedral and octahedral holes of closest packing.
- To calculate geometric properties of the model.
- Apply these properties to interpret crystal chemistry.

Tetrahedral and Octahedral Sites in Closest Packing

Tetrahedral and octahedral sites in closest packing can be occupied by other atoms or ions in crystal structures of salts and alloys. Thus, recognizing their existence and their geometrical constraints helps the study and interpretation of crystal chemistry. The packing of spheres and the formation of tetrahedral and octahedral sites or holes are shown below.



Whenever you put four (4) spheres together touching each other, you've got a tetrahedral arrangement of spheres. The space in the center is called a **tetrahedral site**. The **octahedral site** is formed by six spheres. These sites are also called **holes** in some literature, and they are shown in the diagrams above.

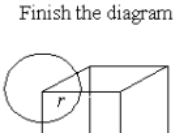
Example 1

What is the radius of the largest sphere that can be placed in a tetrahedral hole without pushing the spheres apart?

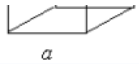
Suggestion for Solution

To solve a problem of this type, we need to construct a model for the analysis. The following statement explicitly tells you how to construct such a model.

Use the diagram shown here as a starting point, and construct a tetrahedral arrangement by placing four spheres of radius *R* at alternate corners of a cube. Once complete, work out the following:



- What is the length of the face diagonal *fd* of this cube in terms of *R*?



Since the spheres are in contact at the centre of each cube face, $fd = 2R$.

- What is the length of the edge for such a cube, in terms of *R*?
  Cube edge length $a = \sqrt{2}\,R$
- What is the length of the body diagonal *bd* of the cube in *R*?
  $bd = \sqrt{6}\,R$
- Is the center of the cube also the center of the tetrahedral hole?
  Yes, but do you know why?
- Let the radius of the tetrahedral hole be *r*. Express *bd* in terms of *R* and *r*.
  If you put a small ball there, it will be in contact with all four spheres. Thus,

$$bd = 2(R+r)$$

$$r = \frac{2.45R}{2} - R \tag{8.8.1}$$
$$= 1.225R - R \tag{8.8.2}$$
$$= 0.225R \tag{8.8.3}$$

- What is the radius ratio of tetrahedral holes to the spheres?

$$\frac{r}{R} = 0.225$$

Example 2

What is the radius of the largest sphere that can be placed in an octahedral hole without pushing the spheres apart?

Solution

The octahedral hole is located at the center of any four spheres that form a square. If we represent the radius of a ball fitting in the octahedral holes by *r*, and the radius of the sphere as *R*, then we have the relationship:

$$r + R = \left(\frac{1}{\sqrt{2}}\right)(2R)$$

$$\frac{r}{R} = \sqrt{2} - 1 \tag{8.8.4}$$
$$= 0.414 \tag{8.8.5}$$

The implication:

Pure geometric consideration shows that only small balls fit in the tetrahedral holes of packed spheres. However, if the radii of cations are smaller than 0.225 *R*, the structure of having ions in the tetrahedral site is unstable. The anions may be pushed apart slightly to reduce the repulsion by fitting a cation in the tetrahedral site.

For ionic crystal structure consideration, the cations are usually smaller than anions. Cations fitting into the tetrahedral sites cannot be smaller than 0.225 R. Usually, most ions are slightly larger than 0.225 R, but smaller than 0.414 R. In such cases, the cation coordination is tetrahedral, and a typical structure is **ZnS**, although covalent bonding is also involved in **ZnS**. The animated diagram is a model of **ZnS** structure.

When the cation radii are greater than or equal to 0.414 *R*, but less than 0.732 *R*, the cations occupy the octahedral sites. Sodium chloride is one such structure, and it serves as an important structure type.

If the cations are large such that $r \geq 0.732\ R$, the cation will have a cubic coordination of 8. The structure is typified by **CsCl**.

The above discussion is summarized below:

r/R	0.225	between	0.414	between	0.732	<
Coordination & number	"	tetrahedral 4	"	octahedral 8	"	cubic 8
Typical	"	ZnS	"	NaCl	"	CsCl

structure

Discussion

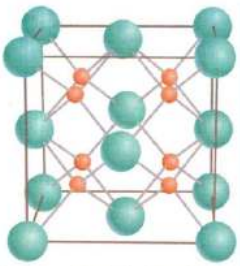
What is the radius of the largest sphere that can be placed in an octahedral hole without pushing the spheres apart? (Answer: 0.731)

Example 3

Is there a structure in which all the tetrahedral sites are occupied by a different type of atoms or ions?

Solution

The outline of a unit cell for PuO_2 is shown here, and all the tetrahedral sites are occupied by small O^{2-} ions.



Face-centered-cubic (fcc) crystal structure of PuO_2 (Pu atoms in green, O atoms in red).

Actually, the crystal structure of UO_2 has the same structure as PuO_2. A common salt CaF_2 also has the same structure, but the fluoride ions are by no means small compared to the calcium ions. However, the Pu^{4+} and U^{4+} ions are large compared to the oxygen ions.

Questions

1. **In the $NaCl$ structure, which ion is larger?**

   Hint: The chloride ion is larger.

   Discussion -
   Usually anions are larger than cations if they have similar electronic configurations. In this case, the Na^+ and Cl^- ions have electronic configurations of Ne and Ar respectively. We already know that Ar is larger than Ne.

2. **The ionic radii of Na^+ and Cl^- ions are 91 and 181 pm respectively. Calculate the radii ratio of cation to anions.**

   Hint: 91/181 = 0.5

   Discussion -
   Since the ratio of 0.5 is between 0.414 and 0.732, the sodium ion prefers an octahedral coordination.

3. **The ionic radii of K^+ and I^- ions are 133 and 220 pm respectively. What type of structure should KI have?**

   Hint: The ratio = 133/220 = 0.605; the $NaCl$ structure type prevails.

   Discussion -
   Structure of KI is indeed $NaCl$ type, with a = 706 pm. The data agree with the ionic radii of the ions: 706 = 2 (133 + 220).

4. **The ionic radii of Cs^+ and Cl^- ions are 167 and 181 pm respectively. What type of coordination should Cs^+ have?**

   Hint: The ratio = 167/181 = 0.923; Cs ion has cubic coordination.

   Discussion -
   The $CsCl$ structure is an important type of structure. The diagram shows a unit cell of the $CsCl$ structure.

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CHAPTER OVERVIEW

9: Electronic Properties of Materials - Superconductors and Semiconductors

Learning Objectives

- Explain the physical basis of the Hubbard and Mott models of metal-insulator transitions.
- Understand why good superconductors derive from bad metals.
- Know the structures and the periodic trends in band gaps and colors of semiconductors.
- Obtain the band gap of an intrinsic semiconductor from the temperature dependence of the conductivity.
- Predict the doping type when impurities or defects are introduced into a semiconductor.
- Correlate the band picture and Fermi level with n- or p-type doping.
- Understand the physical principles of operation of diodes, LEDs, solar cells, and FETs.
- Explain the differences in structures and electronic properties of crystalline and amorphous semiconductors.

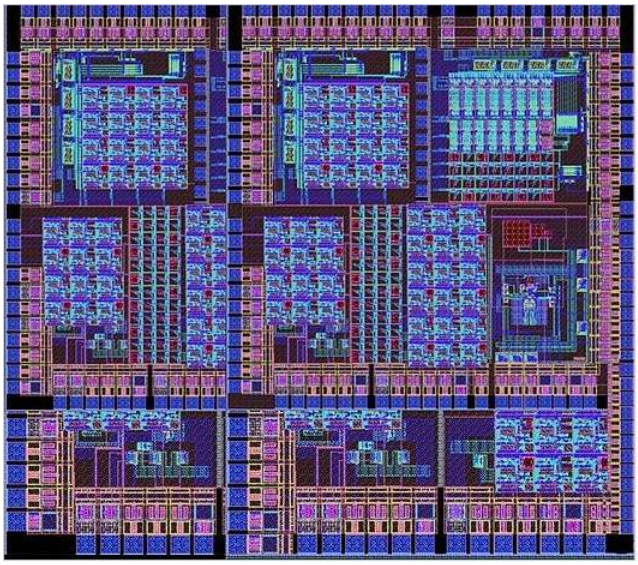
The band model (like MO theory) is based on a *one-electron* model. This was an approximation we made at the very beginning of our discussion of MO theory: we used hydrogen-like (one-electron) solutions to the Schrodinger equation to give us the shapes of s, p, d, and f atomic orbitals. In a one-electron atom, these orbitals are degenerate within a given shell, and the energy differences between, e.g., 2s and 2p orbitals arise only when we consider the energy of an electron in the field of other electrons in the atom. Moving from atoms to molecules, we made linear combinations to generate one-electron molecular orbitals (and, in solids, one-electron energy bands). But as in multi-electron atoms, life is not so simple for real molecules and solids that contain many electrons. Electrons repel each other and so their movement in molecules and in solids is ***correlated***.

9.1: Prelude to Electronic Properties of Materials - Superconductors and Semiconductors
9.2: Bonding in Metals
9.3: Band Theory of Solids
9.4: Semiconductors and Doping
9.5: Resistivity
9.6: Metal-Insulator Transitions
9.7: Superconductors
9.8: Periodic Trends- Metals, Semiconductors, and Insulators
9.9: Semiconductors- Band Gaps, Colors, Conductivity and Doping
9.10: Semiconductor p-n Junctions
9.11: Diodes, LEDs and Solar Cells
9.12: Amorphous Semiconductors
9.13: References

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9.1: Prelude to Electronic Properties of Materials - Superconductors and Semiconductors

In Chapter 6 we developed an energy band picture for metals, starting from atomic orbitals and building up the molecular orbitals of the solid metallic crystal. This treatment gave us a useful picture of how electrons behave in metals, moving at very fast speed between scattering events, and migrating in an electric field at a slow drift velocity. It also taught us that a metal is something with a partially filled band, meaning that the Fermi level cuts through one of its bands of orbitals. An insulator or a semiconductor has a similar band picture, except that the bands are either completely full or completely empty. In this case the Fermi level lies in the gap between fully occupied and unoccupied bands. We will see in this chapter that the properties of semiconductors (along with their useful electronic applications) depend on the addition of small amounts of impurities ("dopants") that change the position of the Fermi level, resulting in conduction by electrons or "holes."



Modern integrated circuits contain billions of nanoscale transistors and diodes that are essential for logic and memory functions. Both kinds of devices rely on junctions between crystalline silicon regions that contain a few parts per million of boron or phosphorus impurities.

While the band picture works well for most crystalline materials, it does not tell us the whole story of conduction in solids. That is because the band model (like MO theory) is based on a *one-electron* model. This was an approximation we made at the very beginning of our discussion of MO theory: we used hydrogen-like (one-electron) solutions to the Schrödinger equation to give us the shapes of s, p, d, and f atomic orbitals. In a one-electron atom, these orbitals are degenerate within a given shell, and the energy differences between, e.g., 2s and 2p orbitals arise only when we consider the energy of an electron in the field of other electrons in the atom. Moving from atoms to molecules, we made linear combinations to generate one-electron molecular orbitals (and, in solids, one-electron energy bands). But as in multi-electron atoms, life is not so simple for real molecules and solids that contain many electrons. Electrons repel each other and so their movement in molecules and in solids is ***correlated***. While this effect is weak in a "good" metal such as sodium - where the wavefunctions are highly delocalized - it can be quite important in other materials such as transition metal oxides. Correlated electron effects give rise to **metal-insulator transitions** that are driven by small changes in temperature, pressure, or composition, as well as to **superconductivity** - the passage of current with zero resistance at low temperatures. In this chapter we will develop some simple models to understand these interesting and important electronic properties of solids.

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9.2: Bonding in Metals

Bonding in metals and semiconductors can be described using band theory, in which a set of molecular orbitals is generated that extends throughout the solid. The primary learning objective of this Module is to describe the electrical properties of solid using band theory.

Band Theory

To explain the observed properties of metals, a more sophisticated approach is needed than the electron-sea model commonly described. The molecular orbital theory used to explain the delocalized π bonding in polyatomic ions and molecules such as NO_2^-, ozone, and 1,3-butadiene can be adapted to accommodate the much higher number of atomic orbitals that interact with one another simultaneously in metals.

In a 1 mol sample of a metal, there can be more than 10^{24} orbital interactions to consider. In our molecular orbital description of metals, however, we begin by considering a simple one-dimensional example: a linear arrangement of n metal atoms, each containing a single electron in an s orbital. We use this example to describe an approach to metallic bonding called band theory, which assumes that the valence orbitals of the atoms in a solid interact, generating a set of molecular orbitals that extend throughout the solid.

One-Dimensional Systems

If the distance between the metal atoms is short enough for the orbitals to interact, they produce bonding, antibonding, and nonbonding molecular orbitals. The left portion of Figure 9.2.1 shows the pattern of molecular orbitals that results from the interaction of ns orbitals as n increases from 2 to 5.

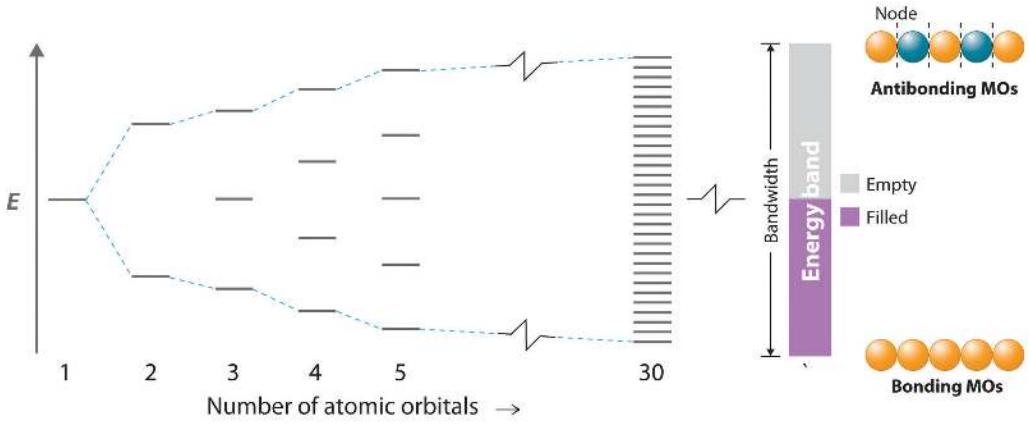


Figure 9.2.1: The Molecular Orbital Energy-Level Diagram for a Linear Arrangement of n Atoms, Each of Which Contains a Singly Occupied s Orbital. As n becomes very large, the energy separation between adjacent levels becomes so small that a single continuous band of allowed energy levels results. The lowest-energy molecular orbital corresponds to positive overlap between all the atomic orbitals to give a totally bonding combination, whereas the highest-energy molecular orbital contains a node between each pair of atoms and is thus totally antibonding.

As we saw previously, the lowest-energy orbital is the completely bonding molecular orbital, whereas the highest-energy orbital is the completely antibonding molecular orbital. Molecular orbitals of intermediate energy have fewer nodes than the totally antibonding molecular orbital. The energy separation between adjacent orbitals decreases as the number of interacting orbitals increases. For n = 30, there are still discrete, well-resolved energy levels, but as n increases from 30 to a number close to Avogadro's number, the spacing between adjacent energy levels becomes almost infinitely small. The result is essentially a continuum of energy levels, as shown on the right in Figure 9.2.1, each of which corresponds to a particular molecular orbital extending throughout the linear array of metal atoms. The levels that are lowest in energy correspond to mostly bonding combinations of atomic orbitals, those highest in energy correspond to mostly antibonding combinations, and those in the middle correspond to essentially nonbonding combinations.

The continuous set of allowed energy levels shown on the right in Figure 9.2.1 is called an energy band. The difference in energy between the highest and lowest energy levels is the bandwidth and is proportional to the strength of the interaction between orbitals on adjacent atoms: the stronger the interaction, the larger the bandwidth. Because the band contains as many energy levels as molecular orbitals, and the number of molecular orbitals is the same as the number of interacting atomic orbitals, the band in Figure

9.2.1 contains n energy levels corresponding to the combining of s orbitals from n metal atoms. Each of the original s orbitals could contain a maximum of two electrons, so the band can accommodate a total of 2n electrons. Recall, however, that each of the metal atoms we started with contained only a single electron in each s orbital, so there are only n electrons to place in the band. Just as with atomic orbitals or molecular orbitals, the electrons occupy the lowest energy levels available. Consequently, only the lower half of the band is filled. This corresponds to filling all of the bonding molecular orbitals in the linear array of metal atoms and results in the strongest possible bonding.

Multidimensional Systems

The previous example was a one-dimensional array of atoms that had only s orbitals. To extrapolate to two- or three-dimensional systems and atoms with electrons in p and d orbitals is straightforward in principle, even though in practice the mathematics becomes more complex, and the resulting molecular orbitals are more difficult to visualize. The resulting energy-level diagrams are essentially the same as the diagram of the one-dimensional example in Figure 9.2.1, with the following exception: they contain as many bands as there are different types of interacting orbitals. Because different atomic orbitals interact differently, each band will have a different bandwidth and will be centered at a different energy, corresponding to the energy of the parent atomic orbital of an isolated atom.

Band Gap

Because the 1s, 2s, and 2p orbitals of a period 3 atom are filled core levels, they do not interact strongly with the corresponding orbitals on adjacent atoms. Hence they form rather narrow bands that are well separated in energy (Figure 9.2.2). These bands are completely filled (both the bonding and antibonding levels are completely populated), so they do not make a net contribution to bonding in the solid. The energy difference between the highest level of one band and the lowest level of the next is the band gap. It represents a set of forbidden energies that do not correspond to any allowed combinations of atomic orbitals.

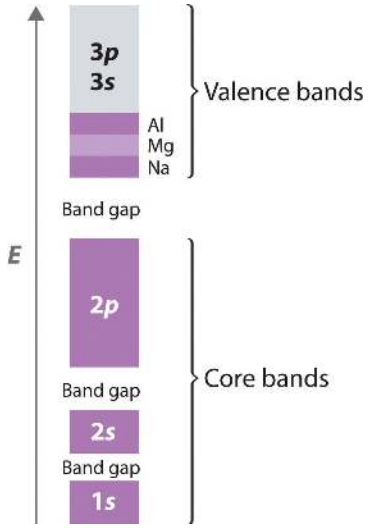


Figure 9.2.2: The Band Structures of the Period 3 Metals Na, Mg, and Al. The 3s and 3p valence bands overlap in energy to form a continuous set of energy levels that can hold a maximum of eight electrons per atom.

Because they extend farther from the nucleus, the valence orbitals of adjacent atoms (3s and 3p in Figure 9.2.2) interact much more strongly with one another than do the filled core levels; as a result, the valence bands have a larger bandwidth. In fact, the bands derived from the 3s and 3p atomic orbitals are wider than the energy gap between them, so the result is overlapping bands. These have molecular orbitals derived from two or more valence orbitals with similar energies. As the valence band is filled with one, two, or three electrons per atom for Na, Mg, and Al, respectively, the combined band that arises from the overlap of the 3s and 3p bands is also filling up; it has a total capacity of eight electrons per atom (two electrons for each 3s orbital and six electrons for each set of 3p orbitals). With Na, therefore, which has one valence electron, the combined valence band is one-eighth filled; with Mg (two valence electrons), it is one-fourth filled; and with Al, it is three-eighths filled, as indicated in Figure 9.2.2. The partially filled valence band is absolutely crucial for explaining metallic behavior because it guarantees that there are unoccupied energy levels at an infinitesimally small energy above the highest occupied level.

Band theory can explain virtually all the properties of metals. Metals conduct electricity, for example, because only a very small amount of energy is required to excite an electron from a filled level to an empty one, where it is free to migrate rapidly throughout

the crystal in response to an applied electric field. Similarly, metals have high heat capacities (as you no doubt remember from the last time a doctor or a nurse placed a stethoscope on your skin) because the electrons in the valence band can absorb thermal energy by being excited to the low-lying empty energy levels. Finally, metals are lustrous because light of various wavelengths can be absorbed, causing the valence electrons to be excited into any of the empty energy levels above the highest occupied level. When the electrons decay back to low-lying empty levels, they emit light of different wavelengths. Because electrons can be excited from many different filled levels in a metallic solid and can then decay back to any of many empty levels, light of varying wavelengths is absorbed and reemitted, which results in the characteristic shiny appearance that we associate with metals.

Requirements for Metallic Behavior

For a solid to exhibit metallic behavior,

- it must have a set of delocalized orbitals forming a band of allowed energy levels, and
- the resulting band must be partially filled (10%–90%) with electrons.

Without a set of delocalized orbitals, there is no pathway by which electrons can move through the solid.

Band theory explains the correlation between the valence electron configuration of a metal and the strength of metallic bonding. The valence electrons of transition metals occupy either their valence ns, (n − 1)d, and np orbitals (with a total capacity of 18 electrons per metal atom) or their ns and (n − 1)d orbitals (a total capacity of 12 electrons per metal atom). These atomic orbitals are close enough in energy that the derived bands overlap, so the valence electrons are not confined to a specific orbital. Metals with 6 to 9 valence electrons (which correspond to groups 6–9) are those most likely to fill the valence bands approximately halfway. Those electrons therefore occupy the highest possible number of bonding levels, while the number of antibonding levels occupied is minimal. Not coincidentally, the elements of these groups exhibit physical properties consistent with the presence of the strongest metallic bonding, such as very high melting points.

Insulators

In contrast to metals, electrical insulators are materials that conduct electricity poorly because their valence bands are full. The energy gap between the highest filled levels and the lowest empty levels is so large that the empty levels are inaccessible: thermal energy cannot excite an electron from a filled level to an empty one. The valence-band structure of diamond, for example, is shown in Figure 9.2.3*a*. Because diamond has only 4 bonded neighbors rather than the 6 to 12 typical of metals, the carbon 2s and 2p orbitals combine to form two bands in the solid, with the one at lower energy representing bonding molecular orbitals and the one at higher energy representing antibonding molecular orbitals. Each band can accommodate four electrons per atom, so only the lower band is occupied. Because the energy gap between the filled band and the empty band is very large (530 kJ/mol), at normal temperatures thermal energy cannot excite electrons from the filled level into the empty band. Thus there is no pathway by which electrons can move through the solid, so diamond has one of the lowest electrical conductivities known.

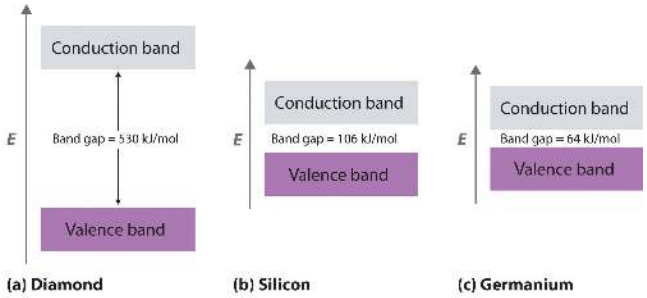


Figure 9.2.2: Energy-Band Diagrams for Diamond, Silicon, and Germanium. The band gap gets smaller from C to Ge.

Semiconductors

What if the difference in energy between the highest occupied level and the lowest empty level is intermediate between those of electrical conductors and insulators? This is the case for silicon and germanium, which have the same structure as diamond. Because Si–Si and Ge–Ge bonds are substantially weaker than C–C bonds, the energy gap between the filled and empty bands becomes much smaller as we go down group 14 (part (b) and part (c) of Figure 9.2.2). Consequently, thermal energy is able to excite a small number of electrons from the filled valence band of Si and Ge into the empty band above it, which is called the conduction band.

Exciting electrons from the filled valence band to the empty conduction band causes an increase in electrical conductivity for two reasons:

1. The electrons in the previously vacant conduction band are free to migrate through the crystal in response to an applied electric field.
2. Excitation of an electron from the valence band produces a “hole” in the valence band that is equivalent to a positive charge. The hole in the valence band can migrate through the crystal in the direction opposite that of the electron in the conduction band by means of a “bucket brigade” mechanism in which an adjacent electron fills the hole, thus generating a hole where the second electron had been, and so forth.

Consequently, Si is a much better electrical conductor than diamond, and Ge is even better, although both are still much poorer conductors than a typical metal (Figure 9.2.4).

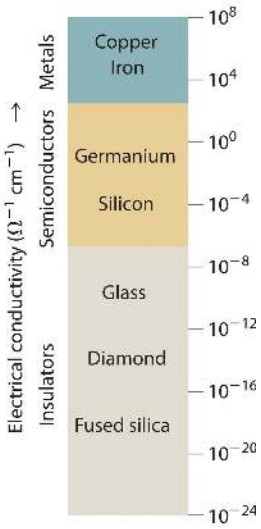


Figure 9.2.4: A Logarithmic Scale Illustrating the Enormous Range of Electrical Conductivities of Solids

Substances such as Si and Ge that have conductivities between those of metals and insulators are called semiconductors. Many binary compounds of the main group elements exhibit semiconducting behavior similar to that of Si and Ge. For example, gallium arsenide (GaAs) is isoelectronic with Ge and has the same crystalline structure, with alternating Ga and As atoms; not surprisingly, it is also a semiconductor. The electronic structure of semiconductors is compared with the structures of metals and insulators in Figure 9.2.5.

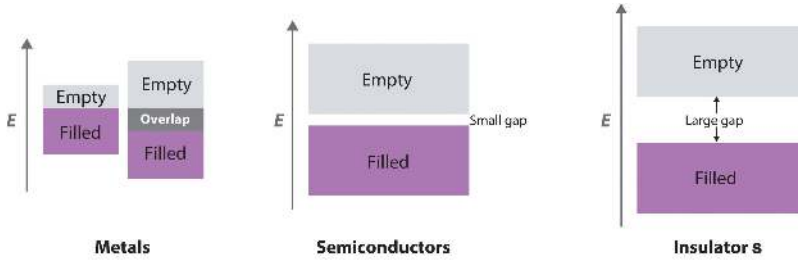


Figure 9.2.5: A Comparison of the Key Features of the Band Structures of Metals, Semiconductors, and Insulators. Metallic behavior can arise either from the presence of a single partially filled band or from two overlapping bands (one full and one empty).

Temperature and Conductivity

Because thermal energy can excite electrons across the band gap in a semiconductor, increasing the temperature increases the number of electrons that have sufficient kinetic energy to be promoted into the conduction band. The electrical conductivity of a semiconductor therefore increases rapidly with increasing temperature, in contrast to the behavior of a purely metallic crystal. In a metal, as an electron travels through the crystal in response to an applied electrical potential, it cannot travel very far before it encounters and collides with a metal nucleus. The more often such encounters occur, the slower the net motion of the electron through the crystal, and the lower the conductivity. As the temperature of the solid increases, the metal atoms in the lattice acquire more and more kinetic energy. Because their positions are fixed in the lattice, however, the increased kinetic energy increases only

the extent to which they vibrate about their fixed positions. At higher temperatures, therefore, the metal nuclei collide with the mobile electrons more frequently and with greater energy, thus decreasing the conductivity. This effect is, however, substantially smaller than the increase in conductivity with temperature exhibited by semiconductors. For example, the conductivity of a tungsten wire decreases by a factor of only about two over the temperature range 750–1500 K, whereas the conductivity of silicon increases approximately 100-fold over the same temperature range. These trends are illustrated in Figure 9.2.6.

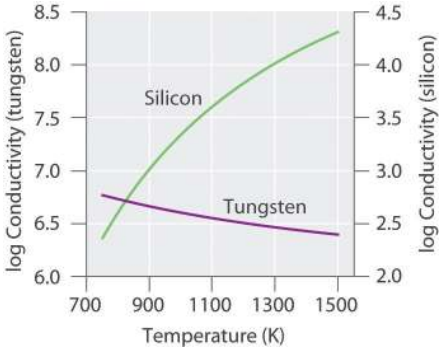


Figure 9.2.6: The Temperature Dependence of the Electrical Conductivity of a Metal versus a Semiconductor. The conductivity of the metal (tungsten) decreases relatively slowly with increasing temperature, whereas the conductivity of the semiconductor (silicon) increases much more rapidly.

n- and p-Type Semiconductors

Doping is a process used to tune the electrical properties of commercial semiconductors by deliberately introducing small amounts of impurities. If an impurity contains more valence electrons than the atoms of the host lattice (e.g., when small amounts of a group 15 atom are introduced into a crystal of a group 14 element), then the doped solid has more electrons available to conduct current than the pure host has. As shown in Figure 9.2.7*a*, adding an impurity such as phosphorus to a silicon crystal creates occasional electron-rich sites in the lattice. The electronic energy of these sites lies between those of the filled valence band and the empty conduction band but closer to the conduction band. Because the atoms that were introduced are surrounded by host atoms, and the electrons associated with the impurity are close in energy to the conduction band, those extra electrons are relatively easily excited into the empty conduction band of the host. Such a substance is called an n-type semiconductor, with the n indicating that the added charge carriers are negative (they are electrons).

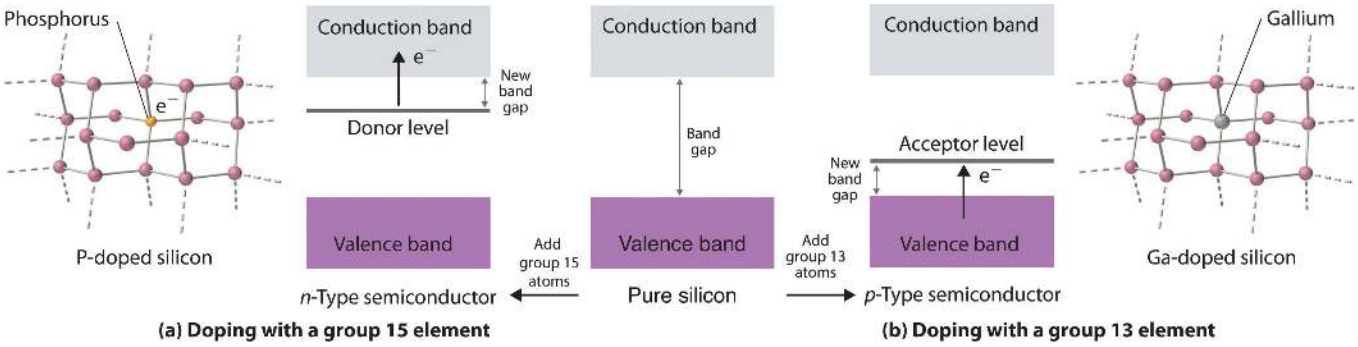


Figure 9.2.7: Structures and Band Diagrams of n-Type and p-Type Semiconductors. (a) Doping silicon with a group 15 element results in a new filled level between the valence and conduction bands of the host. (b) Doping silicon with a group 13 element results in a new empty level between the valence and conduction bands of the host. In both cases, the effective band gap is substantially decreased, and the electrical conductivity at a given temperature increases dramatically.

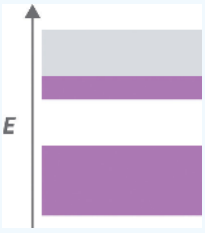
If the impurity atoms contain fewer valence electrons than the atoms of the host (e.g., when small amounts of a group 13 atom are introduced into a crystal of a group 14 element), then the doped solid has fewer electrons than the pure host. Perhaps unexpectedly, this also results in increased conductivity because the impurity atoms generate holes in the valence band. As shown in Figure 9.2.7*b*, adding an impurity such as gallium to a silicon crystal creates isolated electron-deficient sites in the host lattice. The electronic energy of these empty sites also lies between those of the filled valence band and the empty conduction band of the host but much closer to the filled valence band. It is therefore relatively easy to excite electrons from the valence band of the host to the isolated impurity atoms, thus forming holes in the valence band. This kind of substance is called a *p-type semiconductor*, with the p standing for positive charge carrier (i.e., a hole). Holes in what was a filled band are just as effective as electrons in an empty band at conducting electricity.

The electrical conductivity of a semiconductor is roughly proportional to the number of charge carriers, so doping is a precise way to adjust the conductivity of a semiconductor over a wide range. The entire semiconductor industry is built on methods for preparing samples of Si, Ge, or GaAs doped with precise amounts of desired impurities and assembling silicon chips and other complex devices with junctions between n- and p-type semiconductors in varying numbers and arrangements.

Because silicon does not stand up well to temperatures above approximately 100°C, scientists have been interested in developing semiconductors made from diamonds, a more thermally stable material. A new method has been developed based on vapor deposition, in which a gaseous mixture is heated to a high temperature to produce carbon that then condenses on a diamond kernel. This is the same method now used to create cultured diamonds, which are indistinguishable from natural diamonds. The diamonds are heated to more than 2000°C under high pressure to harden them even further. Doping the diamonds with boron has produced p-type semiconductors, whereas doping them with boron and deuterium achieves n-type behavior. Because of their thermal stability, diamond semiconductors have potential uses as microprocessors in high-voltage applications.

Example 9.2.1

A crystalline solid has the following band structure, with the purple areas representing regions occupied by electrons. The lower band is completely occupied by electrons, and the upper level is about one-third filled with electrons.



a. Predict the electrical properties of this solid.
b. What would happen to the electrical properties if all of the electrons were removed from the upper band? Would you use a chemical oxidant or reductant to effect this change?
c. What would happen to the electrical properties if enough electrons were added to completely fill the upper band? Would you use a chemical oxidant or reductant to effect this change?

Given: band structure

Asked for: variations in electrical properties with conditions

Strategy:

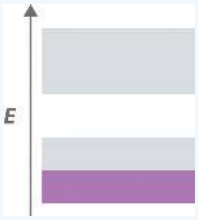
A. **B**ased on the occupancy of the lower and upper bands, predict whether the substance will be an electrical conductor. Then predict how its conductivity will change with temperature.
B. After all the electrons are removed from the upper band, predict how the band gap would affect the electrical properties of the material. Determine whether you would use a chemical oxidant or reductant to remove electrons from the upper band.
C. Predict the effect of a filled upper band on the electrical properties of the solid. Then decide whether you would use an oxidant or a reductant to fill the upper band.

Solution:

A. The material has a partially filled band, which is critical for metallic behavior. The solid will therefore behave like a metal, with high electrical conductivity that decreases slightly with increasing temperature.
B. Removing all of the electrons from the partially filled upper band would create a solid with a filled lower band and an empty upper band, separated by an energy gap. If the band gap is large, the material will be an electrical insulator. If the gap is relatively small, the substance will be a semiconductor whose electrical conductivity increases rapidly with increasing temperature. Removing the electrons would require an oxidant because oxidants accept electrons.
C. Adding enough electrons to completely fill the upper band would produce an electrical insulator. Without another empty band relatively close in energy above the filled band, semiconductor behavior would be impossible. Adding electrons to the solid would require a reductant because reductants are electron donors.

Exercise 9.2.1

A substance has the following band structure, in which the lower band is half-filled with electrons (purple area) and the upper band is empty.



a. Predict the electrical properties of the solid.
b. What would happen to the electrical properties if all of the electrons were removed from the lower band? Would you use a chemical oxidant or reductant to effect this change?
c. What would happen to the electrical properties if enough electrons were added to completely fill the lower band? Would you use a chemical oxidant or reductant to effect this change?

Answer:

a. The solid has a partially filled band, so it has the electrical properties of a conductor.
b. Removing all of the electrons from the lower band would produce an electrical insulator with two empty bands. An oxidant is required.
c. Adding enough electrons to completely fill the lower level would result in an electrical insulator if the energy gap between the upper and lower bands is relatively large, or a semiconductor if the band gap is relatively small. A reductant is required.

- Metallic behavior requires a set of delocalized orbitals and a band of allowed energy levels that is partially occupied.
- The electrical conductivity of a semiconductor increases with increasing temperature, whereas the electrical conductivity of a metal decreases with increasing temperature.
- n-Type semiconductors are negative charge carriers; the impurity has more valence electrons than the host. p-Type semiconductors are positive charge carriers; the impurity has fewer valence electrons than the host.

Summary

Band theory assumes that the valence orbitals of the atoms in a solid interact to generate a set of molecular orbitals that extend throughout the solid; the continuous set of allowed energy levels is an energy band. The difference in energy between the highest and lowest allowed levels within a given band is the bandwidth, and the difference in energy between the highest level of one band and the lowest level of the band above it is the band gap. If the width of adjacent bands is larger than the energy gap between them, overlapping bands result, in which molecular orbitals derived from two or more kinds of valence orbitals have similar energies. Metallic properties depend on a partially occupied band corresponding to a set of molecular orbitals that extend throughout the solid to form a band of energy levels. If a solid has a filled valence band with a relatively low-lying empty band above it (a conduction band), then electrons can be excited by thermal energy from the filled band into the vacant band where they can then migrate through the crystal, resulting in electrical conductivity. Electrical insulators are poor conductors because their valence bands are full. Semiconductors have electrical conductivities intermediate between those of insulators and metals. The electrical conductivity of semiconductors increases rapidly with increasing temperature, whereas the electrical conductivity of metals decreases slowly with increasing temperature. The properties of semiconductors can be modified by doping, or introducing impurities. Adding an element with more valence electrons than the atoms of the host populates the conduction band, resulting in an n-type semiconductor with increased electrical conductivity. Adding an element with fewer valence electrons than the atoms of the host generates holes in the valence band, resulting in a p-type semiconductor that also exhibits increased electrical conductivity.

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9.3: Band Theory of Solids

Learning Objectives

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

- Describe two main approaches to determining the energy levels of an electron in a crystal
- Explain the presence of energy bands and gaps in the energy structure of a crystal
- Explain why some materials are good conductors and others are good insulators
- Differentiate between an insulator and a semiconductor

The free electron model explains many important properties of conductors but is weak in at least two areas. First, it assumes a constant potential energy within the solid. (Recall that a constant potential energy is associated with no forces.) Figure $9.3.1$ compares the assumption of a constant potential energy (dotted line) with the periodic Coulomb potential, which drops as $-1/r$ at each lattice point, where **r** is the distance from the ion core (solid line). Second, the free electron model assumes an impenetrable barrier at the surface. This assumption is not valid, because under certain conditions, electrons can escape the surface—such as in the photoelectric effect. In addition to these assumptions, the free electron model does not explain the dramatic differences in electronic properties of conductors, semiconductors, and insulators. Therefore, a more complete model is needed.

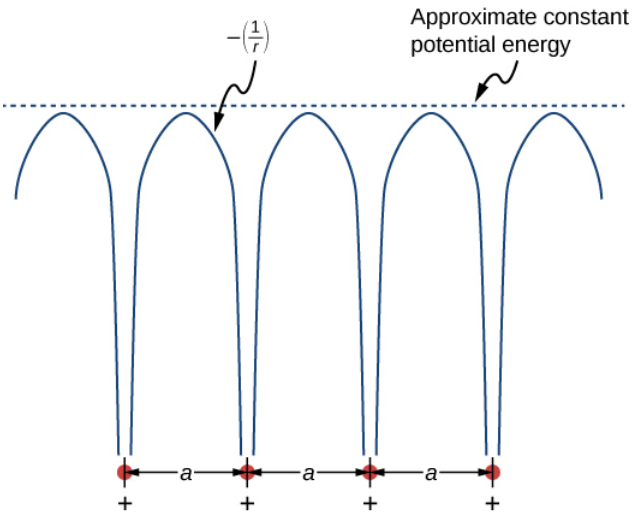


Figure $9.3.1$: The periodic potential used to model electrons in a conductor. Each ion in the solid is the source of a Coulomb potential. Notice that the free electron model is productive because the average of this field is approximately constant.

We can produce an improved model by solving Schrödinger's equation for the periodic potential shown in Figure $9.3.1$. However, the solution requires technical mathematics far beyond our scope. We again seek a qualitative argument based on quantum mechanics to find a way forward.

We first review the argument used to explain the energy structure of a covalent bond. Consider two identical hydrogen atoms so far apart that there is no interaction whatsoever between them. Further suppose that the electron in each atom is in the same ground state: a 1**s** electron with an energy of $-13.6\,eV$ (ignore spin). When the hydrogen atoms are brought closer together, the individual wave functions of the electrons overlap and, by the exclusion principle, can no longer be in the same quantum state, which splits the original equivalent energy levels into two different energy levels. The energies of these levels depend on the interatomic distance, a (Figure $9.3.2a$).

If four hydrogen atoms are brought together, four levels are formed from the four possible symmetries—a single sine wave "hump" in each well, alternating up and down, and so on. In the limit of a very large number **N** of atoms, we expect a spread of nearly continuous bands of electronic energy levels in a solid (Figure $9.3.2c$). Each of these bands is known as an **energy band**. (The allowed states of energy and wave number are still technically quantized, but for large numbers of atoms, these states are so close together that they are consider to be continuous or "in the continuum.")

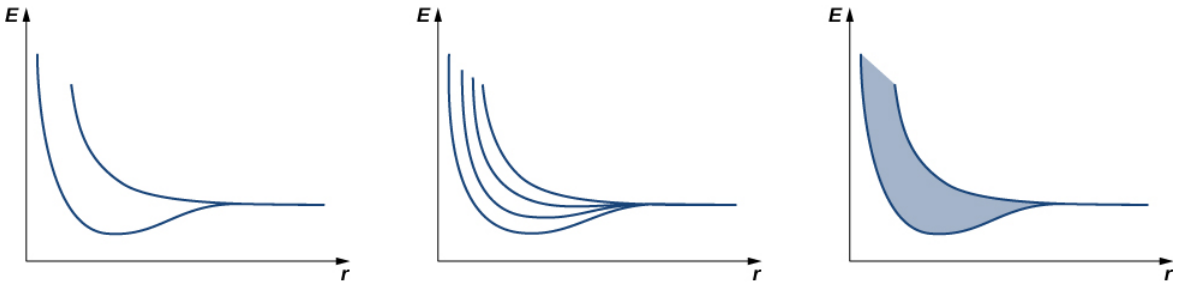


Figure 9.3.2 The dependence of energy-level splitting on the average distance between (a) two atoms, (b) four atoms, and (c) a large number of atoms. For a large number of electrons, a continuous band of energies is produced

Energy bands differ in the number of electrons they hold. In the 1**s** and 2**s** energy bands, each energy level holds up to two electrons (spin up and spin down), so this band has a maximum occupancy of 2**N** electrons. In the 2**p** energy band, each energy level holds up to six electrons, so this band has a maximum occupancy of 6**N** electrons (Figure 9.3.3).

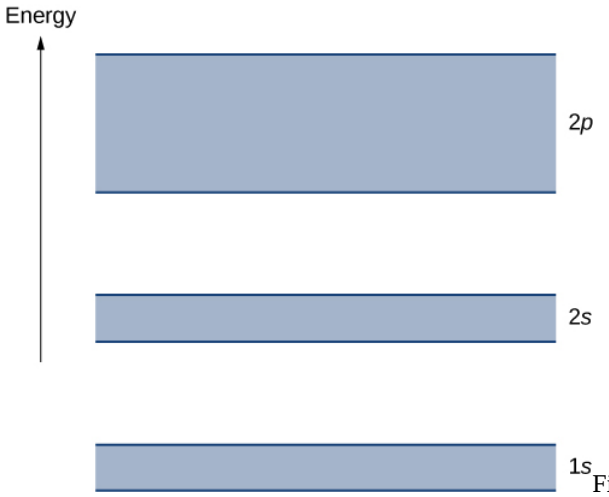


Figure 9.3.3 A simple representation of the energy structure of a solid. Electrons belong to energy bands separated by energy gaps.

Each energy band is separated from the other by an **energy gap**. The electrical properties of conductors and insulators can be understood in terms of energy bands and gaps. The highest energy band that is filled is known as a **valence band**. The next available band in the energy structure is known as a **conduction band**. In a conductor, the highest energy band that contains electrons is partially filled, whereas in an insulator, the highest energy band containing electrons is completely filled. The difference between a conductor and insulator is illustrated in Figure 9.3.4.

A conductor differs from an insulator in how its electrons respond to an applied electric field. If a significant number of electrons are set into motion by the field, the material is a conductor. In terms of the band model, electrons in the partially filled conduction band gain kinetic energy from the electric field by filling higher energy states in the conduction band. By contrast, in an insulator, electrons belong to completely filled bands. When the field is applied, the electrons cannot make such transitions (acquire kinetic energy from the electric field) due to the exclusion principle. As a result, the material does not conduct electricity.

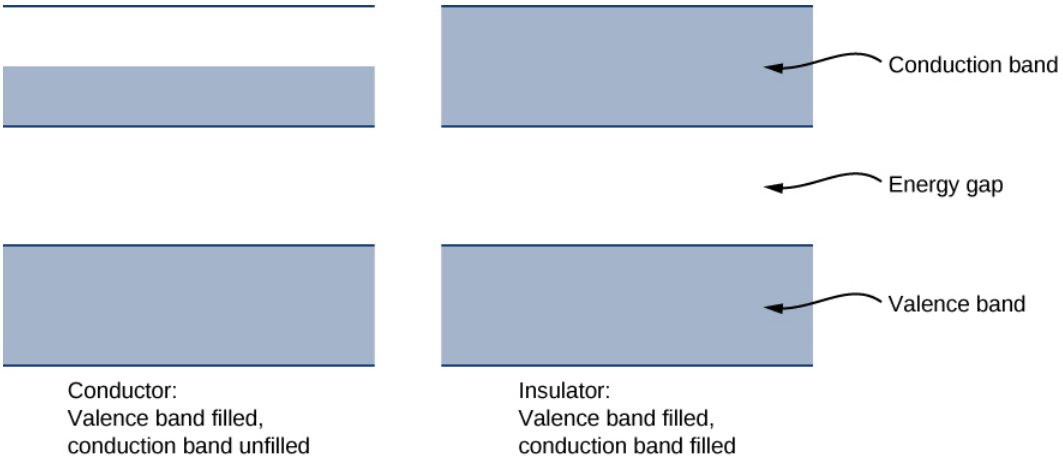


Figure 9.3.4 Comparison of a conductor and insulator. The highest energy band is partially filled in a conductor but completely filled in an insulator.

Simulation

Visit this simulation to learn about the origin of energy bands in crystals of atoms and how the structure of bands determines how a material conducts electricity. Explore how band structure creates a lattice of many wells.

A semiconductor has a similar energy structure to an insulator except it has a relatively small energy gap between the lowest completely filled band and the next available unfilled band. This type of material forms the basis of modern electronics. At $T = 0\ K$, the semiconductor and insulator both have completely filled bands. The only difference is in the size of the energy gap (or **band gap**) $\mathbf{E_g}$ between the highest energy band that is filled (the valence band) and the next-higher empty band (the conduction band). In a semiconductor, this gap is small enough that a substantial number of electrons from the valence band are thermally excited into the conduction band at room temperature. These electrons are then in a nearly empty band and can respond to an applied field. As a general rule of thumb, the band gap of a semiconductor is about 1 eV. (Table 9.3.1 for silicon.) A band gap of greater than approximately 1 eV is considered an insulator. For comparison, the energy gap of diamond (an insulator) is several electron-volts.

Table 9.3.1: Energy Gap for Various Materials at 300 KNote: Except for diamond, the materials listed are all semiconductors.

Material	Energy Gap $E_g(eV)$
Si	1.14
Ge	0.67
GaAs	1.43
GaP	2.26
GaSb	0.69
InAs	0.35
InP	1.35
InSb	0.16
C(diamond)	5.48

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9.4: Semiconductors and Doping

Learning Objectives

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

- Describe changes to the energy structure of a semiconductor due to doping
- Distinguish between an n-type and p-type semiconductor
- Describe the Hall effect and explain its significance
- Calculate the charge, drift velocity, and charge carrier number density of a semiconductor using information from a Hall effect experiment

In the preceding section, we considered only the contribution to the electric current due to electrons occupying states in the conduction band. However, moving an electron from the valence band to the conduction band leaves an unoccupied state or **hole** in the energy structure of the valence band, which a nearby electron can move into. As these holes are filled by other electrons, new holes are created. The electric current associated with this filling can be viewed as the collective motion of many negatively charged electrons or the motion of the positively charged electron holes.

To illustrate, consider the one-dimensional lattice in Figure 9.4.1. Assume that each lattice atom contributes one valence electron to the current. As the hole on the right is filled, this hole moves to the left. The current can be interpreted as the flow of positive charge to the left. The density of holes, or the number of holes per unit volume, is represented by **p**. Each electron that transitions into the conduction band leaves behind a hole. If the conduction band is originally empty, the conduction electron density **p** is equal to the hole density, that is, $n = p$.

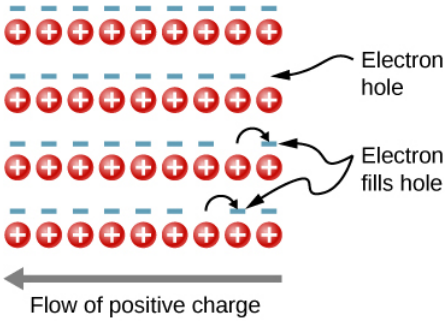


Figure 9.4.1: The motion of holes in a crystal lattice. As electrons shift to the right, an electron hole moves to the left.

As mentioned, a semiconductor is a material with a filled valence band, an unfilled conduction band, and a relatively small energy gap between the bands. Excess electrons or holes can be introduced into the material by the substitution into the crystal lattice of an impurity atom, which is an atom of a slightly different valence number. This process is known as doping. For example, suppose we add an arsenic atom to a crystal of silicon (Figure 9.4.2*a*).

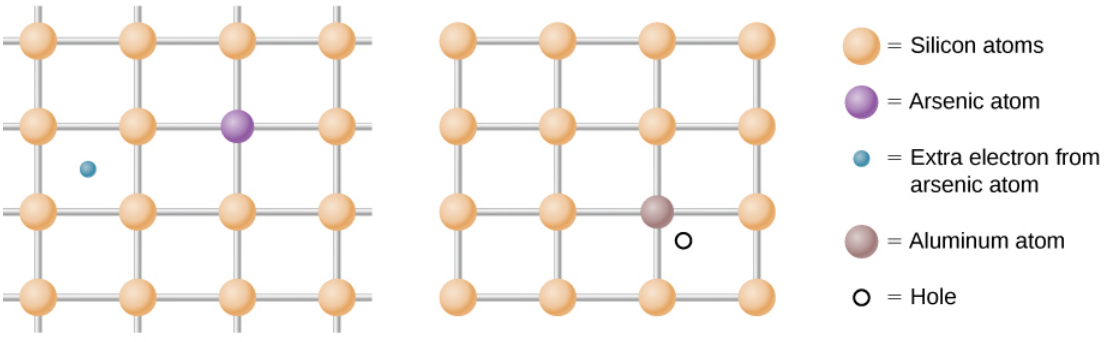


Figure 9.4.2 (a) A donor impurity and (b) an acceptor impurity. The introduction to impurities and acceptors into a semiconductor significantly changes the electronic properties of this material.

Arsenic has five valence electrons, whereas silicon has only four. This extra electron must therefore go into the conduction band, since there is no room in the valence band. The arsenic ion left behind has a net positive charge that weakly binds the delocalized electron. The binding is weak because the surrounding atomic lattice shields the ion's electric field. As a result, the binding energy of the extra electron is only about 0.02 eV. In other words, the energy level of the impurity electron is in the band gap below the conduction band by 0.02 eV, a much smaller value than the energy of the gap, 1.14 eV. At room temperature, this impurity electron is easily excited into the conduction band and therefore contributes to the conductivity (Figure 9.4.3*a*). An impurity with an extra electron is known as a **donor impurity**, and the doped semiconductor is called an **n**-type semiconductor because the primary carriers of charge (electrons) are negative.

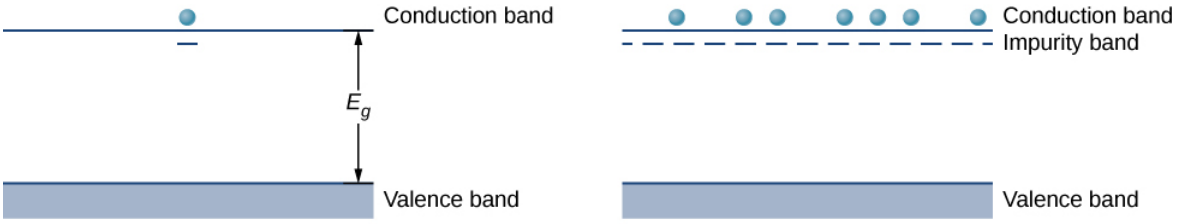


Figure 9.4.3
The extra electron from a donor impurity is excited into the conduction band; (b) formation of an impurity band in an n-type semiconductor.

By adding more donor impurities, we can create an **impurity band**, a new energy band created by semiconductor doping, as shown in Figure 9.4.3*b*. The Fermi level is now between this band and the conduction band. At room temperature, many impurity electrons are thermally excited into the conduction band and contribute to the conductivity. Conduction can then also occur in the impurity band as vacancies are created there. Note that changes in the energy of an electron correspond to a change in the motion (velocities or kinetic energy) of these charge carriers with the semiconductor, but not the bulk motion of the semiconductor itself.

Doping can also be accomplished using impurity atoms that typically have one **fewer** valence electron than the semiconductor atoms. For example, Al, which has three valence electrons, can be substituted for Si, as shown in Figure 9.4.2*b*. Such an impurity is known as an **acceptor impurity**, and the doped semiconductor is called a **p**-type semiconductor, because the primary carriers of charge (holes) are positive. If a hole is treated as a positive particle weakly bound to the impurity site, then an empty electron state is created in the band gap just above the valence band. When this state is filled by an electron thermally excited from the valence band (Figure 9.4.1*a*), a mobile hole is created in the valence band. By adding more acceptor impurities, we can create an impurity band, as shown in Figure 9.4.1*b*.

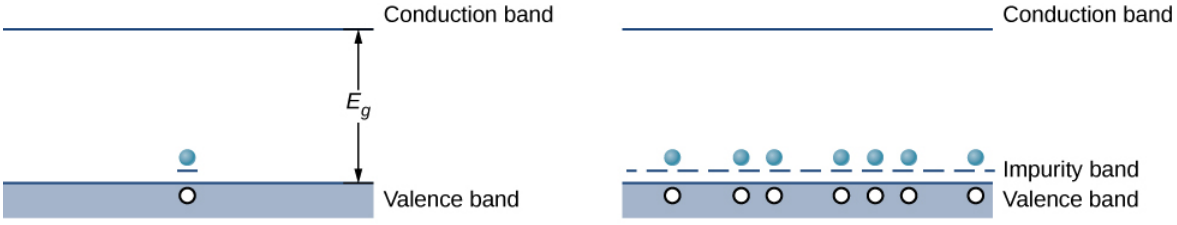


Figure 9.4.4 (a)
An electron from the conduction band is excited into the empty state resulting from the acceptor impurity; (b) formation of an impurity band in a p-type semiconductor.

The electric current of a doped semiconductor can be due to the motion of a **majority carrier**, in which holes are contributed by an impurity atom, or due to a **minority carrier**, in which holes are contributed purely by thermal excitations of electrons across the energy gap. In an **n**-type semiconductor, majority carriers are free electrons contributed by impurity atoms, and minority carriers are free electrons produced by thermal excitations from the valence to the conduction band. In a **p**-type semiconductor, the majority carriers are free holes contributed by impurity atoms, and minority carriers are free holes left by the filling of states due to thermal excitation of electrons across the gap. In general, the number of majority carriers far exceeds the minority carriers. The concept of a majority and minority carriers will be used in the next section to explain the operation of diodes and transistors.

Hall Effect

In studying **p**- and **n**-type doping, it is natural to ask: Do "electron holes" really act like particles? The existence of holes in a doped **p**-type semiconductor is demonstrated by the Hall effect. The Hall effect is the production of a potential difference due to the

motion of a conductor through an external magnetic field. A schematic of the Hall effect is shown in Figure 9.4.5a.

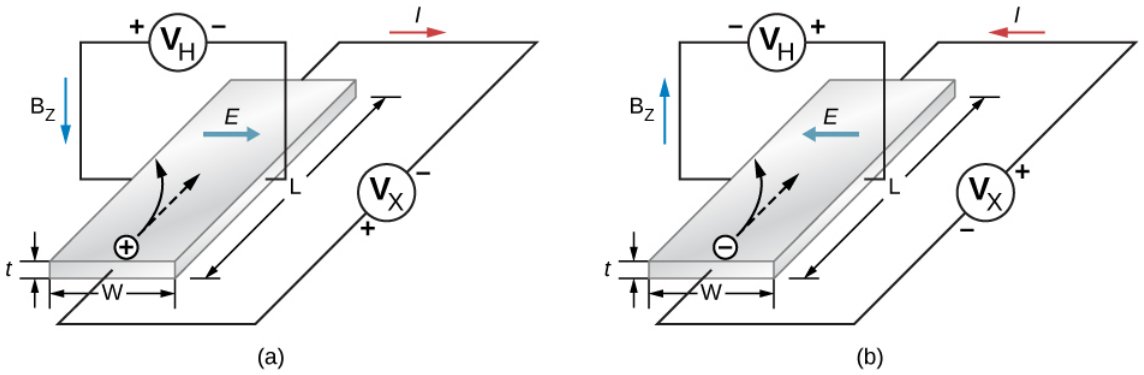


Figure 9.4.5 The Hall effect. (a) Positively charged electron holes are drawn to the left by a uniform magnetic field that points downward. An electric field is generated to the right. (b) Negative charged electrons are drawn to the left by a magnetic field that points up. An electric field is generated to the left.

A semiconductor strip is bathed in a uniform magnetic field (which points into the paper). As the electron holes move from left to right through the semiconductor, a **Lorentz force** drives these charges toward the upper end of the strip. (Recall that the motion of the positively charged carriers is determined by the right-hand rule.) Positive charge continues to collect on the upper edge of the strip until the force associated with the downward electric field between the upper and lower edges of the strip ($F_E = E_q$) just balances the upward magnetic force ($F_B = qvB$). Setting these forces equal to each other, we have $E = vB$. The voltage that develops across the strip is therefore

$$V_H = vBw,$$

where V_H is the Hall voltage; v is the hole's **drift velocity**, or average velocity of a particle that moves in a partially random fashion; **B** is the magnetic field strength; and **w** is the width of the strip. Note that the Hall voltage is transverse to the voltage that initially produces current through the material. A measurement of the sign of this voltage (or potential difference) confirms the collection of holes on the top side of the strip. The magnitude of the Hall voltage yields the drift velocity (**v**) of the majority carriers.

Additional information can also be extracted from the Hall voltage. Note that the electron current density (the amount of current per unit cross-sectional area of the semiconductor strip) is

$$j = nqv, \tag{9.4.1}$$

where **q** is the magnitude of the charge, **n** is the number of charge carriers per unit volume, and **v** is the drift velocity. The current density is easily determined by dividing the total current by the cross-sectional area of the strip, **q** is charge of the hole (the magnitude of the charge of a single electron), and **u** is determined by Equation 9.4.1. Hence, the above expression for the electron current density gives the number of charge carriers per unit volume, **n**. A similar analysis can be conducted for negatively charged carriers in an **n**-type material (see Figure 9.4.5).

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9.5: Resistivity

Resistivity is the material property that pertains to how difficult it is for electrical current to flow through said material. Materials with high resistivity are known as insulators while materials with low resistivity are known as conductors. Spanning from 10^{-8} Ωm to 10^{20} Ωm (see Figure 9.5.1), resistivity possess the largest range of values for any physical property. Resistivity is essential in many material applications including resistors in electrical circuits, dielectrics, resistive heating, and superconducting.

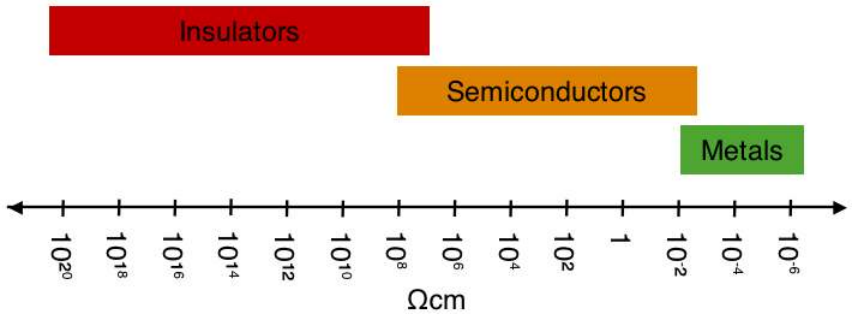


Figure 9.5.1 Regimes of materials according to resistivity.

Introduction

The fundamental relationship that explores a materials opposition to electron flow was first derived in 1826 by Georg Ohm, a German physicist and mathematician. Ohm's Law is represented by the following equation:

$$V = IR$$

where

- V [Volts: J/C] is the voltage applied to the material,
- I [Amperes: C/s] is the electrical current flow, and
- R [ohms: V/A] is the resistance of the material specimen.

It is important to note that resistance is dependent on the specific geometry of a material specimen as seen in Figure 2.

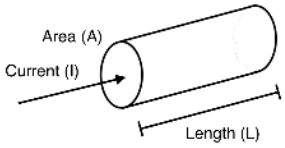


Figure 9.5.2 Material specimen dimensions that relate resistance to resistivity.

To represent the electrical resistivity as an intrinsic material property, the voltage must be divided by the length L at which it is applied to and the current must be divided by the area A it flows through to produce an electric field ξ and current density J respectively. This translation to electric field and current density yields the following equation for resistivity:

$$\rho = \frac{\xi}{J}$$

where ρ is the resistivity of a material $[\Omega m]$. When comparing materials, it is common to invert the value of resistivity to make conductivity σ [Siemens] which can easily be used to rank materials on the basis of how well each conducts electrons. Due to the significant temperature dependence on resistivity and conductivity, a material's resistiveness measured at room temperature [20°C].

As mentioned above, materials are broken into three essential regimes: insulators, semiconductors, and metals. The manifestation of resistivity in conducting materials, metals and semiconductors, can be fully realized by evaluating the behavior of electrons at the quantum mechanical level.

Resistivity of Pure Metals

Metals are structured by a lattice of atoms that are metallically bonded to one another. The sea of delocalized electrons found in metallic bonding is created by having a high density of states (i.e. electrons) at the Fermi level which are easily excited into the conduction band. From this bonding, electrons a can be thought of as free electrons moving through the metal matrix. As the

electron flows, it will interact with individual atoms, causing scattering events, which decrease the effectiveness of electrons at traversing the metal. The mobility of the electrons play an important role in quantifying the resistivity of a metal as seen in the following equation:

$$\rho = \frac{3}{e^2 v_f^2 T N(E_f)}$$

where e is the charge of an electron, V_F Fermi velocity of a conduction electron, τ is the relaxation time between scattering events, and $N(E_F)$ is the population density of electrons at the Fermi energy. Additionally, it is seen that the population density of electrons at the Fermi level is taken in to account as opposed to the total number of valance electrons, which explains the exceptionally low resistivity of silver, copper and gold.

Temperature Dependence

The equation above shows that the resistivity of a metal is inversely proportionally to the relaxation time. This means the number of scattering events plays a substantial role in the resistivity of a metal. A large contributor to the number of scattering events iin a metal is the thermal vibrations of each atom in the lattice. As the temperature of a material increases, each atom beings to oscillate about its central position, increasing the probability that an electron would collide with it. This relationship is visualized by measuring the resistivity of silver as a function of temperature, Figure 9.5.3.

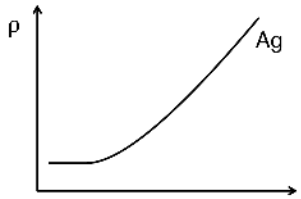


Figure 9.5.3Resistivity of bulk silver as a function of temperature.

Metals exhibit a minimal resistivity at temperatures approaching 0 Kelvin, known as a residual resistivity, and a linear increase in resistivity as the metal reaches its melting point.

Residual Resistivity and Matthiessen's Rule

At low enough temperatures, the degrees of thermal vibration are not yet activated meaning the residual resistivity of a metal is a collection of all other scattering sites present in the material specifically defects and impurities. With polycrystalline metals, there will be a number of sources of defects in the microstructure including Grain boundaries, dislocations, and vacancies. Along with defects, impurities in a metal can host a scattering site. In 1864 Augustus Matthiessen, a British chemist and physicist, was the first to incorporate all of these aspects into the resistivity of a metal. Matthiessen's Rule is as follows:

$$\rho = \rho_{th} + \rho_{imp} + \rho_{def}$$

where ρ_{th} is the resistivity due to temperature, ρ_{imp} is the resistivity due to impurities and ρ_{def} is the the resistivity due to defects. While temperature, defects, and impurities do in fact contribute to resistivity, some deviation from the simple summation postulated by Matthiessen has been reported for specific metals.

Resistivity of Alloys

From Matthiessen's Rule it was seen that the resistivity of a metal was influenced by the impurities present. This portion of the resistivity begins to have a significant contribution when metals are alloyed together. An alloy can be viewed as a metal with a large number of impurities, meaning there is a great deal more scattering sites to increase the residual resistivity of the metal. The result of this increase is a translation of the plot in Figure 9.5.3 upward. At varying compositions of a simple binary alloy, the resistivity of the system is a linear interpolation of the resistivity of each pure metal. If the system exhibits an energetically favorable phase transition that results in a more ordered structure than that of the solute atoms in solution, a drop in resistivity at that composition will be observed. An example of a binary system that has ordered phases that affect resistivity is copper and platinum.

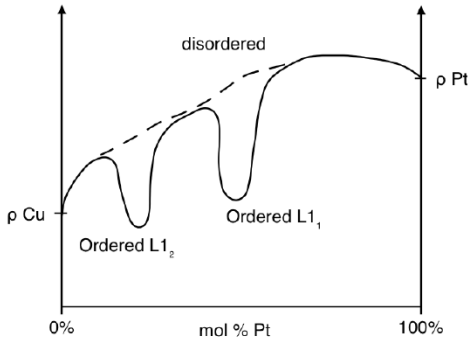


Figure 9.5.4 Resistivity of the binary system of copper and platinum at 500 K as a function of composition. The dashed line models standard linear interpolation of the two pure metals while the solid line represents the actual resistivity due to the formation of ordered phases.

The plot of the copper platinum binary system demonstrates the result of the ordered phases L_2 and L_1. Similar to the deviations from Matthiessen's Rule, formulation of the relationship of resistivity of any alloy has not been adequately developed because of the complexity of the structures created by any given alloy system. Several rules have been created with little implication because each emphasizes a specific subset of alloys with particular characteristics.

Resistivity of Semiconductors

The primary distinguishing factor between metals and any other material is that metals do not possess a band gap or a range of energy levels that are not allowed for electrons to inhabit. It has been observed that the size of the band gap of a material how insulative it is and at low enough band gaps, the material can be partially conductive. These materials are, of course, semiconductors. Similar to metals, through band theory, the following relationship can be determined for the resistivity of a semiconductor.

$$\rho = \frac{m_e*}{e^2 \tau_e N_e} + \frac{m_h*}{e^2 \tau_h N_h}$$

where m_e^* and m_h^* are the effective masses of electrons and holes respectively, N_e and N_h are the number of electrons and holes respectively, and T_e and T_h are the relaxation times for electrons and hole respectively. Acknowledging the inverse dependence of the number of both electrons and holes on the resistivity, extrinsic semiconductors would be expected to have a lower resistivity due to there addition of more charge carriers.

Temperature Dependence

The temperature dependence of semiconductors act very different to metals. With the band gap limiting the excitation of electrons to the conduction band, energy must be supplied to the semiconductor to decrease the resistivity. This energy is supplied thermally, and corresponds to the band gap energy.

$$\rho = \rho_0 exp(\frac{-E_g}{2kT})$$

where ρ_0 is the resistivity of the semiconductor as determined from the equation above, E_g is the band gap energy, k is the Boltzmann's constant and T is the temperature.

For intrinsic semiconductors, that contain equal numbers of electron and holes, the temperature dependence resolves the trend seen in Figure 9.5.5. From Figure 9.5.5, the promotion of more electrons at higher temperatures is observed as well as a freeze out region at low temperatures where no charge carrying species are excited to the conduction band.

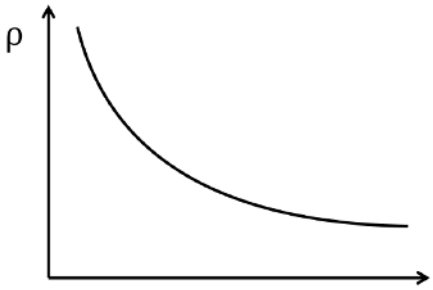


Figure 9.5: 9.5.5Resistivity as a function of temperature for intrinsic semiconductors.

As is expected, extrinsic semiconductors exhibit a similar temperature dependence to their intrinsic counterparts with the small deviation during a portion of the temperature range.

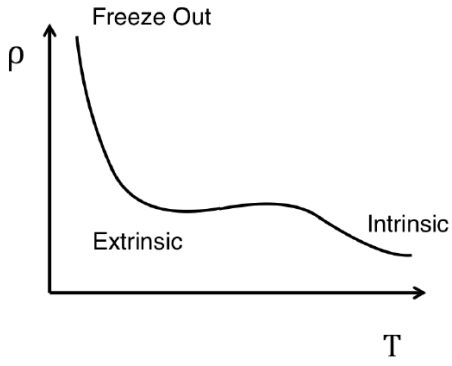


Figure 9.5: 9.5.6Resistivity as a function of temperature for an extrinsic semiconductor.

For a temperature range in the middle of Figure 9.5.6, the resistivity remained relatively constant while the material heats. This accounts for the additional charge carriers found in extrinsic semiconductors that have already decreased the resistivity of the semiconductor below the value for the intrinsic counterpart. During the region of temperatures when the resistivity is not changing, the number of electrons being thermally excited to the conduction band is not yet large enough to influence the resistivity as much as the extrinsic doping has. Eventually the number of excited electrons becomes great enough to resume the intrinsic temperature dependent trend.

Questions

1. What distinguishes resistance from resistivity? Why is it important to quantify resistivity?
2. According to Matthiessen's Rule, what contributes to the residual resistivity of a metal?
3. Calculate the resistance through a rectangular wafer of Germanium at 350°C. Dimensions: width= 3cm thickness= 5mm length= 15cm. Resistivity at room temperature: 1 Ωm Band Gap energy: 0.67 eV

Answers

1. Resistance is a value specific to the particular specimen geometry of the material while resistivity does not depend on geometry. It is important to refer to resistivity when comparing materials because it is an intrinsic property.
2. According to Matthiessen's Rule, residual resistivity is accounts for the resistivity brought upon by impurities and defects, specifically grain boundaries, dislocations, and vacancies, in the material.
3. R=1.95 Ω at 350°C

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9.6: Metal-Insulator Transitions

In Chapter 6 we learned that metals and insulators not only have different electrical properties but also have very different crystal structures. Metals tend to have high coordination numbers (typically 8 or 12) whereas insulators have low coordination numbers that can be rationalized as "octet" bonding arrangements. For example, in crystalline Si or Ge (diamond structure), each atom has four nearest neighbors. There are two electrons per bond, and thus each atom has eight electrons in its valence shell. Sn, the element below Ge, exists in two different forms, one (gray tin) with the diamond structure that is a brittle narrow-gap semiconductor, and the other (white tin) with a body-centered tetragonal structure that is a malleable metal. These two forms are very close in energy, and in fact metallic white tin transforms to the brittle semiconducting gray form at low temperature. Extremely cold weather in 18th century Europe caused many tin organ pipes to break and eventually turn to dust. This transformation has been called tin blight, tin disease, tin pest or tin leprosy. The dust is actually grey tin, which lacks the malleability of its metallic cousin white tin.

Under experimentally accessible temperatures and pressures, Si and Ge are always semiconducting (i.e., insulating), and Pb is always metallic. Why is Sn different? The reason has to do with orbital overlap. Theory tells us in fact that any (and all) insulators should become metallic at high enough pressure, or more to the point, at high enough density. For most insulators, however, the pressures required are far beyond those that we can achieve in the laboratory.

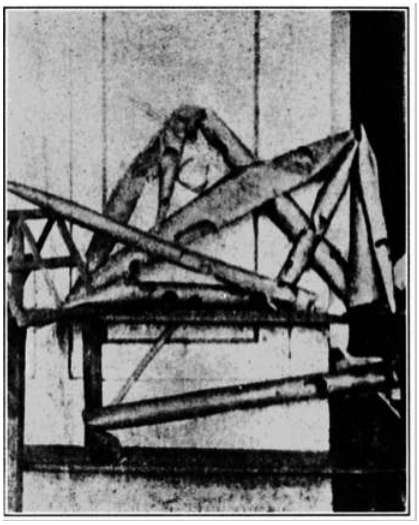
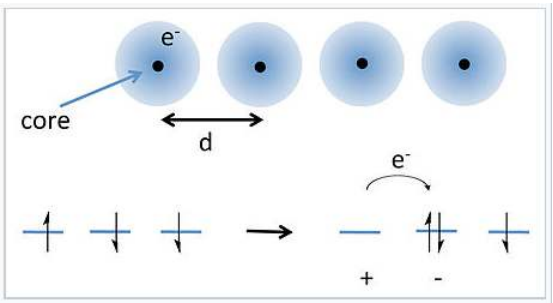


Figure 9.6.1: Organ pipes destroyed by "tin blight"

How can we rationalize the transition of insulators to the metallic state? Indeed, how can we understand the existence of insulators at all?

The Hubbard Model

Let's consider a chain of a large number (N) of atoms as we did in Chapter 6. For convenience, we can say that these are atoms such as H, Na, or Cs that have one valence electron. The simple band model we developed earlier suggests that the chain should be metallic, because N atoms combine to make N orbitals, and the N valence electrons only fill the band of orbitals halfway. But this conclusion doesn't depend on the density, which creates a paradox. If atoms in the chain are very far apart, we suspect that the electrons should localize on the atoms.

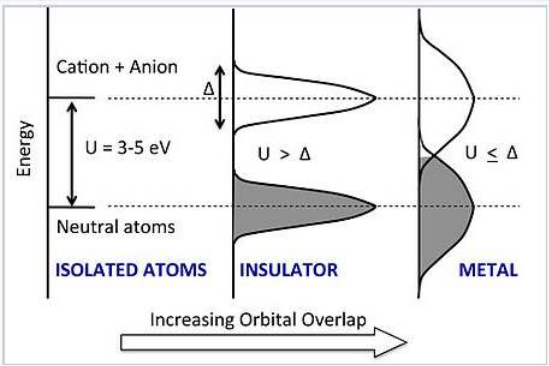


Electron hopping in a 1-D chain of atoms.

A solution to this problem was proposed by J. Hubbard in 1963.[1] Hubbard considered the energy required to transfer an electron from an atom to its nearest neighbor, as shown in the picture at the right. Because each atom already has one electron (with random spin), moving an electron over by one atom requires overcoming the energy of electron-electron repulsion to make a cation-anion pair. For well-separated atoms this energy (U) is given by:

$$U = IP - Ea - \frac{e^2}{4\pi\varepsilon_0 d} \tag{9.6.1}$$

where IP and EA are the ionization energy and electron affinity, ε_0 is the permittivity of free space, and the last term in the equation represents the coulombic attraction between the cation and the anion. For atoms such as alkali metals, U is on the order of 3–5 eV, which is much larger than the thermal energy kT. Thus we expect there to be very few anion-cation pairs at room temperature, and the chain of atoms should be insulating.

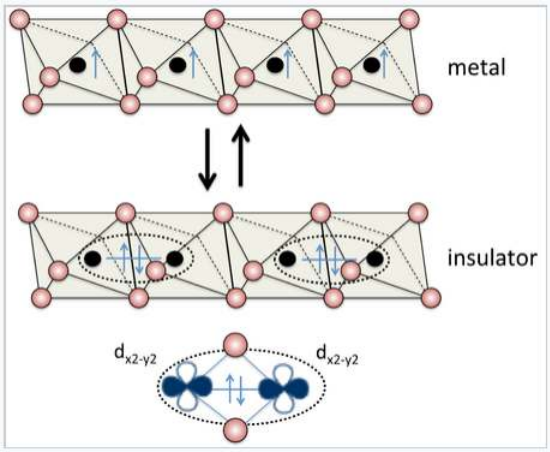


Energy vs. DOS for the chain of atoms as the density and degree of orbital overlap between atoms increases. Increasing overlap broadens the neutral atom and anion-cation states into bands, each of which has a bandwidth Δ. A transition to the metallic state occurs abruptly when Δ exceeds the Hubbard gap U.

What happens when we squeeze the atoms together? In the Hubbard model, as the distance between atoms decreases, the energies of both the neutral atom states and the anion-cation states broaden into bands, each of which has a band width Δ. The lower band can accommodate exactly *N* electrons (not *2N* as in the MO picture we developed earlier) because each orbital can only take one electron without spin-pairing. Thus for small Δ the lower band is full and the upper band is empty. However, as we continue to compress the chain, the orbital overlap becomes so strong that Δ ≈ U. At this point, the bands overlap and some of the electrons fill the anion-cation states. The chain then becomes conducting and the material is metallic.

Some materials, such as Sn and VO_2, happen to have just the right degree of orbital overlap to make the Hubbard transition occur by changing the temperature or pressure. Such materials can be very useful for electrical switching, as illustrated at the right for rutile structure VO_2. Most materials are far away from the transition, either on the metallic or insulating side. An interesting periodic trend that illustrates this concept can be seen among the transition metal monoxides, MO (M = Ti, V, Cr, Mn, Fe, Co, Ni), all of which have the NaCl structure. TiO and VO are metallic, because the 3d orbitals have significant overlap in the structure. However, CrO, MnO, FeO, CoO, and NiO are all insulators, because the 3d orbitals contract (and therefore Δ < U) going across the transition metal series. In contrast, the analogous sulfides (TiS, VS,....NiS) are all metallic. The sulfides have the NiAs structure, in

which all the metal atoms are eclipsed along the stacking axis (the hexagonal c-axis). The short metal-metal distances along that axis result in strong orbital overlap, making Δ > U.



Vanadium dioxide has the rutile structure, and in its undistorted form it is metallic, with one valence electron per V atom. Distortion of the lattice makes pairs of V atoms, resulting in an electronically insulating state. The metal-insulator transition can be driven reversibly by changing the temperature, pressure, or orbital occupancy. Electrical switching of this transition in VO_2 is being studied for applications in high performance thin film transistors[2]

The Mott Model

A simpler, less atomistic model of the metal-insulator transition was formulated by Neville Mott.[3] The Mott model considers the behavior of an electron in a material as a function of the density of all the other valence electrons. We know for a one-electron hydrogen-like atom (H, Na, Cs, etc.) the Schrödinger equation contains a potential energy term:

$$V(r) = -(\frac{e^2}{4\pi\varepsilon_0 r}) \tag{9.6.2}$$

This potential energy function gives rise to familiar ladder of allowed energy levels in the hydrogen atom. However, in a metal, this Coulomb potential must be modified to include the screening of nuclear charge by the other electrons in the solid. In this case there is a **screened Coulomb potential**:

$$V(r) = -(\frac{e^2}{4\pi\varepsilon_0 r})exp(-qr) \tag{9.6.3}$$

where q, which is the inverse of the **screening length**, is given by:

$$q^2 = 4m_e^2(\frac{3n}{\pi})^{\frac{1}{3}}(\frac{2\pi}{h}) \tag{9.6.4}$$

Here n is the density of atoms (or valence electrons), m_e is the electron mass, and h is Planck's constant. At distances much larger than the screening length q^{-1}, the electron no longer "feels" the charge on the nucleus. Mott showed that there is a critical density of electrons n_c above which the valence electrons are no longer bound by individual nuclei and are free to roam the crystal. This critical density marks the transition to the metallic state, and is given by the Mott criterion:

$$\mathbf{n_c^{\frac{1}{3}}\, a_H \approx 0.26} \tag{9.6.5}$$

In this equation, a_H is an effective Bohr radius for the valence electrons in the low-density limit, e.g. the average orbital radius of electrons in the 6s shell of a Cs atom when computing the value for Cs metal.



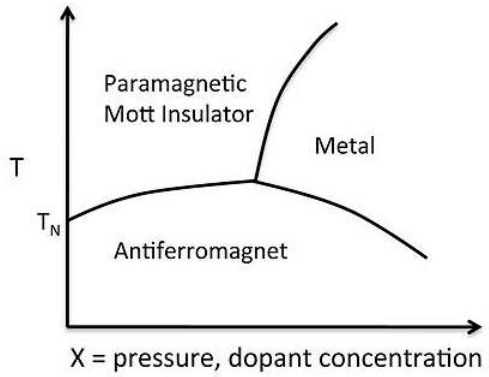
Solutions of lithium metal in liquid ammonia at low (top, ionic conductor) and higher (bottom, metal) Li concentration. From a video by Joshua Judkins

The important concept from the Mott model is that the metal-insulator transition depends very strongly on the **density of valence electrons.** This is consistent with the orbital overlap model of Hubbard, but also more general in the sense that it does not depend on a periodic structure of atoms. The Mott model is thus applicable to such diverse systems as metal atoms dissolved in liquid ammonia, metal atoms trapped in frozen gas matrices, and dopants in semiconductors.[4] In some systems, it is possible to continuously tune the density of valence electrons with rather striking results. For example, dissolving alkali metal (Li, Na, ...) in liquid ammonia (bp -33 ^{o}C) produces a blue liquid. The solvated alkali cations and negatively charged electrons impart ionic conductivity (as in a salt solution) but not electronic conductivity to the blue liquid ammonia solution. But as the concentration of electrons increases, a reflective, bronze-colored liquid phase forms that floats over the blue phase. This bronze phase is metallic and highly conducting. Eventually, with enough alkali metal added, the entire liquid is converted to the electronically conducting bronze phase.

The electrical switching of VO_2 between insulating and metallic phases (see above) can also be rationalized in terms of the Mott transition. Adding more electron density (by chemical or electric field doping) increases the concentration of valence electrons, driving the phase transition to the metallic state.

Thermodynamics and phase transitions

Thermodynamically, the metal-insulator transition is a **first-order phase transition**. In such a transition, the structure and properties change abruptly (think of the breakfast-to-lunch transition at McDonalds - there is just no way to get pancakes after, or hamburgers before 10:30 AM![5]). Thus in the case of Sn metal, the changes in structure (from four- to eight-coordination) and in electronic conductivity (insulator to metal) occur simultaneously. As in other first order phase transitions such as ice to water to steam, there is a latent heat associated with the transition and a discontinuity in derivative properties such as the heat capacity.



A typical phase diagram for a metal-insulator transition is shown at the right for V_2O_3. The octahedrally coordinated V^{3+} ion has a d^2 electron count, so there are two unpaired spins per atom, and at low temperature the spins in the lattice order

antiferromagnetically. As we learned in Chapter 8, above the Néel temperature an antiferromagnet becomes a paramagnet, which is also a Mott insulator. Increasing the pressure, or doping with electrons (e.g., by substituting some d^3 Cr^{3+} for V^{3+}) pushes the electron density over the Mott transition, the spins pair, and the solid becomes metallic.

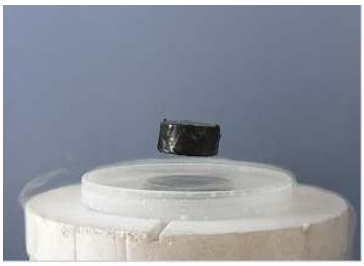
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9.7: Superconductors

Superconductivity refers to the flow of electrical current in a material with zero resistance. Such materials are very important for use in electromagnets, e.g., in magnetic resonance imaging (MRI) and nuclear magnetic resonance (NMR) machines, because once the current starts flowing in the coils of these magnets it doesn't stop. Magnetic levitation using superconductors - which, below a critical field strength, are perfect diamagnets that are not penetrated by magnetic flux lines - is also potentially relevant to future technologies such as magnetically levitated trains.

The phenomenon of superconductivity, first discovered in Hg metal in 1911 by Onnes, continues to be only partially understood. It is of great interest to physicists as a macroscopic quantum phenomenon, and to chemists and materials scientists who try to make better superconductors (especially those that superconduct at higher temperatures) and devices derived from them, such as superconducting quantum interference devices (SQUIDs), which are extremely sensitive magnetometers.

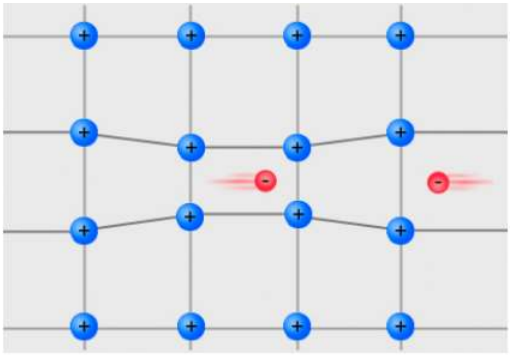


A magnet levitating above a high-temperature superconductor, cooled with liquid nitrogen. Persistent electric current flows on the surface of the superconductor, excluding the magnetic field of the magnet. This current effectively forms an electromagnet that repels the magnet.

Spin pairing and zero resistance

The transition from the metallic to the superconducting state is related to the quantum phenomena of Bose-Einstein condensation and superfluidity. Individual electrons have spin = 1/2, and as such are fermions (particles with half-integer spin). Because of the Pauli exclusion principle, no more than two fermions can occupy the same quantum state (such as an orbital in a molecule or a solid). The familiar consequence of this rule is the aufbau filling of orbitals with spin-paired electrons in each energy level. In contrast, particles with integer spins - which are called bosons - do not have this restriction, and any number of bosons can occupy the same quantized energy level.

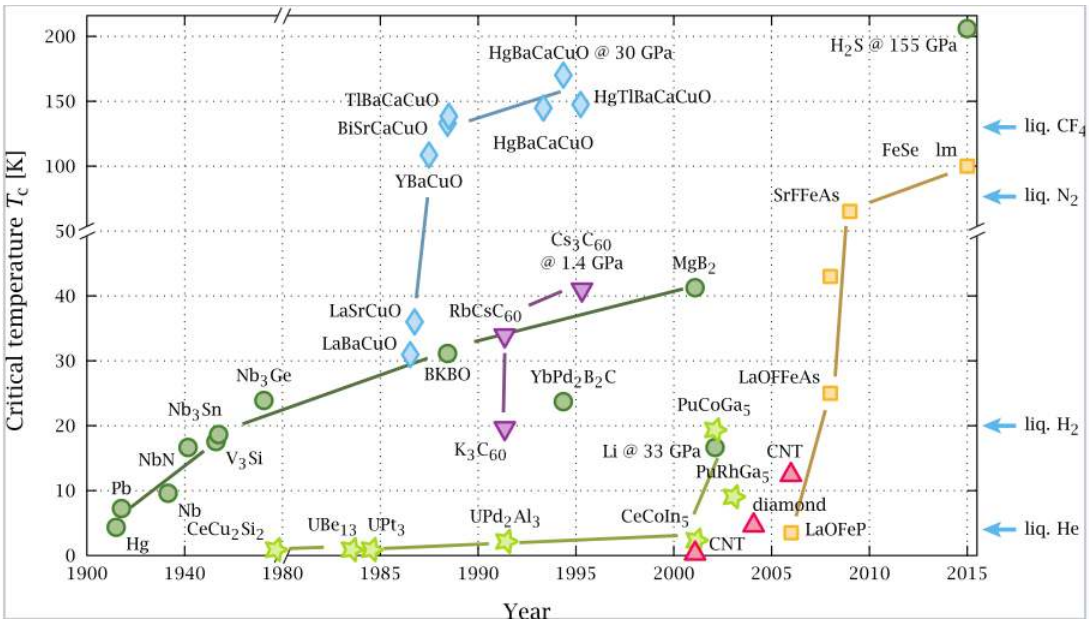
Superconductivity occurs when electrons spin pair into so-called Cooper pairs, which can travel through the lattice together. The electrons in a Cooper pair, although spin-paired, have a long-distance relationship: the spatial extent of a Cooper pair is a few nanometers in cuprate superconductors, and up to one micron in low T_c superconductors such as aluminum. Because its overall spin angular momentum is zero, a Cooper pair is a boson. When the temperature is low enough, the Cooper pairs "condense" into the lowest energy level. The second lowest energy level - which is typically a few meV above the ground state - is not accessible to them as long as the energy gap is larger than the thermal energy, kT. The scattering of electrons by the lattice then becomes forbidden by energy conservation because scattering dissipates energy, and the Cooper pairs cannot change their energy state. Thus the resistance (which arises from scattering, as we learned in Ch. 6) drops abruptly to zero below T_c. However, the Cooper pairs can be broken apart when they move fast, and thus superconductors turn back into normal metals (even below T_c) above some critical current density j_c. This phenomenon is also related to the critical magnetic field, H_c, that quenches superconductivity.



A trampoline for electrons

What causes electrons, which repel each other because of their negative charge, to pair up and travel together in superconductors? The mechanism - which must involve some kind of attractive interaction between electrons - is well understood for "conventional" superconductors which have relatively low transition temperatures, but is not yet known with certainty for high temperature oxide superconductors. In conventional, or BCS superconductors, the spin pairing is mediated by the lattice as shown in the figure at the left. A strong electron-lattice interaction causes a distortion in the lattice as an electron moves through. This elastic deformation is felt as an attractive force by a second electron moving in the opposite direction. This can be thought of as analogous to the interaction of two people jumping on a trampoline. The weight of the first person on the trampoline creates a "well" that attracts the second one, and they tend to move together (even if they don't like each other). Strange as this interaction seems, it is supported experimentally by isotope effects on T_c and by quantitative predictions of T_c values in conventional superconductors.

Bad metals make good superconductors. All superconductors are "normal" metals - with finite electrical resistance - above their critical transition temperature, T_c. If you ask where in the periodic table one might look for superconductors, the answer is surprising. The most conductive metals (Ag, Au, Cu, Cs, etc.) make the worst superconductors, i.e., they have the lowest superconducting transition temperatures, in many cases below 0.01 K. Conversely "bad" metals, such as niobium alloys, certain copper oxides, $K_xBa_{1-x}BiO_3$, MgB_2, FeSe, and alkali salts of C_{60}^{n-} anions, can have relatively high transition temperatures.

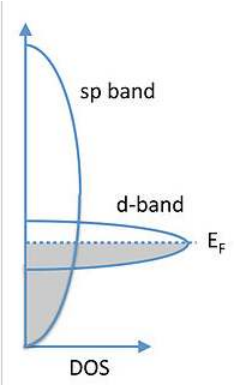


Timeline of superconducting materials, showing T_c vs. year of discovery.

We observe that most good superconductors appear in composition space very **near a metal-insulator transition**. In terms of our microscopic picture, orbital overlap in superconductors is poor, just barely enough to make them act as metals ($\Delta \approx U$) above T_c. In the normal state, superconductors with high T_c - which can be as high as 150 K - are typically "bad" metals. An important characteristic of such metals is that the **mean free path** of electrons (in the normal state, above T_c) is on the order of the lattice

spacing, i.e., **only a few Å**. In contrast, we learned in Ch. 6 that good metals such as Au, Ag, and Cu have electron mean free paths that are two orders of magnitude longer (ca. 40 nm). In a bad metal, the electron "feels" the lattice rather strongly, whereas in a good metal, the electrons are insensitive to small changes in the distance between metals atoms.

What does the band picture look like for a bad metal? The key point is that because orbital overlap is poor, the metal has a **high density of states** at the Fermi level. This is a universal property of high temperature superconductors and provides a clue of where to look for new and improved superconducting materials. Recall that transition elements in the middle of the 3d series (Cr, Fe, Co, Ni) were magnetic because of poor orbital overlap and weak d-d bonding. The elements below these - especially Nb, Ta, and W - have just barely enough d-d orbital overlap to be on the metallic side of the metal-insulator transition and to be "bad" metals. Carbides and nitrides of these elements are typically superconducting, with the carbon and nitrogen atoms serving to adjust the valence electron density, as illustrated in the table below.



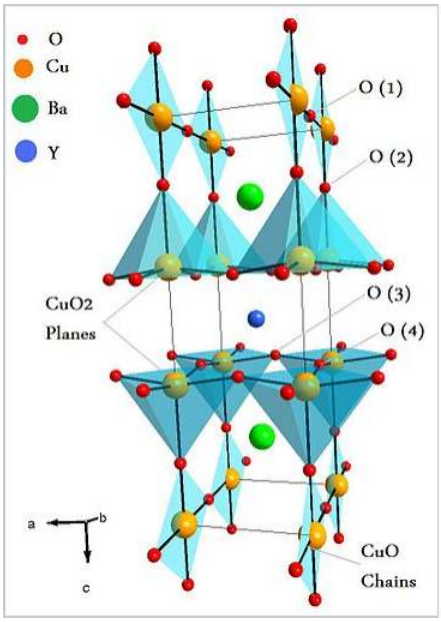
Generic E vs. DOS for a bad metal.

Compound	NbC	Mo_2N	TaC	VN	NbN	TaN	Nb_3Ge
T_c (K)	11.1	5.0	9.7	7.5	15.2	17.8	22.3

High T_c superconductors

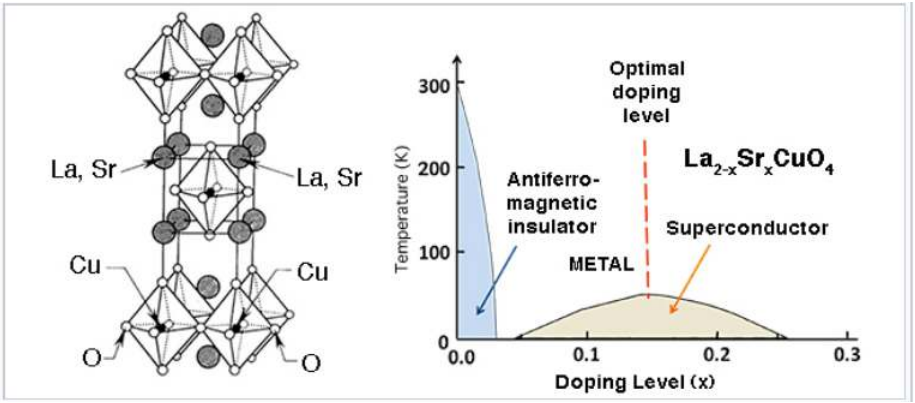
In addition to having weak orbital overlap in the metallic state - which results in a high DOS at E_F - high temperature superconductors also typically contain elements in mixed oxidation states (for example, $Cu^{2+/3+}$ or $Bi^{3+/5+}$) that are close in energy to the O^{2-}/O^- couple in the lattice. At ambient pressure, cuprate superconductors have the highest known T_c values, ranging between about 35 and 150 K. The crystal structures of these materials are almost all variants of the perovskite lattice, as shown at the right for the 1-2-3 superconductor $YBa_2Cu_3O_{7-\delta}$. An ideal perovskite lattice would have formula $ABO_3 = A_3B_3O_9$. In $YBa_2Cu_3O_{7-\delta}$, Y and Ba occupy the A cation sites, Cu occupies the B sites, and two of the nine O atoms are missing.

The $YBa_2Cu_3O_{7-\delta}$ lattice consists of mixed-valent copper(II/III) oxide sheets capped by oxygen atoms to form CuO_5 square pyramids. These sheets encapsulate the Y^{3+} cations. Copper(II) oxide ribbons that share the apical oxygen atoms of the square pyramids run in one direction through the structure. In $YBa_2Cu_3O_{7-\delta}$ and related materials, one component of the structure (here the Cu-O ribbons) acts as a **charge reservoir** to control the doping of the planar CuO_2 sheets, which are the elements of the structure that carry the supercurrent. Cuprate superconductors with Bi, Tl, or Hg-containing charge reservoir layers and multiple, eclipsed CuO_2 sheets in the unit cell tend to have the highest T_c values.



Crystal structure of $YBa_2Cu_3O_{7-\delta}$ (YBCO), the first superconductor with T_c above the boiling point of liquid nitrogen.

The connection between the metal-insulator transtion and superconductivity is nicely illustrated in the phase diagram of $La_{2-x}Sr_xCuO_4$, the first cuprate superconductor, which was discovered in 1986 by Georg Bednorz and K. Alex Müller. This compound has a rather simple structure in which rocksalt La(Sr)O layers are intergrown with perovskite $La(Sr)CuO_3$ layers. Undoped La_2CuO_4 contains only Cu^{2+} ions and is an antiferromagnetic insulator. As a small amount of Sr^{2+} is substituted for La^{3+}, some of the Cu^{2+} is oxidized to Cu^{3+}, and the lattice is doped with holes. As the doping level increases, the antiferromagnetic phase undergoes a first-order phase transition to a "bad" metal, and at slightly higher doping density the superconducting phase appears. The proximity of the superconducting phase to the metal-insulator transition is a hallmark of cuprate superconductors. A maximum T_c of 35K is observed at x = 0.15. Doping at higher levels moves the Fermi level beyond the point of highest DOS in the d-band of Cu and the superconducting phase then gradually disappears. It is interesting to compare this phase diagram with that of V_2O_3 (above), which also undergoes an antiferromagnetic insulator to "bad" metal transition as it is doped.



Crystal structure and phase diagram of the cuprate superconductor $La_{2-x}Sr_xCuO_4$. (LSCO)

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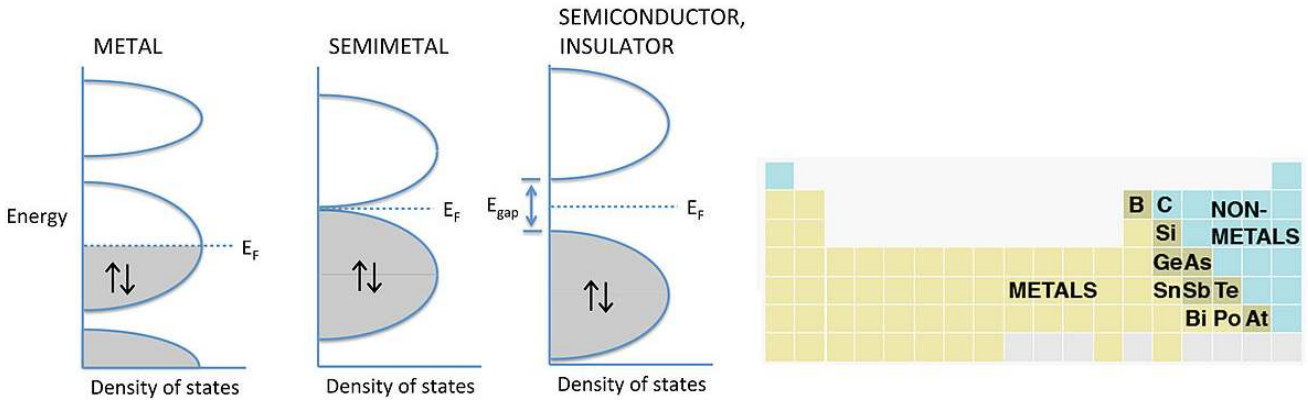
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9.8: Periodic Trends- Metals, Semiconductors, and Insulators

As we consider periodic trends in the electronic properties of materials, it is important to review some of the key bonding trends we have learned in earlier chapters:

- Going down the periodic table, atoms in solids tend to adopt structures with higher coordination numbers.
- The second row of the periodic table is special, with strong s-p hybridization and π-bonding between atoms.
- Electrons in higher quantum shells are less strongly bound, so the energy difference between bonding and antibonding orbitals becomes smaller for heavier atoms.

We also know that most of the elements in the periodic table are metals, but the elements in the top right corner are insulating under ordinary conditions (1 atm. pressure) and tend to obey the octet rule in their compounds.



At the transition between metals and non-metals in the periodic table we encounter a crossover in electronic properties, as well as in other properties such as the acidity of the oxides (see Ch. 3). The group of elements at the border is loosely referred to as the metalloids. Several of these elements (such as C, Sn, and As) can exist as different allotropes that can be metals, insulators, or something in between.

A more rigorous delineation of the electronic properties of these elements (and of many compounds) can be made by considering their band structures and the **temperature dependence of the electronic conductivity**. As we have previously discussed, metals have partially filled energy bands, meaning that the Fermi level intersects a partially filled band. With increasing temperature, metals become poorer conductors because lattice vibrations (which are called phonons in the physics literature) scatter the mobile valence electrons. In contrast, semiconductors and insulators, which have filled and empty bands, become better conductors at higher temperature, since some electrons are thermally excited to the lowest empty band. The distinction between insulators and semiconductors is arbitrary, and from the point of view of metal-insulator transitions, all semiconductors are insulators. We typically call an insulator a semiconductor if its band gap (E_{gap}) is less than about 3 eV. A semimetal is a material that has a band gap near zero, examples being single sheets of sp^2-bonded carbon (graphene) and elemental Bi. Like a narrow gap semiconductor, a semimetal has higher conductivity at higher temperature.

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9.9: Semiconductors- Band Gaps, Colors, Conductivity and Doping

Semiconductors, as we noted above, are somewhat arbitrarily defined as insulators with **band gap energy ≤ 3.0 eV** (~290 kJ/mol). This cutoff is chosen because, as we will see, the conductivity of undoped semiconductors drops off exponentially with the band gap energy and at 3.0 eV it is very low. Also, materials with wider band gaps (e.g. $SrTiO_3$, E_{gap} = 3.2 eV) do not absorb light in the visible part of the spectrum

There are a number of places where we find semiconductors in the periodic table:

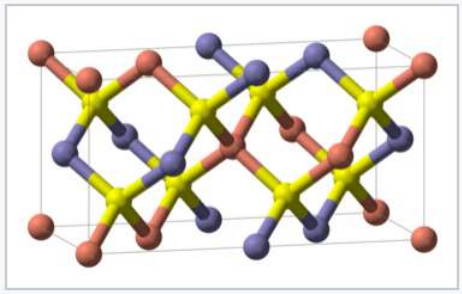
- Early transition metal oxides and nitrides, especially those with d^0 electron counts such as TiO_2, TaON, and WO_3
- Oxides of later 3d elements such as Fe_2O_3, NiO, and Cu_2O
- Layered transition metal chalcogenides with d^0, d^2 and d^6 electron counts including TiS_2, ZrS_2, MoS_2, WSe_2, and PtS_2
- d^{10} copper and sliver halides, e.g., CuI, AgBr, and AgI
- Zincblende- and wurtzite-structure compounds of the p-block elements, especially those that are isoelectronic with Si or Ge, such as GaAs and CdTe. While these are most common, there are other p-block semiconductors that are not isoelectronic and have different structures, including GaS, PbS, and Se.



A 2" wafer cut from a GaAs single crystal. GaAs, like many p-block semiconductors, has the zincblende structure.

The **p-block octet semiconductors** are by far the most studied and important for technological applications, and are the ones that we will discuss in detail.

Zincblende- and wurtzite-structure semiconductors have 8 valence electrons per 2 atoms. These combinations include 4-4 (Si, Ge, SiC,…), 3-5 (GaAs, AlSb, InP,…), 2-6 (CdSe, HgTe, ZnO,…), and 1-7 (AgCl, CuBr,…) semiconductors. Other variations that add up to an octet configuration are also possible, such as $Cu^{I}In^{III}Se_2$, which has the **chalcopyrite** structure, shown at the right.



The **chalcopyrite structure** is adopted by ABX_2 octet semiconductors such as $Cu^{I}In^{III}Se_2$ and $Cd^{II}Sn^{IV}P_2$. The unit cell is doubled relative to the parent **zincblende structure** because of the ordered arrangement of cations. Each anion (yellow) is coordinated by two cations of each type (blue and red).

How does the **band gap energy** vary with **composition**? There are two important trends

(1) Going **down a group** in the periodic table, the gap **decreases**:

C (diamond) > Si > Ge > α-Sn

E_{gap} (eV): 5.4 1.1 0.7 0.0

This trend can be understood by recalling that E_{gap} is related to the **energy splitting between bonding and antibonding orbitals**. This difference decreases (and bonds become weaker) as the principal quantum number increases.

(2) For isoelectronic compounds, **increasing ionicity** results in a **larger band gap**.

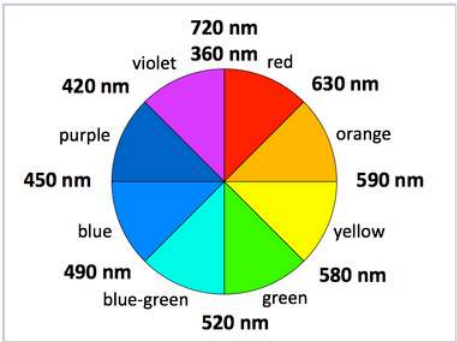
Ge < GaAs < ZnSe
0.7 1.4 2.8 eV

Sn < InSb < CdTe < AgI
0.0 0.2 1.6 2.8 eV

This trend can also be understood from a simple MO picture, as we discussed in Ch. 2. As the electronegativity difference $\Delta\chi$ increases, so does the energy difference between bonding and antibonding orbitals.

The band gap is a very important property of a semiconductor because it determines its color and conductivity. Many of the applications of semiconductors are related to band gaps:

- Narrow gap materials ($Hg_xCd_{1-x}Te$, VO_2, InSb, Bi_2Te_3) are used as infrared photodetectors and thermoelectrics (which convert heat to electricity).
- Wider gap materials (Si, GaAs, GaP, GaN, CdTe, $CuIn_xGa_{1-x}Se_2$) are used in electronics, light-emitting diodes, and solar cells.



Color wheel showing the colors and wavelengths of emitted light.

Semiconductor solid solutions such as $GaAs_{1-x}P_x$ have band gaps that are intermediate between the end member compounds, in this case GaAs and GaP (both zincblende structure). Often, there is a linear relation between composition and band gap, which is referred to as **Vegard's Law**. This "law" is often violated in real materials, but nevertheless offers useful guidance for designing materials with specific band gaps. For example, red and orange light-emitting diodes (LED's) are made from solid solutions with compositions of $GaP_{0.40}As_{0.60}$ and $GaP_{0.65}As_{0.35}$, respectively. Increasing the mole fraction of the lighter element (P) results in a larger band gap, and thus a higher energy of emitted photons.

Colors of semiconductors

The color of absorbed and emitted light both depend on the band gap of the semiconductor. Visible light covers the range of approximately 390-700 nm, or 1.8-3.1 eV. The **color of emitted light** from an LED or semiconductor laser corresponds to the band gap energy and can be read off the color wheel shown at the right.



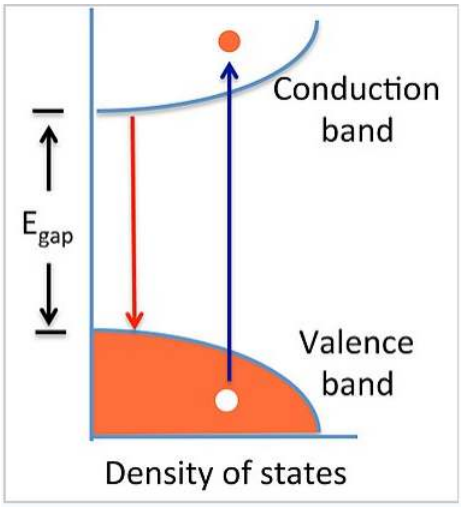
Fe_2O_3 powder is reddish orange because of its 2.2 eV band gap

The color of **absorbed light** includes the band gap energy, but also all colors of higher energy (shorter wavelength), because electrons can be excited from the valence band to a range of energies in the conduction band. Thus semiconductors with band gaps in the infrared (e.g., Si, 1.1 eV and GaAs, 1.4 eV) appear black because they absorb all colors of visible light. Wide band gap semiconductors such as TiO_2 (3.0 eV) are white because they absorb only in the UV. Fe_2O_3 has a band gap of 2.2 eV and thus absorbs light with $\lambda < 560$ nm. It thus appears reddish-orange (the colors of light reflected from Fe_2O_3) because it absorbs green, blue, and violet light. Similarly, CdS (E_{gap} = 2.6 eV) is yellow because it absorbs blue and violet light.

Electrons and holes in semiconductors

Pure (undoped) semiconductors can conduct electricity when electrons are promoted, either by heat or light, from the valence band to the conduction band. The promotion of an **electron** (e^-) leaves behind a **hole** (h^+) in the valence band. The hole, which is the absence of an electron in a bonding orbital, is also a mobile charge carrier, but with a positive charge. The motion of holes in the lattice can be pictured as analogous to the movement of an empty seat in a crowded theater. An empty seat in the middle of a row can move to the end of the row (to accommodate a person arriving late to the movie) if everyone moves over by one seat. Because the movement of the hole is in the opposite direction of electron movement, it acts as a positive charge carrier in an electric field.

The opposite process of excitation, which creates an electron-hole pair, is their recombination. When a conduction band electron drops down to recombine with a valence band hole, both are annihilated and energy is released. This release of energy is responsible for the emission of light in LEDs.



An electron-hole pair is created by adding heat or light energy $E \geq E_{gap}$ to a semiconductor (blue arrow). The electron-hole pair recombines to release energy equal to E_{gap} (red arrow).

At equilibrium, the creation and annihilation of electron-hole pairs proceed at equal rates. This dynamic equilibrium is analogous to the dissociation-association equilibrium of H^+ and OH^- ions in water. We can write a mass action expression:

$$n \times p = K_{eq} = n_i^2$$

where n and p represent the number density of electrons and holes, respectively, in units of cm^{-3}. The intrinsic carrier concentration, n_i, is equal to the number density of electrons or holes in an undoped semiconductor, where $n = p = n_i$.

Note the similarity to the equation for water autodissociation:

$[H^+][OH^-] = K_w$

By analogy, we will see that when we increase n (e.g., by doping), p will decrease, and vice-versa, but their product will remain constant at a given temperature.

Temperature dependence of the carrier concentration. Using the equations $K_{eq} = e^{(\frac{-\Delta G^o}{RT})}$ and $\Delta G^o = \Delta H^o - T\Delta S^o$, we can write:

$$n \times p = n_i^2 = e^{(\frac{\Delta S^o}{R})} e^{(\frac{-\Delta H^o}{RT})} \tag{9.9.1}$$

The entropy change for creating electron hole pairs is given by:

$$\Delta S^o = Rln(N_V) + Rln(N_V) = Rln(N_C N_V) \tag{9.9.2}$$

where N_V and N_C are the effective density of states in the valence and conduction bands, respectively.

and thus we obtain

$$n_i^2 = N_C N_V e^{(-\Delta H^o RT)} \tag{9.9.3}$$

Since the volume change is negligible, $\Delta H^o \approx \Delta E^o$, and therefore $\frac{\Delta H^o}{R} \approx \frac{E_{gap}}{k}$, from which we obtain

$$n_i^2 = N_C N_V e^{(\frac{-E_{gap}}{kT})} \tag{9.9.4}$$

and finally

$$\mathbf{n = p = n_i = (N_C N_V)^{\frac{1}{2}} e^{(\frac{-E_{gap}}{2kT})}} \tag{9.9.5}$$

For pure Si (E_{gap} = 1.1 eV) with N ≈ $10^{22}/cm^3$, we can calculate from this equation a carrier density n_i of approximately $10^{10}/cm^3$ at 300 K. This is about 12 orders of magnitude lower than the valence electron density of Al, the element just to the left of Si in the periodic table. Thus we expect the conductivity of pure semiconductors to be many orders of magnitude lower than those of metals.

Conductivity of intrinsic semiconductors

The conductivity (σ) is the product of the number density of carriers (n or p), their charge (e), and their mobility (μ). Recall from Chapter 6 that μ is the ratio of the carrier drift velocity to the electric field and has units of cm^2/Volt-second. Typically electrons and holes have somewhat different mobilities (μ_e and μ_h, respectively) so the conductivity is given by:

$$\sigma = ne\mu_e + pe\mu_h \tag{9.9.6}$$

For either type of charge carrier, we recall from Ch. 6 that the mobility μ is given by:

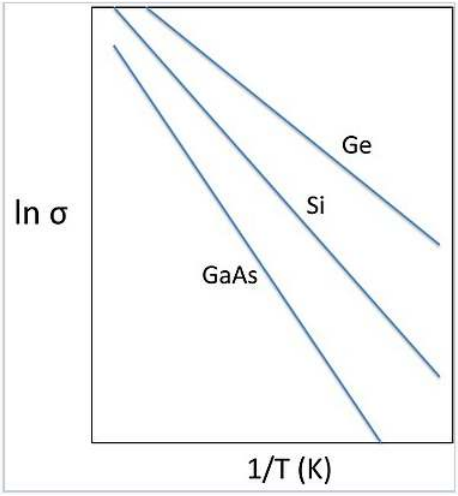
$$\mu = \frac{v_{drift}}{E} = \frac{e\tau}{m} \tag{9.9.7}$$

where e is the fundamental unit of charge, τ is the scattering time, and m is the effective mass of the charge carrier.

Taking an average of the electron and hole mobilities, and using n = p, we obtain

$$\sigma = \sigma_o \mathbf{e}^{(\frac{-E_{gap}}{2kT})},\ where\ \sigma_o = 2(N_C N_V)^{\frac{1}{2}} e\mu \tag{9.9.8}$$

By measuring the conductivity as a function of temperature, it is possible to obtain the activation energy for conduction, which is $E_{gap}/2$. This kind of plot, which resembles an Arrhenius plot, is shown at the right for three different undoped semiconductors. The slope of the line in each case is $-E_{gap}/2k$.

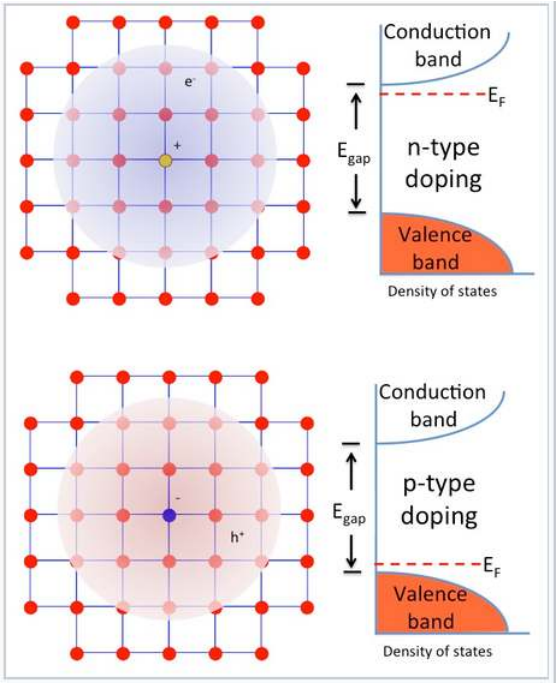


Plots of ln(σ) vs. inverse temperature for intrinsic semiconductors Ge (E_{gap} = 0.7 eV), Si (1.1 eV) and GaAs (1.4 eV). The slope of the line is $-E_{gap}/2k$.

Doping of semiconductors. Almost all applications of semiconductors involve controlled **doping**, which is the substitution of impurity atoms, into the lattice. Very small amounts of dopants (in the parts-per-million range) dramatically affect the conductivity of semiconductors. For this reason, very pure semiconductor materials that are carefully doped - both in terms of the concentration and spatial distribution of impurity atoms - are needed.

n- and p-type doping. In crystalline Si, each atom has four valence electrons and makes four bonds to its neighbors. This is exactly the right number of electrons to completely fill the valence band of the semiconductor. Introducing a phosphorus atom into the lattice (the positively charged atom in the figure at the right) adds an extra electron, because P has five valence electrons and only needs four to make bonds to its neighbors. The extra electron, at low temperature, is bound to the phosphorus atom in a hydrogen-like molecular orbital that is much larger than the 3s orbital of an isolated P atom because of the high dielectric constant of the semiconductor. In silicon, this "expanded" Bohr radius is about 42 Å, i.e., 80 times larger than in the hydrogen atom. The energy needed to ionize this electron – to allow it to move freely in the lattice - is only about 40–50 meV, which is not much larger the thermal energy (26 meV) at room temperature. Therefore the Fermi level lies just below the conduction band edge, and a large fraction of these extra electrons are promoted to the conduction band at room temperature, leaving behind fixed positive charges on the P atom sites. The crystal is **n-doped**, meaning that the majority carrier (electron) is negatively charged.

Alternatively, boron can be substituted for silicon in the lattice, resulting in **p-type** doping, in which the majority carrier (hole) is positively charged. Boron has only three valence electrons, and "borrows" one from the Si lattice, creating a positively charged hole that exists in a large hydrogen-like orbital around the B atom. This hole can become delocalized by promoting an electron from the valence band to fill the localized hole state. Again, this process requires only 40–50 meV, and so at room temperature a large fraction of the holes introduced by boron doping exist in delocalized valence band states. The Fermi level (the electron energy level that has a 50% probability of occupancy at zero temperature) lies just above the valence band edge in a p-type semiconductor.



n- and p-type doping of semiconductors involves substitution of electron donor atoms (light orange) or acceptor atoms (blue) into the lattice. These substitutions introduce extra electrons or holes, respectively, which are easily ionized by thermal energy to become free carriers. The Fermi level of a doped semiconductor is a few tens of mV below the conduction band (n-type) or above the valence band (p-type).

As noted above, the doping of semiconductors dramatically changes their conductivity. For example, the intrinsic carrier concentration in Si at 300 K is about 10^{10} cm^{-3}. The mass action equilibrium for electrons and holes also applies to doped semiconductors, so we can write:

$$n \times p = n_i^2 = 10^{20} cm^{-6} \; at \; 300K \tag{9.9.9}$$

If we substitute P for Si at the level of one part-per-million, the concentration of electrons is about 10^{16} cm^{-3}, since there are approximately 10^{22} Si atoms/cm^3 in the crystal. According to the mass action equation, if n = 10^{16}, then p = 10^4 cm^{-3}. There are three consequences of this calculation:

- The density of carriers in the doped semiconductor (10^{16} cm^{-3}) is much higher than in the undoped material (~10^{10} cm^{-3}), so the conductivity is also many orders of magnitude higher.
- The activation energy for conduction is only 40–50 meV, so the conductivity does not change much with temperature (unlike in the intrinsic semiconductor)
- The minority carriers (in this case holes) do not contribute to the conductivity, because their concentration is so much lower than that of the majority carrier (electrons).

Similarly, for p-type materials, the conductivity is dominated by holes, and is also much higher than that of the intrinsic semiconductor.

Chemistry of semiconductor doping. Sometimes it is not immediately obvious what kind of doping (n- or p-type) is induced by "messing up" a semiconductor crystal lattice. In addition to substitution of impurity atoms on normal lattice sites (the examples given above for Si), it is also possible to dope with vacancies - missing atoms - and with interstitials - extra atoms on sites that are not ordinarily occupied. Some simple rules are as follows:

- For substitutions, adding an **atom to the right** in the periodic table results in **n-type** doping, and an atom to the **left** in **p-type** doping.

  For example, when TiO_2 is doped with Nb on some of the Ti sites, or with F on O sites, the result is n-type doping. In both cases, the impurity atom has one more valence electron than the atom for which it was substituted. Similarly, substituting a small amount of Zn for Ga in GaAs, or a small amount of Li for Ni in NiO, results in p-type doping.

- **Anion vacancies** result in **n-type** doping, and **cation vacancies** in **p-type** doping.

  Examples are anion vacancies in CdS_{1-x} and WO_{3-x}, both of which give n-type semiconductors, and copper vacancies in $Cu_{1-x}O$, which gives a p-type semiconductor.

- **Interstitial cations** (e.g. Li) donate electrons to the lattice resulting in **n-type** doping. Interstitial anions are rather rare but would result in p-type doping.

Sometimes, there can be both p- and n-type dopants in the same crystal, for example B and P impurities in a Si lattice, or cation and anion vacancies in a metal oxide lattice. In this case, the two kinds of doping **compensate** each other, and the doping type is determined by the one that is in higher concentration. A dopant can also be present on more than one site. For example, Si can occupy both the Ga and As sites in GaAs, and the two substitutions compensate each other. Si has a slight preference for the Ga site, however, resulting in n-type doping.

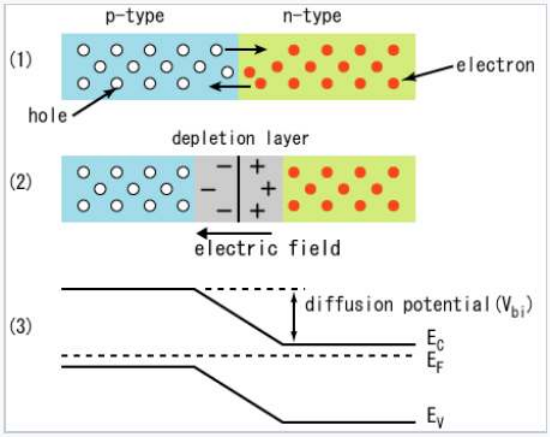
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9.10: Semiconductor p-n Junctions

Semiconductor p-n junctions are important in many kinds of electronic devices, including diodes, transistors, light-emitting diodes, and photovoltaic cells. To understand the operation of these devices, we first need to look at what happens to electrons and holes when we bring p-type and n-type semiconductors together. At the junction between the two materials, mobile electrons and holes annihilate each other, leaving behind the fixed + and - charges of the electron donor and electron acceptor dopants, respectively. For example, on the n-side of a silicon p-n junction, the positively charged dopants are P^+ ions and on the p-side the negatively charged dopants are B^-. The presence of these uncompensated electrical charges creates an electric field, the **built-in field** of the p-n junction. The region that contains these charges (and a very low density of mobile electrons or holes) is called the **depletion region**.

The electric field, which is created in the depletion region by electron-hole recombination, repels both the electrons (on the n-side) and holes (on the p-side) away from the junction. The concentration gradient of electrons and holes, however, tends to move them in the opposite direction by diffusion. At equilibrium, the flux of mobile carriers is zero because the field-driven migration flux is equal and opposite to the concentration-driven diffusion flux.



When p-type and n-type semiconductors are joined, electrons and holes are annihilated at the interface, leaving a depletion region that contains positively and negatively charged donor and acceptor atoms, respectively. At equilibrium, the Fermi level (E_F) is uniform throughout the junction. E_F lies just above the valence band on the p-type side of the junction and just below the conduction band on the n-type side.

The width of the depletion layer depends on the screening length in the semiconductor, which in turn depends on the dopant density. At high doping levels, the depletion layer is narrow (tens of nanometers across), whereas at low doping density it can be as thick as 1 µm. The depletion region is the only place where the electric field is nonzero, and the only place where the bands bend. Elsewhere in the semiconductor the field is zero and the bands are flat.

In the middle of p-n junction, the Fermi level energy, E_F, is halfway between the valence band, VB, and the conduction band, CB, and the semiconductor is intrinsic ($n = p = n_i$)

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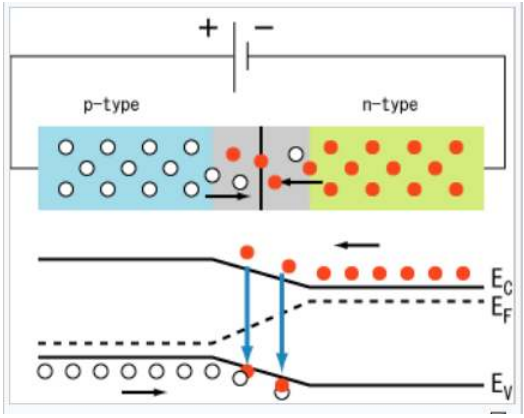
9.11: Diodes, LEDs and Solar Cells

Diodes are semiconductor devices that allow current to flow in only one direction. Diodes act as rectifiers in electronic circuits, and also as efficient light emitters (in LEDs) and solar cells (in photovoltaics). The basic structure of a diode is a junction between a p-type and an n-type semiconductor, called a p-n junction. Typically, diodes are made from a single semiconductor crystal into which p- and n- dopants are introduced.



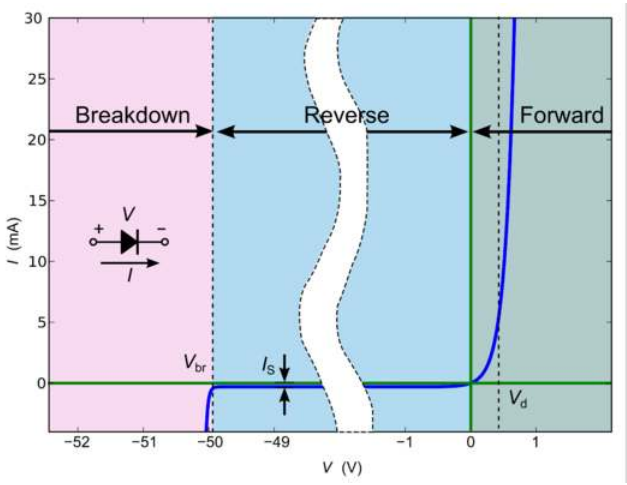
Closeup of a diode, showing the square-shaped semiconductor crystal *(black object on left)* (John Maushammer, Wikipedia, CC-BY-SA)

If the n-side of a diode is biased at positive potential and the p-side is biased negative, electrons are drawn to the n-side and holes to the p-side. This reinforces the built in potential of the p-n junction, the width of the depletion layer increases, and very little current flows. This polarization direction is referred to as "back bias." If the diode is biased the other way, carriers are driven into the junction where they recombine. The electric field is diminished, the bands are flattened, and current flows easily since the applied bias lowers the built-in potential. This is called "forward bias."



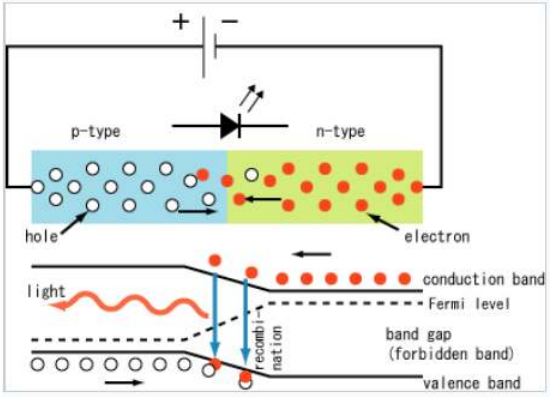
Electrons (red) and holes (white) in a forward-biased diode. (S-kei. Wikipedia, CC-BY-SA)

The figure on the left illustrates a forward-biased diode, through which current flows easily. As electrons and holes are driven into the junction (black arrows in lower left figure), they recombine (downward blue arrows), producing light and/or heat. The Fermi level in the diode is indicated as the dotted line. There is a drop in the Fermi level (equal to the applied bias) across the depletion layer. The corresponding diode i-V curve is shown on the right. The current rises exponentially with applied voltage in the forward bias direction, and there is very little leakage current under reverse bias. At very high reverse bias (typically tens of volts) diodes undergo avalanche breakdown and a large reverse current flows.



Diode i-V curve

A **light-emitting diode** or **LED** is a kind of diode that converts some of the energy of electron-hole recombination into light. This radiative recombination process always occurs in competition with non-radiative recombination, in which the energy is simply converted to heat. When light is emitted from an LED, the photon energy is equal to the bandgap energy. Because of this, LED lights have pure colors and narrow emission spectra relative to other light sources, such as incandescent and fluorescent lights. LED lights are energy-efficient and thus are typically cool to the touch.



Light-emitting diode (LED). (S-kei. Wikipedia, CC-BY-SA)

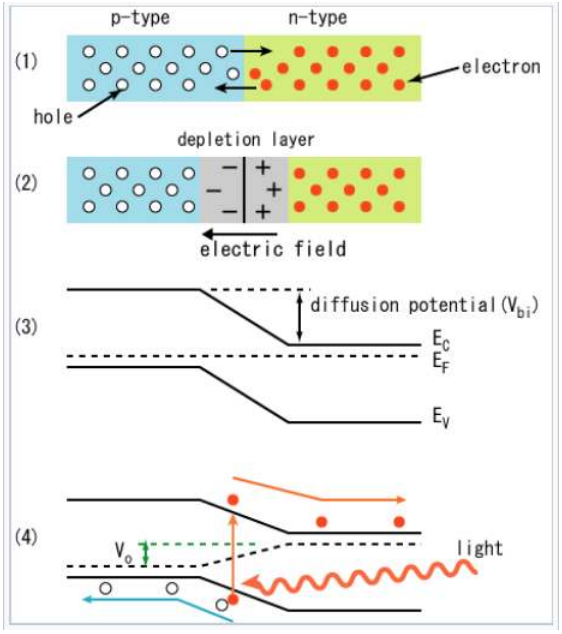
Direct-gap semiconductors such as GaAs and GaP have efficient luminescence and are also good light absorbers. In direct gap semiconductors, there is no momentum change involved in electron-hole creation or recombination. That is, the electrons and holes originate at the same value of the momentum wavevector **k**, which we encountered in Ch. 6. **k** is related to the momentum (also a vector quantity) by **p** = h**k**/2π. In a direct-gap semiconductor, the top of the valence band and the bottom of the conduction band most typically both occur at **k** = 0. Since the momentum of the photon is close to zero, photon absorption and emission are strongly allowed (and thus kinetically fast). Polar semiconductors such as GaAs, GaN, and CdSe are typically direct-gap materials. **Indirect-gap** semiconductors such as Si and Ge absorb and emit light very weakly because the valence band maximum and conduction band minimum do not occur at the same point in k-space. This means that a lattice vibration (a phonon) must also be created or annihilated in order to conserve momentum. Since this "three body" (electron, hole, phonon) process has low probability, the radiative recombination of electrons and holes is slow relative to non-radiative decay - the thermalization of electron-hole energy as lattice vibrations - in indirect-gap semiconductors. The momentum selection rule thus prevents light absorption/emission and there are no pure Si LEDs or Si-based lasers.



Prof. Shuji Nakamura holding a blue LED.

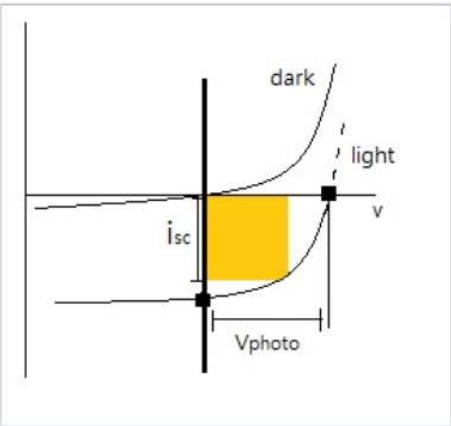
While red, orange, yellow, and green LEDs can be fabricated relatively easily from AlP-GaAs solid solutions, it was initially very difficult to fabricate blue LEDs because the best direct gap semiconductor with a bandgap in the right energy range is a nitride, GaN, which is difficult to make and to dope p-type. Working at Nichia Corporation in Japan, Shuji Nakamura succeeded in developing a manufacturable process for p-GaN, which is the basis of the blue LED. Because of the importance of this work in the development of information storage (Blu-Ray technology) and full-spectrum, energy-efficient LED lighting, Nakamura shared the 2014 Nobel Prize in Physics with Isamu Asaki and Hiroshi Amano, both of whom had made earlier contributions to the development of GaN diodes.

A **Solar cell**, or photovoltaic cell, converts light absorbed in a p-n junction directly to electricity by the photovoltaic effect. Photovoltaics is the field of technology and research related to the development of solar cells for conversion of solar energy to electricity. Sometimes the term solar cell is reserved for devices intended specifically to capture energy from sunlight, whereas the term photovoltaic cell is used when the light source is unspecified.



Photovoltaic effect in a semiconductor p-n junction. (S-kei. Wikipedia, CC-BY-SA)

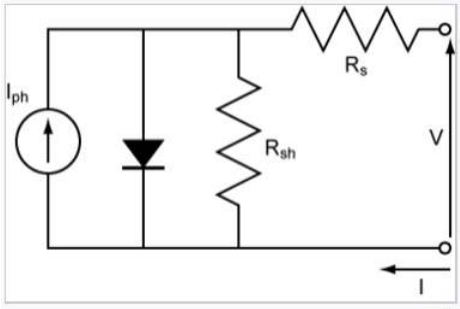
Photocurrent in p-n junction solar cells flows in the diode reverse bias direction. In the dark, the solar cell simply acts as a diode. In the light, the photocurrent can be thought of as a constant current source, which is added to the i-V characteristic of the diode. The relationship between the dark and light current in a photovoltaic cell is shown in the diagram at the left.



Current-voltage characteristic of a solar cell in the dark and under illumination with band gap light. The short-circuit photocurrent is indicated as i_{sc}, and the open-circuit photovoltage is V_{photo}. The maximum power generated by the solar cell is determined by the area of the orange box.

The built-in electric field of the p-n junction separates e^- h^+ pairs that are formed by absorption of bandgap light in the depletion region. The electrons flow downhill, towards the n-type side of the junction, the holes flow uphill towards the p-side. If $h\nu \geq E_{gap}$, light can be absorbed by promoting an electron from the valence band to the conduction band. Any excess energy is rapidly thermalized. Light with $h\nu > E_g$ thus can store only E_g worth of energy in an e^- h^+ pair. If light is absorbed outside of depletion region, i.e., on the n- or p-side of the junction where there is no electric field, minority carriers must diffuse into the junction in order to be collected. This process occurs in competition with electron-hole recombination. Because impurity atoms and lattice defects make efficient recombination centers, semiconductors used in solar cells (especially indirect-gap materials such as Si, which must be relatively thick in order to absorb most of the solar spectrum) must be very pure. Most of the cost of silicon solar cells is associated with the process of purifying elemental silicon and growing large single crystals from the melt.

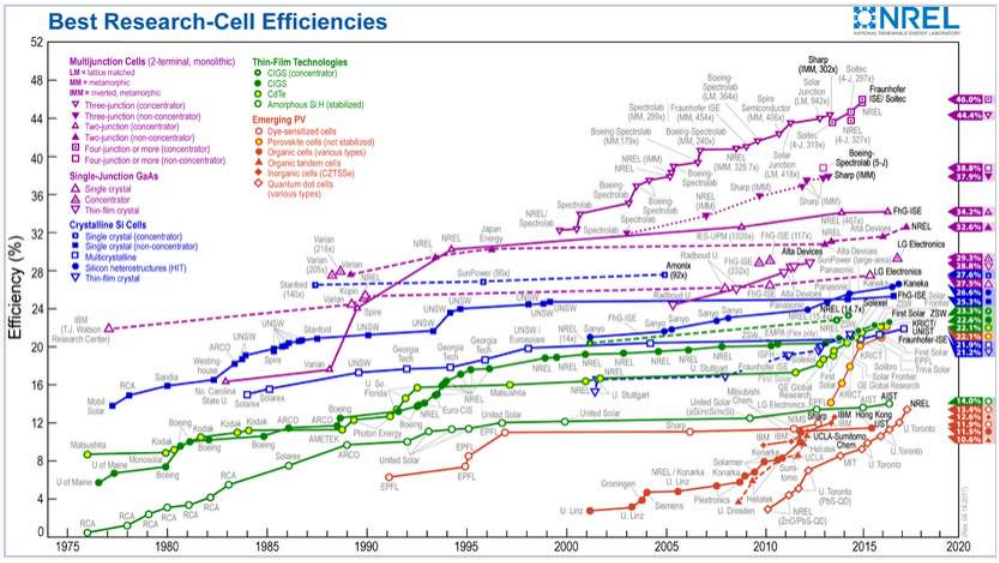
In the photodiode i-V curve above, V_{photo} is typically only about 70% of the bandgap energy E_{gap}. The photocurrent is limited by the photon flux, the recombination rate, and the re-emission of absorbed light.[6] The area of the orange rectangle indicates the power generated by the solar cell, which can be calculated as P = i x V. In good single crystal or polycrystalline solar cells made of Si, GaAs, CdTe, $CuIn_xGa_{1-x}Se_2$, or $(CH_3NH_3)PbI_3$ the quantum yield (the ratio of short circuit photocurrent to photon flux) is close to unity.



The equivalent circuit of a p-n junction solar cell, which results in the "light" i-V curve shown in the figure above. The solar cell is effectively a diode with a reverse-bias current source provided by light-generated electrons and holes. The shunt resistance (R_{sh}) in the equivalent circuit represents parasitic electron-hole recombination. A high shunt resistance (low recombination rate) and low series resistance (R_s) are needed for high solar cell efficiency.

Solar cells have many current applications. Individual cells are used for powering small devices such as electronic calculators. Photovoltaic arrays generate a form of renewable electricity, particularly useful in situations where electrical power from the grid is unavailable such as in remote area power systems, Earth-orbiting satellites and space probes, remote radio-telephones and water pumping applications. Photovoltaic electricity is also increasingly deployed in grid-tied electrical systems.

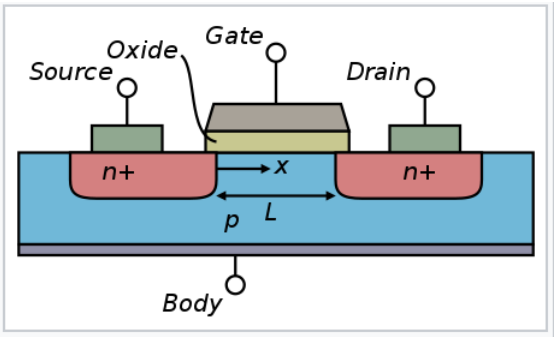
The cost of installed photovoltaics (calculated on a per-watt basis) has dropped over the past decade at a rate of about 13% per year, and has already reached grid parity in Germany and a number of other countries.[7] Photovoltaic grid parity is anticipated in U.S. power markets in the 2020 timeframe.[8] A major driver in the progressively lower cost of photovoltaic power is the steadily increasing efficiency of solar cells, which is shown in the graphic at the right. Higher efficiency solar cells require less area to deliver the same amount of power, and this lowers the "balance of system" costs such as wiring, roof mounting, etc., which scale as the area of the solar panels. Progress towards higher efficiency reflects improved processes for making photovoltaic materials such as silicon and gallium arsenide, as well as the discovery of new materials. Silicon solar cells are a mature technology, so they are now in the flat part of the learning curve and are approaching their maximum theoretical efficiencies. Newer technologies such as organic photovoltaics, quantum dot solar cells, and lead halide perovskite cells are still in the rising part of the learning curve.



Reported timeline of solar cell energy conversion efficiencies since 1976 (National Renewable Energy Laboratory)

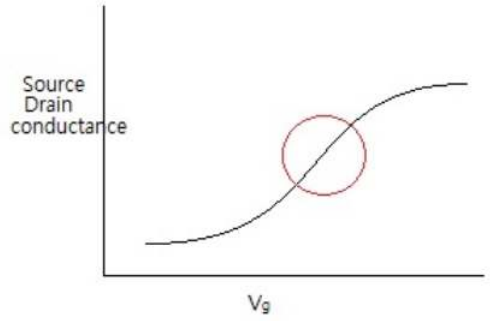
A **field effect transistor (FET)** is a transistor that uses an electric field to control the width of a conducting channel and thus the current in a semiconductor material. It is classified as unipolar transistor, in contrast to bipolar transistors.

Field effect transistors function as current amplifiers. The typical structure of Si-based FETs is one in which two n-type regions (the source and the drain) are separated by a p-type region. An oxide insulator over the p-type region separates a metal gate lead from the semiconductor. This structure is called a metal-oxide-semiconductor FET (or MOSFET). When voltage is applied between source and drain, current cannot flow because either the n-p or the p-n junction is back-biased. When a positive potential is applied to the gate, however, electrons are driven towards the gate, and locally the semiconductor is "inverted" to n-type. Then the current flows easily between the n-type source and drain through the n-channel. The current flow between the source and drain is many times larger than the current through the gate, and thus the FET can act as an amplifier. Current flow can also represent a logical "1," so FETs are also used in digital logic.



Cross section of an n-type MOSFET

In electronic devices such as microprocessors, field-effect transistors are kept in the off-state most of the time in order to minimize background current and power consumption. The FET shown above, which has n-type source and drain regions, is called an NMOS transistor. In a PMOS transistor, the source and drain regions are p-type and the gate is n-type. In **CMOS** (complementary metal-oxide semiconductor) integrated circuits, both NMOS and PMOS transistors are used. CMOS circuits are constructed in such a way that all PMOS transistors must have either an input from the voltage source or from another PMOS transistor. Similarly, all NMOS transistors must have either an input from ground or from another NMOS transistor. This arrangement results in low static power consumption.



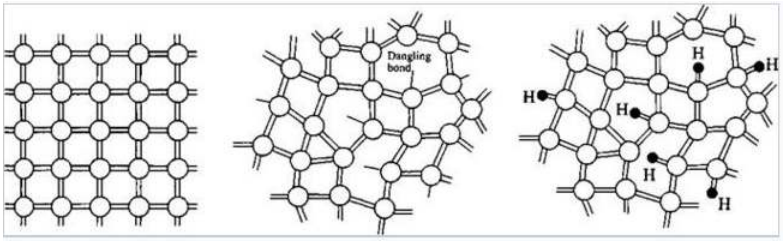
Transistors are most useful in the range of gate voltage (indicated by the red circle in the figure at the left) where the source-drain current changes rapidly. In this region it is possible to effect a large change in current between source and drain when a small signal is applied to the gate. An important figure of merit for FETs is the **subthreshold slope**, which is the slope a plot of log(current) vs. V_{gate}. An ideal subthreshold slope is one decade of current per 60 mV of gate bias. Typically, a decade change in source-drain current can be achieved with a change in gate voltage of ~70 mV. The performance of FETs as switches and amplifiers is limited by the subthreshold slope, which in turn is limited by the capacitance of the gate. It is desirable to have a very high gate capacitance, which requires a thin insulating oxide, but also to have a small leakage current, which requires a thick oxide. A current challenge in the semiconductor industry is to continue to scale FETs to even smaller nanoscale dimensions while maintaining acceptable values of these parameters. This is being done by developing new gate insulator materials that have higher dielectric constants than silicon oxide and do not undergo redox reactions with silicon or with metal gate leads. Only a few known materials (such as hafnium oxynitride and hafnium silicates) currently meet these stringent requirements.

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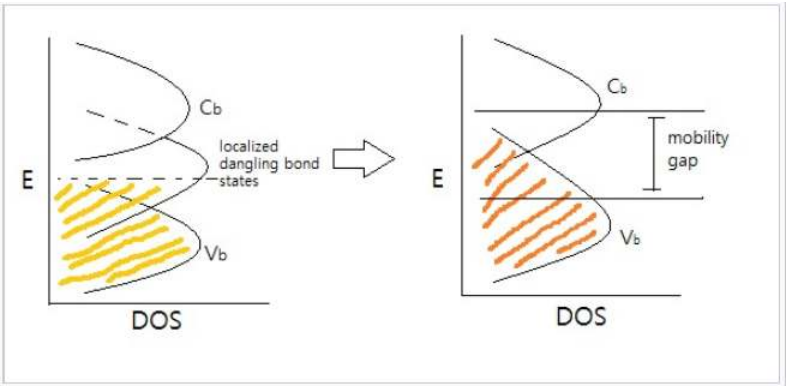
9.12: Amorphous Semiconductors

Amorphous semiconductors are disordered or glassy forms of crystalline semiconductor materials. Like non-conducting glasses, they are network structures with primarily covalent bonding. Crystalline silicon, which has the diamond structure, is an ordered arrangement of fused six-membered silicon rings, all in the "chair" conformation, as we saw in Ch. 8. The local bonding environment of the silicon atoms is tetrahedral. The silicon atoms in amorphous silicon (a-Si) are also predominantly tetrahedrally coordinated, but there is no long-range order in the structure. In addition to six-membered rings, there are five- and seven-membered rings, as well as some "dangling bond" sites in which Si atoms have only three nearest neighbors.



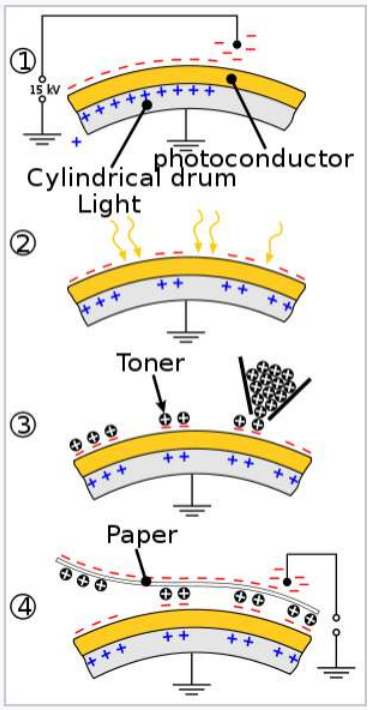
Schematic illustration of the structures of crystalline silicon (left), amorphous silicon (middle), and amorphous hydrogenated silicon (right)

Two of the most widely studied amorphous semiconductors are a-Si and amorphous selenium, a-Se. Si and Se can both be made in glassy form, usually by sputtering or evaporation at relatively low temperature. In a-Se, as in a-Si, locally, most of the atoms have their "normal" valence, but there are many defects and irregularities in the structure. Dangling bonds in amorphous semiconductors have orbital energies in the middle of gap, and electrons in these states are effectively non-bonding. Because these dangling bond sites are far apart from each other, there is little orbital overlap between them, and they also exist over a range of energies. Electrons in these mid-gap states are therefore **localized**, a phenomenon known as Anderson localizaton. Amorphous Si is insulating because electrons the Fermi level (in the middle of the gap) are not mobile in the lattice. These localized states create a mobility gap, and only electrons in states that are strongly bonding or antibonding are delocalized. Therefore, unmodified a-Si is not very useful as a semiconductor. However, by hydrogenating the material as it is formed (typically in a plasma of H atoms), the under-coordinated Si atoms are bonded to hydrogen atoms. This generates filled bonding and empty antibonding orbitals, the energies of which are outside the mobility gap. Hydrogenation thus lowers the density of states in the mobility gap. Hydrogenated amorphous silicon (a-Si:H) is insulating in the dark, but is a good photoconductor because light absorption creates electrons and holes in mobile states that are outside the mobility gap.



Energy vs. DOS for an amorphous semiconductor. Disorder and dangling bonds result in localized mid-gap states.

The photoconductivity of **amorphous Se** is exploited in xerography. A conductive drum coated with a-Se, which is insulating, is charged with static electricity by corona discharge from a wire. When the drum is exposed to a pattern of light and dark (the image to be duplicated), the illuminated a-Se areas become conductive and the static charge is dissipated from those parts of the drum. Carbon-containing toner particles then adhere via static charge to the areas that were not exposed to light, and are transferred and bonded to paper to make the copy. The speed of the process and the high resolution of pattern transfer depend on the very low conductivity of a-Se in the dark and its high conductivity under illumination.



Charging of amorphous Se and pattern transfer in the xerographic cycle.

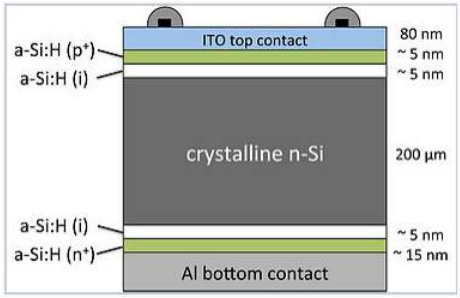
Amorphous hydrogenated Si is used in inexpensive thin film solar cells. The mobility gap is about 1.7 eV, which is larger than the bandgap crystalline of Si (1.1 eV). a-Si:H is a direct-gap material, and therefore thin films are good light absorbers. a-Si:H solar cells can be vapor-deposited in large-area sheets. p^+Si-a-Si:H-n^+Si cells have around 10% power conversion efficiency. However amorphous Si solar cells gradually lose efficiency as they are exposed to light. The mechanism of this efficiency loss, called the Staebler-Wronski effect,[9], involves photogenerated electron-hole pairs which have sufficient energy to cause chemical changes in the material. While the exact mechanism is still unclear, it has been proposed that the energy of electron-hole recombination breaks a weak Si-Si bond, and that one of the resulting dangling bonds abstracts a H atom, leaving a passivated Si-H center and a permanent dangling bond. The effect is minimized by hydrogenating a-Si and can be partially reversed by annealing.



A calculator that runs on solar and battery power

Thin layers of amorphous silicon are used in conjunction with crystalline silicon in heterojunction intrinsic thin-layer (HIT) solar cells.[10] Because the mobility gap of a-Si is wider than the bandgap of c-Si, there is a potential energy barrier at the amorphous-

crystalline interface that reflects electrons and holes away from that interface. At the p^+ contact, only holes can tunnel through the barrier, whereas only electrons can tunnel through the barrier to the n^+ contact. The passivation of surface defects that are sites of electron-hole recombination prevents a major loss mechanism in solar cells, increasing both the photovoltage and the photocurrent relative to conventional c-Si p-n junction cells. Panasonic and Sanyo have announced the production of HIT cells with power conversion efficiencies as high as 23%.



Layered structure of a HIT solar cell. The layers are not drawn to scale. A thick crystalline n-silicon layer is the light absorber, and photogenerated holes, which are the minority carriers, are reflected away from the aluminum back contact by the thin intrinsic a-Si layer there.

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CHAPTER OVERVIEW

10: Metals and Alloys- Structure, Bonding, Electronic and Magnetic Properties

Learning Objectives

- Identify and assign unit cells, coordination numbers, asymmetric units, numbers of atoms contained within a unit cell, and the fraction of space filled in a given structure.
- Relate molecular orbital theory to the delocalization of valence electrons in metals.
- Understand the concepts of electron wavelength and density of states.
- Understand the consequences of the nearly free electron model for the band structure of metals and their conductivity.
- Explain why some metals are magnetic and others are diamagnetic, and how these phenomena relate to bonding and orbital overlap.
- Use the Curie-Weiss law to explain the temperature dependence of magnetic ordering.
- Acquire a physical picture of different kinds of magnetic ordering and the magnetic hysteresis loops of ferro- and ferrimagnets.

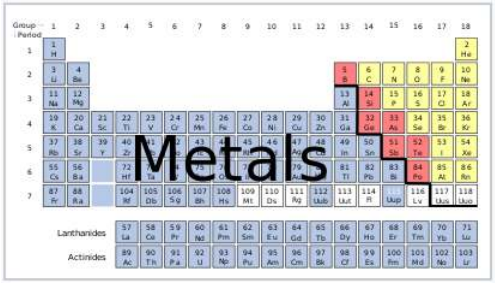
It should come as no surprise that the properties of extended solids are also connected to their structures, and so to understand what they do we should begin with their crystal structures. Most of the metals in the periodic table have relatively simple structures and so this is a good place to begin.

10.1: Prelude to Metals and Alloys
10.2: Unit Cells and Crystal Structures
10.3: Bravais Lattices
10.4: Crystal Structures of Metals
10.5: Bonding in Metals
10.6: Conduction in Metals
10.7: Atomic Orbitals and Magnetism
10.8: Ferro-, Ferri- and Antiferromagnetism
10.9: Hard and Soft Magnets
10.10: Discussion Questions
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10.1: Prelude to Metals and Alloys

In the chemistry of molecular compounds, we are accustomed to the idea that properties depend strongly on structure. For example we can rationalize the polarity of the water molecule based on its shape. We also know that two molecules with the same composition (e.g., ethanol and dimethyl ether) have very different properties based on the bonding arrangements of atoms. It should come as no surprise that the properties of extended solids are also connected to their structures, and so to understand what they do we should begin with their crystal structures. Most of the metals in the periodic table have relatively simple structures and so this is a good place to begin. We will see in Chapter 8 that the structures of more complex compounds are also in many cases related to the simple structures of metals and alloys.



Over 2/3 of the elements in the periodic table exist in their pure form as metals. All elemental metals (except the three - Cs, Ga, Hg - that are liquid) are crystalline solids at room temperature, and most have one of three simple crystal structures.

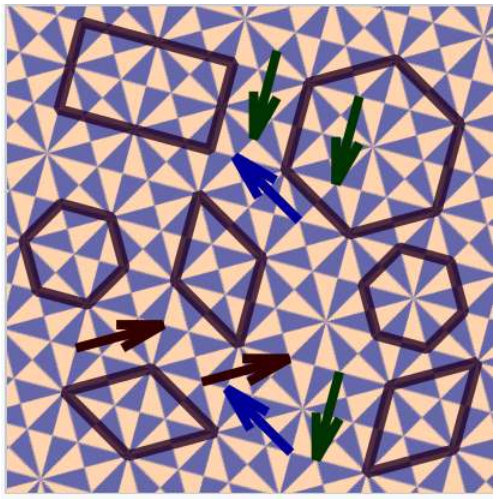
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10.2: Unit Cells and Crystal Structures

Crystals can be thought of as repeating patterns, much like wallpaper or bathroom tiles, but in three dimensions. The fundamental repeating unit of the crystal is called the **unit cell**. It is a three dimensional shape that can be repeated over and over by unit translations to fill space (and leave minimal gaps) in the structure. Some possible unit cells are shown in the tiling pattern at the right, along with arrows that indicate **unit translation vectors**. In three dimensions, the hexagonal or rhombic unit cells of this pattern would be replaced by three dimensional boxes that would stack together to fill all space. As shown in the figure, the origin of the unit cell is arbitrary. The same set of boxes will fill all space no matter where we define the origin of the lattice. We will see that pure metals typically have very simple crystal structures with cubic or hexagonal unit cells. However the crystal structures of alloys can be quite complicated.

When considering the crystal structures of metals and alloys, it is not sufficient to think of each atom and its neighboring ligands as an isolated system. Instead, think of the entire metallic crystal as a network of atoms connected by a sea of shared valence electrons. The **electrons are delocalized** because there are **not enough of them** to fill each "bond" between atoms with an electron pair. For example, in the crystal structures of s-block and p-block metals, each atom has either 8 or 12 nearest neighbors, but the maximum number of s + p electrons is 8. Thus, there are not enough to put two electrons between each pair of atoms. Transition metals can also use their d-orbitals in bonding, but again there are never enough electrons to completely fill all the "bonds."



Possible unit cells in a periodic tile pattern. The arrows connect translationally equivalent points (lattice points) in the pattern.

The atoms in a metal lattice arrange themselves in a certain pattern which can be represented as a 3D box structure known as the **unit cell** which repeats across the entire metal.

Simple Cubic	Body Centered Cubic	Face Centered Cubic	Hexagonal Close Packed
Simple cubic.svg	Lattice body centered cubic.svg	Lattice face centered cubic.svg	Hexagonal close packed.png
1 atom/cell	2 atoms/cell	4 atoms/cell	2 atoms/cell

Metal atoms can be approximated as spheres, and therefore are not 100 % efficient in packing, the same way a stack of cannonballs has some empty spaces between the balls. Different unit cells have different packing efficiencies. The number of atoms that is included in the unit cell only includes the fractions of atoms *inside* of the box. Atoms on the corners of the unit cell count as ⅛ of an atom, atoms on a face count as ½, an atom in the center counts as a full atom. Using this, let's calculate the number of atoms in a simple cubic unit cell, a face centered cubic (fcc) unit cell, and a body centered cubic (bcc) unit cell.

Simple Cubic:

8 corner atoms × ⅛ = 1 atom/cell. The packing in this structure is not efficient (52%) and so this structure type is very rare for metals.

Body Centered Cubic, bcc:

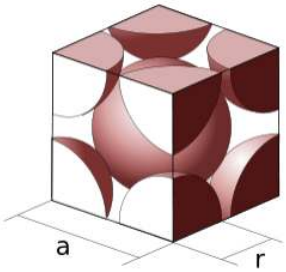
(8 corner atoms × ⅛) + (1 center atom × 1)= 2 atoms/cell. The packing is more efficient (68%) and the structure is a common one for alkali metals and early transition metals. Alloys such as brass (CuZn) also adopt these structures.

Face Centered Cubic, fcc (also called Cubic Close Packed, ccp):

(8 corner atoms × ⅛)+ (6 face atoms × ½)= 4 atoms/cell. This structure, along with its hexagonal relative (hcp), has the most efficient packing (74%). Many metals adopt either the fcc or hcp structure.

Hexagonal Close Packed, hcp:

Like the fcc structure, the packing density of hcp is 74%.

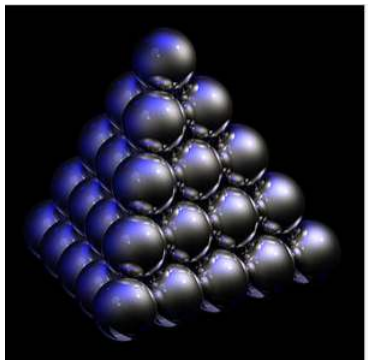


The unit cell of a bcc metal contains two atoms.

Calculating the packing fraction. The packing fractions of the crystal structures shown above can be calculated by dividing the volume of the atoms in the cell by the volume of the cell itself. The volume of the atoms in the cell is equal to the number of atoms/cell times the volume of a sphere, (4/3)πr^3. The volume of the cubic cells is found by cubing the side length. As an example, let's calculate the packing efficiency of a simple cubic unit cell. As we saw earlier in the section, a simple cubic unit cell contains one atom. The side length of the simple cubic unit cell is 2r, since the centers of each atom occupy the corners of the unit cell.

$$\text{Packing efficiency} = \frac{(1\ atom) \times (\frac{4}{3})\pi r^3}{(2r)^3} = 0.523 \tag{10.2.1}$$

The same method can be applied to bcc and fcc structures.



Face-centered cubic stack of cannonballs.

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10.3: Bravais Lattices

Crystal lattices can be classified by their **translational** and **rotational symmetry**. In three-dimensional crytals, these symmetry operations yield 14 distinct lattice types which are called **Bravais lattices**. In these lattice diagrams (shown below) the dots represent lattice points, which are places where the whole structure repeats by translation. For example, in the body-centered cubic (**bcc**) structure of sodium metal, which is discussed below, we put one atom at the corner lattice points and another in the center of the unit cell. In the NaCl structure, which is discussed in Chapter 8, we place one NaCl formula unit on each lattice point in the face-centered cubic (**fcc**) lattice. That is, one atom (Na or Cl) would be placed on the lattice point and the other one would be placed halfway between. Similarly, in the cubic diamond structure, we place one C_2 unit around each lattice point in the fcc lattice.

The fourteen Bravais lattices fall into seven **crystal systems** that are defined by their rotational symmetry. In the lowest symmetry system (**triclinic**), there is no rotational symmetry. This results in a unit cell in which none of the edges are constrained to have equal lengths, and none of the angles are 90º. In the **monoclinic** system, there is one two-fold rotation axis (by convention, the b-axis), which constrains two of the angles to be 90º. In the **orthorhombic** system, there are three mutually perpendicular two-fold axes along the three unit cell directions. **Orthorhombic** unit cells have three unequal unit cell edges that are mutually perpendicular. **Tetragonal** unit cells have a four-fold rotation axis which constrains all the angles to be 90º and makes the a and b axes equivalent. The **rhombohedral** system has a three-fold axis, which constrains all the unit cell edges and angles to be equal, and the **hexagonal** system has a six-fold axis, which constrains the a and b lattice dimensions to be equal and the angle between them to be 120º. The **cubic** system has a three-fold axis along the body diagonal of the cube, as well as two-fold axes along the three perpendicular unit cell directions. In the cubic system, all unit cell edges are equal and the angles between them are 90º.

The translational symmetry of the Bravais lattices (the lattice **centerings**) are classified as follows:

- Primitive (P): lattice points on the cell corners only (sometimes called simple)
- Body-Centered (I): lattice points on the cell corners with one additional point at the center of the cell
- Face-Centered (F): lattice points on the cell corners with one additional point at the center of each of the faces of the cell
- Base-Centered (A, B, or C): lattice points on the cell corners with one additional point at the center of each face of one pair of parallel faces of the cell (sometimes called end-centered)

Not all combinations of the crystal systems and lattice centerings are unique. There are in total 7 × 6 = 42 combinations, but it can be shown that several of these are in fact equivalent to each other. For example, the monoclinic I lattice can be described by a monoclinic C lattice by different choice of crystal axes. Similarly, all A- or B-centred lattices can be described either by a C- or P-centering. This reduces the number of combinations to 14 conventional Bravais lattices, shown in the table below.

When the fourteen Bravais lattices are combined with the **32 crystallographic point groups**, we obtain the **230 space groups**. These space groups describe all the combinations of symmetry operations that can exist in unit cells in three dimensions. For two-dimensional lattices there are only 17 possible plane groups, which are also known as wallpaper groups.

Crystal family	Lattice system	Schönflies	14 Bravais Lattices			
			Primitive	Base-centered	Body-centered	Face-centered
Triclinic		C_i	 Triclinic			
Monoclinic		C_{2h}	 Monoclinic, simple	 Monoclinic, centered		
Orthorhombic		D_{2h}	 Orthorhombic, simple	 Orthorhombic, base-centered	 Orthorhombic, body-centered	 Orthorhombic, face-centered
Tetragonal		D_{4h}	 Tetragonal, simple		 Tetragonal, body-centered	
Hexagonal	rhombohedral	D_{3d}	Rhombohedral			
	hexagonal	D_{6h}	 Hexagonal			
Cubic		O_h	 Cubic, simple		Cubic, body-centered	Cubic, face-centered

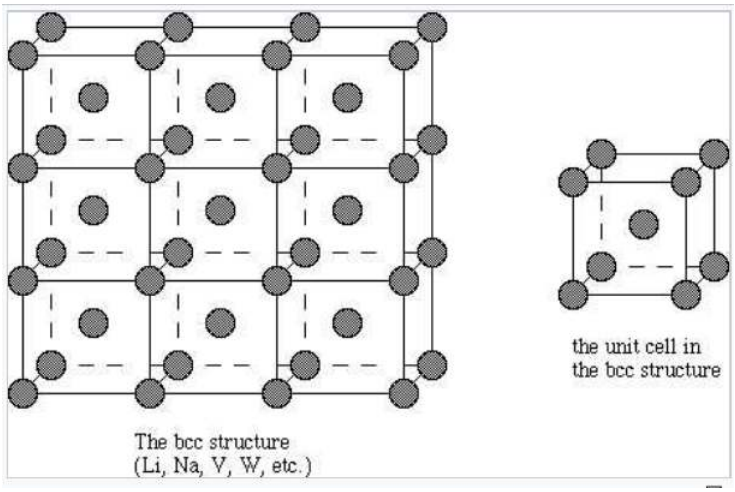
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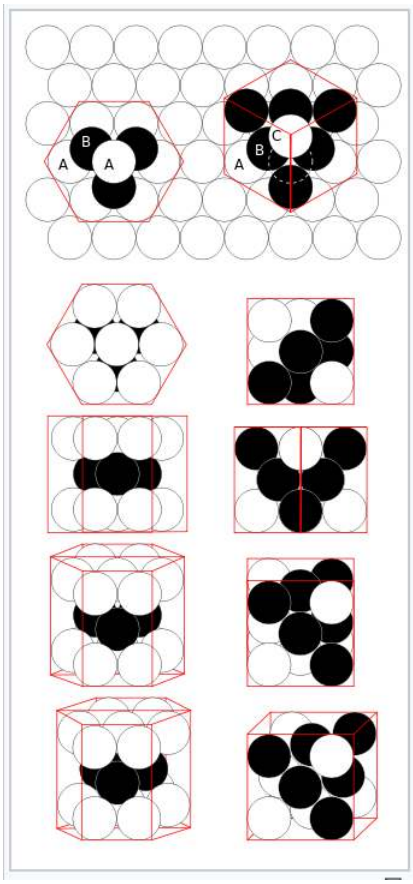
10.4: Crystal Structures of Metals

The Crystalline Nature of Metals

All metallic elements (except Cs, Ga, and Hg) are crystalline solids at room temperature. Like ionic solids, metals and alloys have a very strong tendency to crystallize, whether they are made by thermal processing or by other techniques such as solution reduction or electroplating. Metals crystallize readily and it is difficult to form a glassy metal even with very rapid cooling. Molten metals have low viscosity, and the identical (essentially spherical) atoms can pack into a crystal very easily. Glassy metals can be made, however, by rapidly cooling alloys, particularly if the constituent atoms have different sizes. The different atoms cannot pack in a simple unit cell, sometimes making crystallization slow enough to form a glass.



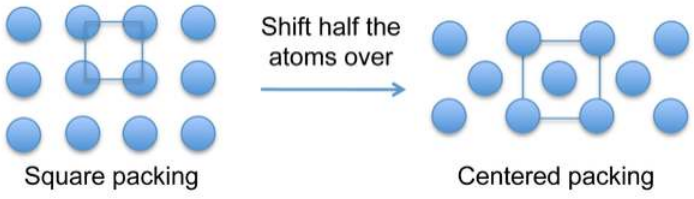
Body-centered cubic



hcp (left) and fcc (right) close-packing of spheres

Crystal structures

Most metals and alloys crystallize in one of three very common structures: body-centered cubic (bcc), hexagonal close packed (hcp), or cubic close packed (ccp, also called face centered cubic, fcc). In all three structures the coordination number of the metal atoms (i.e., the number of equidistant nearest neighbors) is rather high: 8 for bcc, and 12 for hcp and ccp. We can contrast this with the low coordination numbers (i.e., low valences - like 2 for O, 3 for N, or 4 for C) found in nonmetals. In the bcc structure, the nearest neighbors are at the corners of a cube surrounding the metal atom in the center. In the hcp and ccp structures, the atoms pack like stacked cannonballs or billiard balls, in layers with a six-coordinate arrangement. Each atom also has six more nearest neighbors from layers above and below. The stacking sequence is ABCABC... in the ccp lattice and ABAB... in hcp. In both cases, it can be shown that the spheres fill 74% of the volume of the lattice. This is the highest volume fraction that can be filled with a lattice of equal spheres.



Atoms in metallic crystals have a tendency to pack in dense arrangments that fill space efficiently. The simple square packing (above) upon which the simple cubic structure is based is inefficient and thus rare among metallic crystal structures. Body- or face-centered structures fill space more efficiently and more common.

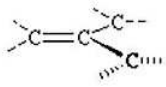
Periodic trends in structure and metallic behavior

Remember where we find the metallic elements in the periodic table - everywhere except the upper right corner. This means that as we go down a group in the p-block (let's say, group IVA, the carbon group, or group VA, the nitrogen group), the properties of the elements gradually change from nonmetals to metalloids to metals. The carbon group nicely illustrates the transition. Starting at the top, the element carbon has two stable allotropes - graphite and diamond. In each one, the valence of carbon atoms is exactly satisfied by making four electron pair bonds to neighboring atoms. In graphite, each carbon has three nearest neighbors, and so there are two single bonds and one double bond. In diamond, there are four nearest neighbors situated at the vertices of a tetrahedron, and so there is a single bond to each one.

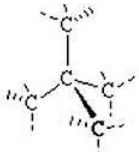
The two elements right under carbon (silicon and germanium) in the periodic table also have the diamond structure (recall that these elements cannot make double bonds to themselves easily, so there is no graphite allotrope for Si or Ge). While diamond is a good insulator, both silicon and germanium are semiconductors (i.e., metalloids). Mechanically, they are hard like diamond. Like carbon, each atom of Si and Ge satisfies its valence of four by making single bonds to four nearest neighbors.

The next element under germanium is tin (Sn). Tin has two allotropes, one with the diamond structure, and one with a slightly distorted bcc structure. The latter has metallic properties (metallic luster, malleability), and conductivity about 10^9 times higher than Si. Finally, lead (Pb), the element under Sn, has the ccp structure, and also is metallic. Note the trends in coordination number and conducting properties:

Element	Structure	Coord. no.	Conductivity
C	graphite, diamond	3, 4	semimetal, insulator
Si	diamond	4	semiconductor
Ge	diamond	4	semiconductor
Sn	diamond, distorted bcc	4, 8	semiconductor, metal
Pb	ccp	12	metal



trigonal bond network in graphite: 1 double bond + 2 single bonds to C



tetrahedral bond network in diamond: 4 single bonds to each C atom

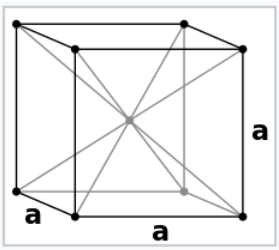
The elements C, Si, and Ge obey the octet rule, and we can easily identify the electron pair bonds in their structures. Sn and Pb, on the other hand, adopt structures with high coordination numbers. They *do not have enough valence electrons* to make electron pair bonds to each neighbor (this is a common feature of metals). What happens in this case is that the valence electrons become "smeared out" or delocalized over all the atoms in the crystal. It is best to think of the bonding in metals as a crystalline arrangement of positively charged cores with a "sea" of shared valence electrons gluing the structure together. Because the electrons are not localized in any particular bond between atoms, they can move in an electric field, which is why metals conduct electricity well. Another way to describe the bonding in metals is nondirectional. That is, an atom's nearest neighbors surround it in every direction, rather than in a few particular directions (like at the corners of a tetrahedron, as we found for diamond). Nonmetals (insulators and semiconductors), on the other hand, have directional bonding. Because the bonding is non-directional and coordination numbers are high, it is relatively easy to deform the coordination sphere (i.e., break or stretch bonds) than it is in the case of a nonmetal. This is why elements like Pb are much more malleable than C, Si, or Ge.

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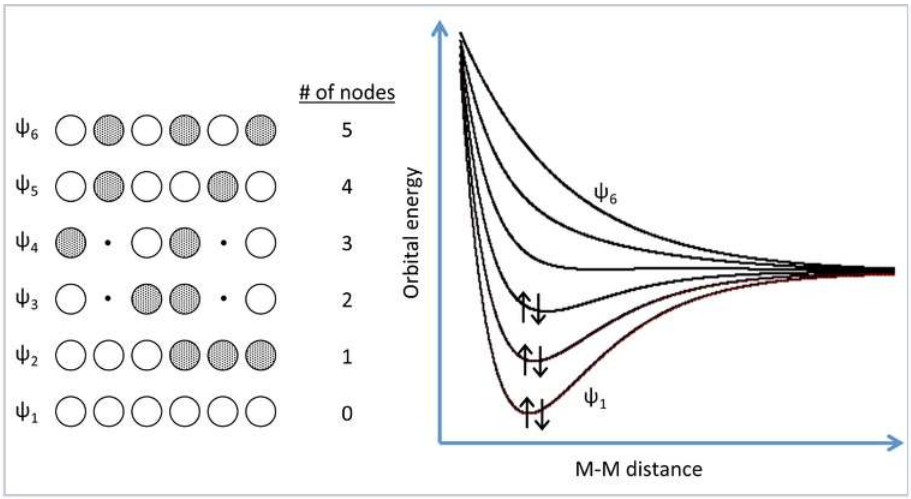
10.5: Bonding in Metals

The electron pair description of chemical bonds, which was the basis of the octet rule for p-block compounds, breaks down for metals. This is illustrated well by Na metal, the structure of which is shown at the left. Na has too few valence electrons to make electron pair bonds between each pair of atoms. We could think of the Na unit cell as having eight no-bond resonance structures in which only one Na-Na bond per cell contains a pair of electrons.



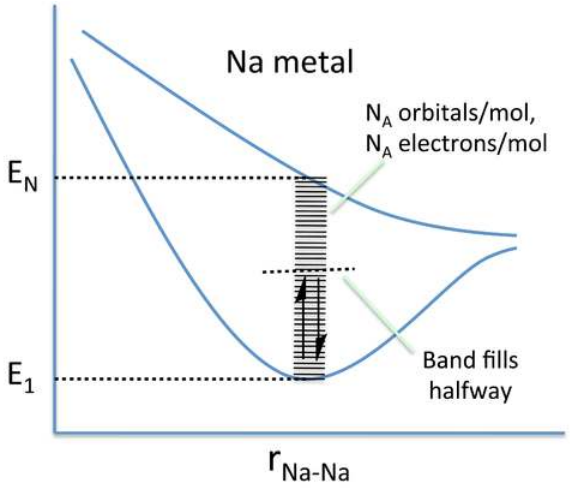
Sodium metal crystallizes in the body-centered cubic structure, in which each atom has eight nearest neighbors. Since the electronic configuration of Na is $[Ar]3s^1$, there are only two valence electrons per unit cell that are shared among eight Na-Na bonds. This means that the Na-Na bond order is 1/8 in Na metal.

A more realistic way to describe the bonding in metals is through **band theory**. The evolution of energy bands in solids from simple MO theory (Chapter 2) is illustrated at the right for a chain of six Na atoms, each of which has one 3s valence orbital and contributes one valence electron. In general, **n** atomic orbitals (in this case the six Na 3s orbitals) will generate **n** molecular orbitals with **n-1** possible nodes. In Chapter 2, we showed that the energy versus internuclear distance graph for a two hydrogen atom system has a low energy level and a high energy level corresponding to the bonding and antibonding molecular orbitals, respectively. These two energy levels were well separated from each other, and the two electrons in H_2 energetically prefer the lower energy level. If more atoms are introduced to the system, there will be a number of additional levels between the lowest and highest energy levels.



MO picture for a linear chain of six Na atoms. Three of the six MOs can accommodate all six valence electrons. Adding more atoms to the chain makes more molecular orbitals of intermediate energy, which eventually merge into a continuous band of orbitals. For Na, the 3s band is always half-filled because each MO can accommodate two electrons.

In band theory, the atom chain is extrapolated to a very large number - on the order of 10^{22} atoms in a crystal - so that the different combinations of bonding and anti-bonding orbitals create "bands" of possible energy states for the metal. In the language of physics, this approach of building the bands from discrete atomic orbitals is called the "tight-binding" approximation. The number of atoms is so large that the energies can be thought of as a continuum rather than a series of distinct levels. A metal will only partially fill this band, as there are fewer valence electrons than there are energy states to fill. In the case of Na metal, this results in a half-filled 3s band.



Nearly free electron model

In metals, the valence electrons are delocalized over many atoms. The total energy of each electron is given by the sum of its kinetic and potential energy:

$$E = KE + PE$$
$$E \approx p^2/2m + V$$

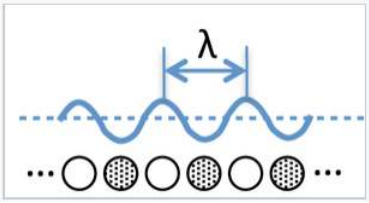
where **p** is the momentum of the electron (a vector quantity), m is its mass, and V is an average potential that the electron feels from the positive cores of the atoms. This potential holds the valence electrons in the crystal but, in the free electron model, is essentially uniform across the crystal.

Electron wavelength and wavenumber

What are the consequences of this model for band theory? For a hypothetical infinite chain (i.e., a 1D crystal) of Na atoms, the molecular orbitals at the bottom of the 3s band are fully bonding and the *wavelength* of electrons (2x the distance between nodes) in these orbitals is very long. At the top of the band, the highest orbital is fully antibonding and the wavelength is 2 times the distance between atoms (2a), since there is one node per atom. Remember that the **wavelength of an electron (λ)** is inversely proportional to its momentum p, according to the de Broglie relation **λ = h/p**.

For a (nearly) free electron, the kinetic energy can be expressed in terms of its wavelength, using KE = $p^2/2m$ and the de Broglie relation:

$$KE = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2} \tag{10.5.1}$$



We can think of the wavelength of an electron in a molecular orbital as twice the distance between nodes. If there are N atoms in a linear chain, the wavelength of the nth orbital is given by λ = 2Na/n, where a is the distance between atoms.

At this point, it is convenient to define the **wavenumber** of the electron as **k**, which has units of inverse length and is inversely proportional to λ. **k** is also directly proportional to the momentum **p**. Like **p**, **k** is a vector quantity. In a 1D crystal, **k** can be either positive or negative, corresponding to an electron moving to the left or right along the chain.

$$k = \frac{2\pi}{\lambda} = \frac{2\pi p}{h} \text{ where h is Planck's constant} \tag{10.5.2}$$

The most important property of **k** is that it is *directly proportional to the number of nodes* **n** in a molecular orbital within the band. For a 1D crystal of sodium atoms that contains **N** unit cells, each separated by a distance a, a molecular orbital with n nodes has a wavelength λ = 2Na/n and the wavenumber k = πn/Na. We can see from this definition that k = 0 at the bottom of the band (where λ is infinite) and k = π/a at the top of the band where the MO contains **N** nodes and λ = 2a.

Energies of orbitals in a metallic crystal

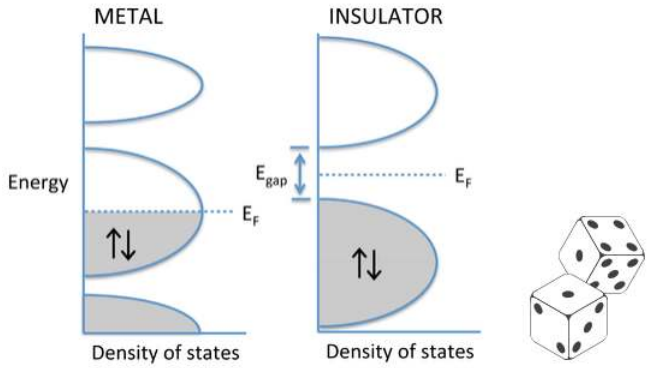
Electrons with long wavelengths do not "feel" the individual atoms in the lattice and so they behave as if they are *nearly free* (but confined to the crystal). Near the bottom of the band, the electron energy increases *parabolically* with the number of nodes (KE $\propto$ $\mathbf{n}^2$), since the momentum **p** is directly proportional to **n**. Because **p** is also directly proportional to **k**, we can write:

$$KE = \frac{p^2}{2m} = \frac{h^2 k^2}{8\pi^2 m} \tag{10.5.3}$$

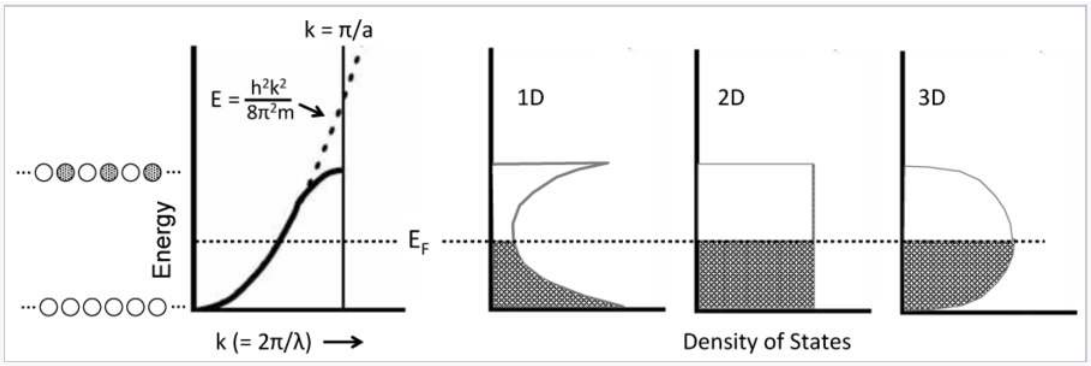
This parabolic relationship is followed as long as the electron wavelength is long compared to the distance between atoms. Near the top of the band, the wavelength becomes shorter and the electrons start to feel the positively charged atomic cores. In particular, the electrons prefer to have the maxima in their wavefunctions line up with the atomic cores, which is the most electrostatically favorable situation. The electron-atom attraction lowers the energy and causes the E vs. k curve to deviate from the parabolic behavior of a "free" electron as shown in the figure below.

Density of States (DOS)

The density of states is defined as the number of orbitals per unit of energy within a band. Because of the parabolic relation between E and k, the density of states for a 1D metallic crystal is highest near the bottom and top of the energy band where the slope of the E vs. k curve is closest to zero. The shape of the DOS curve is different in crystals of higher dimensionality as shown in the figure in the left, because statistically there are more ways to make an orbital with N/2 nodes than there are with zero or N nodes. The situtation is analogous to the numbers you can make by rolling dice. With one die, the numbers 1-6 have equal probability. However, with two dice there is only one way to make a two (snake eyes) or a twelve (boxcars), but many ways to make a seven (a winner!).

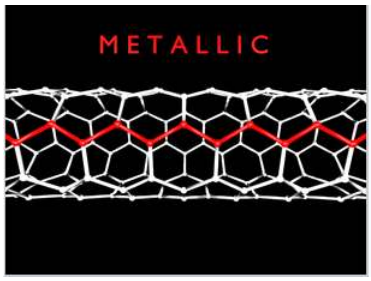


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Electrons in metals follow a parabolic dispersion curve, where the energy increases with the square of the wavenumber, k. Near the top of the band, the dispersion curve deviates from the parabolic dotted line. Because there is one MO for each value of k, the number of orbitals per unit energy (the density of states, DOS) is highest at the bottom and top of the band for a 1D chain of atoms. The density of states is constant with energy for a 2D crystal, and has a maximum in the middle of the band for a 3D crystal. At low temperature, all the MOs below the Fermi level E_F are occupied, and all the MOs above it are empty.

While most of the time we will talk about 3D crystals that have their maximum DOS near the middle of the energy band, there are examples of quasi-1D systems, such as carbon nanotubes. Metallic carbon nanotubes have strong optical absorption bands that correspond to transitions between the two regions of high DOS (the van Hove singularities) near the bottom and top of the bands.



Single-walled carbon nanotubes with "armchair" chirality are metallic and have characteristic sharp absorption bands in the infrared. Prof. Millie Dresselhaus (below) did foundational research on the electronic properties of carbon nanotubes and other low-dimensional conductors.

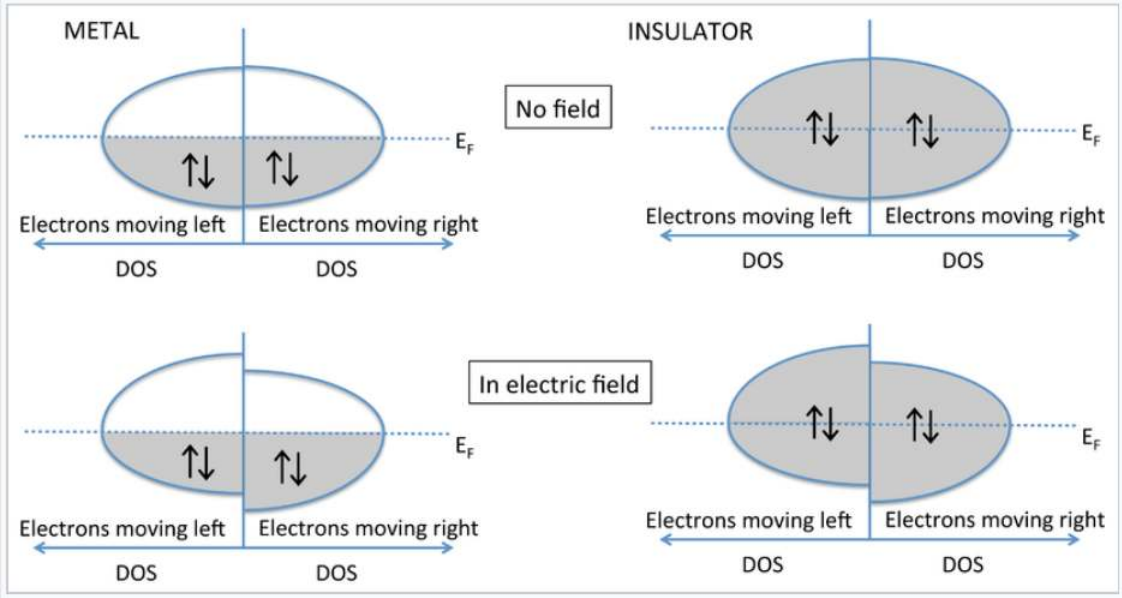


Metals, semiconductors, and insulators

The degree to which bands fill determines whether a crystalline solid is a metal, semiconductor, or insulator. If the highest occupied molecular orbitals lie within a band - i.e., if the Fermi level E_F cuts through a band of orbitals - then the electrons are free to change their speed and direction in an electric field and the solid is metallic. However, if the solid contains just enough electrons to completely fill a band, and the next highest set of molecular orbitals is empty, then it is a semiconductor or insulator. In this case, there is an energy gap between the filled and empty bands, which are called the valence and conduction bands, respectively. Although the distinction is somewhat arbitrary, materials with a large gap (> 3 eV) are called insulators, and those with smaller gaps are called semiconductors. We will learn more about the properties of semiconductors in Chapter 10.

Why don't insulators conduct electricity? The energy vs. DOS diagram below shows what happens when an electric field is applied to a metal or an insulator. In this case we have changed the diagram to show explicitly the energies of electrons moving left and right. These energies are the same in the absence of an electric field. Once we apply a field (e.g., by putting a voltage across a metal

wire), the electrons moving in the direction of the field have lower energy than those moving in the opposite direction. In the case of the metal, the populations of electrons moving with and against the electric field are different, and there is a net flow of current. Note that this can happen only when the Fermi level cuts through a partially filled band. With a semiconductor or insulator, the valence band is filled and the conduction band is empty. Applying an electric field changes the energies of electrons traveling with and against the field, but because the band is filled, the same number are going in both directions and there is no net current flow.



E vs. DOS diagrams comparing the behavior of metals and insulators in an applied electric field.

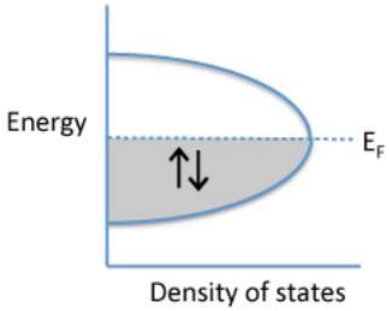
Note that in this picture, all the molecular orbitals extend over the entire crystal. The valence electrons are *delocalized*, even in the case of a semiconductor or insulator. However, there can be no net movement of electrons unless the band is partially filled.

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10.6: Conduction in Metals

In metals, the valence electrons are in molecular orbitals that extend over the entire crystal lattice. As we will learn in Chapter 7, metals are almost always crystalline and the individual crystal grains are typically micron size. This means that the spatial extent of the orbitals is *very large* compared to the size of the atoms or the unit cell. The diagram at the left shows a generic plot of electron energy vs. density of states for a metal such as Na, Cu, or Ag. In these cases, there are N orbitals for N electrons, and each orbital can accommodate two electrons. Therefore the Fermi level, which corresponds to the energy of the highest occupied MO at zero temperature, is somewhere in the middle of the band of orbitals. The energy level spacing between orbitals is very small compared to the thermal energy kT, so we can think of the orbitals as forming a continuous band.



Classically, if the electrons in this band were free to be thermally excited, we would expect them to have a specific heat of 3R per mole of electrons. However, experimentally we observe that C_p is only about 0.02 R per mole. This suggests that *only about 1%* of the electrons in the metal can be thermally excited at room temperature. However, essentially *all* of the valence electrons are free to move in the crystal and contribute to electrical conduction. To understand this apparent paradox, we need to recall that the electrons exist in *quantized energy levels.*

Because of quantization, electrons in metals have a Fermi-Dirac distribution of energies. In this distribution, most of the electrons are spin-paired, although the individual electrons in these pairs can be quite far apart since the orbitals extend over the entire crystal. A relatively small number of electrons at the top of the Fermi sea are unpaired by thermal excitation. This is the origin of the Pauli paramagnetism of metals.

How fast are electrons traveling in a typical metal? Because of the bell shape of the E vs. DOS curve, most of the electrons have $E \approx E_F$. At the midpoint energy (E_F) of the band, the MO's have one node for every two atoms. We can calculate the de Broglie wavelength as twice the distance between nodes and thus:

> **λ = 4a** at the midpoint of the band.

where **a** is the interatomic spacing. Since a typical value of **a** is about 2 Å, we obtain the **de Broglie wavelength λ ≈ 8 Å**.

Using the de Broglie relation p = h/λ, we can write:

$$\mathbf{p} = \frac{\mathbf{h}}{\lambda} = \mathbf{m_e v_F} \tag{10.6.1}$$

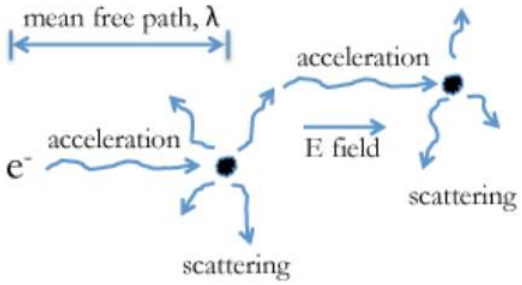
where $\mathbf{m_e}$ is the mass of the electron and $\mathbf{v_F}$ is the velocity of electrons with energy E_F.

Solving for $V_F = \frac{h}{m_e \lambda}$ we obtain $\mathbf{v_F} = \frac{(6.62\times10^{-34}\,Js)}{(9.1\times10^{-31}\,kg)(8\times10^{-10}\,m)} = \mathbf{1.0 \times 10^6 m/s}$

Experimental values of v_F are 1.07 x 10^6 and 1.39 x 10^6 m/s for Na and Ag, respectively, so our approximations are pretty good.

How fast are electrons moving in metals? Really, really fast!! **1,000,000 meters per second!** This is about 1/300 the speed of light, and about 3000 times the speed of sound in air (3 x 10^2 m/s).

However, the **drift velocity** of electrons in metals - the speed at which electrons move in applied electric field - is quite slow, on the order of 0.0001 m/s, or .01 cm/s. You can easily outrun an electron drifting in a metal, even if you have been drinking all night and have been personally reduced to a very slow crawl.



In order to understand the great disparity between the Fermi velocity and the drift velocity of electrons in metals, we need to consider a picture for the scattering of electrons, and their acceleration in an electric field, as shown at the left. If we apply a voltage across a metal (e.g., a metal wire), the electrons are subjected to an electric field **E**, which is the voltage divided by the length of the wire. This electric field exerts a force on the electron, causing it to accelerate. However, the electron is frequently scattered, mostly by phonons (lattice vibrations). Each time the electron is scattered its acceleration starts all over again. The time between scattering events is **τ** and the distance the electrons travel between scattering events is the **mean free path**, **λ**. (Note that this is NOT the same λ as the de Broglie wavelength, they just unfortunately have the same symbol!)

We can write the force on the electron as:

$$\mathbf{F = eE = m_e a = \frac{m_e v_{drift}}{\tau}} \tag{10.6.2}$$

In this equation, **a** is the acceleration in the electric field, $\mathbf{m_e}$ is the mass, and v_{drift} is the **drift velocity** of the electron.

Experimentally, the mean free path is typically obtained by measuring the scattering time. For an electron in Cu metal at 300 K, the scattering time τ is about 2 x 10^{-14} s. From this we can calculate the mean free path as:

$$\lambda = \mathbf{v_{avg}}\tau \approx \mathbf{v_F}\tau = (1 \times 10^6 m/s)(2 \times 10^{-14}) = \mathbf{40nm} \tag{10.6.3}$$

The mean free path (40 nm = 400 Å) is quite long compared to the interatomic spacing (2 Å). To put it in perspective, if the interatomic spacing were scaled to the length of a football (0.3 m), the mean free path would be over half the length of the football field (60 m). Thus an electron travels a fairly long way between scattering events and scarcely notices the atomic structure of the metal in which it is traveling.

To summarize, electrons are traveling in metals at the Fermi velocity v_F, which is very, very fast (10^6 m/s), but the flux of electrons is the same in all directions. That is, they are *going nowhere fast*. In an electric field, a very small but directional *drift velocity* is superimposed on this fast random motion of valence electrons.



For ordinary metals, the mean free path of a valence electron (λ) is quite long relative to the interatomic spacing, represented in this analogy as the length of a football.

We can calculate the drift velocity of electrons as the acceleration in the electric field times the scattering time:

From F = ma, we obtain the acceleration (a) as:

$$\mathbf{a} = \frac{\mathbf{F}}{\mathbf{m_e}} = \frac{\mathbf{eE}}{\mathbf{m_e}} \tag{10.6.4}$$

And thus,

$$\mathbf{v_{drift}} = \mathbf{a}\tau = \frac{\mathbf{eE}\tau}{\mathbf{m_e}} \tag{10.6.5}$$

If we divide both sides of this equation by the magnitude of the electric field (**E**), we obtain the **mobility (μ)**:

$$\mu = \frac{\mathbf{v_{drift}}}{\mathbf{E}} = \frac{\mathbf{e}\tau}{\mathbf{m_e}} \tag{10.6.6}$$

μ has units of velocity/field = cm/s / V/cm = cm^2/Vs

An important consequence of the calculation of v_{drift} is **Ohm's Law**, V = iR. From the equations above, we can see that the drift velocity increases linearly with the applied electric field. The drift velocity (cm/s) is proportional to the current (i, coul/s), and the electric field (E, V/cm) is proportional to the voltage (V):

$$\mathbf{Current\ (i)} = \mathbf{nev_{drift}} \times \mathbf{area} \tag{10.6.7}$$

$$\mathbf{Voltage\ (V)} = \mathbf{E} \times \mathbf{length} \tag{10.6.8}$$

Here **n** is the density of valence electrons (#/cm^3) and **e** is the charge of the electron (coul). Combining these equations with our equation for v_{drift} we obtain:

$$V = i(\frac{m_e}{ne^2\tau})\frac{(}{length}area) = iR \tag{10.6.9}$$

Thus, V = iR, where R is the combination of the two terms in parentheses. The first of these is the **resistivity**, ρ, and the second is a geometrical factor.

The **conductivity (σ)** of a metal, which is the inverse of ρ, is proportional to μ, which in turn is proportional to τ (and λ):

$$\sigma = \mathbf{ne}\mu = \frac{\mathbf{ne^2}\tau}{\mathbf{m_e}} \tag{10.6.10}$$

We can use this equation to work out the conductivity of a specific metal (Cu), for which n = 8.5 x 10^{22} cm^{-3} and τ = 2 x 10^{-14} s. Putting in the numbers for m_e and e, we obtain σ = 7 x 10^5 Ω^{-1} cm^{-1} for Cu, in good agreement with the measured value (6 x 10^5 $\Omega^{-1}cm^{-1}$).

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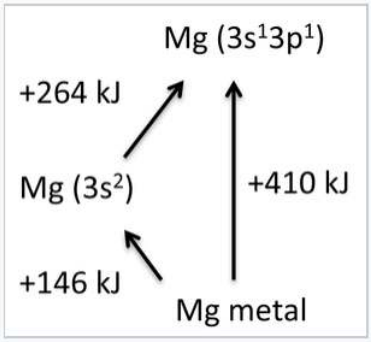
10.7: Atomic Orbitals and Magnetism

The MO picture we developed in Section 6.4 helps us rationalize the electrical conductivity of Na ($3s^1$), but what about Mg, which (as an atom in the gas phase) has a $3s^2$ electronic configuration? The two valence electrons are spin-paired in atomic Mg, as they are in the helium atom ($1s^2$). When the 3s orbitals of Mg combine to form a band, we would expect the band to be completely filled, since Mg has two electrons per orbital. By this reasoning, solid Mg should be an insulator. But Mg has all the properties of a metal: high electrical and thermal conductivity, metallic luster, malleability, etc. In this case the 3s and 3p bands are sufficiently broad (because of strong orbital overlap between Mg atoms) that they form a continuous band. This band, which contains a total of four orbitals (one 3s and three 3p) per atom, is only partially filled by the two valence electrons.



Mg crystals

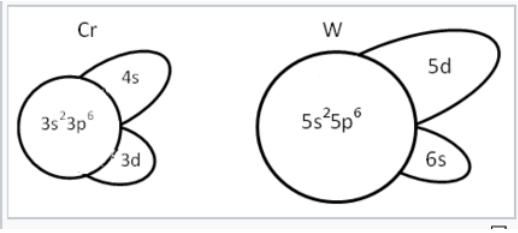
Another way to think about this is to consider the **hybridization** of the 3s and 3p electrons in Mg. Hybridization requires promotion from the $3s^23p^0$ ground state of an Mg atom to a $3s^13p^1$ excited state. The **promotion energy** (+264 kJ/mol) is more than offset by the **bonding energy** (-410 kJ/mol), the energy released when gaseous atoms in the excited state condense to form the metallic solid. The heat of vaporization, or the cohesive energy of a metal, is the difference between the bonding energy and the promotion energy. Experimentally, we can measure the vaporization energy (+146 kJ/mol) and the promotion energy and use them to calculate the bonding energy. From this we learn that each s or p electron is worth about 200 kJ/mol in bonding energy. The concepts of promotion energy and bonding energy are very useful in rationalizing periodic trends in the bond strengths and magnetic properties of metals, which are described below.



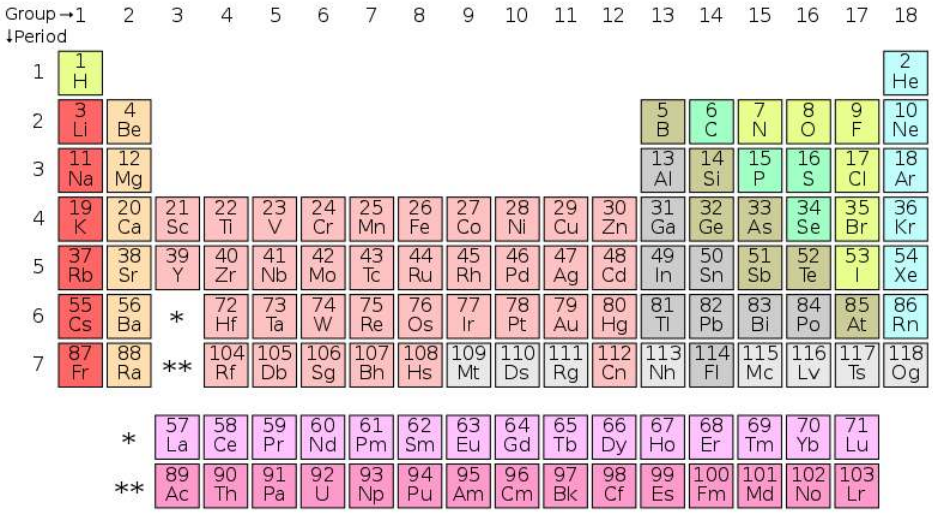
The cohesive energy of Mg metal is the difference between the bonding and promotion energies. The ground state of a gas phase Mg atom is $[Ar]3s^2$, but it can be promoted to the $[Ar]3s^13p^1$ state, which is 264 kJ/mol above the ground state. Mg uses two electrons per atom to make bonds, and the sublimation energy of the metal is 146 kJ/mol.

Periodic trends in d-electron bonding

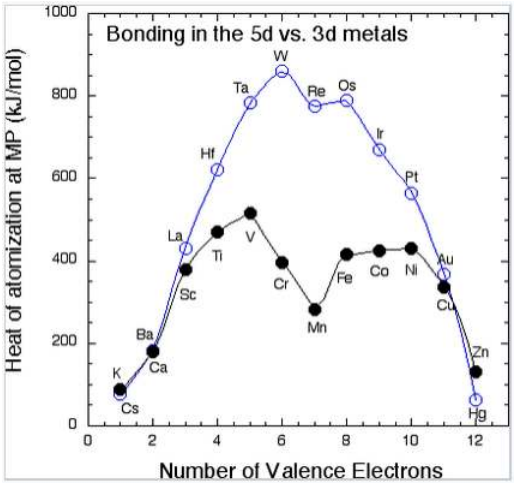
While electrons in s and p orbitals tend to form strong bonds, d-electron bonds can be strong or weak. There are two important periodic trends that are related to orbital size and orbital overlap. As we move *across the periodic table* (Sc - Ti - V - Cr - Fe), the *d orbitals contract* because of increasing nuclear charge. Moving *down the periodic table* (V - Nb - Ta), the *d orbitals expand* because of the increase in principal quantum number. These trends explain the distinct behavior of the 3d elements relative to those in the 4d and 5d series. In the 3d series, the contraction of orbitals affects the ability of the d electrons to contribute to bonding. Past V in the first row of the transition metals, the 3d electrons become much less effective in bonding because they overlap weakly with their neighbors. Weak overlap of 3d orbitals gives narrow d-bands and results in the emergence of magnetic properties as discussed below.



Schematic representation of the sizes of different orbitals of Cr and W. In the first transition series, shielding of the 3d orbitals is poor. Therefore the 4s and 4p orbitals are more effective in bonding than the 3d. In the third transition series, the situation is reversed. The increased nuclear charge is felt most strongly by the 6s, which takes on the character of an inert electron pair. The 5d orbitals are well shielded by the complete n=4 shell so they have good orbital overlap with neighboring atoms.

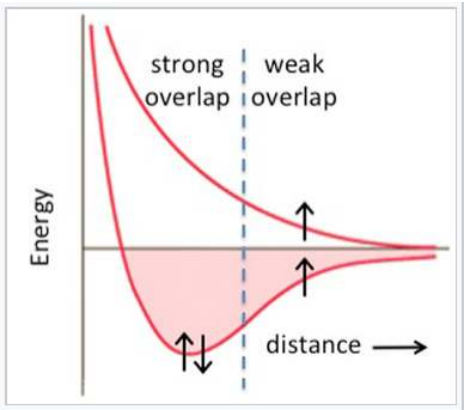


In the **4d and 5d series**, a plot of cohesive energy vs. number of valence electrons (below left) has a "volcano" shape that is peaked at the elements Mo and W ($5s^1 4d^5$ and $6s^1 5d^5$, respectively). The number of bonding electrons, and therefore the bonding energy, increases steadily going from Rb to Mo in the 4d series, and from Cs to W in the 5d series. Mo and W have the most bonding energy because they can use all six of their valence electrons in bonding without promotion. Elements past Mo and W have more d electrons, but some of them are spin paired and so some promotion energy is needed to prepare these electrons for bonding. For example, Pt metal must be promoted from the $6s^1 5d^9$ atomic ground state to $6s^1 5d^7 6p^2$ in order to make six bonds per atom, and the energy cost of promoting electrons from the 5d to the 6p orbitals is reflected in the net bonding energy. Because of their strong bonding energy, elements in the middle of the 4d and 5d series have very high melting points. We do not see magnetism in the 4d or 5d metals or their alloys because orbital overlap is strong and the bonding energy exceeds the electron pairing energy.



The heat of vaporization (the cohesive energy) of metals in the 3d and 5d series, measured at the melting point of the metal.

The **3d elements** (Sc through Zn) are distinctly different from the 4d and 5d elements in their bonding (and consequently in their magnetic properties). In the 3d series, we see the expected increase in cohesive energy going from Ca ($4s^2$) to Sc ($4s^23d^1$) to Ti ($4s^23d^2$) to V ($4s^23d^3$), but then something very odd happens. The 3d series has a "crater" in the cohesive energy plot where there was a peak in the 5d series. The cohesive energy actually *decreases* going from V to Mn, even though the number of valence electrons is increasing. We can explain this effect by remembering that the 3d orbitals are progressively contracting as more protons are added to the nucleus. For elements beyond V, the orbital overlap is so poor that the 3d electrons are no longer effective in bonding, and the valence electrons begin to unpair. At this point the elements become **magnetic**. Depending on the way the spins order, metals and alloys in this part of the periodic table can be ferromagnetic (spins on neighboring atoms aligned parallel, as in the case of Fe or Ni) or antiferromagnetic (spins on neighboring atoms antiparallel, as in the case of Mn). We have seen the trade-off between orbital overlap and magnetism before (in Chapter 5) in the context of paramagnetic transition metal complexes. It is worth recalling that this behavior is predicted in the energy vs. distance diagram of the hydrogen atom (from Chapter 2). At short interatomic distances (or with strong overlap between atomic orbitals), the spins of the electrons pair and a bond is formed. Unpairing the electrons becomes favorable at larger interatomic distances where the overlap between orbitals is poor.



With strong overlap between orbitals of neighboring atoms, the bonding energy exceeds the pairing energy and electrons spin-pair. With weaker overlap, bonding is weak and spins unpair, resulting in magnetic behavior.

Interestingly, many alloys of the **4f elements** (the lanthanides) are also magnetic because the 4f orbitals, like the 3d orbitals, are poorly shielded from the nuclear charge and are ineffective in bonding. Strong permanent magnets often contain alloys of Nd, Sm, or Y, usually with magnetic 3d elements such as Fe and Co.

Because the 4f orbitals are contracted and not very effective in bonding, other physical properties of the lanthanides can also be affected. For example, it has been proposed that oxides of the 4f elements have weak surface interactions with polar molecules such

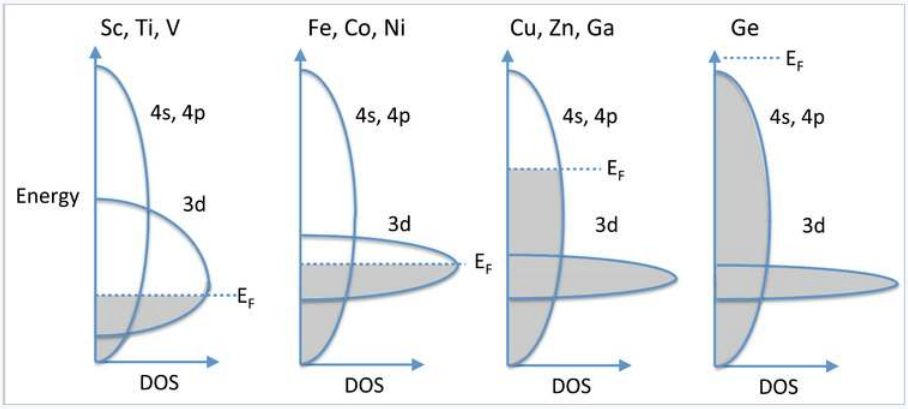
as water because of f-orbital contraction. Experimentally, CeO_2, Er_2O_3, and Ho_2O_3 are observed to be hydrophobic, whereas main group and early transition metal oxides (e.g., Al_2O_3, SiO_2, TiO_2) are quite hydrophilic.[1]

Late transition metal alloys

Although the bonding in the 5d series follows a "normal" volcano plot, the situation is a bit more complex for alloys of Re, Os, Ir, Pt, and Au. There is strong overlap between the 5d orbitals, but because these elements contain more than five d-electrons per atom, they cannot make as many bonds as 4d or 5d elements with half-filled d-shells such as Mo or W. This progressive filling of the d-band explains the steady decrease in bonding energy going from Os to Au. Pt and Au are both soft metals with relatively low heats of vaporization. However, these metals (especially Ir, Pt, and Au) can combine with early transition metals to form stable alloys with very negative heats of formation and high melting points. For example, ZrC and Pt react to form a number of stable alloys (ZrPt, Zr_9Pt_{11}, Zr_3Pt_4, $ZrPt_3$)[2] plus carbon. This reactivity is unusual because we normally think of Pt as a "noble" (i.e., unreactive) metal, and because ZrC is a very stable, refractory metal carbide. The favorable combination of early and late transition metals has been interpreted as arising from a d-electron "acid-base" interaction.[3] For example, in $HfPt_3$, Hf is the "acid" with an electron configuration of $6s^25d^2$, while Pt is the "base" with the electron configuration of $6s^15d^9$. They combine to create a stable "salt" product with a filled 5d electron configuration without promoting any electrons to higher orbitals. The implication is that Pt donates d-electrons to the "d-acid," Zr or Hf. However, electronic structure calculations on model compounds show that much of the bonding energy in ZrPt and $ZrPt_3$ arises from electron transfer from Zr to Pt (not the other way around) and the polarity of the resulting metal-metal bonds.[4] Regardless of the source of their stability, some early-late transition metal alloys are of particular interest for use in catalysis. For example, the alloy $ScPt_3$ is a good catalyst for oxygen reduction in fuel cells. Even though Sc is an active metal that is easily oxidized, it is stabilized in the aqueous acid environment of the fuel cell by its strong interaction with Pt.[5]

Filling of the 3d and 4s,4p bands

In the 3d series, we see magnetic behavior for elements and alloys between Cr and Ni. Past Ni, the elements (Cu, Zn, Ga,...) are no longer magnetic and they are very good electrical conductors, implying that their valence electrons are highly delocalized. We can understand this behavior by considering the overlap of 4s, 4p, and 3d orbitals, all of which are close in energy. The 4s and 4p have strong overlap and form a broad, continuous band. On the other hand, the 3d electrons are contracted and form a relatively narrow band. Progressing from the early 3d elements (Sc, Ti, V), we begin to fill the 3d orbitals, which are not yet so contracted that they cannot contribute to bonding. Thus, the valence electrons in Sc, Ti, and V are all spin-paired, except for a small number near the Fermi level that give rise to a weak Pauli paramagnetism. Moving across the 3d series to the magnetic elements (Fe, Co, Ni), the d-orbitals are now so contracted that their electrons unpair and we see cooperative ordering of spins (ferromagnetism and antiferromagnetism). Referring to the band diagram at the right, the 3d band is only partially filled and the Fermi level cuts through it. For Cu, Zn, and Ga, the 3d orbitals are even more contracted and the 3d band is thus more narrow, but now it is completely filled and the Fermi level is in the 4s,4p band. The strong orbital overlap in these bands results in spin pairing and a high degree of electron delocalization. Consequently, metals in this part of the periodic table (Cu, Ag) are diamagnetic and are among the best electrical conductors at room temperature. Finally, at Ge, the 4s,4p band is completely filled and the solid is a semiconductor.



Progressive filling of the 3d and 4s,4p bands going across the periodic table from Sc to Ge.

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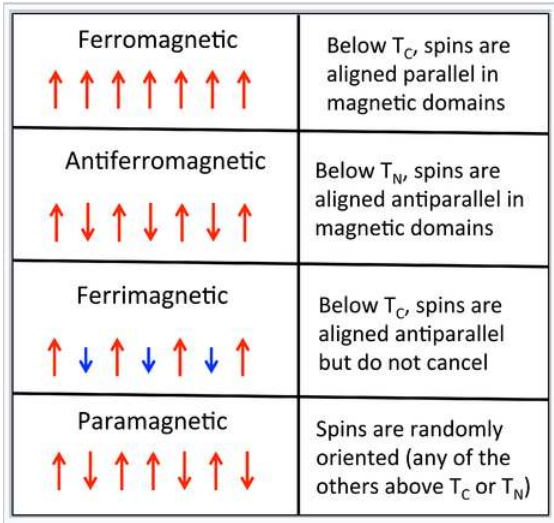
Materials are classified as diamagnetic if they contain no unpaired electrons. Diamagnetic substances are very weakly repelled from an inhomogeneous magnetic field. As we learned in Chapter 5, molecules or ions that have unpaired spins are paramagnetic and are attracted to a magnet, i.e., they move towards the high field region of an inhomogeneous field. This attractive force results from the alignment of spins with the field, but in the case of paramagnetism each molecule acts independently. In metals, alloys, oxides, and other solid state compounds, the unpaired spins interact strongly with each other and can order spontaneously, resulting in the cooperative magnetic phenomena described below.

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10.8: Ferro-, Ferri- and Antiferromagnetism

The magnetism of metals and other materials are determined by the orbital and spin motions of the unpaired electrons and the way in which unpaired electrons align with each other. All magnetic substances are **paramagnetic** at sufficiently high temperature, where the thermal energy (kT) exceeds the interaction energy between spins on neighboring atoms. Below a certain critical temperature, spins can adopt different kinds of ordered arrangements.



A pictorial description of the ordering of spins in ferromagnetism, antiferromagnetism, ferrimagnetism, and paramagnetism

Let's begin by considering an individual atom in the bcc structure of iron metal. Fe is in group VIIIb of the periodic table, so it has eight valence electrons. The atom is promoted to the $4s^1 3d^7$ state in order to make bonds. A localized picture of the d-electrons for an individual iron atom might look like this:



Since each unpaired electron has a spin moment of 1/2, the total spin angular momentum, **S**, for this atom is:

$S = 3\frac{1}{2} = \frac{3}{2}$ (in units of h/2π)

We can think of each Fe atom in the solid as a little bar magnet with a spin-only moment **S** of 3/2. The spin moments of neigboring atoms can align in parallel (↑ ↑), antiparallel (↑ ↓), or random fashion. In bcc Fe, the tendency is to align parallel because of the positive sign of the exchange interaction. This results in **ferromagnetic** ordering, in which all the spins within a magnetic domain (typically hundreds of unit cells in width) have the same orientation, as shown in the figure at the right. Conversely, a negative exchange interaction between neighboring atoms in bcc Cr results in **antiferromagnetic** ordering. A third arrangement, **ferrimagnetic** ordering, results from an antiparallel alignment of spins on neighboring atoms when the magnetic moments of the neighbors are unequal. In this case, the spin moments do not cancel and there is a net magnetization. The ordering mechanism is like that of an antiferromagnetic solid, but the magnetic properties resemble those of a ferromagnet. Ferrimagnetic ordering is most common in metal oxides, as we will learn in Chapter 7.

Magnetization and susceptibility

The **magnetic susceptibility**, **χ**, of a solid depends on the ordering of spins. Paramagnetic, ferromagnetic, antiferromagnetic, and ferrimagnetic solids all have $\chi > 0$, but the magnitude of their susceptibility varies with the kind of ordering and with temperature. We will see these kinds of magnetic ordering primarily among the **3d** and **4f** elements and their alloys and compounds. For example, Fe, Co, Ni, $Nd_2Fe_{14}B$, $SmCo_5$, and YCo_5 are all ferromagnets, Cr and MnO are antiferromagnets, and Fe_3O_4 and $CoFe_2O_4$ are ferrimagnets. Diamagnetic compounds have a weak *negative* susceptibility ($\chi < 0$).

Definitions

- H = applied magnetic field (units: Henry (H))
- B = induced magnetic field in a material (units: Tesla (T))
- M = magnetization, which represents the magnetic moments within a material in the presence of an external field H.

Magnetic susceptibility $\chi = M/H$

Usually, χ is given in *molar* units in the *cgs system*:

χ_M = molar susceptibility (units: cm^3/mol)

Typical values of χ_M:

Compound	Type of Magnetism	χ at 300K (cm^3/mol)
SiO_2	Diamagnetic	-3×10^{-4}
Pt metal	Pauli paramagnetic	$+2 \times 10^{-4}$
$Gd_2(SO_4)_3 \cdot 8H_2O$	Paramagnetic	$+5 \times 10^{-2}$
Ni-Fe alloy	Ferromagnetic	$+10^4 - 10^6$

To correlate χ with the number of unpaired electrons in a compound, we first correct for the small diamagnetic contribution of the core electrons:

$$\chi^{corr} = \chi^{obs} - \chi^{diamagnetic\ cores} \tag{10.8.1}$$

Susceptibility of paramagnets

For a paramagnetic substance,

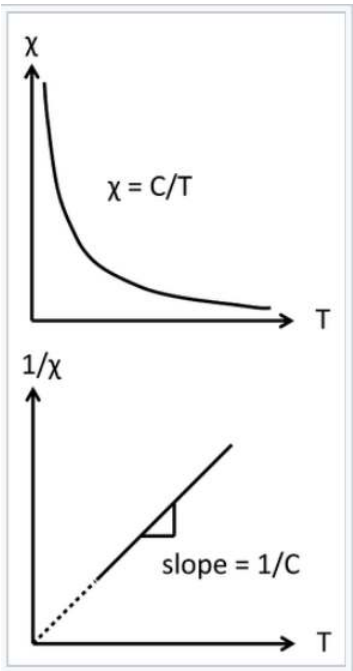
$$\chi_M^{corr} = \frac{C}{T} \tag{10.8.2}$$

The inverse relationship between the magnetic susceptibility and T, the absolute temperature, is called **Curie's Law**, and the proportionality constant C is the **Curie constant**:

$$C = \frac{N_A}{3k_B}\mu_{eff}^2 \tag{10.8.3}$$

Note that C is not a "constant" in the usual sense, because it depends on μ_{eff}, the **effective magnetic moment** of the molecule or ion, which in turn depends on its number of unpaired electrons:

$$\mu_{eff} = \sqrt{n(n+2)}\,\mu_B \tag{10.8.4}$$



Curie law behavior of a paramagnet. A plot of 1/χ vs. absolute temperature is a straight line, with a slope of 1/C and an intercept of zero.

Here μ_B is the Bohr magneton, a physical constant defined as $\mu_B = eh/4\pi m_e = 9.274 \times 10^{-21}$ erg/gauss (in cgs units).

In cgs units, we can combine physical constants,

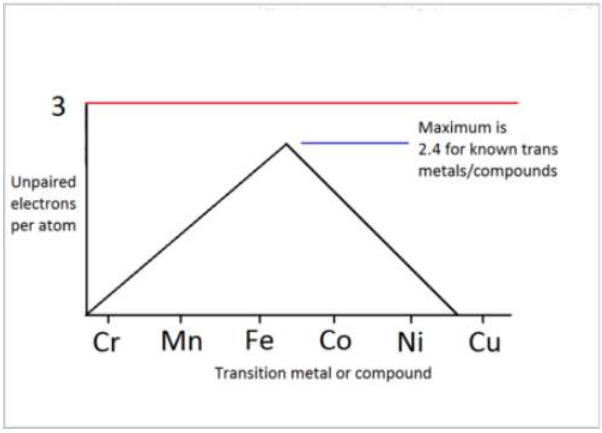
$$\frac{N_A}{3k_B}\mu_B^2 = .125 \tag{10.8.5}$$

Combining these equations, we obtain

$$\chi_M^{corr} = \frac{.125}{T}\left(\frac{\mu_{eff}}{\mu_B}\right)^2 \tag{10.8.6}$$

These equations relate the molar susceptibility, a bulk quantity that can be measured with a magnetometer, to μ_{eff}, a quantity that can be calculated from the number of unpaired electrons, n. Two important points to note about this formula are:

- The magnetic susceptibility is inversely proportional to the absolute temperature, with a proportionality constant C (Curie's Law)
- So far we are talking only about paramagnetic substances, where there is no interaction between neighboring atoms.



Number of unpaired electrons per atom, determined from Curie constants of transition metals and their 1:1 alloys.

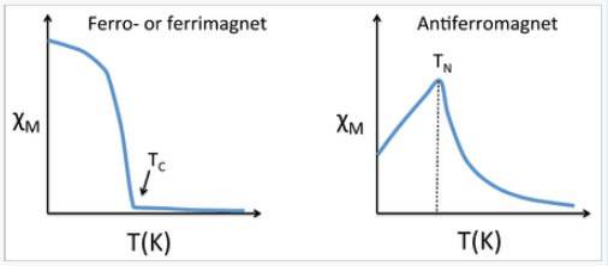
Returning to the isolated Fe atom with its three unpaired electrons, we can measure the Curie constant for iron metal (above the temperature of its transition to a paramagnetic solid) and compare it to the calculation of μ_{eff}. Since n = 3, we calculate:

$$\mu_{eff} = \sqrt{(3)(5)}\mu_B = 3.87\mu_B \tag{10.8.7}$$

The plot at the right shows the number of unpaired electrons per atom, calculated from measured Curie constants, for the magnetic elements and 1:1 alloys in the 3d series. The plot peaks at a value of 2.4 spins per atom, slightly lower than we calculated for an isolated iron atom. This reflects that fact that there is some pairing of d-electrons, i.e., that they do contribute somewhat to bonding in this part of the periodic table.

Susceptibility of ferro-, ferri-, and antiferromagnets

Below a certain critical temperature, the spins of a solid paramagnetic substance order and the susceptibility deviates from simple Curie-law behavior. Because the ordering depends on the short-range exchange interaction, this critical temperature varies widely. Metals and alloys in the 3d series tend to have high critical temperatures because the atoms are directly bonded to each other and the interaction is strong. For example, Fe and Co have critical temperatures (also called the Curie temperature, T_c, for ferromagnetic substances) of 1043 and 1400 K, respectively. The Curie temperature is determined by the strength of the magnetic exchange interaction and by the number of unpaired electrons per atom. The number of unpaired electrons peaks between Fe and Co as the d-band is filled, and the exchange interaction is stronger for Co than for Fe. In contrast to ferromagnetic metals and alloys, paramagnetic salts of transition metal ions typically have critical temperatures below 1K because the magnetic ions are not directly bonded to each other and thus their spins are very weakly coupled in the solid state. For example, in gadolinium sulfate, the paramagnetic Gd^{3+} ions are isolated from each other by SO_4^{2-} ions.

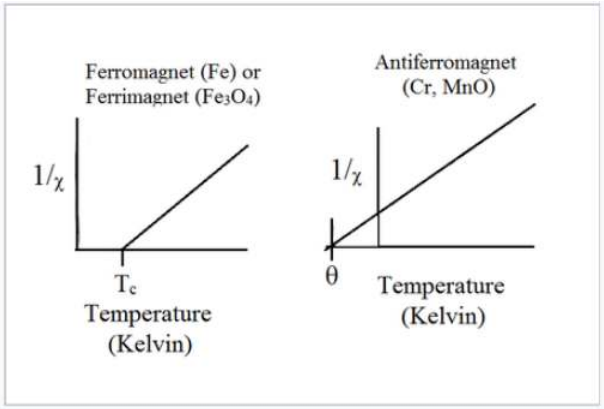


Magnetic susceptibility vs temperature (Kelvin) for ferrimagnetic, ferromagnetic, and antiferromagnetic materials

Above the critical temperature T_C, **ferromagnetic** compounds become paramagnetic and obey the **Curie-Weiss law:**

$$\chi = \frac{C}{T - T_c} \tag{10.8.8}$$

This is similar to the Curie law, except that the plot of $1/\chi$ vs. T is shifted to a positive intercept T_C on the temperature axis. This reflects the fact that ferromagnetic materials (in their paramagnetic state) have a greater tendency for their spins to align in a magnetic field than an ordinary paramagnet in which the spins do not interact with each other. Ferrimagnets follow the same kind of ordering behavior. Typical plots of χ vs. T and $1/\chi$ vs. T for ferro-/ferrimagnets are shown above and below.



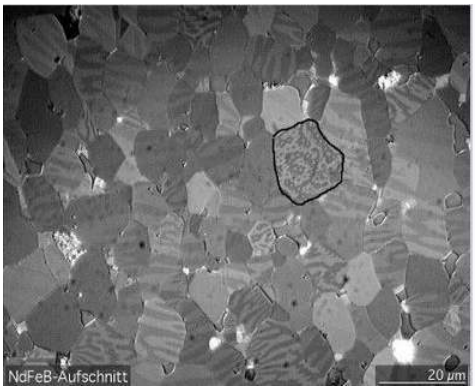
Plots of $1/\chi$ vs. T for ferromagnets, ferrimagnets, and antiferromagnets.

Antiferromagnetic solids are also paramagnetic above a critical temperature, which is called the Néel temperature, T_N. For antiferromagnets, χ reaches a maximum at T_N and is smaller at higher temperature (where the paramagnetic spins are further disordered by thermal energy) and at lower temperature (where the spins pair up). Typically, antiferromagnets retain some positive susceptibility even at very low temperature because of canting of their paired spins. However the maximum value of χ is much lower for an antiferromagnet than it is for a ferro- or ferrimagnet. The Curie-Weiss law is also modified for an antiferromagnet, reflecting the tendency of spins (in the paramagnetic state above T_N) to resist parallel ordering. A plot of $1/\chi$ vs. T intercepts the temperature axis at a negative temperature, $-\theta$, and the Curie-Weiss law becomes:

$$\chi = \frac{C}{T+\theta} \tag{10.8.9}$$

Ordering of spins below T_C

Below T_C, the spins align spontaneously in ferro- and ferrimagnets. Complex magnetization behavior is observed that depends on the history of the sample. For example, if a ferromagnetic material is cooled in the absence of an applied magnetic field, it forms a mosaic structure of magnetic domains that each have internally aligned spins. However, neighboring domains tend to align the opposite way in order to minimize the total energy of the system. This is illustrated in the figure at the left for a Nd-Fe-B magnet. The sample consists of 5-10 µm wide crystal grains that can be easily distinguished by the sharp boundaries in the image. Within each grain are a series of lighter and darker stripes (imaged by using the optical Kerr effect) that are ferromagnetic domains with opposite orientations. Averaged over the whole sample, these domains have random orientation so the net magnetization is zero.

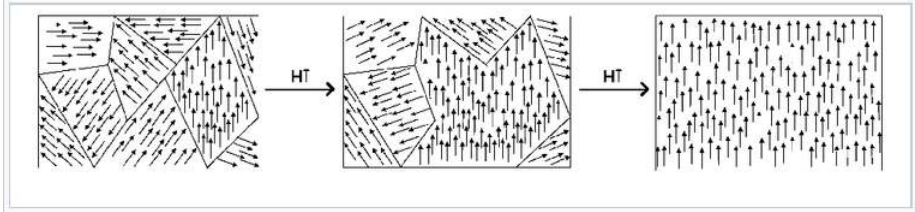


Microcrystalline grains within a piece of $Nd_2Fe_{14}B$ (the alloy used in neodymium magnets) with magnetic domains made visible with a Kerr microscope. The domains are the light and dark stripes visible within each grain.

When a sample like this one is magnetized (i.e., exposed to a strong magnetic field), the domain walls move and the favorably aligned domains grow at the expense of those with the opposite orientation. This transformation can be seen in real time in the Kerr microscope. The domain walls are typically hundreds of atoms wide, so movement of a domain wall involves a cooperative tilting of spin orientation (analogous to "the wave" in a sports stadium) and is a relatively low energy process.

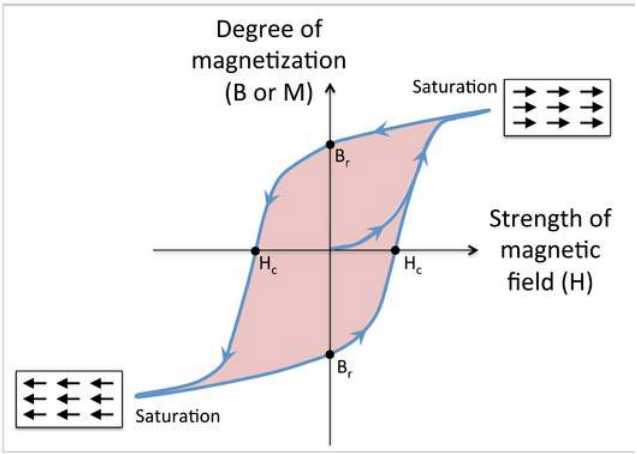
The movement of domain walls in a grain of silicon steel is driven in this movie by increasing the external magnetic field in the "downward" direction, and is imaged using a Kerr microscope. White areas are domains with their magnetization directed up, dark areas - which eventually comprise the entire grain - are domains with their magnetization directed down.

The process of magnetization moves the solid away from its lowest energy state (random domain orientation), so magnetization involves input of energy. When the external magnetic field is removed, the domain walls relax somewhat, but the solid (especially in the case of a "hard" magnet) can retain much of its magnetization. If you have ever magnetized a nail or a paper clip by using a permanent magnet, what you were doing was moving the walls of the magnetic domains inside the ferromagnet. The object thereafter retains the "memory" of its magnetization. However, annealing a permanent magnet destroys the magnetization by returning the system to its lowest energy state in which all the magnetic domains cancel each other.



Rotation of orientation and increase in size of magnetic domains in response to an externally applied magnetic field.

Magnetic hysteresis. Cycling a ferro- or ferrimagnetic material in a magnetic field results in hysteresis in the magnetization of the material, as shown in the figure at the left. At the beginning, the magnetization is zero, but it begins to rise rapidly as the magnetic field is applied. At high field, the magnetic domains are aligned and the magnetization is said to be saturated. When the field is removed, a certain **remanent magnetization** (indicated as the point $\mathbf{B_r}$ on the graph) is retained, i.e., the material is magnetized. Applying a field in the opposite direction begins to orient the magnetic domains in the other direction, and at a field $\mathbf{H_c}$ (the **coercive field**), the magnetization of the sample is reduced to zero. Eventually the material reaches saturation in the opposite direction, and when the field is removed again, it has remanent magnetization Br, but in the opposite direction. As the field continues to reverse, the magnet follows the hysteresis loop as indicated by the arrows. The area of colored region inside the loop is proportional to the magnetic work done in each cycle. When the field cycles rapidly (for example, in the core of a transformer, or in read-write cycles of a magnetic disk) this work is turned into heat.



Magnetization of a ferro- or ferrimagnet vs. applied magnetic field H. Starting at the origin, the upward curve is the initial magnetization curve. The downward curve after saturation, along with the lower return curve, form the main loop. The intercepts Hc and Br are the coercivity and remanent magnetization.

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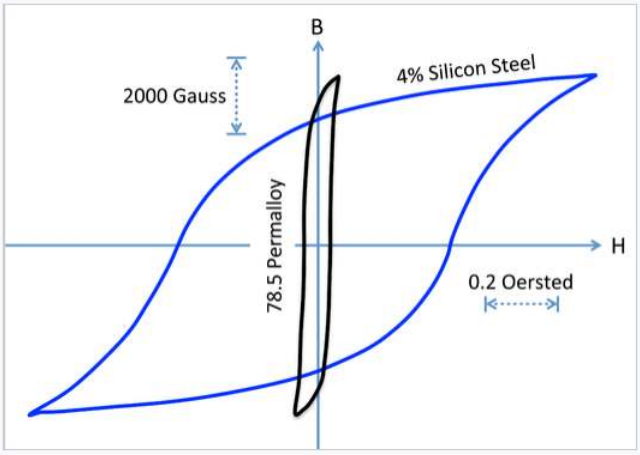
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10.9: Hard and Soft Magnets

Whether a ferro- or ferrimagnetic material is a **hard** or a **soft magnet** depends on the strength of the magnetic field needed to align the magnetic domains. This property is characterized by $\mathbf{H_c}$, the coercivity. Hard magnets have a high coercivity (H_c), and thus retain their magnetization in the absence of an applied field, whereas soft magnets have low values.

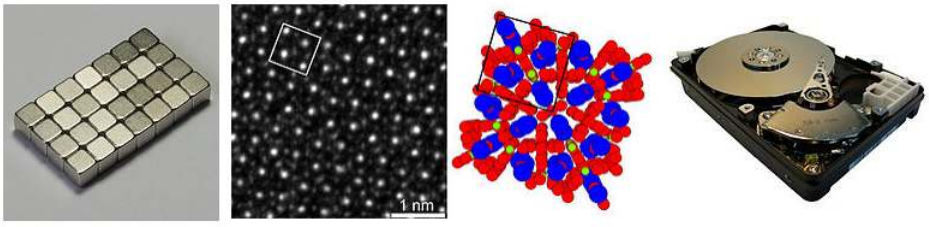
The figure at the right compares hysteresis loops for hard and soft magnets. Recall that the energy dissipated in magnetizing and demagnetizing the material is proportional to the area of the hysteresis loop. We can see that soft magnets, while they can achieve a high value of B_{sat}, dissipate relatively little energy in the loop. This makes **soft magnets** preferable for use in **transformer cores**, where the field is switched rapidly. **Permalloy**, an alloy consisting of about 20% Fe and 80% Ni, is a soft magnet that has very high magnetic permeability μ (i.e., a large maximum slope of the B vs. H curve) and a very narrow hysteresis loop.

Some materials, such as iron metal, can exist as either hard or soft magnets. Whether bcc iron is a hard or soft magnet depends on the crystal grain size. When crystal grains in iron are sub-micron size, and comparable to the size of the magnetic domains, then the magnetic domains are pinned by crystal grain boundaries. When the magnetic domains are pinned a stronger coercive magnetic field needs to be applied to cause them to re-align. When iron is annealed, the crystal grains grow and the magnetic domains become more free to align with applied magnetic fields. This decreases the coercive field and the material becomes a soft magnet.



Hysteresis loops comparing a hard magnet (iron-silicon steel) to a soft magnet (permalloy) on the same scale. H_c for permallloy is 0.05 Oe, about 10 times lower than that of the hard magnet. The remanent magnetizations of the two materials are comparable.

Hard magnets such as CrO_2, γ-Fe_2O_3, and cobalt ferrite ($CoFe_2O_4$) are used in magnetic recording media, where the high coercivity allows them to retain the magnetization state (read as a logical 0 or 1) of a magnetic bit over long periods of time. Hard magnets are also used in disk drives, refrigerator magnets, electric motors and other applications. Drive motors for hybrid and electric vehicles such as the Toyota Prius use the hard magnet $Nd_2Fe_{14}B$ (also used to make strong refrigerator magnets) and require 1 kilogram (2.2 pounds) of neodymium.[6]. A high-resolution transmission electron microscope image of $Nd_2Fe_{14}B$ is shown below and compared to the crystal structure with the unit cell marked.



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10.10: Discussion Questions

- Discuss the relationship between the trends in bonding energy of the transition metals and their magnetic properties.
- Draw the hcp unit cell in sections and show how you would calculate (a) the number of atoms in the unit cell and (b) the fraction of space filled by equal spheres.

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10.11: Problems

1. C-centered Bravais lattices exist in the monoclinic and orthorhombic systems but not in the tetragonal system. That is because the C-centered tetragonal lattice is equivalent to one of the other Bravais lattices. Which one is it? Show with a drawing how that lattice is related to the C-centered tetragonal lattice. How many atoms are in the unit cell of that lattice?

2. Which of the following sequences of close packed layers fills space most efficiently? Explain your answer.

(a) ABACCABA...

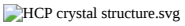
(b) ABABAB...

(c) AABBAABB...

(d) ABACABAC...

3. Calculate the fraction of space that is occupied by packing spheres in the (a) simple cubic, (b) body-centered cubic structure, (c) face-centered cubic (cubic close packed) structures. Assume that nearest neighbor spheres are in contact with each other.

4. The hexagonal close packed (hcp) structure is shown below. If the radius of the spheres is R, what is the vertical distance between layers in units of R? What fraction of space is filled by the spheres in the hcp lattice?



5. Consider a one-dimensional chain of sodium atoms that contains N atoms, where N is a large number. The distance between atoms in the chain is the lattice constant **a**. In the highest occupied molecular orbital of the chain, what is the distance between nodes (in units of **a**)?

6. Starting from the left side of the periodic table, the melting and boiling points of the elements first increase, and then decrease. For example, the order of boiling points is Rb < Sr < Y < Zr < Nb < Mo > Tc ≈ Ru > Rh > Pd > Ag. Briefly explain the reason for this trend.

7. Going across the periodic table from left to right starting from potassium, the bonding energies and heats of vaporization increase in the order K < Ca < Sc < Ti < V, but then decrease going from V to Mn (V > Cr > Mn). The heats of vaporization of V, Cr, and Mn are much less than those of Nb, Mo, and Tc, respectively. Explain these trends.

8. Some alloys of early and late transition metals (e.g., $ZrPt_3$) have much higher enthalpies of vaporization (per metal atom) than either pure metal. Why are such alloys unusually stable, relative to the pure metals?

9. Graphite is a semimetal composed of sheets of fused benzene rings. There are no bonds between sheets, only van der Waals interactions. What is the C-C bond order in graphite? Show why the C-C distance (1.42 Å) is different from that of benzene (1.40 Å).

10. Fe, Co, and Ni are ferromagnetic, whereas Ru, Ir, and Pt are diamagnetic. Explain why magnetic metals are found only among the 3d and 4f elements. Why are Sc and Ti, which are also 3d elements, diamagnetic?

11. The Curie temperature of cobalt is 1127•C, which is higher than that of Fe (770•C) or Ni (358•C). Why does Co have the highest Curie temperature?

12. Iron metal comes in magnetically “soft” and “hard” forms. Briefly explain the structural differences between them and draw magnetic hysteresis curves for each, indicating on your curves the coercive field and the remanent magnetization.

13. Aluminum metal has the fcc structure, a lattice constant of 4.046 Å, three valence electrons per atom, and an electron scattering time (at room temperature) of 11.8 fs. Use these values to calculate the room temperature resistivity (in ohm-cm) of Al metal.

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CHAPTER OVERVIEW

11: Basic Science of Nanomaterials

Learning Objectives

- Understand the physical basis of mesoscopic behavior in nanoscale semiconducting and magnetic particles.
- Describe how the particle-in-a-box equation applies to electrons in quantum wells.
- Use the Brus formula to calculate the band gap energy of nanoscale semiconductor particles.
- Use the surface energy concept to calculate changes in the melting point and vapor pressure of nanoparticles.
- Describe the methods used to make semiconducting and metal nanocrystals of uniform size.
- Explain the origin of the localized surface plasmon resonance effect in metal nanoparticles.
- Describe the emerging analytical and biomedical applications of metal nanoparticles.

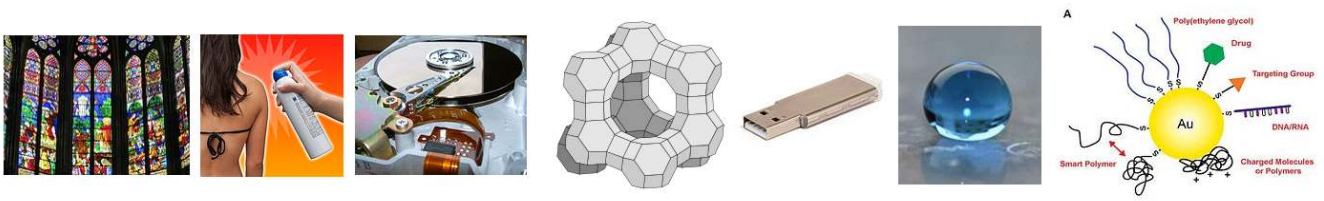
Nanomaterials describe materials of which a single unit is sized (in at least one dimension) between 1 and 1000 nanometers, but is usually 1—100 nm. Nanomaterials research takes a materials science-based approach to nanotechnology, leveraging advances in materials metrology and synthesis which have been developed in support of microfabrication research. Materials with structure at the nanoscale often have unique optical, electronic, or mechanical properties. In this chapter we will learn about the basic science of nanomaterials, i.e., what it is about their size that makes them different.

11.1: Prelude to Basic Science of Nanomaterials
11.2: Physics and Length Scales- Cavity Laser, Coulomb Blockade, Nanoscale Magnets
11.3: Semiconductor Quantum Dots
11.4: Synthesis of Semiconductor Nanocrystals
11.5: Surface Energy
11.6: Nanoscale Metal Particles
11.7: Applications of Nanomaterials
11.8: Discussion Questions
11.9: Problems
11.10: References

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11.1: Prelude to Basic Science of Nanomaterials

What do stained glass, sunscreen, magnetic hard drives, heterogeneous catalysts, consumer electronics, stain-resistant clothing, self-cleaning glass, and medical diagnostics all have in common? All of them derive some special property and utility from **nanoscale materials**: ordinary elements and inorganic compounds such as gold, silver, TiO_2, chromium, SiO_2, and silicon that acquire different properties when their characteristic dimensions are somewhere between **1 and 100 nm**. In this chapter we will learn about the basic science of nanomaterials, i.e., what it is about their size that makes them different.



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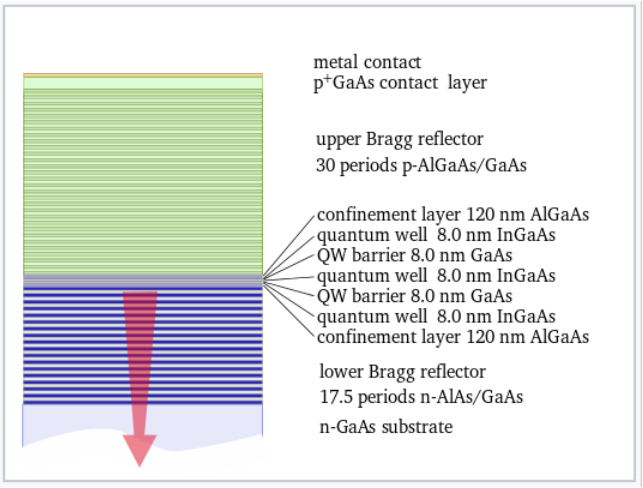
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11.2: Physics and Length Scales- Cavity Laser, Coulomb Blockade, Nanoscale Magnets

The special properties of nanomaterials do not derive from different laws of physics, which are the same for objects large and small. For example, Newton's second law ($F = ma$), Coulomb's law ($E = \frac{q_1 q_2}{4\pi\varepsilon_0 r}$), and the laws of energy and momentum conservation are the same for buckyballs (C_{60}) and full-size soccer balls. Nevertheless, the physics of electrons, atoms, and photons naturally produce **characteristic length scales**, some of which we have already seen. For example, in Chapter 6 we discovered that the mean free path of an electron in a good metal is about 40 nm. In Chapter 10, we learned that the Bohr radius of an electron or hole in doped Si is about 4 nm, and that the coherence length of Cooper pairs in semiconductors is somewhere between a few nm and 1 μm. When objects become small relative to these characteristic lengths, their physical properties change in interesting ways. Materials that exist at the relevant length scale are called ***mesoscopic*** (meso = "between," scopic = "size") meaning that they cross over from one kind of behavior - the bulk behavior of large objects - to another. This length scale is different for different kinds of properties, but for many it happens between 1 and 100 nm. We illustrate this point with a few examples.

The cavity laser

A vertical cavity surface-emitting laser (or VCSEL) is a semiconductor-based device that emits light in the vertical direction relative to the plane of the chip. These devices are being developed and used for high power applications such as laser surgery, infrared illumination for military surveillance, and laser cutting tools. The basic design of a VCSEL is shown at the right. The VCSEL is basically a light-emitting diode, incorporating p-type and n-type regions of the III-V semiconductor (Al,Ga)As. However, it has two special features. First, the refractive index of the semiconductor is modulated above and below the junction to make Bragg mirrors. These mirrors reflect light emitted in the junction, so that the photon density becomes very high there, a necessary condition for stimulated emission and lasing. The Bragg mirror stack is asymmetric (thinner on the bottom), so that light can escape from the junction in one direction only. Second, the junction itself consists of a thin "quantum well" layer of (In,Ga)As, a III-V semiconductor with a smaller band gap than the surrounding (Al,Ga)As layers.

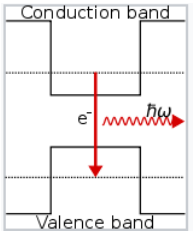


A VCSEL device structure. This is a *bottom-emitting multiple-quantum-well* VCSEL.

The **quantum well** structure, the band diagram of which is illustrated at the left, is the nanoscale part of the laser. The energies of the conduction and valence bands of (Al,Ga)As flank those of the thin (In,Ga)As layer. Therefore, electrons and holes injected into that layer cannot escape: electrons in (In,Ga)As do not have enough energy to climb "up" to the conduction band of (Al,Ga)As and holes cannot climb "down." Electrons confined to such a small well behave as a particle-in-a-box (as we learned in the context of electrides in Chapter 9).

The electron has a kinetic energy defined by the equation:

$$KE = \frac{h^2 n^2}{8mL^2} \tag{11.2.1}$$



We can calculate the energy difference between the lowest (n=1) and next lowest (n=2) levels, which is inversely proportional to the square of the thickness (L) of the (In,Ga)As layer. In this calculation we need to use the effective mass of the electron in (In,Ga)As, which is about 7% of the electron rest mass[1]. With an 8 nm thick layer, this energy is:

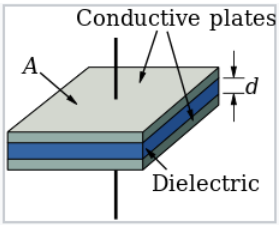
$$E = \frac{(2^2 - 1^2)(6.626 \cdot 10^{-34} Js)^2}{8 \cdot 0.07 \cdot (9.1 \cdot 10^{-31} kg)(8 \cdot 10^{-9} m)^2} = 4.0 \cdot 10^{-20} J = 0.25 eV \tag{11.2.2}$$

The VCSEL cavity will thus have a resonant energy of 0.25 eV and emit photons at this energy in the infrared (λ ≈ 5000 nm). Note that because of the inverse square dependence of the cavity energy on layer thickness, lasers based on this design can only function at nanoscale dimensions. When the cavity is three times thicker, its resonant energy becomes comparable to the thermal energy at room temperature (kT = 0.026 eV), and the lasing effect is thermally "washed out."

Coulomb blockade

A capacitor is a (macroscopic) device that stores electrical charge. The basic structure of a capacitor is shown at the right. When a voltage is applied to such a device, it develops a charge (± Q) on the two plates that is proportional to the voltage:

$$C = \frac{Q}{V} \tag{11.2.3}$$



Basic design of a parallel plate capacitor of area *A* and with a dielectric thickness of *d*

The magnitude of the capacitance C is determined by the permittivity ε and the dimensions of the dielectric layer, A and d.

$$C = \frac{\varepsilon A}{d} \tag{11.2.4}$$

We can also calculate the work done in charging the capacitor up (i.e., the energy stored by charging the capacitor) by integrating the voltage times the charge:

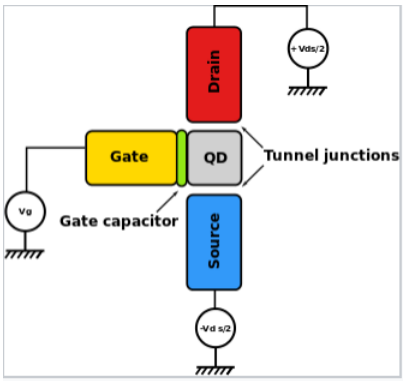
$$E = int_0^Q V(q)dq = \int_0^Q \frac{q}{C} dq = \frac{1}{2}\frac{Q^2}{C} = \frac{1}{2}CV^2 = \frac{1}{2}VQ \tag{11.2.5}$$

Now it is interesting to ask, what happens to a capacitor when we make it very small? This is of particular interest in a device called a **single electron transistor**, a schematic diagram of which is shown at the right. The metallic gate lead is separated from a "quantum dot," which can be a metal or semiconductor particle, by a thin dielectric layer. This metal-dielectric-metal sandwich acts as a capacitor, and from the equation above, the energy needed to charge it by a single electron (Q = e) is:

$$E = \frac{e^2}{2C} \tag{11.2.6}$$

where e is the charge of the electron, 1.602 x 10^{-19} Coulomb. If the gate width and lateral dimensions are very small - say 2 nm as is readily achievable in self-assembled Coulomb blockade devices[2][3] - then for a typical insulating dielectric, a voltage of about

200 mV is needed to charge the quantum dot by a single electron. Again, this effect is unique to the nanoscale, because a 10 times larger device area would make the single-electron charging voltage about 20 mV, which is smaller than the thermal energy kT (26 meV). Thus for devices larger than about 5-6 nm, individual electron charging events are washed out at room temperature by thermal fluctuations.

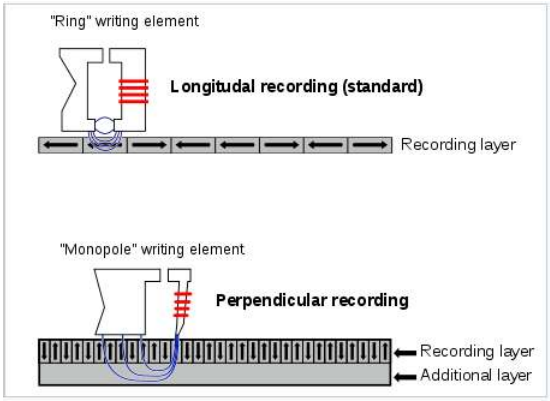


Schematic of a single-electron transistor.

How can a **nanoscale capacitor** like this act as a **transistor**, which functions as a switch in an electrical circuit? The effect comes from the mutual repulsion of electrons. An electron on the quantum dot repels any other electron that would be forced onto it by applying a small voltage between the source and the drain. Hence the conductance of the quantum dot is very low at a gate bias of zero volts, or at any gate bias (200, 400, 600 mV...) that places an integer number (1, 2, 3,...) of electrons on the dot. But halfway in between these voltages (e.g., at 100, 300, 500 mV) the energy is the same whether there are n or n+1 electrons on the dot. This means that electrons can hop on and off without changing their energy, i.e., they can tunnel through the dot from source to drain. This effect gives peaks in the conductance of the dot at regular steps in the gate voltage. In effect, the gate can act as a switch, as in a conventional field-effect transistor. Single-electron transistors are being researched as ultra-sensitive electrometers and single-molecule chemical sensors, since a tiny change in the electrostatic environment of the dot can switch the device on or off.

Nanoscale magnets

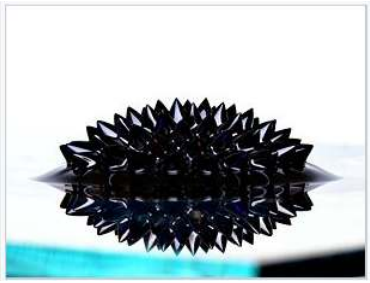
Ferro- and ferrimagnetic materials such as iron and chromium oxide are used for digitial storage of information in hard disks. The individual memory bits, which can be oriented perpendicular or parallel to the plane of the disk as shown at the right, store a logical "0" or "1" depending on the orientation of their magnetic dipole. To be useful, this information must be non-volatile, i.e., the magnetic bit must retain its polarization in the absence of an applied field from the read/write head.



Longitudinal and perpendicular recording, two types of writing heads on a hard disk.

The storage density of such magnetic memories is impressive. A 2.5" hard drive can now store 1 TB of information, using rod-shaped magnetic grains that are approximately 0.5 µm long. We now have good synthetic methods for making these same materials as crystals with dimensions of only a few nanometers. Why aren't those nanocrystals used to make even more dense memory disks?

The reason is that the energy needed to flip the magnetization (i.e., to turn a "0" into a "1" and vice-versa) is strongly size-dependent. For a ferro- or ferrimagnet this energy is equal to Mr^3, where M is the magnetic energy per unit volume and r is the characteristic dimension (e.g., the length of the edge of a cube, or the diameter of a sphere) of the magnetic grain. For typical materials such as iron, this energy becomes comparable to kT when r is about 3-5 nm. Such small particles are superparamagnetic, meaning that they still have a large magnetic moment because of the ordering of their spins, but they do not retain a permanent polarization in the absence of an applied magnetic field. Superparamagnetic particles are thus not useful for magnetic memories, but they are interesting and practical in other ways, for example in ferrofluids, magnetic resonance imaging (MRI), and some emerging medical diagnostic and therapeutic applications.



A ferrofluid containing superparamagnetic Fe_3O_4 nanoparticles, which are coated with oleic acid and suspended in oil, in the field of a strong permanent magnet.

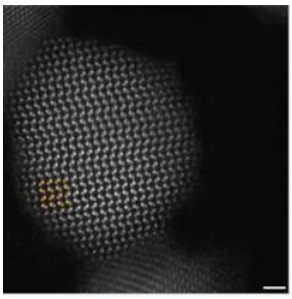
In these three illustrative examples (involving light emission, electronic conduction, and magnetic behavior), the transition to new properties involves a crossover in which the characteristic energy of the system is comparable to the thermal energy kT. It just so happens that for many physical phenomena, this crossover occurs on the length scale of nanometers.

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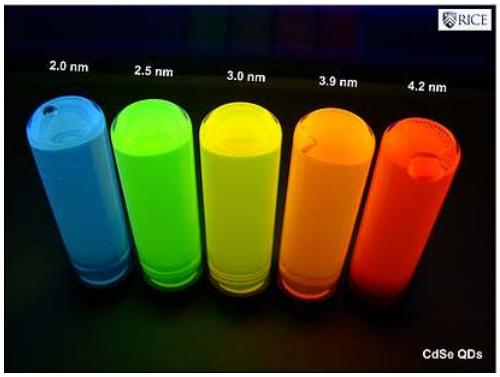
11.3: Semiconductor Quantum Dots

One of the most fascinating and well-studied mesoscopic effects occurs with semiconductor particles of various shapes when one or more of their dimensions is in the range of a few nanometers. These so-called "quantum dots" (0D), "quantum rods" (1D) and "nanosheets" (2D) acquire striking new electronic and optical properties.



Atomic resolution image of a CdSe nanoparticle.

The synthesis of semiconductor quantum dots, which is discussed in more detail below, is sufficiently well controlled to give essentially perfect crystals of a few thousand atoms, something that is statistically impossible in a macroscopic crystal. An image of such a crystal is shown at the right. In the synthesis, these crystals can be capped with an epitaxial layer of ligands or by a shell of a wider bandgap semiconductor (such as ZnS in the case of CdSe), so that the inner core is effectively a quantum well. Electron-hole pairs formed by excitation of the core semiconductor are confined there and cannot reach the external surface of the particle, where they might otherwise be trapped and recombine thermally. Consequently, the quantum yield for bandgap emission of semiconductor quantum dots is typically high, giving rise to the bright emission colors shown at the right for CdSe particles of different sizes. Because of their strong and narrow emission bands, quantum dots are of interest as luminescent tags for biological imaging applications, and also as light absorbers and emitters in solar cells and LEDs.



Emission colors of CdSe nanoparticles of different sizes. Smaller particles emit blue light because the exciton energy increases as the size decreases.

The size-dependence of the emission color comes primarily from a particle-in-a-box effect. The electron and hole that are created when the quantum dot absorbs light are bound together as an **exciton** by the confines of the "box". Louis Brus used first-order perturbation theory to determine that the bandgap of a semiconductor quantum dot is given approximately by:[4]

$$E_{gap} = E_{gap,bulk} + \frac{h^2}{8\mu R^2} - \frac{1.8e^2}{4R\pi\varepsilon\varepsilon_0} + \ldots \tag{11.3.1}$$

where R is the particle radius, μ is the electron-hole reduced mass ($1/\mu = 1/m_e^* + 1/m_h^*$), m_e^* and m_h^* are the electron and hole effective masses, and ε is the dielectric constant of the semiconductor. In this equation, the first term after the bulk bandgap is the kinetic energy due to confinement of the exciton, and the second term represents the electrostatic attractive energy between the confined electron and hole. Because the energy is a function of R^2, it can be widely tuned across the visible spectrum by changing the size of the quantum dot.

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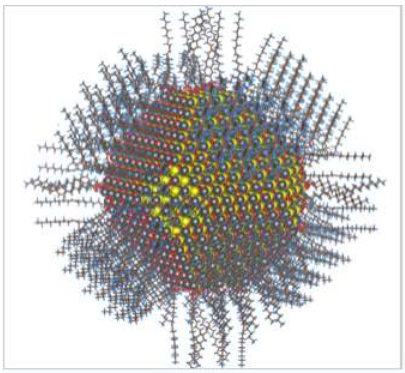
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11.4: Synthesis of Semiconductor Nanocrystals

Early work on the quantum size effect in semiconductor nanoparticles used simple metathesis reactions in the synthesis. For example, CdSe and PbS can be precipitated at ambient temperature by the reactions:

$$CdCl_{2(aq)} + H_2Se_{(g)} = CdSe_{(s)} + 2\,HCl_{(aq)}$$

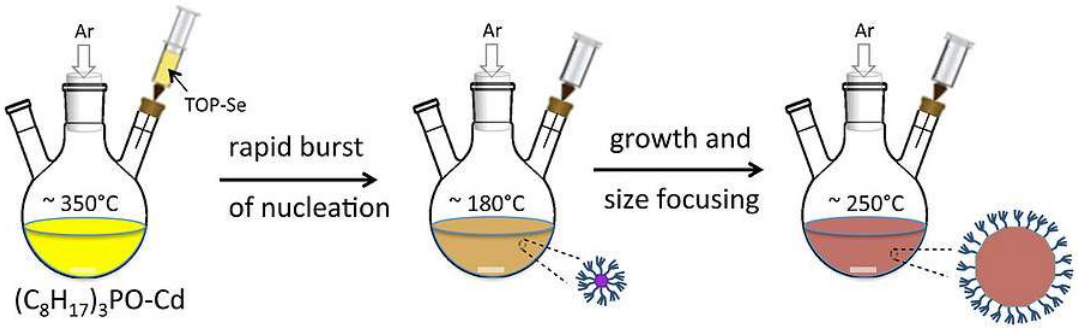
$$Pb(NO_3)_2 + H_2S_{(g)} = PbS_{(s)} + 2\,HNO_{3(aq)}$$



Complete atomistic model of a 5 nm diameter colloidal lead sulfide nanoparticle with surface passivation by oleic acid, oleyl and hydroxyl groups.

The growth of the particles was restricted by carrying out these reactions in different matrices, such as in polymer films or the silicate cages of zeolites, and capping ligands were also sometimes used to limit particle growth. While these reactions did produce nanoparticles, in general a broad distribution of particle sizes was obtained. The particles were also unstable to **Ostwald ripening** - in which large particles grow at the expense of smaller ones in order to minimize the total surface energy - because of the reversibility of the acid-forming synthetic reactions in aqueous media. The lack of good samples prevented detailed studies and the development of applications for semiconductor quantum dots.

A very important development in nanoparticle synthesis came in the early 1990's, when Murray, Norris, and Bawendi introduced the first non-aqueous, controlled growth process for II-VI semiconductor quantum dots.[5] The keys to this synthesis were (1) to use non-aqueous solvents and capping ligands to stabilize the products against ripening, (2) to carry out the reaction at high temperature to ensure good crystallinity, and (3) to separate the steps of particle **nucleation** and **growth**, and thereby obtain particles of uniform size. This procedure is illustrated below:

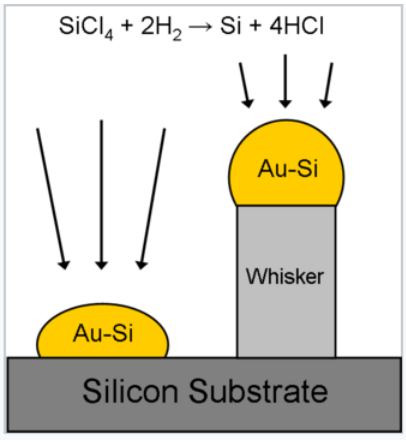


The synthesis is carried out in a coordinating, high boiling solvent that is a mixture of trioctylphosphine (**TOP**) and trioctylphosphine oxide (**TOPO**). In early experiments, organometallic cadmium compounds such as diethylcadmium were used as the metal source, but it was later found that these highly toxic and pyrophoric compounds could be replaced by CdO. At the start of the reaction, a selenium source, typically bis(trimethylsilyl)selenium, $[(CH_3)_3Si]_2Se$, dissolved in TOP is rapidly injected into the hot (350 °C) reaction mixture. The reaction causes a rapid burst of nanoparticle nucleation, but the temperature also drops as the cold solvent is injected and so the nucleation event ends quickly. The cooled solution now contains nanocrystal seeds. It is supersaturated in TOPO-Cd and TOP-Se, but particle growth proceeds slowly until the solution is heated again to the growth temperature, ca. 250°C. Particle growth and **size-focusing** occurs because small particles require less added material to grow by an

amount ΔR than larger particles. This is because the volume of an added shell around a spherical seed is $4\pi R^2\Delta R$, so for larger R, ΔR is smaller. Very narrow particle size distributions can be obtained under conditions of high supersaturation, where the rate of nanoparticle growth is fast relative to particle dissolution and Ostwald ripening.[6] The size distribution can then be narrowed further by adding a non-solvent such as hexane to the cooled reaction mixture. The largest particles precipitate first, followed by smaller particles. Because the nanoparticles are capped with a ligand shell of TOP, they can be re-suspended in organic solvents once they are size-separated.

The high temperature synthesis of semiconductor quantum dots has been applied to a broad variety of materials including II-VI, III-V, and IV-VI semiconductors. Monodisperse nanoparticles of **controlled shapes** can be made by variants of this method. For example, it is possible to adjust the conditions so that CdSe nucleates in the zincblende polymorph as tetrahedrally shaped seeds, and then grow polar wurtzite "arms" onto each triangular face, resulting in nanocrystal tetrapods. Numerous other nanocrystal shapes such as rods, arrowheads, rice (tapered rods), and polar structures such as Janus rods can be made by variants of this technique. These shape-control strategies often involve the use of ligands that adsorb specifically to certain crystal faces and inhibit their growth. For example, hexylphosphonic acid ligands adsorb selectively to Cd-rich crystal faces and thus lead to the growth of prismatic wurtzite-phase CdSe nanocrytals.

A second widely used method of semiconductor nanocrystal synthesis involves growth from molecular precursors and molten metal droplets, as shown in the figure at the right. The **vapor-liquid-solid (VLS)** and related **solution-liquid-solid (SLS)** growth processes rely on the fact that semiconductors such as Si, Ge, GaAs, InP, and others are soluble at high temperatures in liquid metals such as Au and Cu. The catalytic reduction of a molecule such as silicon tetrachloride ($SiCl_4$) at the surface of a gold nanocrystal liberates HCl gas and creates a solid solution of Si in Au. The presence of Si lowers the melting point of Au, and as more $SiCl_4$ reacts, a liquid **eutectic** droplet of the Si-Au alloy is formed. When this droplet becomes supersaturated in Si, a silicon nanocrystal nucleates and grows. This reaction can be performed on the surface of a macroscopic Si crystal, in which case nanocrystal "whiskers" grow from the surface, typically as single crystals and with an epitaxial orientation that is determined by the Si crystal face of the substrate. The diameter of the whiskers is controlled by the radius of the Au drops, which can be as small as a few nanometers and as large as several microns. Using this technique, "forests" of nanowires or microwires can be grown. Because the composition of the nanowire depends on the precursor being fed to the Au droplets, it is possible to make "totem pole" structures with varied compositions along the nanowire axis. Semiconductor shells can also be grown around the wires by **chemical vapor deposition (CVD)**. The VLS process can also be adapted to complex compositions for which no molecular precursor is available by using a laser to ablate the semiconductor from a solid target.



Epitaxial growth of silicon nanowires catalyzed by gold nanoparticles in the vapor-liquid-solid (VLS) process.

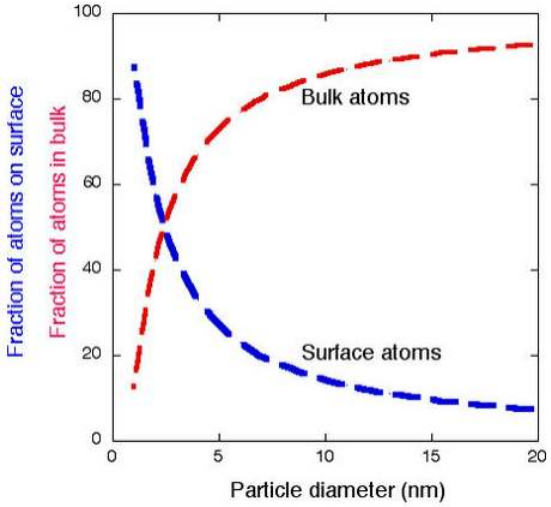
Semiconductor nanowires made by this method are the basis of extremely sensitive **biosensors**, in which a molecular binding event anywhere along the wire strongly affects its electrical conductivity.[7] Nanowire and microwire arrays are also being studied as **solar cell** and **lithium battery** materials, as well as nanoscale electronic and optoelectronic devices.

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11.5: Surface Energy

Nanoparticles have a substantial fraction of their atoms on the surface, as shown in the plot at the right.[8] This high surface area to volume ratio is an important factor in many of the physical properties of nanoparticles, such as their **melting point** and **vapor pressure**, and also in their **reactivity**. Heterogeneous catalysts, for example, are often based on nanoparticles because the catalytically reactive atoms are those that are on the surface of the particle.



The surface energy is always positive. A key quantity that is connected with the chemistry of all surfaces is the **surface energy**. This is the (thermodynamically unfavorable) energy of making "dangling bonds" at the surface. Atoms at the surface are under-coordinated, and because breaking bonds costs energy, surface atoms always have higher energy than atoms in the bulk. This happens regardless of whether the bonding is covalent (as in a metal), ionic (in a salt), or non-covalent (in a liquid such as water). We see this effect, for example, in water droplets that bead up on a waxy surface. The droplet contracts into a sphere (against the force of gravity that works to flatten it) in order to minimize the number of dangling hydrogen bonds at the surface.

In the case of metal or semiconductor particles, strong covalent bonds are broken at the surface. For example, a gold atom in bulk face-centered cubic Au has 12 nearest neighbors, but a gold atom on the (111) surface of the crystal (the most dense crystal plane of gold) has six nearest neighbors in-plane and three underneath, for a total of 9. We might expect the surface energy of this crystal face to be a little less (because the remaining bonds will become slightly stronger) than 3/12 = **1/4 of the bonding energy** of bulk Au, and this is in fact a fairly good rule of thumb for many materials. When translated into energy per unit area, the surface energy of metals and inorganic salts is usually in the range of 1-2 J/m^2.

Example: The sublimation energy of bulk gold is 334 kJ/mol, and the surface energy is 1.5 J/m^2. What percentage of the bulk bonding energy is lost by atoms at the (111) surface of a gold crystal?

To solve this problem, we need to know the surface area per Au atom. Gold has the face-centered cubic structure, and the unit cell edge length is 4.08 Å. From this we can determine that the Au-Au distance is 4.08/1.414 = 2.88 Å. In a hexagonal array of gold atoms with this interatomic spacing, the surface area per atom is (2.88 Å)^2 x 0.866 = 7.2 Å^2. Multiplying by Avogadro's number, we find that the area per mole of Au surface atoms on the (111) crystal face is **4.3 x 10^4 m^2.**

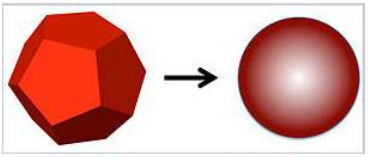
Now we multiply this area by the surface energy:

$(4.3 \times 10^4 \frac{m^2}{mol}) \times (1.5 \frac{J}{mol}) \times (\frac{1kJ}{1000J}) = \mathbf{+65kJ}$ per mole of Au surface atoms.

$\frac{65kJ}{334kJ} \times 100\% = \mathbf{19\%}$ of the bulk bonding energy is lost by atoms at the surface.

It is clear from this example that the surface energy of nanoparticles can have a major effect on their physical properties, since a large fraction of the atoms in a nanoparticle are on the surface. A good example of this is the dramatic depression of the **melting point**.

Solid nanocrystals are in general faceted, whereas liquid droplets made by melting nanocrystals adopt a spherical shape to minimize the surface area.



A faceted solid nanocrystal melts into a spherical droplet in order to minimize its surface energy.

Let's consider melting a silver nanocrystal that is 2 nm in diameter, meaning that about 1/2 of the atoms are on the surface. The spherical liquid droplet has lower surface area than the faceted crystal. For example, a cube has 1.24 times the surface area of a sphere of the same volume. If the decrease in surface area is about 20% upon melting, and the surface energy is about 1/4 of the bulk bonding energy of the atoms, then for a 2 nm diameter nanocrystal we would estimate that:

$$\Delta H^o_{fusion} \approx \Delta H^o_{fusion,\ bulk} - (\frac{1}{2})(0.25)(\frac{1}{4})\Delta H^o_{vap} = \Delta H^o_{fusion,\ bulk} - 0.025\Delta H^o_{vap,\ bulk} \quad (11.5.1)$$

where $\Delta H°_{vap,\ bulk}$, the heat of vaporization, is the total bonding energy of atoms in a bulk crystal. For silver, $\Delta H°_{fusion,\ bulk}$ = 11.3 kJ/mol and $\Delta H°_{vap,\ bulk}$ = 250 kJ/mol. From this we can calculate the heat of fusion of a 2 nm Ag nanocrystal:

$$\Delta H^o_{fusion} \approx 11.3 - (0.025)(25) = 5.1 \frac{kJ}{mol} \quad (11.5.2)$$

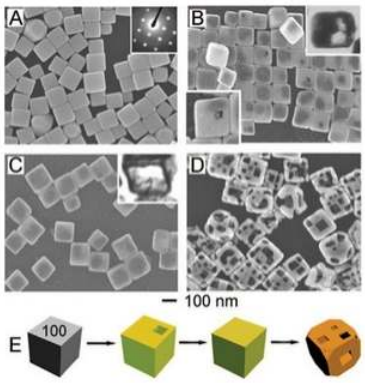
The melting point of bulk silver is 962 °C = 1235 K. Assuming that the entropy of fusion is the same in the bulk and in the nanocrystal, the melting point of the nanocrystal should be $1234K \times (\frac{5.1}{11.3}) = 557K = 284^{\circ}C$, a drop of almost 700 degrees from the bulk value. Experimentally, the melting point of a 2 nm diameter silver nanocrystal drops about **800 degrees below that of the bulk,** to 127 °C.[9] This is a whopping big change in the melting point, which is in reasonable agreement with our rough estimate.

The same effect - energetic destabilization of the surface atoms relative to bulk atoms - results in the **lower boiling point**, **higher vapor pressure**, **higher solubility**, and **higher reactivity** of nanocrystals relative to microcrystals (or larger crystals) of the same material.

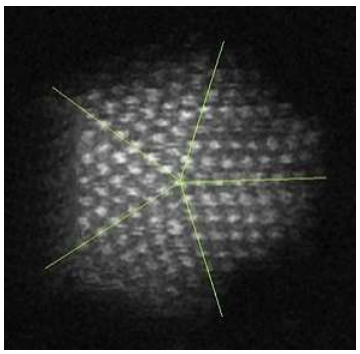
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11.6: Nanoscale Metal Particles



Nanoscale metal particles have been the subject of intense research over the past 20 years, especially because of their unusual **optical**, **magnetic**, and **catalytic** properties. The synthesis of metal nanocrystals in various shapes has become increasingly sophisticated and rational, like the synthesis of semiconductor nanocrystals described above. By controlling the separate phases of nucleation and growth, and by using ligands that cap specific crystal faces during growth, it is possible to make metal nanocrystals of uniform size in a variety of interesting and useful shapes including cubes, truncated cubes, octahedra, triangular prisms, and high aspect ratio rods. By exploiting displacement reactions that replace one metal with another, complex hollow shapes such as nanocages (as shown at the left) can be made starting with other shapes. In this case, solid silver nanocubes are transformed to gold nanocages.



Five-fold twinning in a gold nanoparticle

The interesting optical properties of nanocrystalline Au, Ag, Cu, and a number of other metals, derive from the collective oscillation of their valence electrons, a phenomenon known as **plasmon resonance**. Remember that in these metals, the electron mean free path is long (about 100 times larger than the size of the atoms), so the valence electrons feel only the average positive charge of the atomic cores as they zoom around the crystal. Light impinging on the metal acts as an oscillating electric field, pushing and pulling on the valence electrons at the characteristic frequency of the light wave. The situation is very much like a pendulum or a weight on a spring. The electrons, pushed away from their equilibrium positions, feel a restoring force that is proportional to their displacement. Their motion can be described by **Hooke's Law**:

$$F = kx \tag{11.6.1}$$

where the spring constant k determines the "stiffness" of the spring. In the case of the plasmon resonance, k is proportional to the number density of valence electrons n, and the square of the electronic charge e:

$$k = \frac{ne^2}{\varepsilon_0} \tag{11.6.2}$$

The **resonant frequency** of the plasma oscillation is given by:

$$\omega_p = (\frac{k}{m})^{\frac{1}{2}} = (\frac{ne^2}{m_e \varepsilon_0}^{\frac{1}{2}} \tag{11.6.3}$$

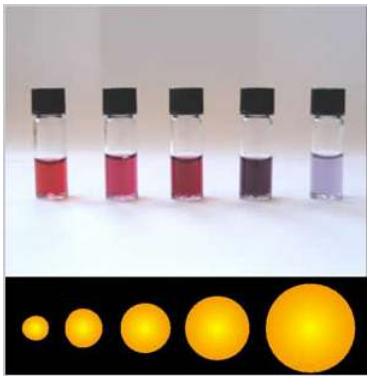
where m_e is the electron mass. For most metals, the plasmon resonance is in the ultraviolet part of the spectrum, but for a few metals like Au, Ag, and Cu it is in the visible.



The Lycurgus cup (4th century Roman glass) derives its unique coloration from noble metal nanoparticles. The cup is red in transmitted light and green in scattered (reflected) light.

For metal particles that are much smaller than the wavelength of light, this effect is called the **localized surface plasmon resonance**, or LSPR. There are three important consequences of the LSPR effect:

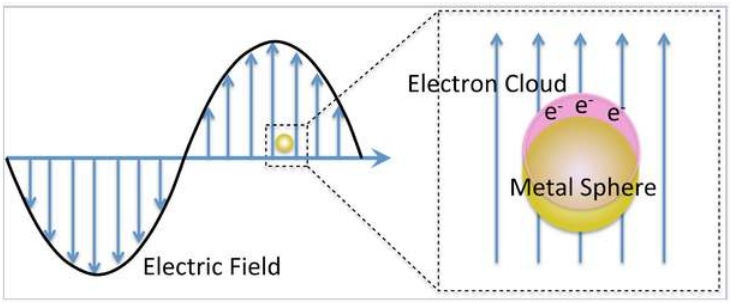
- The **local electric field** of the incoming light wave is greatly **enhanced** at the particle surface. This gives rise to huge enhancement factors in optical processes such as **Raman scattering** and **fluorescence**. Thus, certain analytical spectroscopic techniques are greatly enhanced by LSPR.
- Near the plasmon resonance frequency, metal nanocrystals **absorb** and **scatter light** very strongly. This makes them brightly reflective, and the strong light absorption can be exploited for light-induced local heating. These properties are being applied in medical diagnostics and therapy, e.g., for detection and photothermal destruction of cancer cells. By adjusting the size and shape of the gold nanoparticles, which are more stable than Ag and Cu in biological media, the plasmon frequency can be tuned to the tissue-transparent near-IR region of the spectrum between 700 and 900 nm. Small quantities of plasmonic Ag and Au particles also make brightly colored and strongly scattering pigments, e.g. in stained glass as shown above at the right.
- The plasmon frequency is sensitive to the refractive index of the particle's surroundings, i.e., its chemical environment. This makes metal nanoparticles of special interest for **sensing and biosensing** applications.



The colors of plasmonic gold nanoparticles depend on their size and shape.

Theory of light scattering and absorption by metal nanoparticles

The valence electrons in metal nanoparticles oscillate in the electric field of a light wave. While the nature of these oscillations is somewhat complex in metal particles that are non-spherical, the theory for spherical particles is relatively simple and in fact was worked out over 100 years ago by German physicist Gustav Mie.



Mie considered the interaction of a spherical particle with a **uniform electric field, E,** oscillating at angular frequency ω (= 2π f). This is a good approximation when the particle diameter is much smaller than the wavelength of light, as shown on the left. The particle is embedded in a uniform, insulating material (e.g. a solvent) that has a dielectric constant ε_{diel}. For insulators, ε_{diel} is a positive real number.

The dielectric constant ε of a metal is actually a complex number:

$$\varepsilon = \varepsilon^{'} + i\varepsilon'' \tag{11.6.4}$$

Here the real part, ε', is related to the refraction of light, and the imaginary part, ε", is related to light absorption. Both ε' and ε" are dependent on the frequency of the light. For metals near the plasmon resonance frequency, ε' is typically a *negative number.*

The **cross-section for absorption** of the light wave by the particle is:

$$\sigma_{absorption} = \frac{9\omega}{c}\epsilon_{diel}^{\frac{3}{2}} V \frac{\epsilon''_{metal}}{(\epsilon^{'}_{metal} + 2\epsilon_{diel})^2 + (\epsilon''_{metal})^2} \tag{11.6.5}$$

and the **cross-section for scattering** is:

$$\sigma_{scattering} = \frac{3}{2\pi}(\frac{\omega^4}{c})\epsilon_{diel}^2 V^2 \frac{(\epsilon^{'}_{metal} - \epsilon_{diel})^2 + (\epsilon''_{metal})^2}{(\epsilon^{'}_{metal} + 2\epsilon_{diel})^2 + (\epsilon''_{metal})^2} \tag{11.6.6}$$

The sum of these two is the **cross-section for extinction**:

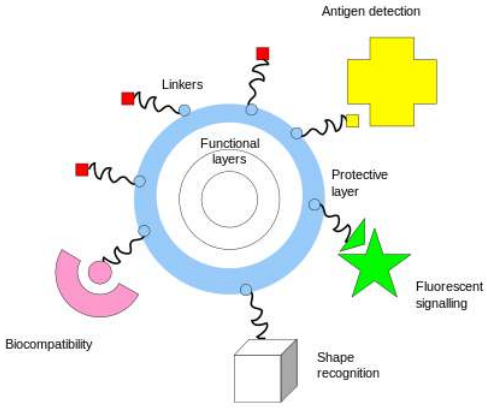
$$\sigma_{extinction} = \sigma_{absorption} + \sigma_{scattering} \tag{11.6.7}$$

These cross-sections become large when the (ε'_{metal} + $2\varepsilon_{diel}$) term in the denominator becomes small. This occurs when

$$\epsilon^{'}_{metal} \simeq -2\epsilon_{diel} \tag{11.6.8}$$

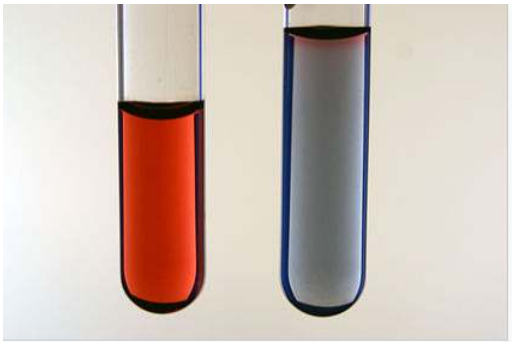
For 15 nm diameter gold nanoparticles in water, this happens at about 580 nm, resulting in the characteristic wine-red color of colloidal gold solutions. Changing the solution environment (e.g., by adsorbing a molecule onto the gold surface) changes ε_{diel} and thus alters the color slightly.

It is important to note that the cross-section for **scattering** is proportional to the **square of the volume** of the particle, V^2, whereas the absorption is proportional to V. This means that very small gold particles (< 5 nm) are strongly absorbing but not strongly scattering. Larger particles (>30 nm) scatter light very strongly. Depending on the application, therefore, we choose larger or smaller particles.



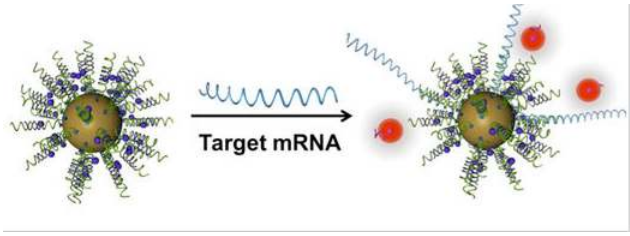
One of the key complementary properties of noble metal nanoparticles that is important to their use in biomedicine is the ease with which they can be **covalently conjugated** with polymers or small molecules, typically via thiol or amine bonds at their surface. This imparts biological recognition properties to the particles that enables them to bind to specific biomolecular targets. The figure at the left illustrates some of the functionality that can be imparted to nanoparticles through surface functionalization.

Functionalization of gold nanoparticles with thiol-terminated single-stranded DNA was the basis of one of the first nanoparticle sensors, developed by the Mirkin group at Northwestern University. **DNA-coated nanoparticles** have the characterstic wine-red plasmonic color of spherical nano-gold. However, when these particles are linked together by a complementary DNA strand, the resonance frequency shifs, resulting in a blue color. This color change, illustrated in the figure at the right, provides a "litmus test" for the presence of the target DNA sequence.[10] "Melting" of the DNA - heating it to the temperature at which double stranded DNA dissociates to make single strands - reverses the color change. The DNA hybridization/melting transition is highly **cooperative** because of the aggregation of many gold particles, so the transition temperature is very sharp. With proper temperature control, the color change can be sensitive to a **single base mismatch** in the target DNA that is detected by this method.



Aggregation of Au nanoparticles (in this case by adding salt to a colloidal solution) causes a color change from wine red (left) to blue (right). Photo credit: George Lisensky, Beloit College

Subsequent research has developed sophisticated diagnostic and therapeutic ("theranostic") applications for these **spherical nucleic acid**[11] particles. These particles easily penetrate cell membranes and can report on the chemistry happening inside living cells.



General schematic of nanoflare-based detection.

An important property of gold nanoparticles in these applications is their ability to **quench** the **fluorescence** of reporter molecules that are near their surface. Nucleic acid strands that contain a hairpin loop can position fluorescent molecules near the gold surface, where their fluorescence is turned off by nanoparticle quenching. Hybridization of these sequences to target RNA or DNA causes the fluorescence to turn on by moving the fluorescent molecule away from the nanoparticle surface. These so called "nanoflares" can thus signal the up- or down-regulation of specific genes inside cells. Nanoflares are the basis of the Verigene System, developed and commercialized by Nanosphere, Inc. to detect markers for infectious diseases and cancers.

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11.7: Applications of Nanomaterials

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11.8: Discussion Questions

- Explain how separating the nucleation and growth steps leads to nanoparticles of uniform size.
- A recent paper by Delia Milliron and coworkers (*Nature*, 2013, *500*, 323–326, doi:10.1038/nature12398) describes plasmonic indium-tin-oxide (ITO) nanoparticles that can control the infrared transparency of windows. Explain how the plasmon resonance wavelength of the nanoparticles can be tuned by electrochemical doping, and how the invention could save some of the energy used to heat and cool buildings.

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11.9: Problems

1. Consider a spherical gold nanoparticle that contains 500 atoms. If the diameter of an atom is approximately 3 Å, what fraction of the gold atoms in the particle are on the surface?

2. Now consider small droplets of mercury that contains 500 atoms. Mercury atoms are also about 3 Å in diameter. The heat of vaporization of bulk mercury is 64.0 kJ/mol, and the vapor pressure of mercury is 0.00185 torr = 2.43 x 10^{-6} atm. The surface tension of mercury (γ_{Hg}) is 0.518 N/m, and the surface excess energy can be calculated as $\gamma_{Hg}A$, where A is the surface area. Using this information and the Clausius-Clapyron equation ($P = const \cdot \exp(-\Delta H_{vap}/RT)$), calculate the vapor pressure of these small droplets of mercury.

3. James Heath and coworkers (Phys. Rev. Lett. 1995, 75, 3466) have observed Ostwald ripening in thin films of gold nanoparticles at room temperature. Starting with an uneven distribution of particle sizes, they find that the large particles grow at the expense of smaller ones. Can you explain this observation, based on your answers to problems (1) and (2)?

4. The bandgap of bulk germanium is 0.67 eV. What bandgap would you expect for a 4 nm diameter Ge nanocrystal? Use the Brus formula,

$$\Delta E_{gap} \approx \frac{h^2}{8\mu R^2} - \frac{1.8e^2}{4R\pi\varepsilon\varepsilon_0} + \ldots \tag{11.9.1}$$

where R is the particle radius, ε_{Ge} = 16.2, h = 6.6 10^{-34} J s, 1 eV = 1.6 10^{-19} J, 1 J = 1 kg m^2/s^2. and $e^2/4\pi\varepsilon_0$ = 1.44 10^{-9} eV m. Assume that the electron-hole reduced mass μ is approximately 40% of the free electron mass, m_e = 9.1 10^{-31} kg.

5. Grecian Formula (a hair coloring product) until recently contained lead acetate, which reacts with the cysteine in hair to make PbS. In bulk form, PbS is a semiconductor with a band gap of 0.3 eV (1 eV = 1240 nm). The particles are initially very small but grow as more Grecian Formula is applied and reacts with cysteine. As the particles grow, they change progressively from colorless to yellow to black. Explain why the particles are initially colorless and why their color changes. (Grecian formula now uses Bi, which is less toxic than Pb, and works by the same mechanism)

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