CHE 310: Inorganic Chemistry

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CHAPTER OVERVIEW

1: Introduction to Inorganic Chemistry

This chapter will introduce the breadth of the field of inorganic chemistry

> **◐ Learning Objectives**
>
> - Identify different subfields of inorganic chemistry
> - Recognize the historical and modern distinction between the fields of inorganic and organic chemistry

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1.1: What is Inorganic Chemistry?

Where did the name "Inorganic Chemistry" come from? Well, the term "Organic Chemistry" literally means the *chemistry of life*. Organic chemistry is the study of carbon-based molecules because the first molecules that were isolated from living organisms contained carbon. On the other hand, minerals and other non-living things seemed to be made of other elements. For some time in our history, scientists believed that the chemical difference between living and non-living things was carbon. So, if "organic" molecules are the molecules of life, then is "inorganic chemistry" the "chemistry of death"? Almost? "Inorganic" chemistry historically meant the chemistry of "non-living" things; and these were non-carbon based molecules and ions.

The names "organic" and "inorganic" come from science history, and still today a generally-accepted definition of *Inorganic Chemistry is the study of non-carbon molecules, or all the elements on the periodic table except carbon* (Figure 1.1.1. But, this definition is not completely correct because the field of Inorganic Chemistry also includes organometallic compounds and the study of some carbon-based molecules that have properties that are familiar to metals (like conduction of electricity). This makes the field of inorganic chemistry very broad, and practically limitless. A great way to understand the breadth of the field is to take a look at the abstracts in the latest article of Inorganic Chemistry. Or, check out the 20 most-read articles from this past year using the links below.
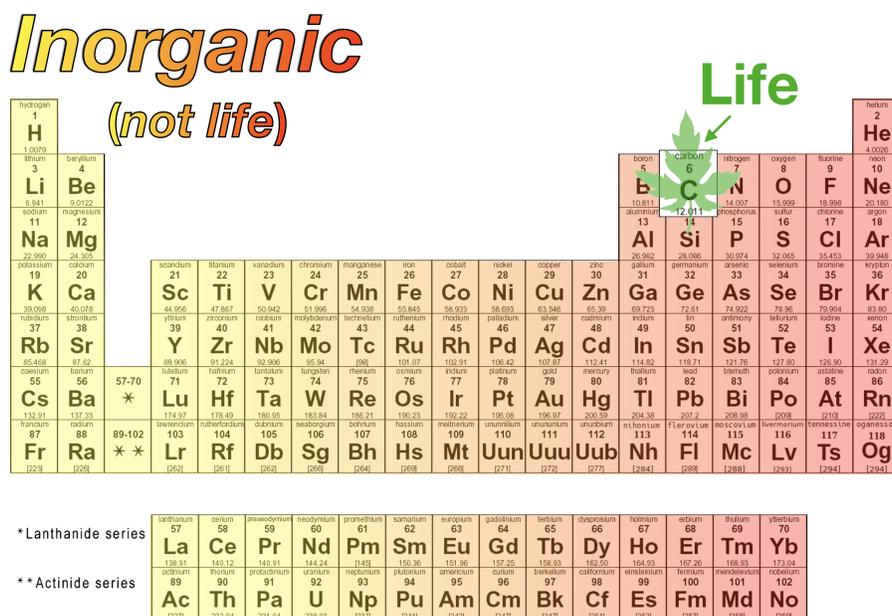
Figure 1.1.1. An illustration of the historic meaning of "organic" and "inorganic". The modern understanding of organic and inorganic chemistry is not consistent with these historical meanings. (Kathryn Haas; CC-NC-BY-SA)

External links:

- The journal, Inorganic Chemistry: https://pubs.acs.org/journal/inocaj
- The latest issue of Inorganic chemistry: https://pubs.acs.org/toc/inocaj/current
- The most popular Inorganic Chemistry articles from the past month and the past year:
  https://pubs.acs.org/action/showMostReadArticles?journalCode=inocaj

Practice

? What are the Sub-Fields of Inorganic Chemistry?

To appreciate the breadth of Inorganic Chemistry, go to the most recent issue of Inorganic Chemistry and look at the titles and visual abstracts. Identify at least 4 sub-fields of Inorganic Chemistry.

Answer

There are a lot of correct answers here! The point here is that you notice that Inorganic Chemistry is a very broad field. It has something for almost everyone because many other fields overlap with Inorganic Chemistry. You might notice that

some of the sub-fields you identified are also interdisciplinary fields between inorganic chemistry and another discipline. For a list of some of the subfields of Inorganic Chemistry, check this Wikipedia article.

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1.2: Inorganic vs Organic Chemistry

The division between the fields of Inorganic and Organic chemistry has become blurred. For example, let's look at one of the major classes of catalysts used for organic synthesis reactions: organometalic catalysts (Figure 1.2.1). Organometallic catalysts like these, and all organometallic compounds, contain metals that are bonded to carbon or carbon-containing molecules. So, are they "inorganic" because they contain metals, or "organic" because they contain carbon? These illustrate that clear divisions between organic and inorganic chemistry do not exist. Further, metal ions are common in biology and so the idea that metals are "inorganic" and thus classed as "non-living or non-biological" is incorrect. A canonical example is the organometallic catalyst adenosylcobalbumin, which is an important biological cofactor containing a cobalt (Co) ion (Figure 1.2.1, right) and a cobalt-carbon bond.
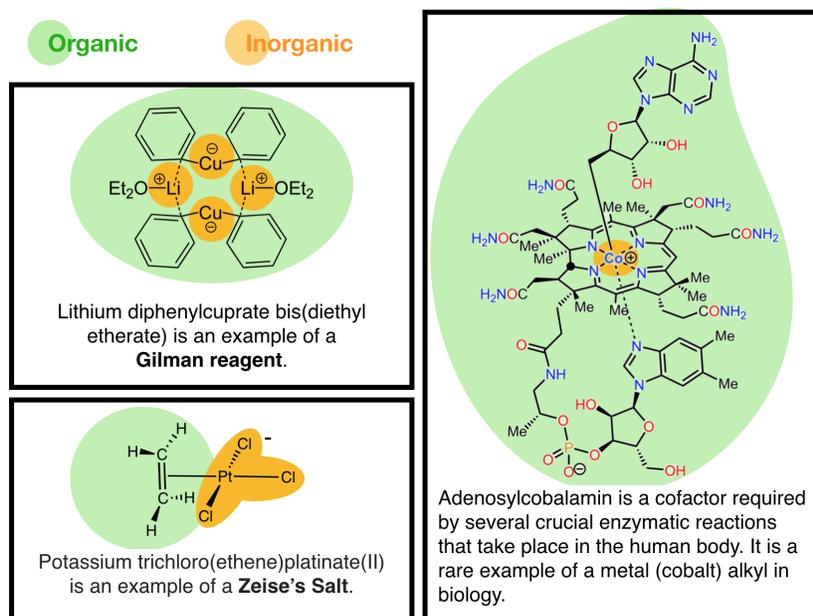
Figure 1.2.1: Some examples of organometallic catalysts. These compounds catalyze organic reactions or biochemical reactions and they are compounds that contain both carbon and metals. These compounds are examples of molecules that cannot be defined only as organic molecules or only as inorganic molecules. Adenosylcobalbumin is an example of an organometallic catalyst that is present in biology, further illustrating that "inorganic" metals are important cofactors in biology. This image is based on information on the Wikipedia article on Organometallic Chemistry and is created from images found there; attribution to images created by Alsosaid1987, AdoCbl-ColorCoded, CC BY-SA 4.0 and Smokefoot, Zeise'sSalt, CC BY-SA 3.0. (Kathryn Haas; CC-BY-SA)

Some of the subfields of Inorganic Chemistry focus on electrical conductivity of inorganic materials (i.e., conduction, superconduction, and semiconduction) and on the study of optical and electronic properties of inorganic nanomaterials. Electrical conductivity is a canonical property of metals, but carbon-based materials also demonstrate electrical conductivity. For example, carbon nanotubes conduct electricity through their extended conjugated π systems. Fullerenes, of which the most famous is Buckminsterfullerene, or Buckeyball (C_{60}), demonstrate interesting properties that are similar to nanoparticles, and when combined with metals and crystallized can demonstrate superconductivity.

Buckminsterfullerene is a type of fullerene with the formula C_{60}
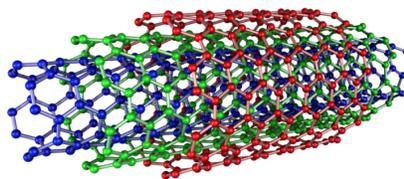
Triple-walled armchair **carbon nanotube**

Figure 1.2.2: This figure is created from information found on the Wikipedia articles for Buckmisterfullerene and carbon nanotubes. Attribution Eric Wieser, Multi-walled Carbon Nanotube, CC BY-SA 3.0. (Kathryn Haas; CC-BY-SA)

Although carbon nanotubes and fullerenes are allotropes of carbon, their material properties are somewhat foreign to many organic chemists, who traditionally have focused on smaller organic molecules having very different properties. However, these properties are familiar to inorganic chemists. Thus, inorganic chemists have embraced these molecules as "inorganic" due to the fact that they behave more like inorganic materials than smaller organic molecules. This class of carbon-based molecules serves as another example of molecules that are not perfectly matched to the traditional definitions of "organic" and "inorganic" chemistry. Certainly, the future will hold more and more examples of molecules that do not fit into the traditional disciplines of chemistry.

1.3: History of Inorganic Chemistry

Metals serve an essential role in many aspects of human civilization and have defined Ages of human history. The period of time from about 3300 BC to 1200 BC is often referred to as the Bronze Age. During this period our ancestors first started using metal and learned to mix various elements with copper to make a strong alloy, called bronze. This Age yielded significant advancement in crafting of sharper knives and stronger weapons out of metal instead of rock, wood and bone. Around 1200 BC the human race found an even harder metal and discovered a much stronger alloy called steel. This period is known as the Iron Age. More recently, periods of time known as Gold Rushes have caused huge changes in population distributions and wealth in some countries. Metal has obvious importance in our modern way of life. Today, iron and steel are used for making buildings, machines, automobiles, jewelry, cooking pots, tools, weapons, vehicles, electronics, surgical instruments and symbolic structures like the Eiffel Tower. Gold, silver, and copper still serve as currency for trade and exchange of goods and services.

The existence of Chemistry as a field of study owes much to the fact that gold was a valuable commodity throughout our history. In both the ancient Egyptian society and during the Roman Empire, the gold mines were the property of the state, not an individual or group. So there were few ways for most people to legally get any gold for themselves. The Alchemists were a varied group of scholars and charlatans who aimed to solve this problem by creating the **Philosopher's Stone** (which caused the transmutation of lead into gold). Three major streams of alchemy are known, Chinese, Indian, and European, with all three streams having some factors in common. Techniques developed in the European stream ultimately influenced the development of the science of chemistry.
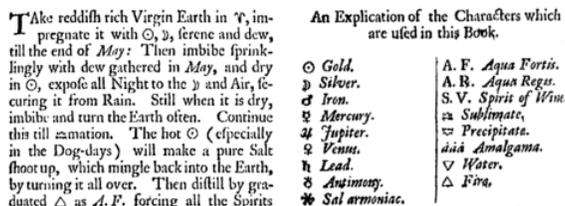
Figure 1.3.1. Alchemist recipe. Many of the specific approaches that alchemists used when they tried changing lead into gold are vague and unclear. Each alchemist had his own code for recording his data. The processes were kept secret so others could not profit from them. Different scholars developed their own set of symbols as they recorded the information they came up with. Many alchemists were not very honest, taking money from a nobleman by claiming to be able to make gold from lead, then leaving town in the middle of the night. Sometimes the nobleman would detect the fraud and have the alchemist hung. By the 1300's, several European rulers had declared alchemy to be illegal and set out strict punishments for those practicing the alchemical arts.

Although alchemists were never successful in changing lead into gold, they made several contributions to modern-day chemistry. Strong acids and bases were discovered, including nitric acid (H_2NO_3), sulfuric acid (H_3SO_4), and hydrochloric acid (HCl), and sodium hydroxide (NaOH). Glassware for running chemical reactions were developed, as well as methods for distillation, crystallization, sublimation. Alchemy helped improve the study of metallurgy and the extraction of metals from ores. More systematic approaches to research were developed that allowed the discovery of atoms and laid the groundwork for development of the periodic table. For more about the History of Chemistry in general, try the LibreText page History of Chemistry.

Inorganic compounds have been known and used since antiquity; probably the oldest is the deep blue pigment called Prussian blue, $Fe_4[Fe(CN)_6]$. However, the chemical nature of these substances was unknown until the late nineteenth and early twentieth century when the modern field of Coordination Chemistry emerged. Much of what we know about inorganic chemistry is based largely on the work of and debates between of Alfred Werner (1866–1919; Nobel Prize in Chemistry in 1913) and Sophus Mads Jørgensen (1837 –1914). After Werner succeeded in these debates, the field of Inorganic Chemistry declined in popularity until the mid twentieth century when the second world war stimulated renewed interest. During the post-war era, several important discoveries and theories were developed. For example, important theories of bonding in coordination compounds were developed. Soon after World War II, Crystal Field Theory (CFT) and Ligand Field Theory (LFT) were developed. These are two critical and complimentary theories that provide explanation of spectroscopic, chemical, and structural properties of inorganic coordination compounds; CFT being more simple, and LFT more accurate. In the 1950's, organometallic catalysts were discovered that catalyzed important organic reactions.

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \tag{1.3.1}$$
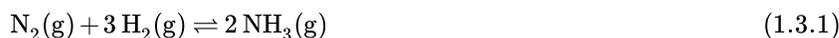
The Haber-Bosch Process is catalyzed by an inorganic oxide catalyst and is one of the world's most important industrial reactions. It provides for the synthesis of ammonia directly from elemental nitrogen, N_2, and hydrogen, H_2. Since its development in the early

twentieth century, it has led to the production of an enormous quantity of fertilizer, vastly increasing global food production. As a result, it is estimated that a significant fraction of the nitrogen content in the typical human body is ultimately derived from this process. Yet while the reaction must be run at high temperatures and pressures in the industrial setting, the nitrogenase enzyme on the roots of plants can carry out this reaction at the mild conditions within soil. Intense investigations were then aimed to improve inorganic catalysts through understanding the metal cofactors in enzymes. The link between the Haber-Bosch industrial process and the nitrogenase enzyme was an early bridge between the fields of organometallic chemistry and biochemistry.

Contributions

Part of this page is adapted from K.Haas Ph.D. dissertation

Part of this page is adapted from the following LibreTexts pages

- Alchemy contributed by CK-12 Foundation by Sharon Bewick, Richard Parsons, Therese Forsythe, Shonna Robinson, and Jean Dupon.
- Werner's Theory of Coordination Compounds
- The Haber-Bosch Process Worksheet

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1.4: Exercises

1. Why is inorganic chemistry considered more diverse than organic chemistry?
2. Can inorganic compounds contain carbon? Provide an example.
3. Mention one historical application of inorganic compounds.
4. What was Alfred Werner's significant contribution to inorganic chemistry?
5. Describe the significance of the Haber-Bosch process.
6. Inorganic chemistry is the chemistry of non-living things. Do you agree with this statement? Provide an example
7. This image shows the structure of the Fe-porphyrin subunit of heme B. Indicate the organic and inorganic elements for this structure (image by Yikrazuul, Public domain, via Wikimedia Commons)
8.
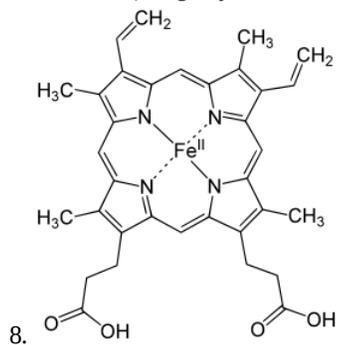
CHAPTER OVERVIEW

2: Atoms, Molecules, and Ions

This chapter will describe some of the fundamental chemical principles related to the composition of matter, including those central to the concept of molecular identity.

2.1: Introduction

Lung diseases and lung cancers are among the world's most devastating illnesses partly due to delayed detection and diagnosis. Most noninvasive screening procedures aren't reliable, and patients often resist more accurate methods due to discomfort with the procedures or with the potential danger that the procedures cause. But what if you could be accurately diagnosed through a simple breath test?
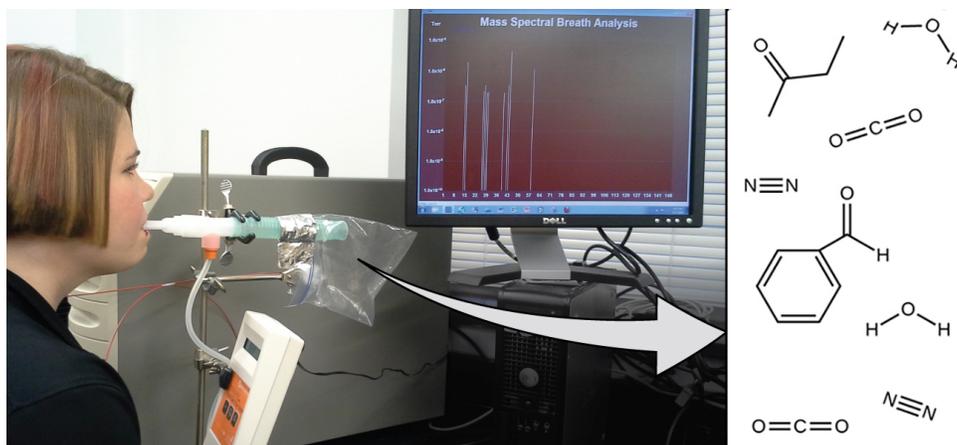
Figure 2.1.1: Analysis of molecules in an exhaled breath can provide valuable information, leading to early diagnosis of diseases or detection of environmental exposure to harmful substances. (credit: modification of work by Paul Flowers)

Early detection of biomarkers, substances that indicate an organism's disease or physiological state, could allow diagnosis and treatment before a condition becomes serious or irreversible. Recent studies have shown that your exhaled breath can contain molecules that may be biomarkers for recent exposure to environmental contaminants or for pathological conditions ranging from asthma to lung cancer. Scientists are working to develop biomarker "fingerprints" that could be used to diagnose a specific disease based on the amounts and identities of certain molecules in a patient's exhaled breath. In Sangeeta Bhatia's lab at MIT, a team used substances that react specifically inside diseased lung tissue; the products of the reactions will be present as biomarkers that can be identified through mass spectrometry (an analytical method discussed later in the chapter). A potential application would allow patients with early symptoms to inhale or ingest a "sensor" substance, and, minutes later, to breathe into a detector for diagnosis. Similar research by scientists such as Laura López-Sánchez has provided similar processes for lung cancer. An essential concept underlying this goal is that of a molecule's identity, which is determined by the numbers and types of atoms it contains, and how they are bonded together. This chapter will describe some of the fundamental chemical principles related to the composition of matter, including those central to the concept of molecular identity.

2.2: Early Ideas in Atomic Theory

> **◑ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - State the postulates of Dalton's atomic theory
> - Use postulates of Dalton's atomic theory to explain the laws of definite and multiple proportions

The earliest recorded discussion of the basic structure of matter comes from ancient Greek philosophers, the scientists of their day. In the fifth century BC, Leucippus and Democritus argued that all matter was composed of small, finite particles that they called *atomos*, a term derived from the Greek word for "indivisible." They thought of atoms as moving particles that differed in shape and size, and which could join together. Later, Aristotle and others came to the conclusion that matter consisted of various combinations of the four "elements"—fire, earth, air, and water—and could be infinitely divided. Interestingly, these philosophers thought about atoms and "elements" as philosophical concepts, but apparently never considered performing experiments to test their ideas.

The Aristotelian view of the composition of matter held sway for over two thousand years, until English schoolteacher John Dalton helped to revolutionize chemistry with his hypothesis that the behavior of matter could be explained using an atomic theory. First published in 1807, many of Dalton's hypotheses about the microscopic features of matter are still valid in modern atomic theory. Here are the postulates of Dalton's atomic theory.

1. Matter is composed of exceedingly small particles called atoms. An atom is the smallest unit of an element that can participate in a chemical change.
2. An element consists of only one type of atom, which has a mass that is characteristic of the element and is the same for all atoms of that element (Figure 2.2.1). A macroscopic sample of an element contains an incredibly large number of atoms, all of which have identical chemical properties.
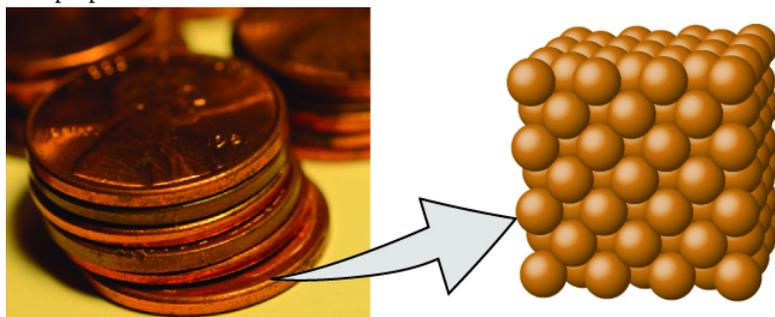
Figure 2.2.1: A pre-1982 copper penny (left) contains approximately 3 10^{22} copper atoms (several dozen are represented as brown spheres at the right), each of which has the same chemical properties. (credit: modification of work by "slgckgc"/Flickr)

3. Atoms of one element differ in properties from atoms of all other elements.
4. A compound consists of atoms of two or more elements combined in a small, whole-number ratio. In a given compound, the numbers of atoms of each of its elements are always present in the same ratio (Figure 2.2.2).
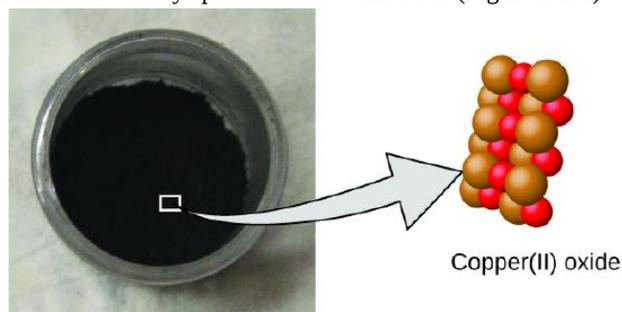
Copper(II) oxide

Figure 2.2.2: Copper(II) oxide, a powdery, black compound, results from the combination of two types of atoms—copper (brown spheres) and oxygen (red spheres)—in a 1:1 ratio. (credit: modification of work by "Chemicalinterest"/Wikimedia Commons)

5. Atoms are neither created nor destroyed during a chemical change, but are instead rearranged to yield substances that are different from those present before the change (Figure 2.2.3).

The elements
copper and oxygen

The compound
copper(II) oxide
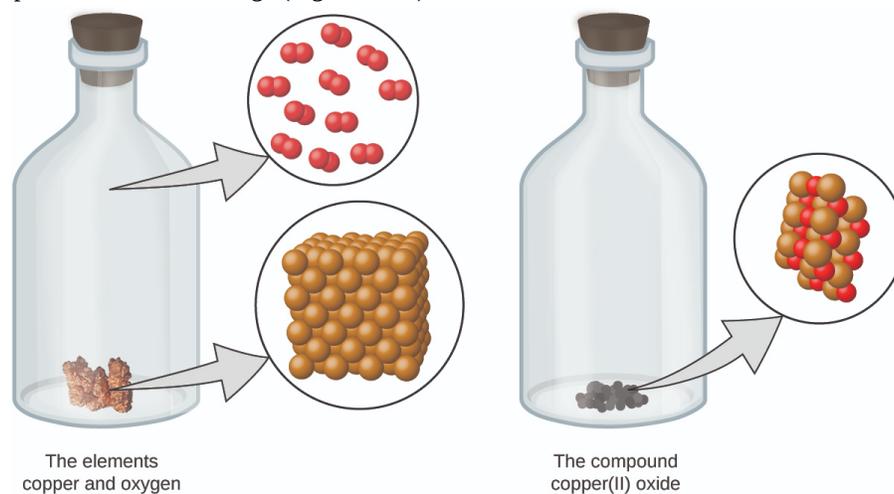
Figure 2.2.3: When the elements copper (a shiny, red-brown solid, shown here as brown spheres) and oxygen (a clear and colorless gas, shown here as red spheres) react, their atoms rearrange to form a compound containing copper and oxygen (a powdery, black solid). (credit copper: modification of work by http://images-of-elements.com/copper.php)

Dalton's atomic theory provides a microscopic explanation of the many macroscopic properties of matter that you've learned about. For example, if an element such as copper consists of only one kind of atom, then it cannot be broken down into simpler substances, that is, into substances composed of fewer types of atoms. And if atoms are neither created nor destroyed during a chemical change, then the total mass of matter present when matter changes from one type to another will remain constant (the law of conservation of matter).

✔ **Example 2.2.1: Testing Dalton's Atomic Theory**

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres touch, they are part of a single unit of a compound. Does the following chemical change represented by these symbols violate any of the ideas of Dalton's atomic theory? If so, which one?

Starting materials   Products of the change

Solution

The starting materials consist of two green spheres and two purple spheres. The products consist of only one green sphere and one purple sphere. This violates Dalton's postulate that atoms are neither created nor destroyed during a chemical change, but are merely redistributed. (In this case, atoms appear to have been destroyed.)

? **Exercise 2.2.1**

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres touch, they are part of a single unit of a compound. Does the following chemical change represented by these symbols violate any of the ideas of Dalton's atomic theory? If so, which one?

Starting materials   Products of the change

Answer

> The starting materials consist of four green spheres and two purple spheres. The products consist of four green spheres and two purple spheres. This does not violate any of Dalton's postulates: Atoms are neither created nor destroyed, but are redistributed in small, whole-number ratios.

Dalton knew of the experiments of French chemist Joseph Proust, who demonstrated that *all samples of a pure compound contain the same elements in the same proportion by mass*. This statement is known as the law of definite proportions or the law of constant composition. The suggestion that the numbers of atoms of the elements in a given compound always exist in the same ratio is consistent with these observations. For example, when different samples of isooctane (a component of gasoline and one of the standards used in the octane rating system) are analyzed, they are found to have a carbon-to-hydrogen mass ratio of 5.33:1, as shown in Table 2.1.

Table 2.1: Constant Composition of Isooctane

Sample	Carbon	Hydrogen	Mass Ratio
A	14.82 g	2.78 g	14.82 g C / 2.78 g H = 5.33 / 1
B	22.33 g	4.19 g	22.33 g C / 4.19 g H = 5.33 / 1
C	19.40 g	3.64 g	19.40 4 C / 3.64 g H = 5.33 / 1

It is worth noting that although all samples of a particular compound have the same mass ratio, the converse is not true in general. That is, samples that have the same mass ratio are not necessarily the same substance. For example, there are many compounds other than isooctane that also have a carbon-to-hydrogen mass ratio of 5.33:1.00.

Dalton also used data from Proust, as well as results from his own experiments, to formulate another interesting law. The law of multiple proportions states that *when two elements react to form more than one compound, a fixed mass of one element will react with masses of the other element in a ratio of small, whole numbers*. For example, copper and chlorine can form a green, crystalline solid with a mass ratio of 0.558 g chlorine to 1 g copper, as well as a brown crystalline solid with a mass ratio of 1.116 g chlorine to 1 g copper. These ratios by themselves may not seem particularly interesting or informative; however, if we take a ratio of these ratios, we obtain a useful and possibly surprising result: a small, whole-number ratio.

This 2-to-1 ratio means that the brown compound has twice the amount of chlorine per amount of copper as the green compound.

This can be explained by atomic theory if the copper-to-chlorine ratio in the brown compound is 1 copper atom to 2 chlorine atoms, and the ratio in the green compound is 1 copper atom to 1 chlorine atom. The ratio of chlorine atoms (and thus the ratio of their masses) is therefore 2 to 1 (Figure 2.2.4).
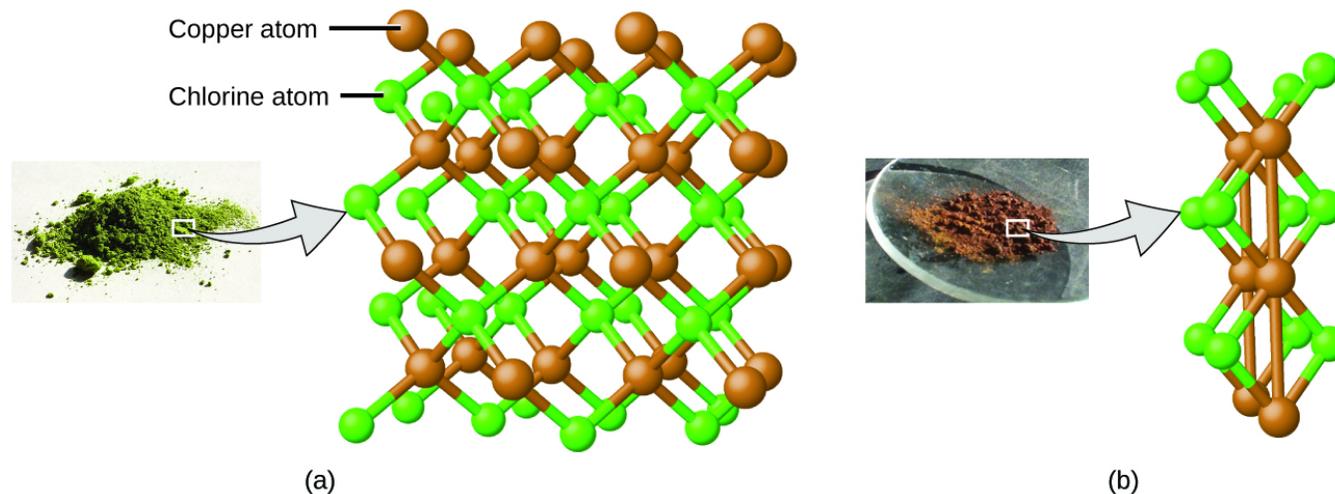
Figure 2.2.4: Compared to the copper chlorine compound in (a), where copper is represented by brown spheres and chlorine by green spheres, the copper chlorine compound in (b) has twice as many chlorine atoms per copper atom. (credit a: modification of work by "Benjah-bmm27"/Wikimedia Commons; credit b: modification of work by "Walkerma"/Wikimedia Commons)

✔ Example 2.2.2: Laws of Definite and Multiple Proportions

A sample of compound A (a clear, colorless gas) is analyzed and found to contain 4.27 g carbon and 5.69 g oxygen. A sample of compound B (also a clear, colorless gas) is analyzed and found to contain 5.19 g carbon and 13.84 g oxygen. Are these data an example of the law of definite proportions, the law of multiple proportions, or neither? What do these data tell you about substances A and B?

Solution

In compound A, the mass ratio of oxygen to carbon is: 5.69 g O / 4.27 g C = 1.33 /1

In compound B, the mass ratio of oxygen to carbon is: 13.84 g O / 5.19 g C = 2.66 /1

The ratio of these ratios is: 1.33/2.66 = 0.5 = 1/2

This supports the law of multiple proportions. This means that A and B are different compounds, with A having one-half as much oxygen per amount of carbon (or twice as much carbon per amount of oxygen) as B. A possible pair of compounds that would fit this relationship would be A = CO and B = CO_2.

? Exercise 2.2.1

A sample of compound X (a clear, colorless, combustible liquid with a noticeable odor) is analyzed and found to contain 14.13 g carbon and 2.96 g hydrogen. A sample of compound Y (a clear, colorless, combustible liquid with a noticeable odor that is slightly different from X's odor) is analyzed and found to contain 19.91 g carbon and 3.34 g hydrogen. Are these data an example of the law of definite proportions, the law of multiple proportions, or neither? What do these data tell you about substances X and Y?

Answer

In compound X, the mass ratio of carbon to hydrogen is 4.77/1. In compound Y, the mass ratio of carbon to hydrogen is 5.96/1. The ratio of these ratios is 0.800 = 4/5. This small, whole-number ratio supports the law of multiple proportions. This means that X and Y are different compounds.

2.3: Evolution of Atomic Theory

> ### Learning Objectives
>
> By the end of this section, you will be able to:
>
> - Outline milestones in the development of modern atomic theory
> - Summarize and interpret the results of the experiments of Thomson, Millikan, and Rutherford
> - Describe the three subatomic particles that compose atoms
> - Define isotopes and give examples for several elements

If matter is composed of atoms, what are atoms composed of? Are they the smallest particles, or is there something smaller? In the late 1800s, a number of scientists interested in questions like these investigated the electrical discharges that could be produced in low-pressure gases, with the most significant discovery made by English physicist J. J. Thomson using a cathode ray tube. This apparatus consisted of a sealed glass tube from which almost all the air had been removed; the tube contained two metal electrodes. When high voltage was applied across the electrodes, a visible beam called a cathode ray appeared between them. This beam was deflected toward the positive charge and away from the negative charge, and was produced in the same way with identical properties when different metals were used for the electrodes. In similar experiments, the ray was simultaneously deflected by an applied magnetic field, and measurements of the extent of deflection and the magnetic field strength allowed Thomson to calculate the charge-to-mass ratio of the cathode ray particles. The results of these measurements indicated that these particles were much lighter than atoms (Figure 2.3.1).
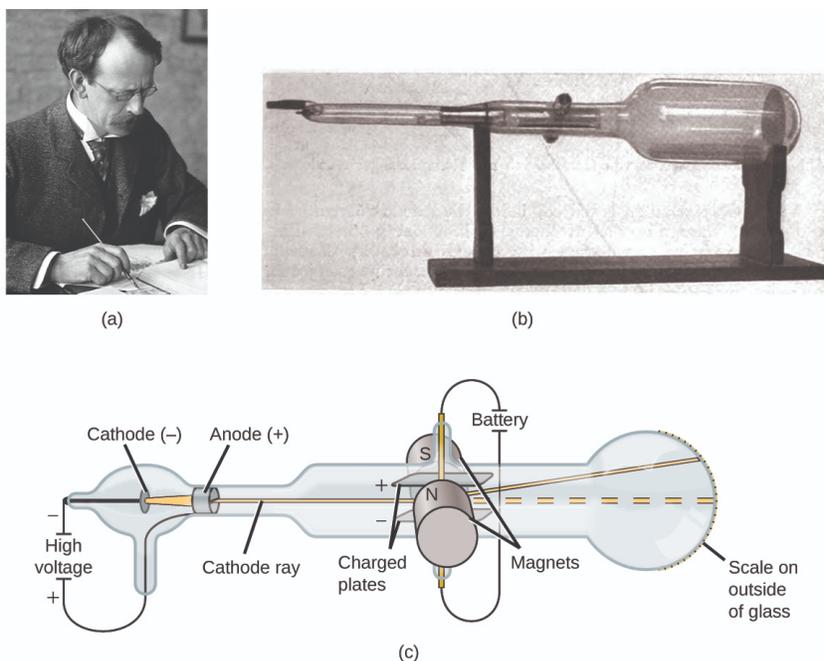
Figure 2.3.1: (a) J. J. Thomson produced a visible beam in a cathode ray tube. (b) This is an early cathode ray tube, invented in 1897 by Ferdinand Braun. (c) In the cathode ray, the beam (shown in yellow) comes from the cathode and is accelerated past the anode toward a fluorescent scale at the end of the tube. Simultaneous deflections by applied electric and magnetic fields permitted Thomson to calculate the mass-to-charge ratio of the particles composing the cathode ray. (credit a: modification of work by Nobel Foundation; credit b: modification of work by Eugen Nesper; credit c: modification of work by "Kurzon"/Wikimedia Commons)

Based on his observations, here is what Thomson proposed and why: The particles are attracted by positive (+) charges and repelled by negative (−) charges, so they must be negatively charged (like charges repel and unlike charges attract); they are less massive than atoms and indistinguishable, regardless of the source material, so they must be fundamental, subatomic constituents of all atoms. Although controversial at the time, Thomson's idea was gradually accepted, and his cathode ray particle is what we now call an electron, a negatively charged, subatomic particle with a mass more than one thousand-times less that of an atom. The term "electron" was coined in 1891 by Irish physicist George Stoney, from "*electr*ic i*on*."

In 1909, more information about the electron was uncovered by American physicist Robert A. Millikan via his "oil drop" experiments. Millikan created microscopic oil droplets, which could be electrically charged by friction as they formed or by using X-rays. These droplets initially fell due to gravity, but their downward progress could be slowed or even reversed by an electric field lower in the apparatus. By adjusting the electric field strength and making careful measurements and appropriate calculations, Millikan was able to determine the charge on individual drops (Figure 2.3.2).

Oil drop	Charge in coulombs (C)
A	4.8×10^{-19} C
B	3.2×10^{-19} C
C	6.4×10^{-19} C
D	1.6×10^{-19} C
E	4.8×10^{-19} C
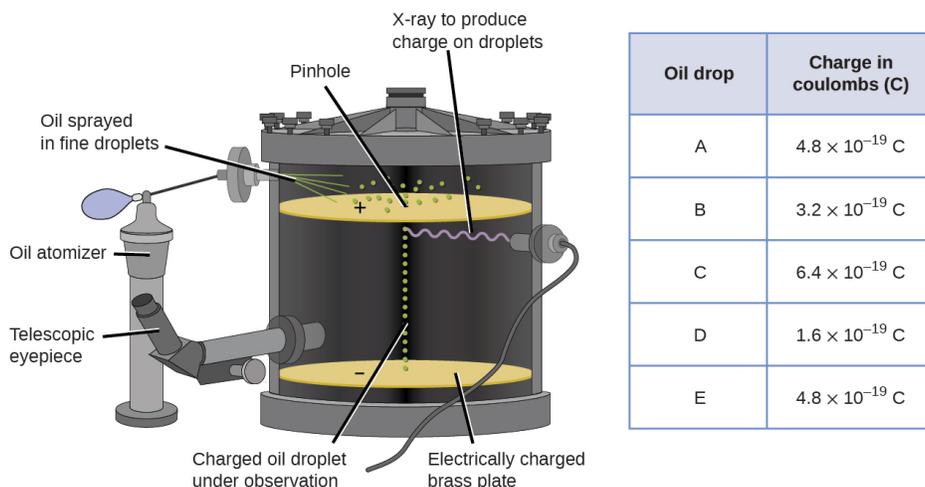
Figure 2.3.2: Millikan's experiment measured the charge of individual oil drops. The tabulated data are examples of a few possible values.

Looking at the charge data that Millikan gathered, you may have recognized that the charge of an oil droplet is always a multiple of a specific charge, 1.6×10^{-19} C. Millikan concluded that this value must therefore be a fundamental charge—the charge of a single electron—with his measured charges due to an excess of one electron (1 times 1.6×10^{-19} C), two electrons (2 times 1.6×10^{-19} C), three electrons (3 times 1.6×10^{-19} C), and so on, on a given oil droplet. Since the charge of an electron was now known due to Millikan's research, and the charge-to-mass ratio was already known due to Thomson's research (1.759×10^{11} C/kg), it only required a simple calculation to determine the mass of the electron as well.

Scientists had now established that the atom was not indivisible as Dalton had believed, and due to the work of Thomson, Millikan, and others, the charge and mass of the negative, subatomic particles—the electrons—were known. However, the positively charged part of an atom was not yet well understood. In 1904, Thomson proposed the "plum pudding" model of atoms, which described a positively charged mass with an equal amount of negative charge in the form of electrons embedded in it, since all atoms are electrically neutral. A competing model had been proposed in 1903 by Hantaro Nagaoka, who postulated a Saturn-like atom, consisting of a positively charged sphere surrounded by a halo of electrons (Figure 2.3.3).
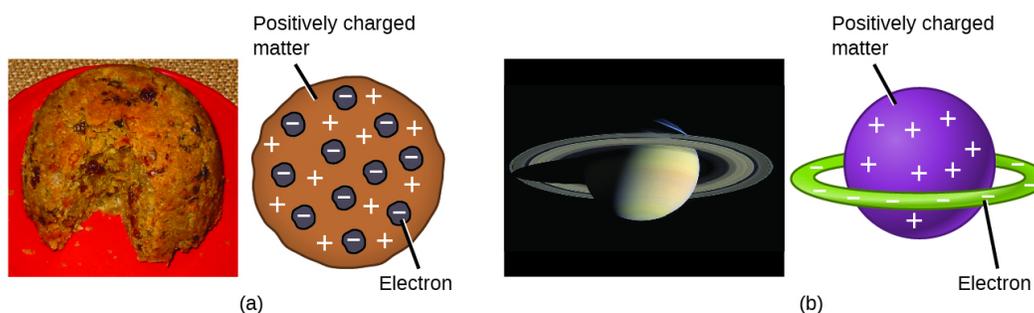
Figure 2.3.3: (a) Thomson suggested that atoms resembled plum pudding, an English dessert consisting of moist cake with embedded raisins ("plums"). (b) Nagaoka proposed that atoms resembled the planet Saturn, with a ring of electrons surrounding a positive "planet." (credit a: modification of work by "Man vyi"/Wikimedia Commons; credit b: modification of work by "NASA"/Wikimedia Commons)

The next major development in understanding the atom came from Ernest Rutherford, a physicist from New Zealand who largely spent his scientific career in Canada and England. He performed a series of experiments using a beam of high-speed, positively charged alpha particles (α particles) that were produced by the radioactive decay of radium; α particles consist of two protons and two neutrons (you will learn more about radioactive decay in the chapter on nuclear chemistry). Rutherford and his colleagues Hans Geiger (later famous for the Geiger counter) and Ernest Marsden aimed a beam of α particles, the source of which was embedded in a lead block to absorb most of the radiation, at a very thin piece of gold foil and examined the resultant scattering of the α particles using a luminescent screen that glowed briefly where hit by an α particle.

What did they discover? Most particles passed right through the foil without being deflected at all. However, some were diverted slightly, and a very small number were deflected almost straight back toward the source (Figure 2.3.4). Rutherford described finding these results: "It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you."[1]
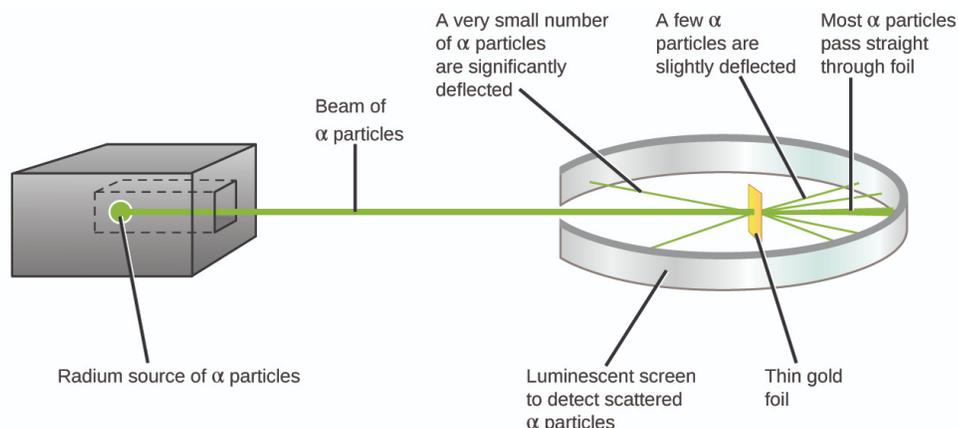
Figure 2.3.4: Geiger and Rutherford fired α particles at a piece of gold foil and detected where those particles went, as shown in this schematic diagram of their experiment. Most of the particles passed straight through the foil, but a few were deflected slightly and a very small number were significantly deflected.

Here is what Rutherford deduced: Because most of the fast-moving α particles passed through the gold atoms undeflected, they must have traveled through essentially empty space inside the atom. Alpha particles are positively charged, so deflections arose when they encountered another positive charge (like charges repel each other). Since like charges repel one another, the few positively charged α particles that changed paths abruptly must have hit, or closely approached, another body that also had a highly concentrated, positive charge. Since the deflections occurred a small fraction of the time, this charge only occupied a small amount of the space in the gold foil. Analyzing a series of such experiments in detail, Rutherford drew two conclusions:

1. The volume occupied by an atom must consist of a large amount of empty space.
2. A small, relatively heavy, positively charged body, the nucleus, must be at the center of each atom.

📌 Link to Learning

View this simulation of the Rutherford gold foil experiment. Adjust the slit width to produce a narrower or broader beam of α particles to see how that affects the scattering pattern.

This analysis led Rutherford to propose a model in which an atom consists of a very small, positively charged nucleus, in which most of the mass of the atom is concentrated, surrounded by the negatively charged electrons, so that the atom is electrically neutral (Figure 2.3.5). After many more experiments, Rutherford also discovered that the nuclei of other elements contain the hydrogen nucleus as a "building block," and he named this more fundamental particle the proton, the positively charged, subatomic particle found in the nucleus. With one addition, which you will learn next, this nuclear model of the atom, proposed over a century ago, is still used today.
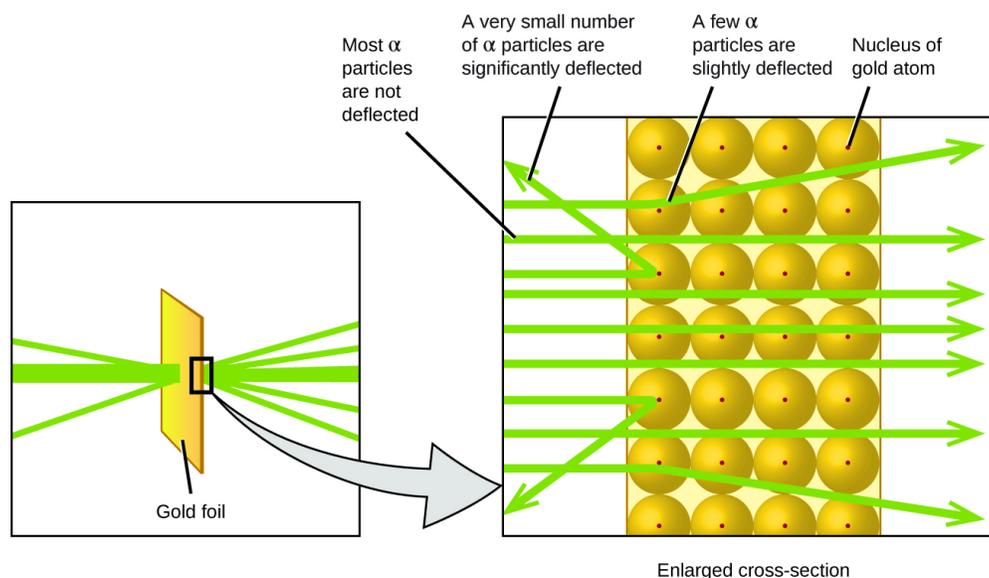
Figure 2.3.5: The α particles are deflected only when they collide with or pass close to the much heavier, positively charged gold nucleus. Because the nucleus is very small compared to the size of an atom, very few α particles are deflected. Most pass through the relatively large region occupied by electrons, which are too light to deflect the rapidly moving particles.

📌 Link to Learning

The Rutherford Scattering simulation allows you to investigate the differences between a "plum pudding" atom and a Rutherford atom by firing α particles at each type of atom.

Another important finding was the discovery of isotopes. During the early 1900s, scientists identified several substances that appeared to be new elements, isolating them from radioactive ores. For example, a "new element" produced by the radioactive decay of thorium was initially given the name mesothorium. However, a more detailed analysis showed that mesothorium was chemically identical to radium (another decay product), despite having a different atomic mass. This result, along with similar findings for other elements, led the English chemist Frederick Soddy to realize that an element could have types of atoms with different masses that were chemically indistinguishable. These different types are called isotopes—atoms of the same element that differ in mass. Soddy was awarded the Nobel Prize in Chemistry in 1921 for this discovery.

One puzzle remained: The nucleus was known to contain almost all of the mass of an atom, with the number of protons only providing half, or less, of that mass. Different proposals were made to explain what constituted the remaining mass, including the existence of neutral particles in the nucleus. As you might expect, detecting uncharged particles is very challenging, and it was not until 1932 that James Chadwick found evidence of neutrons, uncharged, subatomic particles with a mass approximately the same as that of protons. The existence of the neutron also explained isotopes: They differ in mass because they have different numbers of neutrons, but they are chemically identical because they have the same number of protons. This will be explained in more detail later in this chapter.

Footnotes

- 1Ernest Rutherford, "The Development of the Theory of Atomic Structure," ed. J. A. Ratcliffe, in *Background to Modern Science*, eds. Joseph Needham and Walter Pagel, (Cambridge, UK: Cambridge University Press, 1938), 61–74. Accessed September 22, 2014, https://ia600508.us.archive.org/3/it...e032734mbp.pdf.

2.4: Atomic Structure and Symbolism

Learning Objectives

By the end of this section, you will be able to:

- Write and interpret symbols that depict the atomic number, mass number, and charge of an atom or ion
- Define the atomic mass unit and average atomic mass
- Calculate average atomic mass and isotopic abundance

The development of modern atomic theory revealed much about the inner structure of atoms. It was learned that an atom contains a very small nucleus composed of positively charged protons and uncharged neutrons, surrounded by a much larger volume of space containing negatively charged electrons. The nucleus contains the majority of an atom's mass because protons and neutrons are much heavier than electrons, whereas electrons occupy almost all of an atom's volume. The diameter of an atom is on the order of 10^{-10} m, whereas the diameter of the nucleus is roughly 10^{-15} m—about 100,000 times smaller. For a perspective about their relative sizes, consider this: If the nucleus were the size of a blueberry, the atom would be about the size of a football stadium (Figure 2.4.1).
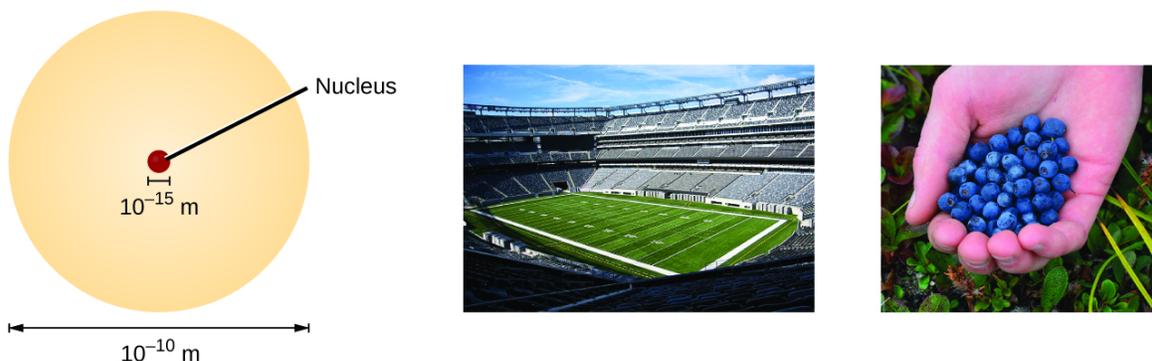
Figure 2.4.1: If an atom could be expanded to the size of a football stadium, the nucleus would be the size of a single blueberry. (credit middle: modification of work by "babyknight"/Wikimedia Commons; credit right: modification of work by Paxson Woelber)

Atoms—and the protons, neutrons, and electrons that compose them—are extremely small. For example, a carbon atom weighs less than 2×10^{-23} g, and an electron has a charge of less than 2×10^{-19} C (coulomb). When describing the properties of tiny objects such as atoms, we use appropriately small units of measure, such as the atomic mass unit (amu) and the fundamental unit of charge (e). The amu was originally defined based on hydrogen, the lightest element, then later in terms of oxygen. Since 1961, it has been defined with regard to the most abundant isotope of carbon, atoms of which are assigned masses of exactly 12 amu. (This isotope is known as "carbon-12" as will be discussed later in this module.) Thus, one amu is exactly $\frac{1}{12}$ of the mass of one carbon-12 atom: 1 amu = 1.6605×10^{-24} g. (The **Dalton** (Da) and the **unified atomic mass** unit (u) are alternative units that are equivalent to the amu.) The fundamental unit of charge (also called the elementary charge) equals the magnitude of the charge of an electron (e) with e = 1.602×10^{-19} C.

A proton has a mass of 1.0073 amu and a charge of 1+. A neutron is a slightly heavier particle with a mass 1.0087 amu and a charge of zero; as its name suggests, it is neutral. The electron has a charge of 1− and is a much lighter particle with a mass of about 0.00055 amu (it would take about 1800 electrons to equal the mass of one proton). The properties of these fundamental particles are summarized in Table 2.4.1. (An observant student might notice that the sum of an atom's subatomic particles does not equal the atom's actual mass: The total mass of six protons, six neutrons, and six electrons is 12.0993 amu, slightly larger than 12.00 amu. This "missing" mass is known as the mass defect, and you will learn about it in the chapter on nuclear chemistry.)

Table 2.4.1: Properties of Subatomic Particles

Name	Location	Charge (C)	Unit Charge	Mass (amu)	Mass (g)
electron	outside nucleus	-1.602×10^{-19}	1−	0.00055	0.00091×10^{-24}
proton	nucleus	1.602×10^{-19}	1+	1.00727	1.67262×10^{-24}

Name	Location	Charge (C)	Unit Charge	Mass (amu)	Mass (g)
neutron	nucleus	0	0	1.00866	$1.67493 \ 10^{-24}$

The number of protons in the nucleus of an atom is its **atomic number** (Z). This is the defining trait of an element: Its value determines the identity of the atom. For example, any atom that contains six protons is the element carbon and has the atomic number 6, regardless of how many neutrons or electrons it may have. A neutral atom must contain the same number of positive and negative charges, so the number of protons equals the number of electrons. Therefore, the atomic number also indicates the number of electrons in an atom. The total number of protons and neutrons in an atom is called its **mass number** (A). The number of neutrons is therefore the difference between the mass number and the atomic number: A – Z = number of neutrons.

$$\text{atomic number } (Z) = \text{ number of protons}$$
$$\text{mass number } (A) = \text{ number of protons } + \text{ number of neutrons}$$
$$A - Z = \text{ number of neutrons}$$

Atoms are electrically neutral if they contain the same number of positively charged protons and negatively charged electrons. When the numbers of these subatomic particles are *not* equal, the atom is electrically charged and is called an **ion**. The charge of an atom is defined as follows:

$$\text{Atomic charge} = \text{number of protons} - \text{number of electrons}$$

As will be discussed in more detail later in this chapter, atoms (and molecules) typically acquire charge by gaining or losing electrons. An atom that gains one or more electrons will exhibit a negative charge and is called an **anion**. Positively charged atoms called **cations** are formed when an atom loses one or more electrons. For example, a neutral sodium atom (Z = 11) has 11 electrons. If this atom loses one electron, it will become a cation with a 1+ charge (11 − 10 = 1+). A neutral oxygen atom (Z = 8) has eight electrons, and if it gains two electrons it will become an anion with a 2− charge (8 − 10 = 2−).

> ✔ Example 2.4.1: Composition of an Atom
>
> Iodine is an essential trace element in our diet; it is needed to produce thyroid hormone. Insufficient iodine in the diet can lead to the development of a goiter, an enlargement of the thyroid gland (Figure 2.4.2).
>
>
>
> (a)   (b)
>
> Figure 2.4.2: (a) Insufficient iodine in the diet can cause an enlargement of the thyroid gland called a goiter. (b) The addition of small amounts of iodine to salt, which prevents the formation of goiters, has helped eliminate this concern in the US where salt consumption is high. (credit a: modification of work by "Almazi"/Wikimedia Commons; credit b: modification of work by Mike Mozart)
>
> The addition of small amounts of iodine to table salt (iodized salt) has essentially eliminated this health concern in the United States, but as much as 40% of the world's population is still at risk of iodine deficiency. The iodine atoms are added as anions, and each has a 1− charge and a mass number of 127. Determine the numbers of protons, neutrons, and electrons in one of these iodine anions.
>
> **Solution**
>
> The atomic number of iodine (53) tells us that a neutral iodine atom contains 53 protons in its nucleus and 53 electrons outside its nucleus. Because the sum of the numbers of protons and neutrons equals the mass number, 127, the number of neutrons is

> **? Exercise 2.4.1**
>
> An ion of platinum has a mass number of 195 and contains 74 electrons. How many protons and neutrons does it contain, and what is its charge?
>
> **Answer**
>
> 78 protons; 117 neutrons; charge is 4+

Chemical Symbols

A chemical symbol is an abbreviation that we use to indicate an element or an atom of an element. For example, the symbol for mercury is Hg (Figure 2.4.3). We use the same symbol to indicate one atom of mercury (microscopic domain) or to label a container of many atoms of the element mercury (macroscopic domain).

Figure 2.4.3: The symbol Hg represents the element mercury regardless of the amount; it could represent one atom of mercury or a large amount of mercury.

The symbols for several common elements and their atoms are listed in Table 2.4.2. Some symbols are derived from the common name of the element; others are abbreviations of the name in another language. Most symbols have one or two letters, but three-letter symbols have been used to describe some elements that have atomic numbers greater than 112. To avoid confusion with other notations, only the first letter of a symbol is capitalized. For example, Co is the symbol for the element cobalt, but CO is the notation for the compound carbon monoxide, which contains atoms of the elements carbon (C) and oxygen (O). All known elements and their symbols are in the periodic table (also found in Appendix A).

Table 2.4.2: Some Common Elements and Their Symbols

Element	Symbol	Element	Symbol
aluminum	Al	iron	Fe (from *ferrum*)
bromine	Br	lead	Pb (from *plumbum*)
calcium	Ca	magnesium	Mg
carbon	C	mercury	Hg (from *hydrargyrum*)
chlorine	Cl	nitrogen	N
chromium	Cr	oxygen	O
cobalt	Co	potassium	K (from *kalium*)
copper	Cu (from *cuprum*)	silicon	Si
fluorine	F	silver	Ag (from *argentum*)
gold	Au (from *aurum*)	sodium	Na (from *natrium*)

Element	Symbol	Element	Symbol
helium	He	sulfur	S
hydrogen	H	tin	Sn (from *stannum*)
iodine	I	zinc	Zn

Traditionally, the discoverer (or discoverers) of a new element names the element. However, until the name is recognized by the International Union of Pure and Applied Chemistry (IUPAC), the recommended name of the new element is based on the Latin word(s) for its atomic number. For example, element 106 was called unnilhexium (Unh), element 107 was called unnilseptium (Uns), and element 108 was called unniloctium (Uno) for several years. These elements are now named after scientists (or occasionally locations); for example, element 106 is now known as *seaborgium* (Sg) in honor of Glenn Seaborg, a Nobel Prize winner who was active in the discovery of several heavy elements. Element 109 was named in honor of Lise Meitner, who discovered nuclear fission, a phenomenon that would have world-changing impacts; Meitner also contributed to the discovery of some major isotopes, discussed immediately below.

> 📌 **Link to Learning**
>
> Visit this site to learn more about IUPAC, the International Union of Pure and Applied Chemistry, and explore its periodic table.

Isotopes

The symbol for a specific isotope of any element is written by placing the mass number as a superscript to the left of the element symbol (Figure 2.4.4). The atomic number is sometimes written as a subscript preceding the symbol, but since this number defines the element's identity, as does its symbol, it is often omitted. For example, magnesium exists as a mixture of three isotopes, each with an atomic number of 12 and with mass numbers of 24, 25, and 26, respectively. These isotopes can be identified as ^{24}Mg, ^{25}Mg, and ^{26}Mg. These isotope symbols are read as "element, mass number" and can be symbolized consistent with this reading. For instance, ^{24}Mg is read as "magnesium 24," and can be written as "magnesium-24" or "Mg-24." ^{25}Mg is read as "magnesium 25," and can be written as "magnesium-25" or "Mg-25." All magnesium atoms have 12 protons in their nucleus. They differ only because a ^{24}Mg atom has 12 neutrons in its nucleus, a ^{25}Mg atom has 13 neutrons, and a ^{26}Mg has 14 neutrons.

Mass number — 4 2+ — Charge   24 2+

He   Mg

Atomic number — 2   12
(often omitted)

Figure 2.4.4: The symbol for an atom indicates the element via its usual two-letter symbol, the mass number as a left superscript, the atomic number as a left subscript (sometimes omitted), and the charge as a right superscript.

Information about the naturally occurring isotopes of elements with atomic numbers 1 through 10 is given in Table 2.4.3. Note that in addition to standard names and symbols, the isotopes of hydrogen are often referred to using common names and accompanying symbols. Hydrogen-2, symbolized ^{2}H, is also called deuterium and sometimes symbolized D. Hydrogen-3, symbolized ^{3}H, is also called tritium and sometimes symbolized T.

Table 2.4.3: Nuclear Compositions of Atoms of the Very Light Elements

Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
hydrogen	$^{1}_{1}$H (protium)	1	1	0	1.0078	99.989
	$^{2}_{1}$H (deuterium)	1	1	1	2.0141	0.0115
	$^{3}_{1}$H (tritium)	1	1	2	3.01605	— (trace)

Element	Symbol	Atomic Number	Number of Protons	Number of Neutrons	Mass (amu)	% Natural Abundance
helium	$_2^3\text{He}$	2	2	1	3.01603	0.00013
	$_2^4\text{He}$	2	2	2	4.0026	100
lithium	$_3^6\text{Li}$	3	3	3	6.0151	7.59
	$_3^7\text{Li}$	3	3	4	7.0160	92.41
beryllium	$_4^9\text{Be}$	4	4	5	9.0122	100
boron	$_5^{10}\text{B}$	5	5	5	10.0129	19.9
	$_5^{11}\text{B}$	5	5	6	11.0093	80.1
carbon	$_6^{12}\text{C}$	6	6	6	12.0000	98.89
	$_6^{13}\text{C}$	6	6	7	13.0034	1.11
	$_6^{14}\text{C}$	6	6	8	14.0032	— (trace)
nitrogen	$_7^{14}\text{N}$	7	7	7	14.0031	99.63
	$_7^{15}\text{N}$	7	7	8	15.0001	0.37
oxygen	$_{81}^{16}\text{O}$	8	8	8	15.9949	99.757
	$_{81}^{17}\text{O}$	8	8	9	16.9991	0.038
	$_{81}^{18}\text{O}$	8	8	10	17.9992	0.205
fluorine	$_9^{19}\text{F}$	9	9	10	18.9984	100
neon	$_{10}^{20}\text{Ne}$	10	10	10	19.9924	90.48
	$_{10}^{21}\text{Ne}$	10	10	11	20.9938	0.27
	$_{10}^{22}\text{Ne}$	10	10	12	21.9914	9.25

📌 Link to Learning

Use this Build an Atom simulator to build atoms of the first 10 elements, see which isotopes exist, check nuclear stability, and gain experience with isotope symbols.

Atomic Mass

Because each proton and each neutron contribute approximately one amu to the mass of an atom, and each electron contributes far less, the **atomic mass** of a single atom is approximately equal to its mass number (a whole number). However, the average masses of atoms of most elements are not whole numbers because most elements exist naturally as mixtures of two or more isotopes.

The mass of an element shown in a periodic table or listed in a table of atomic masses is a weighted, average mass of all the isotopes present in a naturally occurring sample of that element. This is equal to the sum of each individual isotope's mass multiplied by its fractional abundance.

$$\text{average mass} = \sum_i (\text{fractional abundance} \times \text{isotopic mass})_i$$

For example, the element boron is composed of two isotopes: About 19.9% of all boron atoms are ^{10}B with a mass of 10.0129 amu, and the remaining 80.1% are ^{11}B with a mass of 11.0093 amu. The average atomic mass for boron is calculated to be:

$$\text{boron average mass } = (0.199 \times 10.0129\,\text{amu}) + (0.801 \times 11.0093\,\text{amu})$$
$$= 1.99\,\text{amu} + 8.82\,\text{amu}$$
$$= 10.81\,\text{amu}$$

It is important to understand that no single boron atom weighs exactly 10.8 amu; 10.8 amu is the average mass of all boron atoms, and individual boron atoms weigh either approximately 10 amu or 11 amu.

> ✔ Example 2.4.2: Calculation of Average Atomic Mass
>
> A meteorite found in central Indiana contains traces of the noble gas neon picked up from the solar wind during the meteorite's trip through the solar system. Analysis of a sample of the gas showed that it consisted of 91.84% ^{20}Ne (mass 19.9924 amu), 0.47% ^{21}Ne (mass 20.9940 amu), and 7.69% ^{22}Ne (mass 21.9914 amu). What is the average mass of the neon in the solar wind?
>
> **Solution**
> $$\text{average mass } = (0.9184 \times 19.9924\,\text{amu}) + (0.0047 \times 20.9940\,\text{amu}) + (0.0769 \times 21.9914\,\text{amu}$$
> $$= (18.36 + 0.099 + 1.69)\,\text{amu}$$
> $$= 20.15\,\text{amu}$$
>
> The average mass of a neon atom in the solar wind is 20.15 amu. (The average mass of a terrestrial neon atom is 20.1796 amu. This result demonstrates that we may find slight differences in the natural abundance of isotopes, depending on their origin.)

> ? Exercise 2.4.2
>
> A sample of magnesium is found to contain 78.70% of ^{24}Mg atoms (mass 23.98 amu), 10.13% of ^{25}Mg atoms (mass 24.99 amu), and 11.17% of ^{26}Mg atoms (mass 25.98 amu). Calculate the average mass of a Mg atom.
>
> **Answer**
>
> 24.31 amu

We can also do variations of this type of calculation, as shown in the next example.

> ✔ Example 2.4.3: Calculation of Percent Abundance
>
> Naturally occurring chlorine consists of ^{35}Cl (mass 34.96885 amu) and ^{37}Cl (mass 36.96590 amu), with an average mass of 35.453 amu. What is the percent composition of Cl in terms of these two isotopes?
>
> **Solution**
> The average mass of chlorine is the fraction that is ^{35}Cl times the mass of ^{35}Cl plus the fraction that is ^{37}Cl times the mass of ^{37}Cl.
>
> $$\text{average mass } = \left(\text{ fraction of }^{35}Cl \times \text{ mass of }^{35}Cl\right) + \left(\text{ fraction of }^{37}Cl \times \text{ mass of }^{37}Cl\right)$$
>
> If we let x represent the fraction that is ^{35}Cl, then the fraction that is ^{37}Cl is represented by $1.00 - x$.
>
> (The fraction that is ^{35}Cl + the fraction that is ^{37}Cl must add up to 1, so the fraction of ^{37}Cl must equal 1.00 − the fraction of ^{35}Cl.)
>
> Substituting this into the average mass equation, we have:
> $$35.453\,amu = (x \times 34.96885\,amu) + [(1.00 - x) \times 36.96590\,amu]$$
> $$35.453 = 34.96885x + 36.96590 - 36.96590x$$
> $$1.99705x = 1.513$$
> $$x = \frac{1.513}{1.99705} = 0.7576$$

So solving yields: $x = 0.7576$, which means that $1.00 - 0.7576 = 0.2424$. Therefore, chlorine consists of 75.76% ^{35}Cl and 24.24% ^{37}Cl.

> **? Exercise 2.4.3**
>
> Naturally occurring copper consists of ^{63}Cu (mass 62.9296 amu) and ^{65}Cu (mass 64.9278 amu), with an average mass of 63.546 amu. What is the percent composition of Cu in terms of these two isotopes?
>
> **Answer**
>
> 69.15% Cu-63 and 30.85% Cu-65

> **⚲ Link to Learning**
>
> Visit this site to make mixtures of the main isotopes of the first 18 elements, gain experience with average atomic mass, and check naturally occurring isotope ratios using the Isotopes and Atomic Mass simulation.

As you will learn, isotopes are important in nature and especially in human understanding of science and medicine. Let's consider just one natural, stable isotope: Oxygen-18, which is noted in the table above and is referred to as one of the environmental isotopes. It is important in paleoclimatology, for example, because scientists can use the ratio between Oxygen-18 and Oxygen-16 in an ice core to determine the temperature of precipitation over time. Oxygen-18 was also critical to the discovery of metabolic pathways and the mechanisms of enzymes. Mildred Cohn pioneered the usage of these isotopes to act as tracers, so that researchers could follow their path through reactions and gain a better understanding of what is happening. One of her first discoveries provided insight into the phosphorylation of glucose that takes place in mitochondria. And the methods of using isotopes for this research contributed to entire fields of study.

The occurrence and natural abundances of isotopes can be experimentally determined using an instrument called a mass spectrometer. **Mass spectrometry** (MS) is widely used in chemistry, forensics, medicine, environmental science, and many other fields to analyze and help identify the substances in a sample of material. In a typical mass spectrometer (Figure 2.4.5), the sample is vaporized and exposed to a high-energy electron beam that causes the sample's atoms (or molecules) to become electrically charged, typically by losing one or more electrons. These cations then pass through a (variable) electric or magnetic field that deflects each cation's path to an extent that depends on both its mass and charge (similar to how the path of a large steel ball rolling past a magnet is deflected to a lesser extent that that of a small steel ball). The ions are detected, and a plot of the relative number of ions generated versus their mass-to-charge ratios (a *mass spectrum*) is made. The height of each vertical feature or peak in a mass spectrum is proportional to the fraction of cations with the specified mass-to-charge ratio. Since its initial use during the development of modern atomic theory, MS has evolved to become a powerful tool for chemical analysis in a wide range of applications.
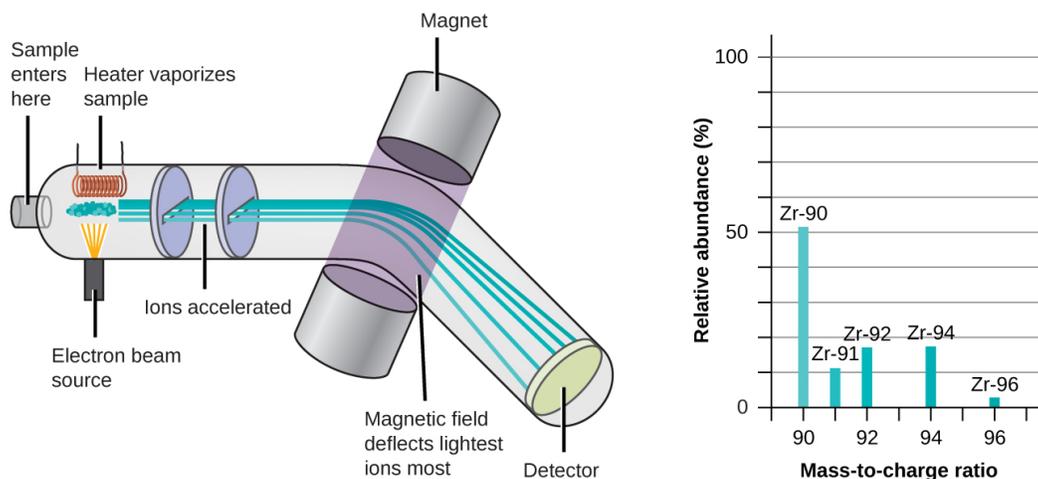

Figure 2.4.5: Analysis of zirconium in a mass spectrometer produces a mass spectrum with peaks showing the different isotopes of Zr.

2.5: Chemical Formulas

> ◗ **Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Symbolize the composition of molecules using molecular formulas and empirical formulas
> - Represent the bonding arrangement of atoms within molecules using structural formulas

A molecular formula is a representation of a molecule that uses chemical symbols to indicate the types of atoms followed by subscripts to show the number of atoms of each type in the molecule. (A subscript is used only when more than one atom of a given type is present.) Molecular formulas are also used as abbreviations for the names of compounds.

The structural formula for a compound gives the same information as its molecular formula (the types and numbers of atoms in the molecule) but also shows how the atoms are connected in the molecule. The structural formula for methane contains symbols for one C atom and four H atoms, indicating the number of atoms in the molecule (Figure 2.5.1). The lines represent bonds that hold the atoms together. (A chemical bond is an attraction between atoms or ions that holds them together in a molecule or a crystal.) We will discuss chemical bonds and see how to predict the arrangement of atoms in a molecule later. For now, simply know that the lines are an indication of how the atoms are connected in a molecule. A ball-and-stick model shows the geometric arrangement of the atoms with atomic sizes not to scale, and a space-filling model shows the relative sizes of the atoms.
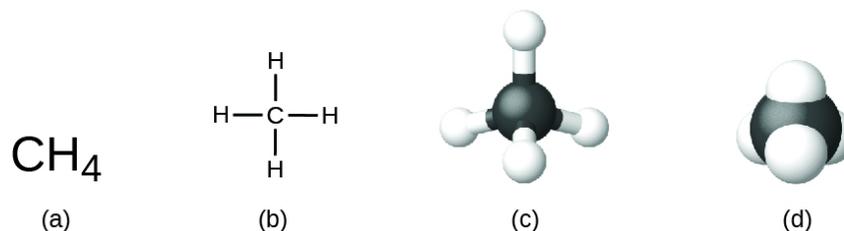
Figure 2.5.1 : A methane molecule can be represented as (a) a molecular formula, (b) a structural formula, (c) a ball-and-stick model, and (d) a space-filling model. Carbon and hydrogen atoms are represented by black and white spheres, respectively.

Although many elements consist of discrete, individual atoms, some exist as molecules made up of two or more atoms of the element chemically bonded together. For example, most samples of the elements hydrogen, oxygen, and nitrogen are composed of molecules that contain two atoms each (called diatomic molecules) and thus have the molecular formulas H_2, O_2, and N_2, respectively. Other elements commonly found as diatomic molecules are fluorine (F_2), chlorine (Cl_2), bromine (Br_2), and iodine (I_2). The most common form of the element sulfur is composed of molecules that consist of eight atoms of sulfur; its molecular formula is S_8 (Figure 2.5.2).
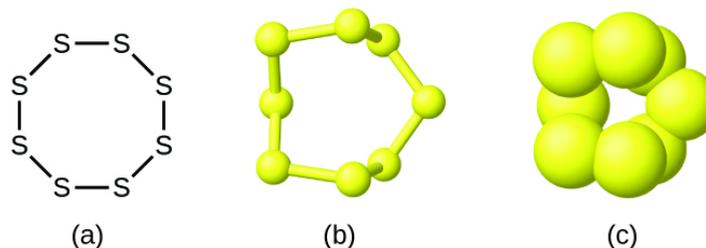
Figure 2.5.2 : A molecule of sulfur is composed of eight sulfur atoms and is therefore written as S_8. It can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. Sulfur atoms are represented by yellow spheres.

It is important to note that a subscript following a symbol and a number in front of a symbol do not represent the same thing; for example, H_2 and 2H represent distinctly different species. H_2 is a molecular formula; it represents a diatomic molecule of hydrogen, consisting of two atoms of the element that are chemically bonded together. The expression 2H, on the other hand, indicates two separate hydrogen atoms that are not combined as a unit. The expression $2H_2$ represents two molecules of diatomic hydrogen (Figure 2.5.3).
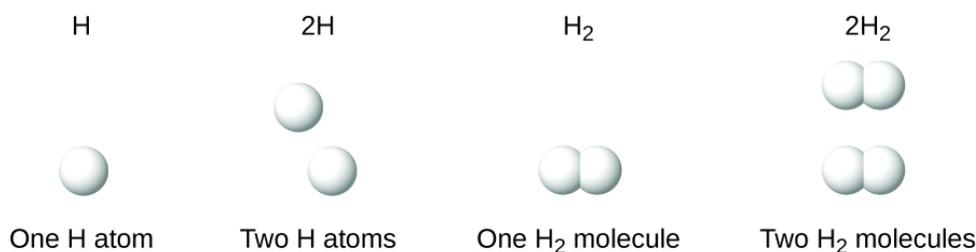
Figure 2.5.3 : The symbols H, 2H, H$_2$, and 2H$_2$ represent very different entities.

Compounds are formed when two or more elements chemically combine, resulting in the formation of bonds. For example, hydrogen and oxygen can react to form water, and sodium and chlorine can react to form table salt. We sometimes describe the composition of these compounds with an empirical formula, which indicates the types of atoms present and *the simplest whole-number ratio of the number of atoms (or ions) in the compound*. For example, titanium dioxide (used as pigment in white paint and in the thick, white, blocking type of sunscreen) has an empirical formula of TiO$_2$. This identifies the elements titanium (Ti) and oxygen (O) as the constituents of titanium dioxide, and indicates the presence of twice as many atoms of the element oxygen as atoms of the element titanium (Figure 2.5.4).
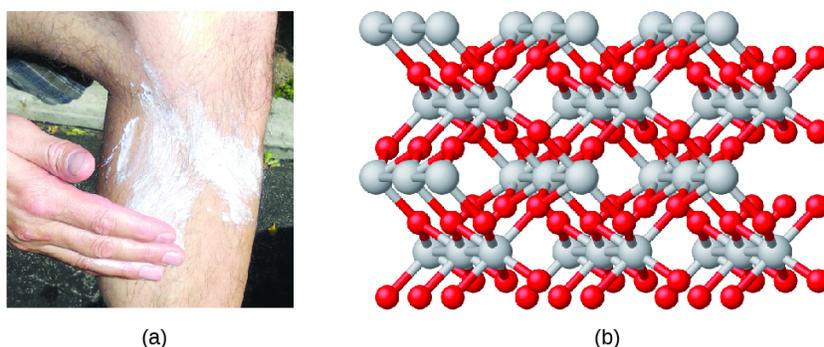
Figure 2.5.4 : (a) The white compound titanium dioxide provides effective protection from the sun. (b) A crystal of titanium dioxide, TiO$_2$, contains titanium and oxygen in a ratio of 1 to 2. The titanium atoms are gray and the oxygen atoms are red. (credit a: modification of work by "osseous"/Flickr)

As discussed previously, we can describe a compound with a molecular formula, in which the subscripts indicate the *actual numbers of atoms* of each element in a molecule of the compound. In many cases, the molecular formula of a substance is derived from experimental determination of both its empirical formula and its molecular mass (the sum of atomic masses for all atoms composing the molecule). For example, it can be determined experimentally that benzene contains two elements, carbon (C) and hydrogen (H), and that for every carbon atom in benzene, there is one hydrogen atom. Thus, the empirical formula is CH. An experimental determination of the molecular mass reveals that a molecule of benzene contains six carbon atoms and six hydrogen atoms, so the molecular formula for benzene is C$_6$H$_6$ (Figure 2.5.5).
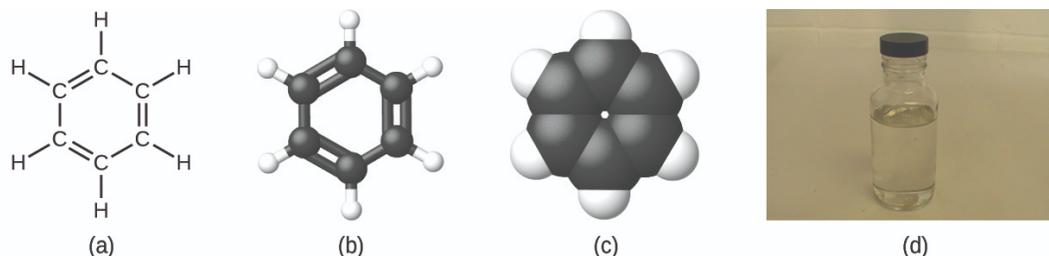
Figure 2.5.5 : Benzene, C$_6$H$_6$, is produced during oil refining and has many industrial uses. A benzene molecule can be represented as (a) a structural formula, (b) a ball-and-stick model, and (c) a space-filling model. (d) Benzene is a clear liquid. (credit d: modification of work by Sahar Atwa)

If we know a compound's formula, we can easily determine the empirical formula. (This is somewhat of an academic exercise; the reverse chronology is generally followed in actual practice.) For example, the molecular formula for acetic acid, the component that gives vinegar its sharp taste, is C$_2$H$_4$O$_2$. This formula indicates that a molecule of acetic acid (Figure 2.5.6) contains two carbon atoms, four hydrogen atoms, and two oxygen atoms. The ratio of atoms is 2:4:2. Dividing by the lowest common

denominator (2) gives the simplest, whole-number ratio of atoms, 1:2:1, so the empirical formula is CH_2O. Note that a molecular formula is always a whole-number multiple of an empirical formula.
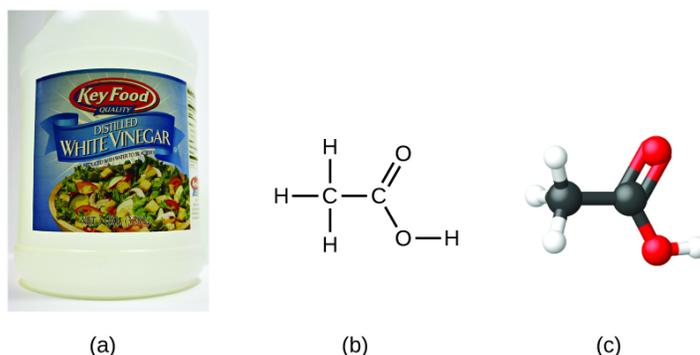
Figure 2.5.6: (a) Vinegar contains acetic acid, $C_2H_4O_2$, which has an empirical formula of CH_2O. It can be represented as (b) a structural formula and (c) as a ball-and-stick model. (credit a: modification of work by "HomeSpot HQ"/Flickr)

✔ **Example 2.5.1: Empirical and Molecular Formulas**

Molecules of glucose (blood sugar) contain 6 carbon atoms, 12 hydrogen atoms, and 6 oxygen atoms. What are the molecular and empirical formulas of glucose?

Solution

The molecular formula is $C_6H_{12}O_6$ because one molecule actually contains 6 C, 12 H, and 6 O atoms. The simplest whole-number ratio of C to H to O atoms in glucose is 1:2:1, so the empirical formula is CH_2O.

? **Exercise 2.5.1**

A molecule of metaldehyde (a pesticide used for snails and slugs) contains 8 carbon atoms, 16 hydrogen atoms, and 4 oxygen atoms. What are the molecular and empirical formulas of metaldehyde?

Answer

Molecular formula, $C_8H_{16}O_4$; empirical formula, C_2H_4O

📌 **Link to Learning**

You can explore molecule building using an online simulation.

📌 **Portrait of a Chemist: Lee Cronin**

What is it that chemists do? According to Lee Cronin (Figure 2.5.7), chemists make very complicated molecules by "chopping up" small molecules and "reverse engineering" them. He wonders if we could "make a really cool universal chemistry set" by what he calls "app-ing" chemistry. Could we "app" chemistry?

Figure 2.5.7: Chemist Lee Cronin has been named one of the UK's 10 most inspirational scientists. The youngest chair at the University of Glasgow, Lee runs a large research group, collaborates with many scientists worldwide, has published over 250 papers in top scientific journals, and has given more than 150 invited talks. His research focuses on complex chemical systems and their potential to transform technology, but also branches into nanoscience, solar fuels, synthetic biology, and even artificial life and evolution. (credit: image courtesy of Lee Cronin)

In a 2012 TED talk, Lee describes one fascinating possibility: combining a collection of chemical "inks" with a 3D printer capable of fabricating a reaction apparatus (tiny test tubes, beakers, and the like) to fashion a "universal toolkit of chemistry." This toolkit could be used to create custom-tailored drugs to fight a new superbug or to "print" medicine personally configured to your genetic makeup, environment, and health situation. Says Cronin, "What Apple did for music, I'd like to do for the discovery and distribution of prescription drugs."[2] View his full talk at the TED website.

It is important to be aware that it may be possible for the same atoms to be arranged in different ways: Compounds with the same molecular formula may have different atom-to-atom bonding and therefore different structures. For example, could there be another compound with the same formula as acetic acid, $C_2H_4O_2$? And if so, what would be the structure of its molecules?

If you predict that another compound with the formula $C_2H_4O_2$ could exist, then you demonstrated good chemical insight and are correct. Two C atoms, four H atoms, and two O atoms can also be arranged to form a methyl formate, which is used in manufacturing, as an insecticide, and for quick-drying finishes. Methyl formate molecules have one of the oxygen atoms between the two carbon atoms, differing from the arrangement in acetic acid molecules. Acetic acid and methyl formate are examples of isomers—compounds with the same chemical formula but different molecular structures (Figure 2.5.8). Note that this small difference in the arrangement of the atoms has a major effect on their respective chemical properties. You would certainly not want to use a solution of methyl formate as a substitute for a solution of acetic acid (vinegar) when you make salad dressing.
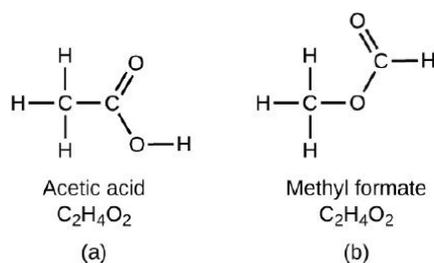
Figure 2.5.8: Molecules of (a) acetic acid and methyl formate (b) are structural isomers; they have the same formula ($C_2H_4O_2$) but different structures (and therefore different chemical properties).

Many types of isomers exist (Figure 2.5.9). Acetic acid and methyl formate are structural isomers, compounds in which the molecules differ in how the atoms are connected to each other. There are also various types of spatial isomers, in which the relative orientations of the atoms in space can be different. For example, the compound carvone (found in caraway seeds, spearmint, and mandarin orange peels) consists of two isomers that are mirror images of each other. *S*-(+)-carvone smells like caraway, and *R*-(−)-carvone smells like spearmint.
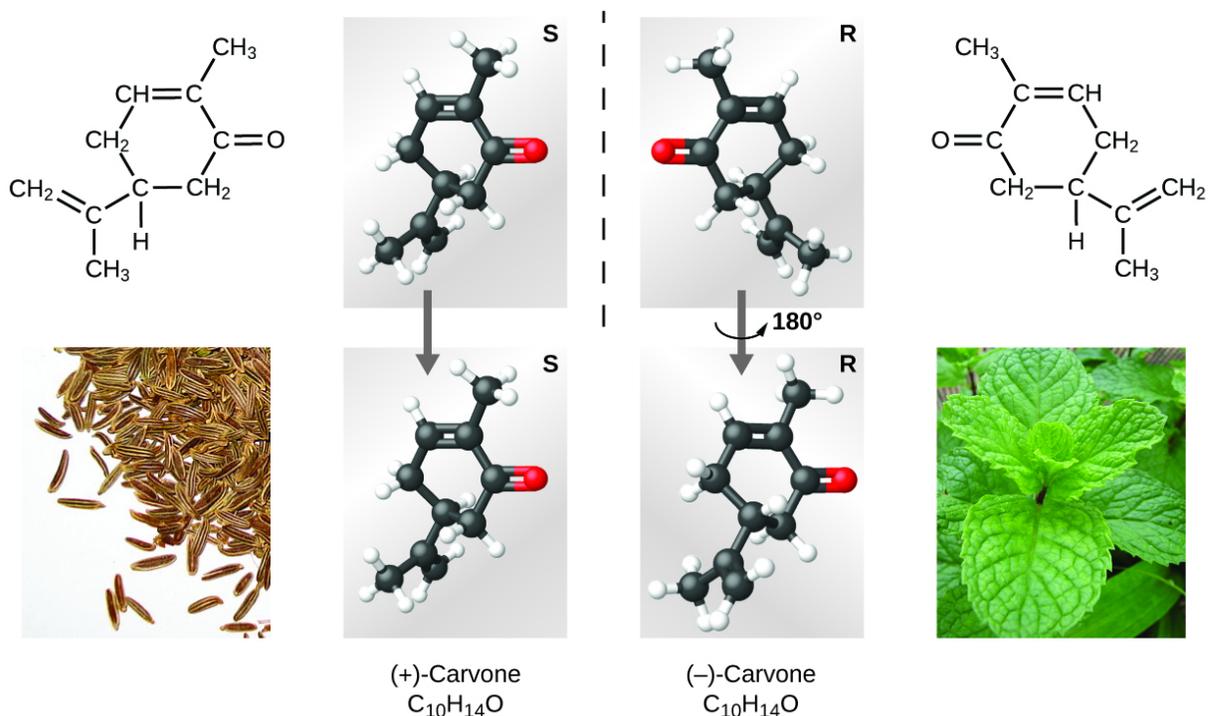
Figure 2.5.0: Molecules of carvone are spatial isomers; they only differ in the relative orientations of the atoms in space. (credit bottom left: modification of work by "Miansari66"/Wikimedia Commons; credit bottom right: modification of work by Forest & Kim Starr)

> 📌 Link to Learning
>
> Select this link to view an explanation of isomers, spatial isomers, and why they have different smells (select the video titled "Mirror Molecule: Carvone").

Footnotes

- 2Lee Cronin, "Print Your Own Medicine," Talk presented at TED Global 2012, Edinburgh, Scotland, June 2012.

2.6: The Periodic Table

◗ Learning Objectives

By the end of this section, you will be able to:

- State the periodic law and explain the organization of elements in the periodic table
- Predict the general properties of elements based on their location within the periodic table
- Identify metals, nonmetals, and metalloids by their properties and/or location on the periodic table

As early chemists worked to purify ores and discovered more elements, they realized that various elements could be grouped together by their similar chemical behaviors. One such grouping includes lithium (Li), sodium (Na), and potassium (K): These elements all are shiny, conduct heat and electricity well, and have similar chemical properties. A second grouping includes calcium (Ca), strontium (Sr), and barium (Ba), which also are shiny, good conductors of heat and electricity, and have chemical properties in common. However, the specific properties of these two groupings are notably different from each other. For example: Li, Na, and K are much more reactive than are Ca, Sr, and Ba; Li, Na, and K form compounds with oxygen in a ratio of two of their atoms to one oxygen atom, whereas Ca, Sr, and Ba form compounds with one of their atoms to one oxygen atom. Fluorine (F), chlorine (Cl), bromine (Br), and iodine (I) also exhibit similar properties to each other, but these properties are drastically different from those of any of the elements above.

Dimitri Mendeleev in Russia (1869) and Lothar Meyer in Germany (1870) independently recognized that there was a periodic relationship among the properties of the elements known at that time. Both published tables with the elements arranged according to increasing atomic mass. But Mendeleev went one step further than Meyer: He used his table to predict the existence of elements that would have the properties similar to aluminum and silicon, but were yet unknown. The discoveries of gallium (1875) and germanium (1886) provided great support for Mendeleev's work. Although Mendeleev and Meyer had a long d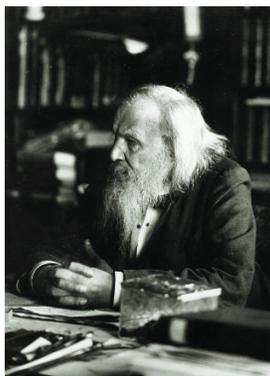ispute over priority, Mendeleev's contributions to the development of the periodic table are now more widely recognized (Figure 2.6.1).

	Gruppo I. — R²O	Gruppo II. — RO	Gruppo III. — R²O³	Gruppo IV. RH⁴ RO²	Gruppo V. RH³ R²O⁵	Gruppo VI. RH² RO³	Gruppo VII. RH R²O⁷	Gruppo VIII. — RO⁴
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,8	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	—=44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	—=68	—=72	As=75	So=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	—=100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce=140	—	—	—	— — — —
9	(—)	—	—	—	—	—	—	
10	—	—	?Er=178	?La=180	Ta=182	W=184	—	Os=195, Ir=197, Pt=198, Au=199.
11	(Au=199)	Hg=200	Tl=204	Pb=207	Bi=208	—	—	— — — —
12	—	—	—	Th=231	—	U=240	—	

(a)   (b)

Figure 2.6.1: (a) Dimitri Mendeleev is widely credited with creating (b) the first periodic table of the elements. (credit a: modification of work by Serge Lachinov; credit b: modification of work by "Den fjättrade ankan"/Wikimedia Commons)

By the twentieth century, it became apparent that the periodic relationship involved atomic numbers rather than atomic masses. The modern statement of this relationship, the **periodic law**, is as follows: *the properties of the elements are periodic functions of their atomic numbers*. A modern **periodic table** arranges the elements in increasing order of their atomic numbers and groups atoms with similar properties in the same vertical column (Figure 2.6.2). Each box represents an element and contains its atomic number, symbol, average atomic mass, and (sometimes) name. The elements are arranged in seven horizontal rows, called **periods** or **series**, and 18 vertical columns, called **groups**. Groups are labeled at the top of each column. In the United States, the labels traditionally were numerals with capital letters. However, IUPAC recommends that the numbers 1 through 18 be used, and these labels are more common. For the table to fit on a single page, parts of two of the rows, a total of 14 columns, are usually written below the main body of the table.

Periodic Table of the Elements

Figure 2.6.2: Elements in the periodic table are organized according to their properties.

Even after the periodic nature of elements and the table itself were widely accepted, gaps remained. Mendeleev had predicted, and others including Henry Moseley had later confirmed, that there should be elements below Manganese in Group 7. German chemists Ida Tacke and Walter Noddack set out to find the elements, a quest being pursued by scientists around the world. Their method was unique in that they did not only consider the properties of manganese, but also the elements horizontally adjacent to the missing elements 43 and 75 on the table. Thus, by investigating ores containing minerals of ruthenium (Ru), tungsten (W), osmium (Os), and so on, they were able to identify naturally occurring elements that helped complete the table. Rhenium, one of their discoveries, was one of the last natural elements to be discovered and is the last stable element to be discovered. (Francium, the last natural element to be discovered, was identified by Marguerite Perey in 1939.)

Many elements differ dramatically in their chemical and physical properties, but some elements are similar in their behaviors. For example, many elements appear shiny, are malleable (able to be deformed without breaking) and ductile (can be drawn into wires), and conduct heat and electricity well. Other elements are not shiny, malleable, or ductile, and are poor conductors of heat and electricity. We can sort the elements into large classes with common properties: **metals** (elements that are shiny, malleable, good conductors of heat and electricity—shaded yellow); **nonmetals** (elements that appear dull, poor conductors of heat and electricity —shaded green); and **metalloids** (elements that conduct heat and electricity moderately well, and possess some properties of metals and some properties of nonmetals—shaded purple).

The elements can also be classified into the main-group elements (or representative elements) in the columns labeled 1, 2, and 13–18; the transition metals in the columns labeled 3–12[3]; and inner transition metals in the two rows at the bottom of the table (the top-row elements are called lanthanides and the bottom-row elements are actinides; Figure 2.6.3). The elements can be subdivided further by more specific properties, such as the composition of the compounds they form. For example, the elements in group 1 (the first column) form compounds that consist of one atom of the element and one atom of hydrogen. These elements (except hydrogen) are known as **alkali metals**, and they all have similar chemical properties. The elements in group 2 (the second column) form compounds consisting of one atom of the element and two atoms of hydrogen: These are called **alkaline earth metals**, with similar properties among members of that group. Other groups with specific names are the **pnictogens** (group 15), **chalcogens** (group 16), halogens (group 17), and the **noble gases** (group 18, also known as inert gases). The groups can also be referred to by

the first element of the group: For example, the chalcogens can be called the oxygen group or oxygen family. Hydrogen is a unique, nonmetallic element with properties similar to both group 1 and group 17 elements. For that reason, hydrogen may be shown at the top of both groups, or by itself.
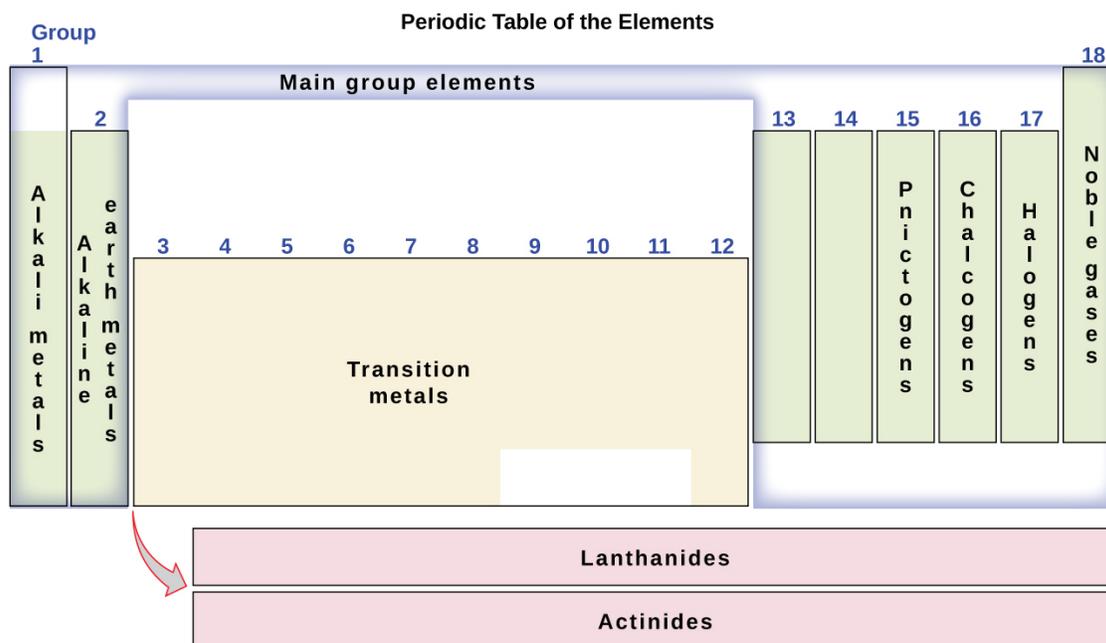
Figure 2.6.3: The periodic table organizes elements with similar properties into groups.

📌 Link to Learning

Click on this link for an interactive periodic table, which you can use to explore the properties of the elements (includes podcasts and videos of each element). You may also want to try this one that shows photos of all the elements.

✔ Example 2.6.1: Naming Groups of Elements

Atoms of each of the following elements are essential for life. Give the group name for the following elements:

a. chlorine
b. calcium
c. sodium
d. sulfur

Solution

The family names are as follows:

a. halogen
b. alkaline earth metal
c. alkali metal
d. chalcogen

❓ Exercise 2.6.1

Give the group name for each of the following elements:

a. krypton
b. selenium
c. barium
d. lithium

> **Answer**
>
> (a) noble gas; (b) chalcogen; (c) alkaline earth metal; (d) alkali metal

As you will learn in your further study of chemistry, elements in groups often behave in a somewhat similar manner. This is partly due to the number of electrons in their outer shell and their similar readiness to bond. These shared properties can have far-ranging implications in nature, science, and medicine. For example, when Gertrude Elion and George Hitchens were investigating ways to interrupt cell and virus replication to fight diseases, they utilized the similarity between sulfur and oxygen (both in Group 16) and their capacity to bond in similar ways. Elion focused on purines, which are key components of DNA and which contain oxygen. She found that by introducing sulfur-based compounds (called purine analogues) that mimic the structure of purines, molecules within DNA would bond to the analogues rather than the "regular" DNA purine. With the normal DNA bonding and structure altered, Elion successfully interrupted cell replication. At its core, the strategy worked because of the similarity between sulfur and oxygen. Her discovery led directly to important treatments for leukemia. Overall, Elion's work with George Hitchens not only led to more treatments, but also changed the entire methodology of drug development. By using specific elements and compounds to target specific aspects of tumor cells, viruses, and bacteria, they laid the groundwork for many of today's most common and important medicines, used to help millions of people each year. They were awarded the Nobel Prize in 1988.

In studying the periodic table, you might have noticed something about the atomic masses of some of the elements. Element 43 (technetium), element 61 (promethium), and most of the elements with atomic number 84 (polonium) and higher have their atomic mass given in square brackets. This is done for elements that consist entirely of unstable, radioactive isotopes (you will learn more about radioactivity in the nuclear chemistry chapter). An average atomic weight cannot be determined for these elements because their radioisotopes may vary significantly in relative abundance, depending on the source, or may not even exist in nature. The number in square brackets is the atomic mass number (an approximate atomic mass) of the most stable isotope of that element.

Footnotes

- [3]Per the IUPAC definition, group 12 elements are not transition metals, though they are often referred to as such. Additional details on this group's elements are provided in a chapter on transition metals and coordination chemistry.

2.7: Molecular and Ionic Compounds

> **◐ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Define ionic and molecular (covalent) compounds
> - Predict the type of compound formed from elements based on their location within the periodic table
> - Determine formulas for simple ionic compounds

In ordinary chemical reactions, the nucleus of each atom (and thus the identity of the element) remains unchanged. Electrons, however, can be added to atoms by transfer from other atoms, lost by transfer to other atoms, or shared with other atoms. The transfer and sharing of electrons among atoms govern the chemistry of the elements. During the formation of some compounds, atoms gain or lose electrons, and form electrically charged particles called ions (Figure 2.7.1).
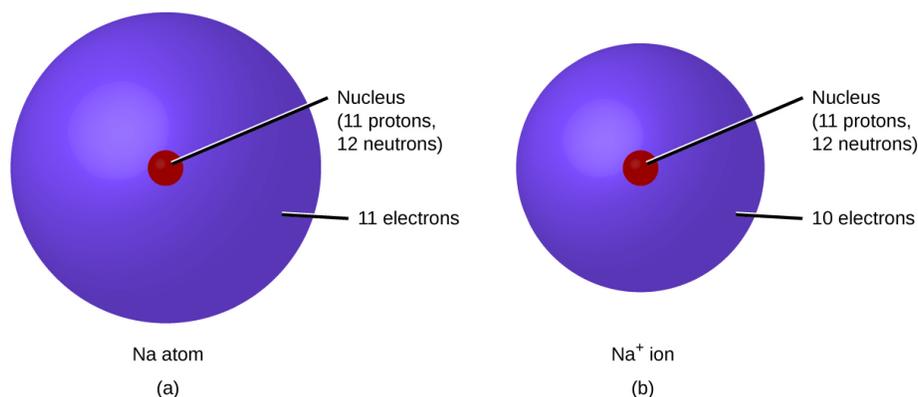
Table 2.7.1: (a) A sodium atom (Na) has equal numbers of protons and electrons (11) and is uncharged. (b) A sodium cation (Na$^+$) has lost an electron, so it has one more proton (11) than electrons (10), giving it an overall positive charge, signified by a superscripted plus sign.

You can use the periodic table to predict whether an atom will form an anion or a cation, and you can often predict the charge of the resulting ion. Atoms of many main-group metals lose enough electrons to leave them with the same number of electrons as an atom of the preceding noble gas. To illustrate, an atom of an alkali metal (group 1) loses one electron and forms a cation with a 1+ charge; an alkaline earth metal (group 2) loses two electrons and forms a cation with a 2+ charge, and so on. For example, a neutral calcium atom, with 20 protons and 20 electrons, readily loses two electrons. This results in a cation with 20 protons, 18 electrons, and a 2+ charge. It has the same number of electrons as atoms of the preceding noble gas, argon, and is symbolized Ca^{2+}. The name of a metal ion is the same as the name of the metal atom from which it forms, so Ca^{2+} is called a calcium ion.

When atoms of nonmetal elements form ions, they generally gain enough electrons to give them the same number of electrons as an atom of the next noble gas in the periodic table. Atoms of group 17 gain one electron and form anions with a 1− charge; atoms of group 16 gain two electrons and form ions with a 2− charge, and so on. For example, the neutral bromine atom, with 35 protons and 35 electrons, can gain one electron to provide it with 36 electrons. This results in an anion with 35 protons, 36 electrons, and a 1− charge. It has the same number of electrons as atoms of the next noble gas, krypton, and is symbolized Br$^-$. (A discussion of the theory supporting the favored status of noble gas electron numbers reflected in these predictive rules for ion formation is provided in a later chapter of this text.)

Note the usefulness of the periodic table in predicting likely ion formation and charge (Figure 2.7.2). Moving from the far left to the right on the periodic table, main-group elements tend to form cations with a charge equal to the group number. That is, group 1 elements form 1+ ions; group 2 elements form 2+ ions, and so on. Moving from the far right to the left on the periodic table, elements often form anions with a negative charge equal to the number of groups moved left from the noble gases. For example, group 17 elements (one group left of the noble gases) form 1− ions; group 16 elements (two groups left) form 2− ions, and so on. This trend can be used as a guide in many cases, but its predictive value decreases when moving toward the center of the periodic table. In fact, transition metals and some other metals often exhibit variable charges that are not predictable by their location in the table. For example, copper can form ions with a 1+ or 2+ charge, and iron can form ions with a 2+ or 3+ charge.

Periodic Table of the Elements

Period / Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1																		He
2	Li^+	Be^{2+}												C^{4-}	N^{3-}	O^{2-}	F^-	Ne
3	Na^+	Mg^{2+}											Al^{3+}		P^{3-}	S^{2-}	Cl^-	Ar
4	K^+	Ca^{2+}				Cr^{3+} Cr^{6+}	Mn^{2+}	Fe^{2+} Fe^{3+}	Co^{2+}	Ni^{2+}	Cu^+ Cu^{2+}	Zn^{2+}			As^{3-}	Se^{2-}	Br^-	Kr
5	Rb^+	Sr^{2+}									Ag^+	Cd^{2+}				Te^{2-}	I^-	Xe
6	Cs^+	Ba^{2+}								Pt^{2+}	Au^+ Au^{3+}	Hg_2^{2+} Hg^{2+}					At^-	Rn
7	Fr^+	Ra^{2+}																

Table 2.7.2: Some elements exhibit a regular pattern of ionic charge when they form ions.

✔ **Example 2.7.1: Composition of Ions**

An ion found in some compounds used as antiperspirants contains 13 protons and 10 electrons. What is its symbol?

Solution

Because the number of protons remains unchanged when an atom forms an ion, the atomic number of the element must be 13. Knowing this lets us use the periodic table to identify the element as Al (aluminum). The Al atom has lost three electrons and thus has three more positive charges (13) than it has electrons (10). This is the aluminum cation, Al^{3+}.

? **Exercise 2.7.1**

Give the symbol and name for the ion with 34 protons and 36 electrons.

Answer

Se^{2-}, the selenide ion

✔ **Example 2.7.2: Formation of Ions**

Magnesium and nitrogen react to form an ionic compound. Predict which forms an anion, which forms a cation, and the charges of each ion. Write the symbol for each ion and name them.

Solution

Magnesium's position in the periodic table (group 2) tells us that it is a metal. Metals form positive ions (cations). A magnesium atom must lose two electrons to have the same number electrons as an atom of the previous noble gas, neon. Thus, a magnesium atom will form a cation with two fewer electrons than protons and a charge of 2+. The symbol for the ion is Mg^{2+}, and it is called a magnesium ion.

Nitrogen's position in the periodic table (group 15) reveals that it is a nonmetal. Nonmetals form negative ions (anions). A nitrogen atom must gain three electrons to have the same number of electrons as an atom of the following noble gas, neon. Thus, a nitrogen atom will form an anion with three more electrons than protons and a charge of 3−. The symbol for the ion is N^{3-}, and it is called a nitride ion.

? Exercise 2.7.2

Aluminum and carbon react to form an ionic compound. Predict which forms an anion, which forms a cation, and the charges of each ion. Write the symbol for each ion and name them.

Answer

Al will form a cation with a charge of 3+: Al^{3+}, an aluminum ion. Carbon will form an anion with a charge of 4−: C^{4-}, a carbide ion.

The ions that we have discussed so far are called monatomic ions, that is, they are ions formed from only one atom. We also find many polyatomic ions. These ions, which act as discrete units, are electrically charged molecules (a group of bonded atoms with an overall charge). Some of the more important polyatomic ions are listed in Table 2.7.1. Oxyanions are polyatomic ions that contain one or more oxygen atoms. At this point in your study of chemistry, you should memorize the names, formulas, and charges of the most common polyatomic ions. Because you will use them repeatedly, they will soon become familiar.

Table 2.7.1: Common Polyatomic Ions

Name	Formula	Related Acid	Formula
ammonium	NH_4^+		
hydronium	H_3O		
peroxide	O_2^{2-}		
hydroxide	OH^-		
acetate	CH_3COO^-	acetic acid	CH_3COOH
cyanide	CN^-	hydrocyanic acid	HCN
azide	N_3^-	hydrazoic acid	HN_3
carbonate	CO_3^{2-}	carbonic acid	H_2CO_3
bicarbonate	HCO_3^-		
nitrate	NO_3^-	nitric acid	HNO_3
nitrite	NO_2^-	nitrous acid	HNO_2
sulfate	SO_{42}^-	sulfuric acid	H_2SO_4
hydrogen sulfate	HSO_4^-		
sulfite	SO_3^{2-}	sulfurous acid	H_2SO_3
hydrogen sulfite	HSO_3^-		
phosphate	PO_4^{3-}	phosphoric acid	H_3PO_4
hydrogen phosphate	HPO_4^{2-}		
dihydrogen phosphate	$H_2PO_4^-$		
perchlorate	ClO_4^-	perchloric acid	$HClO_4$
chlorate	ClO_3^-	chloric acid	$HClO_3$
chlorite	ClO_2^-	chlorous acid	$HClO_2$
hypochlorite	ClO^-	hypochlorous acid	$HClO$
chromate	CrO_4^{2-}	chromic acid	H_2CrO_4
dichromate	$Cr_2O_7^{2-}$	dichromic acid	$H_2Cr_2O_7$

Name	Formula	Related Acid	Formula
permanganate	MnO_4^-	permanganic acid	$HMnO_4$

Note that there is a system for naming some polyatomic ions; -ate and -ite are suffixes designating polyatomic ions containing more or fewer oxygen atoms. Per- (short for "hyper") and hypo- (meaning "under") are prefixes meaning more oxygen atoms than -ate and fewer oxygen atoms than -ite, respectively. For example, perchlorate is ClO_4^-, chlorate is ClO_3^-, chlorite is ClO_2^- and hypochlorite is ClO^-. Unfortunately, the number of oxygen atoms corresponding to a given suffix or prefix is not consistent; for example, nitrate is NO_3^- while sulfate is SO_4^{2-}. This will be covered in more detail in the next module on nomenclature.

The nature of the attractive forces that hold atoms or ions together within a compound is the basis for classifying chemical bonding. When electrons are transferred and ions form, ionic bonds result. Ionic bonds are electrostatic forces of attraction, that is, the attractive forces experienced between objects of opposite electrical charge (in this case, cations and anions). When electrons are "shared" and molecules form, covalent bonds result. Covalent bonds are the attractive forces between the positively charged nuclei of the bonded atoms and one or more pairs of electrons that are located between the atoms. Compounds are classified as ionic or molecular (covalent) on the basis of the bonds present in them.

Ionic Compounds

When an element composed of atoms that readily lose electrons (a metal) reacts with an element composed of atoms that readily gain electrons (a nonmetal), a transfer of electrons usually occurs, producing ions. The compound formed by this transfer is stabilized by the electrostatic attractions (ionic bonds) between the ions of opposite charge present in the compound. For example, when each sodium atom in a sample of sodium metal (group 1) gives up one electron to form a sodium cation, Na^+, and each chlorine atom in a sample of chlorine gas (group 17) accepts one electron to form a chloride anion, Cl^-, the resulting compound, NaCl, is composed of sodium ions and chloride ions in the ratio of one Na^+ ion for each Cl^- ion. Similarly, each calcium atom (group 2) can give up two electrons and transfer one to each of two chlorine atoms to form $CaCl_2$, which is composed of Ca^{2+} and Cl^- ions in the ratio of one Ca^{2+} ion to two Cl^- ions.

A compound that contains ions and is held together by ionic bonds is called an ionic compound. The periodic table can help us recognize many of the compounds that are ionic: When a metal is combined with one or more nonmetals, the compound is usually ionic. This guideline works well for predicting ionic compound formation for most of the compounds typically encountered in an introductory chemistry course. However, it is not always true (for example, aluminum chloride, $AlCl_3$, is not ionic).

You can often recognize ionic compounds because of their properties. Ionic compounds are solids that typically melt at high temperatures and boil at even higher temperatures. For example, sodium chloride melts at 801 °C and boils at 1413 °C. (As a comparison, the molecular compound water melts at 0 °C and boils at 100 °C.) In solid form, an ionic compound is not electrically conductive because its ions are unable to flow ("electricity" is the flow of charged particles). When molten, however, it can conduct electricity because its ions are able to move freely through the liquid (Figure 2.7.3).
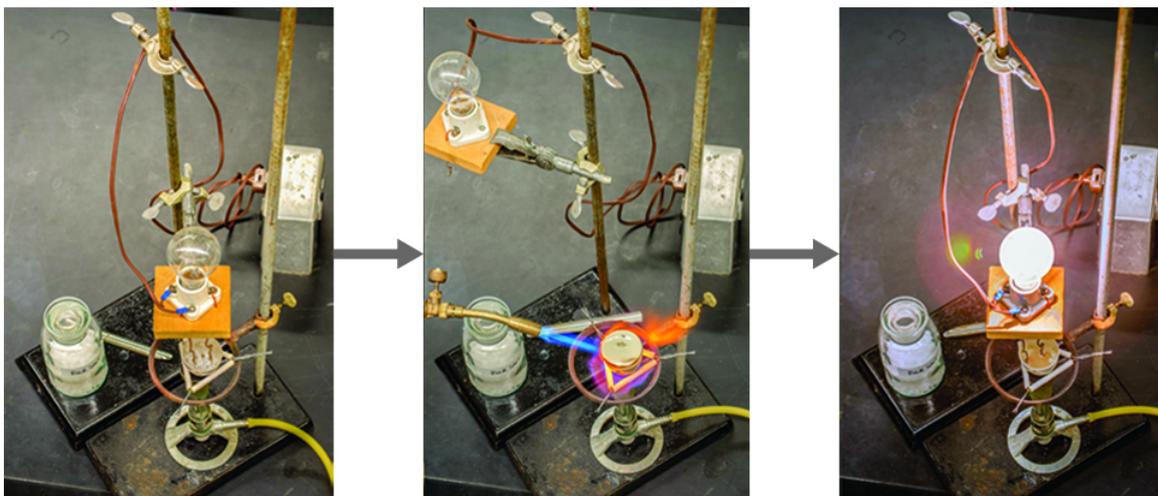

Table 2.7.3: Sodium chloride melts at 801 °C and conducts electricity when molten. (credit: modification of work by Mark Blaser and Matt Evans)

In every ionic compound, the total number of positive charges of the cations equals the total number of negative charges of the anions. Thus, ionic compounds are electrically neutral overall, even though they contain positive and negative ions. We can use this observation to help us write the formula of an ionic compound. The formula of an ionic compound must have a ratio of ions such that the numbers of positive and negative charges are equal.

✔ Example 2.7.3: Predicting the Formula of an Ionic Compound

The gemstone sapphire (Figure 2.7.4) is mostly a compound of aluminum and oxygen that contains aluminum cations, Al^{3+}, and oxygen anions, O^{2-}. What is the formula of this compound?

Table 2.7.4: Although pure aluminum oxide is colorless, trace amounts of iron and titanium give blue sapphire its characteristic color. (credit: modification of work by Stanislav Doronenko via Wikipedia)

Solution

Because the ionic compound must be electrically neutral, it must have the same number of positive and negative charges. Two aluminum ions, each with a charge of 3+, would give us six positive charges, and three oxide ions, each with a charge of 2−, would give us six negative charges. The formula would be Al_2O_3.

❓ Exercise 2.7.3

Predict the formula of the ionic compound formed between the sodium cation, Na^+, and the sulfide anion, S^{2-}.

Answer

Na_2S

Many ionic compounds contain polyatomic ions (Table 2.7.1) as the cation, the anion, or both. As with simple ionic compounds, these compounds must also be electrically neutral, so their formulas can be predicted by treating the polyatomic ions as discrete units. We use parentheses in a formula to indicate a group of atoms that behave as a unit. For example, the formula for calcium phosphate, one of the minerals in our bones, is $Ca_3(PO_4)_2$. This formula indicates that there are three calcium ions (Ca^{2+}) for every two phosphate (PO_4^{3-}) groups. The PO_4^{3-} groups are discrete units, each consisting of one phosphorus atom and four oxygen atoms, and having an overall charge of 3−. The compound is electrically neutral, and its formula shows a total count of three Ca, two P, and eight O atoms.

✔ Example 2.7.4: Predicting the Formula of a Compound with a Polyatomic Anion

Baking powder contains calcium dihydrogen phosphate, an ionic compound composed of the ions Ca^{2+} and $H_2PO_4^-$. What is the formula of this compound?

Solution

The positive and negative charges must balance, and this ionic compound must be electrically neutral. Thus, we must have two negative charges to balance the 2+ charge of the calcium ion. This requires a ratio of one Ca^{2+} ion to two $H_2PO_4^-$ ions. We

designate this by enclosing the formula for the dihydrogen phosphate ion in parentheses and adding a subscript 2. The formula is $Ca(H_2PO_4)_2$.

? Exercise 2.7.4

Predict the formula of the ionic compound formed between the lithium ion and the peroxide ion, O_2^{2-} (Hint: Use the periodic table to predict the sign and the charge on the lithium ion.)

Answer

Li_2O_2

Because an ionic compound is not made up of single, discrete molecules, it may not be properly symbolized using a *molecular* formula. Instead, ionic compounds must be symbolized by a formula indicating the relative numbers of its constituent ions. For compounds containing only monatomic ions (such as $NaCl$) and for many compounds containing polyatomic ions (such as $CaSO_4$), these formulas are just the empirical formulas introduced earlier in this chapter. However, the formulas for some ionic compounds containing polyatomic ions are not empirical formulas. For example, the ionic compound sodium oxalate is comprised of Na^+ and $C_2O_4^{2-}$ ions combined in a 2:1 ratio, and its formula is written as $Na_2C_2O_4$. The subscripts in this formula are not the smallest-possible whole numbers, as each can be divided by 2 to yield the empirical formula, $NaCO_2$. This is not the accepted formula for sodium oxalate, however, as it does not accurately represent the compound's polyatomic anion, $C_2O_4^{2-}$.

Molecular Compounds

Many compounds do not contain ions but instead consist solely of discrete, neutral molecules. These molecular compounds (covalent compounds) result when atoms share, rather than transfer (gain or lose), electrons. Covalent bonding is an important and extensive concept in chemistry, and it will be treated in considerable detail in a later chapter of this text. We can often identify molecular compounds on the basis of their physical properties. Under normal conditions, molecular compounds often exist as gases, low-boiling liquids, and low-melting solids, although many important exceptions exist.

Whereas ionic compounds are usually formed when a metal and a nonmetal combine, covalent compounds are usually formed by a combination of nonmetals. Thus, the periodic table can help us recognize many of the compounds that are covalent. While we can use the positions of a compound's elements in the periodic table to predict whether it is ionic or covalent at this point in our study of chemistry, you should be aware that this is a very simplistic approach that does not account for a number of interesting exceptions. Shades of gray exist between ionic and molecular compounds, and you'll learn more about those later.

✔ Example 2.7.5: Predicting the Type of Bonding in Compounds

Predict whether the following compounds are ionic or molecular:

a. KI, the compound used as a source of iodine in table salt
b. H_2O_2, the bleach and disinfectant hydrogen peroxide
c. $CHCl_3$, the anesthetic chloroform
d. Li_2CO_3, a source of lithium in antidepressants

Solution
a. Potassium (group 1) is a metal, and iodine (group 17) is a nonmetal; KI is predicted to be ionic.
b. Hydrogen (group 1) is a nonmetal, and oxygen (group 16) is a nonmetal; H_2O_2 is predicted to be molecular.
c. Carbon (group 14) is a nonmetal, hydrogen (group 1) is a nonmetal, and chlorine (group 17) is a nonmetal; $CHCl_3$ is predicted to be molecular.
d. Lithium (group 1) is a metal, and carbonate is a polyatomic ion; Li_2CO_3 is predicted to be ionic.

? Exercise 2.7.5

Using the periodic table, predict whether the following compounds are ionic or covalent:

a. SO_2
b. CaF_2

---

c. N_2H_4
d. $Al_2(SO_4)_3$

Answer

a. molecular
b. ionic
c. molecular
d. ionic

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2.8: Chemical Nomenclature

> **◑ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Derive names for common types of inorganic compounds using a systematic approach

Nomenclature, a collection of rules for naming things, is important in science and in many other situations. This module describes an approach that is used to name simple ionic and molecular compounds, such as NaCl, $CaCO_3$, and N_2O_4. The simplest of these are **binary compounds**, those containing only two elements, but we will also consider how to name ionic compounds containing polyatomic ions, and one specific, very important class of compounds known as acids (subsequent chapters in this text will focus on these compounds in great detail). We will limit our attention here to inorganic compounds, compounds that are composed principally of elements other than carbon, and will follow the nomenclature guidelines proposed by IUPAC. The rules for organic compounds, in which carbon is the principle element, will be treated in a later chapter on organic chemistry.

Ionic Compounds

To name an inorganic compound, we need to consider the answers to several questions. First, is the compound ionic or molecular? If the compound is ionic, does the metal form ions of only one type (fixed charge) or more than one type (variable charge)? Are the ions monatomic or polyatomic? If the compound is molecular, does it contain hydrogen? If so, does it also contain oxygen? From the answers we derive, we place the compound in an appropriate category and then name it accordingly.

Compounds Containing Only Monatomic Ions

The name of a binary compound containing monatomic ions consists of the name of the cation (the name of the metal) followed by the name of the anion (the name of the nonmetallic element with its ending replaced by the suffix *–ide*). Some examples are given in Table 2.8.1.

Table 2.8.1: Names of Some Ionic Compounds

NaCl, sodium chloride	Na_2O, sodium oxide
KBr, potassium bromide	CdS, cadmium sulfide
CaI_2, calcium iodide	Mg_3N_2, magnesium nitride
CsF, cesium fluoride	Ca_3P_2, calcium phosphide
LiCl, lithium chloride	Al_4C_3, aluminum carbide

Compounds Containing Polyatomic Ions

Compounds containing polyatomic ions are named similarly to those containing only monatomic ions, i.e. by naming first the cation and then the anion. Examples are shown in Table 2.8.2.

Table 2.8.2: Names of Some Polyatomic Ionic Compounds

$KC_2H_3O_2$, potassium acetate	NH_4Cl, ammonium chloride
$NaHCO_3$, sodium bicarbonate	$CaSO_4$, calcium sulfate
$Al_2(CO_3)_3$, aluminum carbonate	$Mg_3(PO_4)_2$, magnesium phosphate

> **📌 Chemistry in Everyday Life: Ionic Compounds in Your Cabinet**
>
> Every day you encounter and use a large number of ionic compounds. Some of these compounds, where they are found, and what they are used for are listed in Table 2.8.3. Look at the label or ingredients list on the various products that you use during the next few days, and see if you run into any of those in this table, or find other ionic compounds that you could now name or write as a formula.

Table 2.8.3: Everyday Ionic Compounds

Ionic Compound	Use
NaCl, sodium chloride	ordinary table salt
KI, potassium iodide	added to "iodized" salt for thyroid health
NaF, sodium fluoride	ingredient in toothpaste
$NaHCO_3$, sodium bicarbonate	baking soda; used in cooking (and as antacid)
Na_2CO_3, sodium carbonate	washing soda; used in cleaning agents
NaOCl, sodium hypochlorite	active ingredient in household bleach
$CaCO_3$ calcium carbonate	ingredient in antacids
$Mg(OH)_2$, magnesium hydroxide	ingredient in antacids
$Al(OH)_3$, aluminum hydroxide	ingredient in antacids
NaOH, sodium hydroxide	lye; used as drain cleaner
K_3PO_4, potassium phosphate	food additive (many purposes)
$MgSO_4$, magnesium sulfate	added to purified water
Na_2HPO_4, sodium hydrogen phosphate	anti-caking agent; used in powdered products
Na_2SO_3, sodium sulfite	preservative

Compounds Containing a Metal Ion with a Variable Charge

Most of the transition metals and some main group metals can form two or more cations with different charges. Compounds of these metals with nonmetals are named with the same method as compounds in the first category, except the charge of the metal ion is specified by a Roman numeral in parentheses after the name of the metal. The charge of the metal ion is determined from the formula of the compound and the charge of the anion. For example, consider binary ionic compounds of iron and chlorine. Iron typically exhibits a charge of either 2+ or 3+ (see Figure 2.29), and the two corresponding compound formulas are $FeCl_2$ and $FeCl_3$. The simplest name, "iron chloride," will, in this case, be ambiguous, as it does not distinguish between these two compounds. In cases like this, the charge of the metal ion is included as a Roman numeral in parentheses immediately following the metal name. These two compounds are then unambiguously named iron(II) chloride and iron(III) chloride, respectively. Other examples are provided in Table 2.8.4.

Table 2.8.4: Some Ionic Compounds with Variably Charged Metal Ions

Compound	Name
$FeCl_2$	iron(II) chloride
$FeCl_3$	iron(III) chloride
Hg_2O	mercury(I) oxide
HgO	mercury(II) oxide
SnF_2	tin(II) fluoride
SnF_4	tin(IV) fluoride

Out-of-date nomenclature used the suffixes –*ic* and –*ous* to designate metals with higher and lower charges, respectively: Iron(III) chloride, $FeCl_3$, was previously called ferric chloride, and iron(II) chloride, $FeCl_2$, was known as ferrous chloride. Though this naming convention has been largely abandoned by the scientific community, it remains in use by some segments of industry. For example, you may see the words *stannous fluoride* on a tube of toothpaste. This represents the formula SnF_2, which is more

properly named tin(II) fluoride. The other fluoride of tin is SnF$_4$, which was previously called stannic fluoride but is now named tin(IV) fluoride.

Ionic Hydrates

Ionic compounds that contain water molecules as integral components of their crystals are called **hydrates**. The name for an ionic hydrate is derived by adding a term to the name for the anhydrous (meaning "not hydrated") compound that indicates the number of water molecules associated with each formula unit of the compound. The added word begins with a Greek prefix denoting the number of water molecules (see Table 2.8.5) and ends with "hydrate." For example, the anhydrous compound copper(II) sulfate also exists as a hydrate containing five water molecules and named copper(II) sulfate pentahydrate. Washing soda is the common name for a hydrate of sodium carbonate containing 10 water molecules; the systematic name is sodium carbonate decahydrate.

Formulas for ionic hydrates are written by appending a vertically centered dot, a coefficient representing the number of water molecules, and the formula for water. The two examples mentioned in the previous paragraph are represented by the formulas

$$\text{copper(II) sulfate pentahydrate} \quad CuSO_4 \cdot 5\,H_2O$$

$$\text{sodium carbonate decahydrate} \quad Na_2CO_3 \cdot 10\,H_2O$$
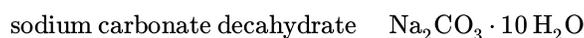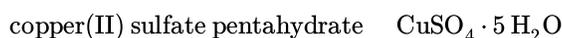
Table 2.8.5: Nomenclature Prefixes

Number	Prefix	Number	Prefix
1 (sometimes omitted)	mono-	6	hexa-
2	di-	7	hepta-
3	tri-	8	octa-
4	tetra-	9	nona-
5	penta-	10	deca-

✔ Example 2.8.1: Naming Ionic Compounds

Name the following ionic compounds

a. Fe$_2$S$_3$
b. CuSe
c. GaN
d. MgSO$_4$·7H$_2$O
e. Ti$_2$(SO$_4$)$_3$

Solution

The anions in these compounds have a fixed negative charge (S^{2-}, Se^{2-}, N^{3-}, and and the compounds must be neutral. Because the total number of positive charges in each compound must equal the total number of negative charges, the positive ions must be Fe^{3+}, Cu^{2+}, Ga^{3+}, Mg^{2+}, and Ti^{3+}. These charges are used in the names of the metal ions:

a. iron(III) sulfide
b. copper(II) selenide
c. gallium(III) nitride
d. magnesium sulfate heptahydrate
e. titanium(III) sulfate

? Exercise 2.8.1

Write the formulas of the following ionic compounds:

a. chromium(III) phosphide
b. mercury(II) sulfide
c. manganese(II) phosphate

d. copper(I) oxide

e. iron(III) chloride dihydrate

Answer

(a) CrP; (b) HgS; (c) $Mn_3(PO_4)_2$; (d) Cu_2O; (e) $FeCl_3 \cdot 2H_2O$

📌 Chemistry in Everyday Life: Erin Brockovich and Chromium Contamination

In the early 1990s, legal file clerk Erin Brockovich (Figure 2.8.1) discovered a high rate of serious illnesses in the small town of Hinckley, California. Her investigation eventually linked the illnesses to groundwater contaminated by Cr(VI) used by Pacific Gas & Electric (PG&E) to fight corrosion in a nearby natural gas pipeline. As dramatized in the film *Erin Brockovich* (for which Julia Roberts won an Oscar), Erin and lawyer Edward Masry sued PG&E for contaminating the water near Hinckley in 1993. The settlement they won in 1996—$333 million—was the largest amount ever awarded for a direct-action lawsuit in the US at that time.
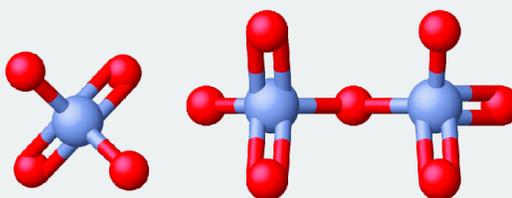
(a) (b)

Figure 2.8.1: (a) Erin Brockovich found that Cr(VI), used by PG&E, had contaminated the Hinckley, California, water supply. (b) The Cr(VI) ion is often present in water as the polyatomic ions chromate, (left), and dichromate, (right).

Chromium compounds are widely used in industry, such as for chrome plating, in dye-making, as preservatives, and to prevent corrosion in cooling tower water, as occurred near Hinckley. In the environment, chromium exists primarily in either the Cr(III) or Cr(VI) forms. Cr(III), an ingredient of many vitamin and nutritional supplements, forms compounds that are not very soluble in water, and it has low toxicity. But Cr(VI) is much more toxic and forms compounds that are reasonably soluble in water. Exposure to small amounts of Cr(VI) can lead to damage of the respiratory, gastrointestinal, and immune systems, as well as the kidneys, liver, blood, and skin.

Despite cleanup efforts, Cr(VI) groundwater contamination remains a problem in Hinckley and other locations across the globe. A 2010 study by the Environmental Working Group found that of 35 US cities tested, 31 had higher levels of Cr(VI) in their tap water than the public health goal of 0.02 parts per billion set by the California Environmental Protection Agency.

Molecular (Covalent) Compounds

The bonding characteristics of inorganic molecular compounds are different from ionic compounds, and they are named using a different system as well. The charges of cations and anions dictate their ratios in ionic compounds, so specifying the names of the ions provides sufficient information to determine chemical formulas. However, because covalent bonding allows for significant variation in the combination ratios of the atoms in a molecule, the names for molecular compounds must explicitly identify these ratios.

Compounds Composed of Two Elements

When two nonmetallic elements form a molecular compound, several combination ratios are often possible. For example, carbon and oxygen can form the compounds CO and CO_2. Since these are different substances with different properties, they cannot both have the same name (they cannot both be called carbon oxide). To deal with this situation, we use a naming method that is somewhat similar to that used for ionic compounds, but with added prefixes to specify the numbers of atoms of each element. The name of the more metallic element (the one farther to the left and/or bottom of the periodic table) is first, followed by the name of the more nonmetallic element (the one farther to the right and/or top) with its ending changed to the suffix –*ide*. The numbers of atoms of each element are designated by the Greek prefixes shown in Table 2.8.5.

When only one atom of the first element is present, the prefix *mono-* is usually deleted from that part. Thus, CO is named carbon monoxide, and CO_2 is called carbon dioxide. When two vowels are adjacent, the *a* in the Greek prefix is usually dropped. Some other examples are shown in Table 2.8.6.

Table 2.8.6: Names of Some Molecular Compounds Composed of Two Elements

Compound	Name	Compound	Name
SO_2	sulfur dioxide	BCl_3	boron trichloride
SO_3	sulfur trioxide	SF_6	sulfur hexafluoride
NO_2	nitrogen dioxide	PF_5	phosphorus pentafluoride
N_2O_4	dinitrogen tetroxide	P_4O_{10}	tetraphosphorus decaoxide
N_2O_5	dinitrogen pentoxide	IF_7	iodine heptafluoride

There are a few common names that you will encounter as you continue your study of chemistry. For example, although NO is often called nitric oxide, its proper name is nitrogen monoxide. Similarly, N_2O is known as nitrous oxide even though our rules would specify the name dinitrogen monoxide. (And H_2O is usually called water, not dihydrogen monoxide.) You should commit to memory the common names of compounds as you encounter them.

> ### ✔ Example 2.8.2: Naming Covalent Compounds
>
> Name the following covalent compounds:
>
> a. SF_6
> b. N_2O_3
> c. Cl_2O_7
> d. P_4O_6
>
> **Solution**
>
> Because these compounds consist solely of nonmetals, we use prefixes to designate the number of atoms of each element:
>
> a. sulfur hexafluoride
> b. dinitrogen trioxide
> c. dichlorine heptoxide
> d. tetraphosphorus hexoxide

> ### ? Exercise 2.8.2
>
> Write the formulas for the following compounds:
>
> a. phosphorus pentachloride
> b. dinitrogen monoxide
> c. iodine heptafluoride
> d. carbon tetrachloride
>
> **Answer**
>
> (a) PCl_5; (b) N_2O; (c) IF_7; (d) CCl_4

> ### 📌 Link to Learning
>
> The following website provides practice with naming chemical compounds and writing chemical formulas. You can choose binary, polyatomic, and variable charge ionic compounds, as well as molecular compounds.

Binary Acids

Some compounds containing hydrogen are members of an important class of substances known as **acids**. The chemistry of these compounds is explored in more detail in later chapters of this text, but for now, it will suffice to note that many acids release hydrogen ions, H^+, when dissolved in water. To denote this distinct chemical property, a mixture of water with an acid is given a name derived from the compound's name. If the compound is a binary acid (comprised of hydrogen and one other nonmetallic element):

1. The word "hydrogen" is changed to the prefix *hydro-*
2. The other nonmetallic element name is modified by adding the suffix *-ic*
3. The word "acid" is added as a second word

For example, when the gas HCl (hydrogen chloride) is dissolved in water, the solution is called *hydrochloric acid*. Several other examples of this nomenclature are shown in Table 2.8.7.

Table 2.8.7: Names of Some Simple Acids

Name of Gas	Name of Acid
HF(g), hydrogen fluoride	HF(aq), hydrofluoric acid
HCl(g), hydrogen chloride	HCl(aq), hydrochloric acid
HBr(g), hydrogen bromide	HBr(aq), hydrobromic acid
HI(g), hydrogen iodide	HI(aq), hydroiodic acid
H_2S(g), hydrogen sulfide	H_2S(aq), hydrosulfuric acid

Oxyacids

Many compounds containing three or more elements (such as organic compounds or coordination compounds) are subject to specialized nomenclature rules that you will learn later. However, we will briefly discuss the important compounds known as **oxyacids**, compounds that contain hydrogen, oxygen, and at least one other element, and are bonded in such a way as to impart acidic properties to the compound (you will learn the details of this in a later chapter). Typical oxyacids consist of hydrogen combined with a polyatomic, oxygen-containing ion. To name oxyacids:

1. Omit "hydrogen"
2. Start with the root name of the anion
3. Replace *–ate* with *–ic*, or *–ite* with *–ous*
4. Add "acid"

For example, consider H_2CO_3 (which you might be tempted to call "hydrogen carbonate"). To name this correctly, "hydrogen" is omitted; the *–ate* of carbonate is replace with *–ic*; and acid is added—so its name is carbonic acid. Other examples are given in Table 2.8.8. There are some exceptions to the general naming method (e.g., H_2SO_4 is called sulfuric acid, not sulfic acid, and H_2SO_3 is sulfurous, not sulfous, acid).

Table 2.8.8: Names of Common Oxyacids

Formula	Anion Name	Acid Name
$HC_2H_3O_2$	acetate	acetic acid
HNO_3	nitrate	nitric acid
HNO_2	nitrite	nitrous acid
$HClO_4$	perchlorate	perchloric acid
H_2CO_3	carbonate	carbonic acid
H_2SO_4	sulfate	sulfuric acid
H_2SO_3	sulfite	sulfurous acid

Formula	Anion Name	Acid Name
H_3PO_4	phosphate	phosphoric acid

2.9: Key Terms

actinide | inner transition metal in the bottom of the bottom two rows of the periodic table

alkali metal | element in group 1

alkaline earth metal | element in group 2

alpha particle (α particle) | positively charged particle consisting of two protons and two neutrons

anion | negatively charged atom or molecule (contains more electrons than protons)

atomic mass | average mass of atoms of an element, expressed in amu

atomic mass unit (amu) | (also, unified atomic mass unit, u, or Dalton, Da) unit of mass equal to of the mass of a ^{12}C atom

atomic number (Z) | number of protons in the nucleus of an atom

binary acid | compound that contains hydrogen and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

binary compound | compound containing two different elements.

cation | positively charged atom or molecule (contains fewer electrons than protons)

chalcogen | element in group 16

chemical symbol | one-, two-, or three-letter abbreviation used to represent an element or its atoms

covalent bond | attractive force between the nuclei of a molecule's atoms and pairs of electrons between the atoms

covalent compound | (also, molecular compound) composed of molecules formed by atoms of two or more different elements

Dalton (Da) | alternative unit equivalent to the atomic mass unit

Dalton's atomic theory | set of postulates that established the fundamental properties of atoms

electron | negatively charged, subatomic particle of relatively low mass located outside the nucleus

empirical formula | formula showing the composition of a compound given as the simplest whole-number ratio of atoms

fundamental unit of charge | (also called the elementary charge) equals the magnitude of the charge of an electron (e) with e = 1.602 10^{-19} C

group | vertical column of the periodic table

halogen | element in group 17

hydrate | compound containing one or more water molecules bound within its crystals

inert gas | (also, noble gas) element in group 18

inner transition metal | (also, lanthanide or actinide) element in the bottom two rows; if in the first row, also called lanthanide, or if in the second row, also called actinide

ion | electrically charged atom or molecule (contains unequal numbers of protons and electrons)

ionic bond | electrostatic forces of attraction between the oppositely charged ions of an ionic compound

ionic compound | compound composed of cations and anions combined in ratios, yielding an electrically neutral substance

isomers | compounds with the same chemical formula but different structures

isotopes | atoms that contain the same number of protons but different numbers of neutrons

lanthanide | inner transition metal in the top of the bottom two rows of the periodic table

law of constant composition | (also, law of definite proportions) all samples of a pure compound contain the same elements in the same proportions by mass

law of definite proportions | (also, law of constant composition) all samples of a pure compound contain the same elements in the same proportions by mass

law of multiple proportions | when two elements react to form more than one compound, a fixed mass of one element will react with masses of the other element in a ratio of small whole numbers

main-group element | (also, representative element) element in groups 1, 2, and 13–18

mass number (A) | sum of the numbers of neutrons and protons in the nucleus of an atom

metal | element that is shiny, malleable, good conductor of heat and electricity

metalloid | element that conducts heat and electricity moderately well, and possesses some properties of metals and some properties of nonmetals

molecular compound | (also, covalent compound) composed of molecules formed by atoms of two or more different elements

molecular formula | formula indicating the composition of a molecule of a compound and giving the actual number of atoms of each element in a molecule of the compound.

monatomic ion | ion composed of a single atom

neutron | uncharged, subatomic particle located in the nucleus

noble gas | (also, inert gas) element in group 18

nomenclature | system of rules for naming objects of interest

nonmetal | element that appears dull, poor conductor of heat and electricity

nucleus | massive, positively charged center of an atom made up of protons and neutrons

oxyacid | compound that contains hydrogen, oxygen, and one other element, bonded in a way that imparts acidic properties to the compound (ability to release H^+ ions when dissolved in water)

oxyanion | polyatomic anion composed of a central atom bonded to oxygen atoms

period | (also, series) horizontal row of the periodic table

periodic law | properties of the elements are periodic function of their atomic numbers.

periodic table | table of the elements that places elements with similar chemical properties close together

pnictogen | element in group 15

polyatomic ion | ion composed of more than one atom

proton | positively charged, subatomic particle located in the nucleus

representative element | (also, main-group element) element in columns 1, 2, and 12–18

series | (also, period) horizontal row of the period table

spatial isomers | compounds in which the relative orientations of the atoms in space differ

structural formula | shows the atoms in a molecule and how they are connected

structural isomer | one of two substances that have the same molecular formula but different physical and chemical properties because their atoms are bonded differently

transition metal | element in groups 3–12 (more strictly defined, 3–11; see chapter on transition metals and coordination chemistry)

unified atomic mass unit (u) | alternative unit equivalent to the atomic mass unit

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2.11: Summary

The ancient Greeks proposed that matter consists of extremely small particles called atoms. Dalton postulated that each element has a characteristic type of atom that differs in properties from atoms of all other elements, and that atoms of different elements can combine in fixed, small, whole-number ratios to form compounds. Samples of a particular compound all have the same elemental proportions by mass. When two elements form different compounds, a given mass of one element will combine with masses of the other element in a small, whole-number ratio. During any chemical change, atoms are neither created nor destroyed.

Although no one has actually seen the inside of an atom, experiments have demonstrated much about atomic structure. Thomson's cathode ray tube showed that atoms contain small, negatively charged particles called electrons. Millikan discovered that there is a fundamental electric charge—the charge of an electron. Rutherford's gold foil experiment showed that atoms have a small, dense, positively charged nucleus; the positively charged particles within the nucleus are called protons. Chadwick discovered that the nucleus also contains neutral particles called neutrons. Soddy demonstrated that atoms of the same element can differ in mass; these are called isotopes.

An atom consists of a small, positively charged nucleus surrounded by electrons. The nucleus contains protons and neutrons; its diameter is about 100,000 times smaller than that of the atom. The mass of one atom is usually expressed in atomic mass units (amu), which is referred to as the atomic mass. An amu is defined as exactly of the mass of a carbon-12 atom and is equal to 1.6605 10^{-24} g.

Protons are relatively heavy particles with a charge of 1+ and a mass of 1.0073 amu. Neutrons are relatively heavy particles with no charge and a mass of 1.0087 amu. Electrons are light particles with a charge of 1− and a mass of 0.00055 amu. The number of protons in the nucleus is called the atomic number (Z) and is the property that defines an atom's elemental identity. The sum of the numbers of protons and neutrons in the nucleus is called the mass number and, expressed in amu, is approximately equal to the mass of the atom. An atom is neutral when it contains equal numbers of electrons and protons.

Isotopes of an element are atoms with the same atomic number but different mass numbers; isotopes of an element, therefore, differ from each other only in the number of neutrons within the nucleus. When a naturally occurring element is composed of several isotopes, the atomic mass of the element represents the average of the masses of the isotopes involved. A chemical symbol identifies the atoms in a substance using symbols, which are one-, two-, or three-letter abbreviations for the atoms.

A molecular formula uses chemical symbols and subscripts to indicate the exact numbers of different atoms in a molecule or compound. An empirical formula gives the simplest, whole-number ratio of atoms in a compound. A structural formula indicates the bonding arrangement of the atoms in the molecule. Ball-and-stick and space-filling models show the geometric arrangement of atoms in a molecule. Isomers are compounds with the same molecular formula but different arrangements of atoms.

The discovery of the periodic recurrence of similar properties among the elements led to the formulation of the periodic table, in which the elements are arranged in order of increasing atomic number in rows known as periods and columns known as groups. Elements in the same group of the periodic table have similar chemical properties. Elements can be classified as metals, metalloids, and nonmetals, or as a main-group elements, transition metals, and inner transition metals. Groups are numbered 1–18 from left to right. The elements in group 1 are known as the alkali metals; those in group 2 are the alkaline earth metals; those in 15 are the pnictogens; those in 16 are the chalcogens; those in 17 are the halogens; and those in 18 are the noble gases.

Metals (particularly those in groups 1 and 2) tend to lose the number of electrons that would leave them with the same number of electrons as in the preceding noble gas in the periodic table. By this means, a positively charged ion is formed. Similarly, nonmetals (especially those in groups 16 and 17, and, to a lesser extent, those in Group 15) can gain the number of electrons needed to provide atoms with the same number of electrons as in the next noble gas in the periodic table. Thus, nonmetals tend to form negative ions. Positively charged ions are called cations, and negatively charged ions are called anions. Ions can be either monatomic (containing only one atom) or polyatomic (containing more than one atom).

Compounds that contain ions are called ionic compounds. Ionic compounds generally form from metals and nonmetals. Compounds that do not contain ions, but instead consist of atoms bonded tightly together in molecules (uncharged groups of atoms that behave as a single unit), are called covalent compounds. Covalent compounds usually form from two nonmetals.

Chemists use nomenclature rules to clearly name compounds. Ionic and molecular compounds are named using somewhat-different methods. Binary ionic compounds typically consist of a metal and a nonmetal. The name of the metal is written first, followed by the name of the nonmetal with its ending changed to –*ide*. For example, K_2O is called potassium oxide. If the metal can form ions with different charges, a Roman numeral in parentheses follows the name of the metal to specify its charge. Thus, $FeCl_2$ is iron(II)

chloride and FeCl$_3$ is iron(III) chloride. Some compounds contain polyatomic ions; the names of common polyatomic ions should be memorized. Molecular compounds can form compounds with different ratios of their elements, so prefixes are used to specify the numbers of atoms of each element in a molecule of the compound. Examples include SF$_6$, sulfur hexafluoride, and N$_2$O$_4$, dinitrogen tetroxide. Acids are an important class of compounds containing hydrogen and having special nomenclature rules. Binary acids are named using the prefix *hydro-*, changing the *–ide* suffix to *–ic*, and adding "acid;" HCl is hydrochloric acid. Oxyacids are named by changing the ending of the anion (*–ate* to *–ic* and *–ite* to *–ous*), and adding "acid;" H$_2$CO$_3$ is carbonic acid.

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2.12: Exercises

1.

In the following drawing, the green spheres represent atoms of a certain element. The purple spheres represent atoms of another element. If the spheres of different elements touch, they are part of a single unit of a compound. The following chemical change represented by these spheres may violate one of the ideas of Dalton's atomic theory. Which one?

Starting materials   Products of the change
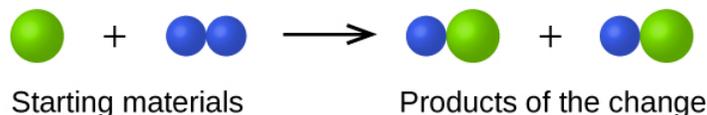
2.

Which postulate of Dalton's theory is consistent with the following observation concerning the weights of reactants and products? When 100 grams of solid calcium carbonate is heated, 44 grams of carbon dioxide and 56 grams of calcium oxide are produced.

3.

Identify the postulate of Dalton's theory that is violated by the following observations: 59.95% of one sample of titanium dioxide is titanium; 60.10% of a different sample of titanium dioxide is titanium.

4.

Samples of compound X, Y, and Z are analyzed, with results shown here.

Compound	Description	Mass of Carbon	Mass of Hydrogen
X	clear, colorless, liquid with strong odor	1.776 g	0.148 g
Y	clear, colorless, liquid with strong odor	1.974 g	0.329 g
Z	clear, colorless, liquid with strong odor	7.812 g	0.651 g

Do these data provide example(s) of the law of definite proportions, the law of multiple proportions, neither, or both? What do these data tell you about compounds X, Y, and Z?

5.

The existence of isotopes violates one of the original ideas of Dalton's atomic theory. Which one?

6.

How are electrons and protons similar? How are they different?

7.

How are protons and neutrons similar? How are they different?

8.

Predict and test the behavior of α particles fired at a "plum pudding" model atom.

a. Predict the paths taken by α particles that are fired at atoms with a Thomson's plum pudding model structure. Explain why you expect the α particles to take these paths.
b. If α particles of higher energy than those in (a) are fired at plum pudding atoms, predict how their paths will differ from the lower-energy α particle paths. Explain your reasoning.
c. Now test your predictions from (a) and (b). Open the Rutherford Scattering simulation and select the "Plum Pudding Atom" tab. Set "Alpha Particles Energy" to "min," and select "show traces." Click on the gun to start firing α particles. Does this match your prediction from (a)? If not, explain why the actual path would be that shown in the simulation. Hit the pause button, or "Reset All." Set "Alpha Particles Energy" to "max," and start firing α particles. Does this match your prediction from (b)? If not, explain the effect of increased energy on the actual paths as shown in the simulation.

9.

Predict and test the behavior of α particles fired at a Rutherford atom model.

   a. Predict the paths taken by α particles that are fired at atoms with a Rutherford atom model structure. Explain why you expect the α particles to take these paths.
   b. If α particles of higher energy than those in (a) are fired at Rutherford atoms, predict how their paths will differ from the lower-energy α particle paths. Explain your reasoning.
   c. Predict how the paths taken by the α particles will differ if they are fired at Rutherford atoms of elements other than gold. What factor do you expect to cause this difference in paths, and why?
   d. Now test your predictions from (a), (b), and (c). Open the Rutherford Scattering simulation and select the "Rutherford Atom" tab. Due to the scale of the simulation, it is best to start with a small nucleus, so select "20" for both protons and neutrons, "min" for energy, show traces, and then start firing α particles. Does this match your prediction from (a)? If not, explain why the actual path would be that shown in the simulation. Pause or reset, set energy to "max," and start firing α particles. Does this match your prediction from (b)? If not, explain the effect of increased energy on the actual path as shown in the simulation. Pause or reset, select "40" for both protons and neutrons, "min" for energy, show traces, and fire away. Does this match your prediction from (c)? If not, explain why the actual path would be that shown in the simulation. Repeat this with larger numbers of protons and neutrons. What generalization can you make regarding the type of atom and effect on the path of α particles? Be clear and specific.

10.

In what way are isotopes of a given element always different? In what way(s) are they always the same?

11.

Write the symbol for each of the following ions:

   a. the ion with a 1+ charge, atomic number 55, and mass number 133
   b. the ion with 54 electrons, 53 protons, and 74 neutrons
   c. the ion with atomic number 15, mass number 31, and a 3− charge
   d. the ion with 24 electrons, 30 neutrons, and a 3+ charge

12.

Write the symbol for each of the following ions:

   a. the ion with a 3+ charge, 28 electrons, and a mass number of 71
   b. the ion with 36 electrons, 35 protons, and 45 neutrons
   c. the ion with 86 electrons, 142 neutrons, and a 4+ charge
   d. the ion with a 2+ charge, atomic number 38, and mass number 87

13.

Open the Build an Atom simulation and click on the Atom icon.

(a) Pick any one of the first 10 elements that you would like to build and state its symbol.

(b) Drag protons, neutrons, and electrons onto the atom template to make an atom of your element.
State the numbers of protons, neutrons, and electrons in your atom, as well as the net charge and mass number.

(c) Click on "Net Charge" and "Mass Number," check your answers to (b), and correct, if needed.

(d) Predict whether your atom will be stable or unstable. State your reasoning.

(e) Check the "Stable/Unstable" box. Was your answer to (d) correct? If not, first predict what you can do to make a stable atom of your element, and then do it and see if it works. Explain your reasoning.

14.

Open the Build an Atom simulation.

   a. Drag protons, neutrons, and electrons onto the atom template to make a neutral atom of Oxygen-16 and give the isotope symbol for this atom.
   b. Now add two more electrons to make an ion and give the symbol for the ion you have created.

15.

Open the Build an Atom simulation.

  a. Drag protons, neutrons, and electrons onto the atom template to make a neutral atom of Lithium-6 and give the isotope symbol for this atom.

  b. Now remove one electron to make an ion and give the symbol for the ion you have created.

16.

Determine the number of protons, neutrons, and electrons in the following isotopes that are used in medical diagnoses:

  a. atomic number 9, mass number 18, charge of 1−

  b. atomic number 43, mass number 99, charge of 7+

  c. atomic number 53, atomic mass number 131, charge of 1−

  d. atomic number 81, atomic mass number 201, charge of 1+

  e. Name the elements in parts (a), (b), (c), and (d).

17.

The following are properties of isotopes of two elements that are essential in our diet. Determine the number of protons, neutrons and electrons in each and name them.

  a. atomic number 26, mass number 58, charge of 2+

  b. atomic number 53, mass number 127, charge of 1−

18.

Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:

  a. Boron-10

  b. Mercury-199

  c. Copper-63

  d. Carbon-13

  e. Selenium-77

19.

Give the number of protons, electrons, and neutrons in neutral atoms of each of the following isotopes:

  a. Lithium-7

  b. Tellurium-125

  c. Silver-109

  d. Nitrogen-15

  e. Phosphorus-31

20.

Click on the site and select the "Mix Isotopes" tab, hide the "Percent Composition" and "Average Atomic Mass" boxes, and then select the element boron.

  a. Write the symbols of the isotopes of boron that are shown as naturally occurring in significant amounts.

  b. Predict the relative amounts (percentages) of these boron isotopes found in nature. Explain the reasoning behind your choice.

  c. Add isotopes to the black box to make a mixture that matches your prediction in (b). You may drag isotopes from their bins or click on "More" and then move the sliders to the appropriate amounts.

  d. Reveal the "Percent Composition" and "Average Atomic Mass" boxes. How well does your mixture match with your prediction? If necessary, adjust the isotope amounts to match your prediction.

  e. Select "Nature's" mix of isotopes and compare it to your prediction. How well does your prediction compare with the naturally occurring mixture? Explain. If necessary, adjust your amounts to make them match "Nature's" amounts as closely as possible.

21.

Repeat Exercise 2.20 using an element that has three naturally occurring isotopes.

22.

An element has the following natural abundances and isotopic masses: 90.92% abundance with 19.99 amu, 0.26% abundance with 20.99 amu, and 8.82% abundance with 21.99 amu. Calculate the average atomic mass of this element.

23.

Average atomic masses listed by IUPAC are based on a study of experimental results. Bromine has two isotopes, ^{79}Br and ^{81}Br, whose masses (78.9183 and 80.9163 amu, respectively) and abundances (50.69% and 49.31%, respectively) were determined in earlier experiments. Calculate the average atomic mass of bromine based on these experiments.

24.

Variations in average atomic mass may be observed for elements obtained from different sources. Lithium provides an example of this. The isotopic composition of lithium from naturally occurring minerals is 7.5% ^{6}Li and 92.5% ^{7}Li, which have masses of 6.01512 amu and 7.01600 amu, respectively. A commercial source of lithium, recycled from a military source, was 3.75% ^{6}Li (and the rest ^{7}Li). Calculate the average atomic mass values for each of these two sources.

25.

The average atomic masses of some elements may vary, depending upon the sources of their ores. Naturally occurring boron consists of two isotopes with accurately known masses (^{10}B, 10.0129 amu and ^{11}B, 11.00931 amu). The actual atomic mass of boron can vary from 10.807 to 10.819, depending on whether the mineral source is from Turkey or the United States. Calculate the percent abundances leading to the two values of the average atomic masses of boron from these two countries.

26.

The ^{18}O:^{16}O abundance ratio in some meteorites is greater than that used to calculate the average atomic mass of oxygen on earth. Is the average mass of an oxygen atom in these meteorites greater than, less than, or equal to that of a terrestrial oxygen atom?

27.

Explain why the symbol for an atom of the element oxygen and the formula for a molecule of oxygen differ.

28.

Explain why the symbol for the element sulfur and the formula for a molecule of sulfur differ.

29.

Write the molecular and empirical formulas of the following compounds:
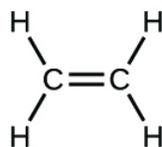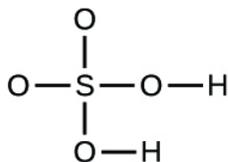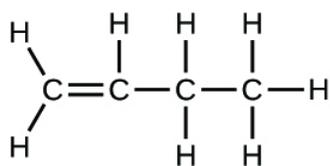
(a)

$$O=C=O$$

(b)

$$H-C\equiv C-H$$

(c)

(d)

30.

Write the molecular and empirical formulas of the following compounds:
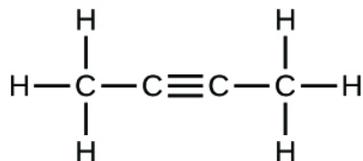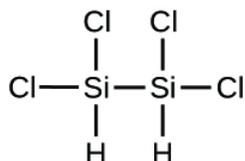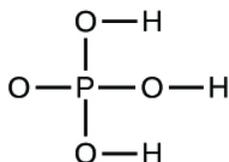
(a)

(b)

(c)

(d)

31.

Determine the empirical formulas for the following compounds:

a. caffeine, $C_8H_{10}N_4O_2$
b. sucrose, $C_{12}H_{22}O_{11}$
c. hydrogen peroxide, H_2O_2
d. glucose, $C_6H_{12}O_6$
e. ascorbic acid (vitamin C), $C_6H_8O_6$

32.

Determine the empirical formulas for the following compounds:

a. acetic acid, $C_2H_4O_2$
b. citric acid, $C_6H_8O_7$
c. hydrazine, N_2H_4
d. nicotine, $C_{10}H_{14}N_2$
e. butane, C_4H_{10}

33.

Write the empirical formulas for the following compounds:

(a)

(b)

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H$$
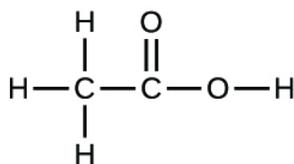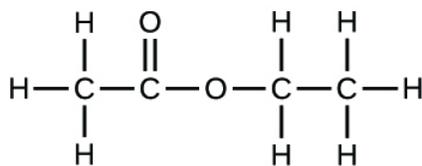
34.

Open the Build a Molecule simulation and select the "Larger Molecules" tab. Select an appropriate atom's "Kit" to build a molecule with two carbon and six hydrogen atoms. Drag atoms into the space above the "Kit" to make a molecule. A name will appear when you have made an actual molecule that exists (even if it is not the one you want). You can use the scissors tool to separate atoms if you would like to change the connections. Click on "3D" to see the molecule, and look at both the space-filling and ball-and-stick possibilities.

 a. Draw the structural formula of this molecule and state its name.
 b. Can you arrange these atoms in any way to make a different compound?

35.

Use the Build a Molecule simulation to repeat Exercise 2.34, but build a molecule with two carbons, six hydrogens, and one oxygen.

 a. Draw the structural formula of this molecule and state its name.
 b. Can you arrange these atoms to make a different molecule? If so, draw its structural formula and state its name.
 c. How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names).?

36.

Use the Build a Molecule simulation to repeat Exercise 2.34, but build a molecule with three carbons, seven hydrogens, and one chlorine.

 a. Draw the structural formula of this molecule and state its name.
 b. Can you arrange these atoms to make a different molecule? If so, draw its structural formula and state its name.
 c. How are the molecules drawn in (a) and (b) the same? How do they differ? What are they called (the type of relationship between these molecules, not their names)?

37.

Using the periodic table, classify each of the following elements as a metal or a nonmetal, and then further classify each as a main-group (representative) element, transition metal, or inner transition metal:

 a. (i) carbon

   (j) potassium

38.

Using the periodic table, classify each of the following elements as a metal or a nonmetal, and then further classify each as a main-group (representative) element, transition metal, or inner transition metal:

 a. (i) rhenium

39.

Using the periodic table, identify the lightest member of each of the following groups:

 a. noble gases
 b. alkaline earth metals
 c. alkali metals
 d. chalcogens

40.

Using the periodic table, identify the heaviest member of each of the following groups:

 a. alkali metals

b. chalcogens

c. noble gases

d. alkaline earth metals

41.

Use the periodic table to give the name and symbol for each of the following elements:

a. the noble gas in the same period as germanium

b. the alkaline earth metal in the same period as selenium

c. the halogen in the same period as lithium

d. the chalcogen in the same period as cadmium

42.

Use the periodic table to give the name and symbol for each of the following elements:

a. the halogen in the same period as the alkali metal with 11 protons

b. the alkaline earth metal in the same period with the neutral noble gas with 18 electrons

c. the noble gas in the same row as an isotope with 30 neutrons and 25 protons

d. the noble gas in the same period as gold

43.

Write a symbol for each of the following neutral isotopes. Include the atomic number and mass number for each.

a. the alkali metal with 11 protons and a mass number of 23

b. the noble gas element with 75 neutrons in its nucleus and 54 electrons in the neutral atom

c. the isotope with 33 protons and 40 neutrons in its nucleus

d. the alkaline earth metal with 88 electrons and 138 neutrons

44.

Write a symbol for each of the following neutral isotopes. Include the atomic number and mass number for each.

a. the chalcogen with a mass number of 125

b. the halogen whose longest-lived isotope is radioactive

c. the noble gas, used in lighting, with 10 electrons and 10 neutrons

d. the lightest alkali metal with three neutrons

45.

Using the periodic table, predict whether the following chlorides are ionic or covalent: KCl, NCl_3, ICl, $MgCl_2$, PCl_5, and CCl_4.

46.

Using the periodic table, predict whether the following chlorides are ionic or covalent: $SiCl_4$, PCl_3, $CaCl_2$, $CsCl$, $CuCl_2$, and $CrCl_3$.

47.

Determine the mass of each of the following:

(a) 0.0146 mol KOH

(b) 10.2 mol ethane, C_2H_6

(c) $1.6 \times \times 10^{-3}$ mol Na_2SO_4

(d) $6.854 \times \times 10^3$ mol glucose, $C_6H_{12}O_6$

(e) 2.86 mol $Co(NH_3)_6Cl_3$

48.

Determine the number of moles of the compound and determine the number of moles of each type of atom in each of the following:

(a) 2.12 g of potassium bromide, KBr

(b) 0.1488 g of phosphoric acid, H_3PO_4

(c) 23 kg of calcium carbonate, $CaCO_3$

(d) 78.452 g of aluminum sulfate, $Al_2(SO_4)_3$

(e) 0.1250 mg of caffeine, $C_8H_{10}N_4O_2$

49.

For each of the following pairs of ions, write the formula of the compound they will form:

  a. Ca^{2+}, S^{2-}
  b.
  c. Al^{3+}, Br^-
  d. Na^+,
  e. Mg^{2+},

50.

For each of the following pairs of ions, write the formula of the compound they will form:

  a. K^+, O^{2-}
  b. SO_4^{2-}, Al^{3+}
  c. Al^{3+}, O^{2-}
  d. Na^+, H^-
  e. Ba^{2+}, PO_4^{3-}

51.

Name the following compounds:

  a. AlF_3
  b. H_2S
  c. CaH_2
  d. $HMnO_4$
  e. $HClO_4$
  f. $Ca(HCO_3)_2$

52.

Name the following compounds:

  a. ICl_3
  b. N_2O_5
  c. $LiSCN$
  d. $Al(HSO_3)_3$
  e. $Cu(HS)_2$

53.

Write the formulas of the following compounds:

  a. rubidium bromide
  b. magnesium selenide
  c. sodium oxide
  d. calcium chloride
  e. hydrogen fluoride
  f. gallium phosphide
  g. aluminum bromide
  h. ammonium sulfate

54.

Write the formulas of the following compounds:

  a. lithium carbonate
  b. sodium perchlorate
  c. barium hydroxide

    d. ammonium carbonate

    e. sulfuric acid

    f. calcium acetate

    g. magnesium phosphate

    h. sodium sulfite

55.

Write the formulas of the following compounds:

    a. silicon dioxide

    b. Hydrogen peroxide

    c. Rubidium sulfite

    d. Potassium dichromate

    e. Diboron tetrahydride

    f. Phosphous trichloride

56.

Write the formulas of the following compounds:

    a. Tin(IV) chloride

    b. Cuprous nitrate

    c. Vanadium(III) bromite

    d. Hypochlorous acid

    e. Ammonium iodate

57.

Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:

    a. MnS_2

    b. $Co_2(SO_3)_3$

    c. Hg_2Cl_2

    d.

58.

Each of the following compounds contains a metal that can exhibit more than one ionic charge. Name these compounds:

    a. (f) Fe_2O_3

59.

The following ionic compounds are found in common household products. Write the formulas for each compound:

    a. sodium bisulfate (the common name for sodium hydrogen sulfate)

    b. Sodium chloride - Table salt

    c. Sodium bicarbonate - Baking soda

    d. Calcium carbonate - Chalk or limestone, also found in antacids

    e. Sodium hypochlorite - Bleach

    f. Ammonia - Found in some household cleaners

    g. Hydrogen peroxide - Used as a disinfectant and bleach

    h. Sulfuric acid - Found in some drain cleaners

60.

The following ionic compounds are found in common household products. Name each of the compounds:

- Calcium hydroxide - Also known as slaked lime, used in some cleaning products
- Magnesium sulfate - Epsom salt, used in bath salts
- Aluminum chloride - Used in some deodorants
- Boric acid - Used as an insecticide or antiseptic
- Sodium carbonate - Washing soda, used in laundry detergents

- Acetic acid - Found in vinegar
- Calcium sulfate - Plaster of Paris
- Sodium nitrate - Used in fertilizers and food preservation

61.

What are the IUPAC names of the following compounds?

a. manganese dioxide
b. mercurous chloride (Hg_2Cl_2)
c. ferric nitrate [$Fe(NO_3)_3$]
d. titanium tetrachloride
e. cupric bromide ($CuBr_2$)

CHAPTER OVERVIEW

3: Electronic Structure and Periodic Properties

The study of chemistry must at some point extend to the molecular level, for the physical and chemical properties of a substance are ultimately explained in terms of the structure and bonding of molecules. This module introduces some basic facts and principles that are needed for a discussion of organic molecules.

3.1: Introduction

In 1054, Chinese astronomers recorded the appearance of a "guest star" in the sky, visible even during the day, which then disappeared slowly over the next two years. The sudden appearance was due to a supernova explosion, which was much brighter than the original star. Even though this supernova was observed almost a millennium ago, the remaining Crab Nebula (Figure 3.1.1) continues to release energy today. It emits not only visible light but also infrared light, X-rays, and other forms of electromagnetic radiation. The nebula emits both continuous spectra (the blue-white glow) and atomic emission spectra (the colored filaments). In this chapter, we will discuss light and other forms of electromagnetic radiation and how they are related to the electronic structure of atoms. We will also see how this radiation can be used to identify elements, even from thousands of light years away.
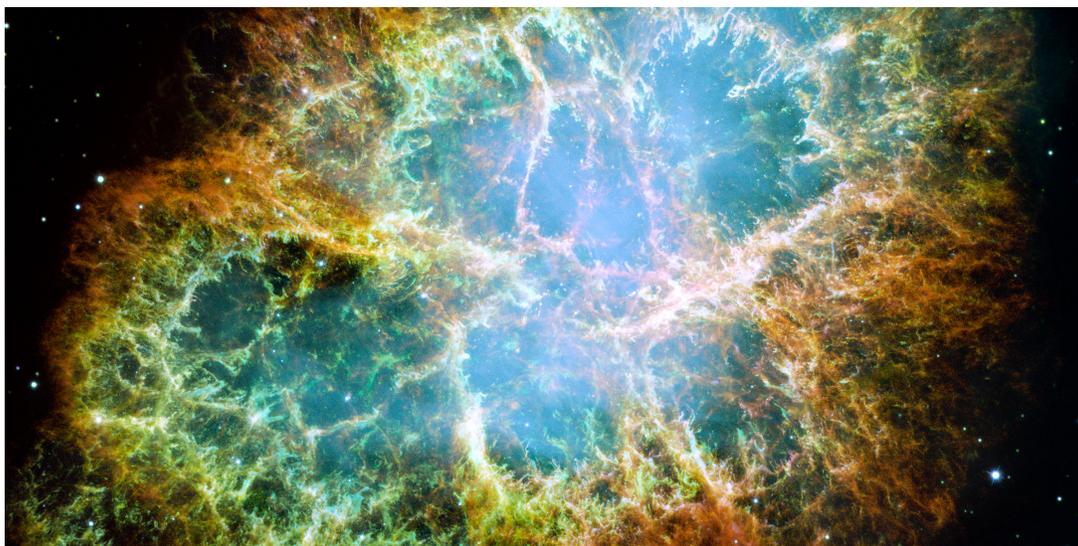

Figure 3.1.1: The Crab Nebula consists of remnants of a supernova (the explosion of a star). NASA's Hubble Space Telescope produced this composite image. Measurements of the emitted light wavelengths enabled astronomers to identify the elements in the nebula, determining that it contains specific ions including S^+ (green filaments) and O^{2+} (red filaments). (credit: modification of work by NASA and ESA)

3.2: Electromagnetic Energy

> **◑ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Explain the basic behavior of waves, including travelling waves and standing waves
> - Describe the wave nature of light
> - Use appropriate equations to calculate related light-wave properties such as frequency, wavelength, and energy
> - Distinguish between line and continuous emission spectra
> - Describe the particle nature of light

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

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

Waves

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

Waves need not be restricted to travel through matter. As Maxwell showed, electromagnetic waves consist of an electric field oscillating in step with a perpendicular magnetic field, both of which are perpendicular to the direction of travel. These waves can travel through a vacuum at a constant speed of 2.998 108 m/s, the speed of light (denoted by c).

All waves, including forms of electromagnetic radiation, are characterized by, a **wavelength** (denoted by λ, the lowercase Greek letter lambda), a **frequency** (denoted by ν, the lowercase Greek letter nu), and an **amplitude**. As can be seen in Figure 3.2.1, the wavelength is the distance between two consecutive peaks or troughs in a wave (measured in meters in the SI system).

Electromagnetic waves have wavelengths that fall within an enormous range-wavelengths of kilometers (10^3 m) to picometers (10^{-12} m) have been observed. The frequency is the number of wave cycles that pass a specified point in space in a specified amount of time (in the SI system, this is measured in seconds). A cycle corresponds to one complete wavelength. The unit for frequency, expressed as cycles per second [s^{-1}], is the **hertz** (Hz). Common multiples of this unit are megahertz, ($1\,\text{MHz} = 1 \times 10^6\,\text{Hz}$) and gigahertz ($1\,\text{GHz} = 1 \times 10^9\,\text{Hz}$). The amplitude corresponds to the magnitude of the wave's displacement and so, in Figure $3.2.1$, this corresponds to one-half the height between the peaks and troughs. The amplitude is related to the intensity of the wave, which for light is the brightness, and for sound is the loudness.
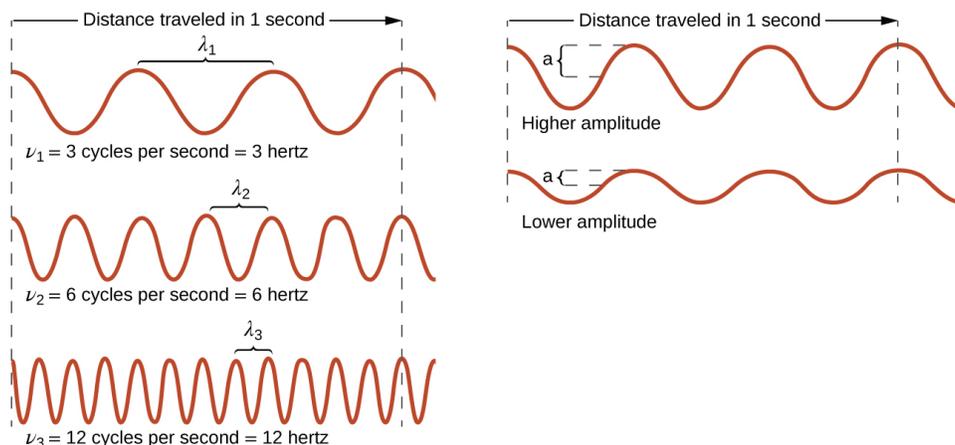

Figure 3.2.1: One-dimensional sinusoidal waves show the relationship among wavelength, frequency, and speed. The wave with the shortest wavelength has the highest frequency. Amplitude is one-half the height of the wave from peak to trough.

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

$$c = 2.998 \times 10^8 m s^{-1} = \lambda\nu$$

Wavelength and frequency are inversely proportional: As the wavelength increases, the frequency decreases. The inverse proportionality is illustrated in Figure $3.2.2$. This figure also shows the electromagnetic spectrum, the range of all types of electromagnetic radiation. Each of the various colors of visible light has specific frequencies and wavelengths associated with them, and you can see that visible light makes up only a small portion of the electromagnetic spectrum. Because the technologies developed to work in various parts of the electromagnetic spectrum are different, for reasons of convenience and historical legacies, different units are typically used for different parts of the spectrum. For example, radio waves are usually specified as frequencies (typically in units of MHz), while the visible region is usually specified in wavelengths (typically in units of nm or angstroms).
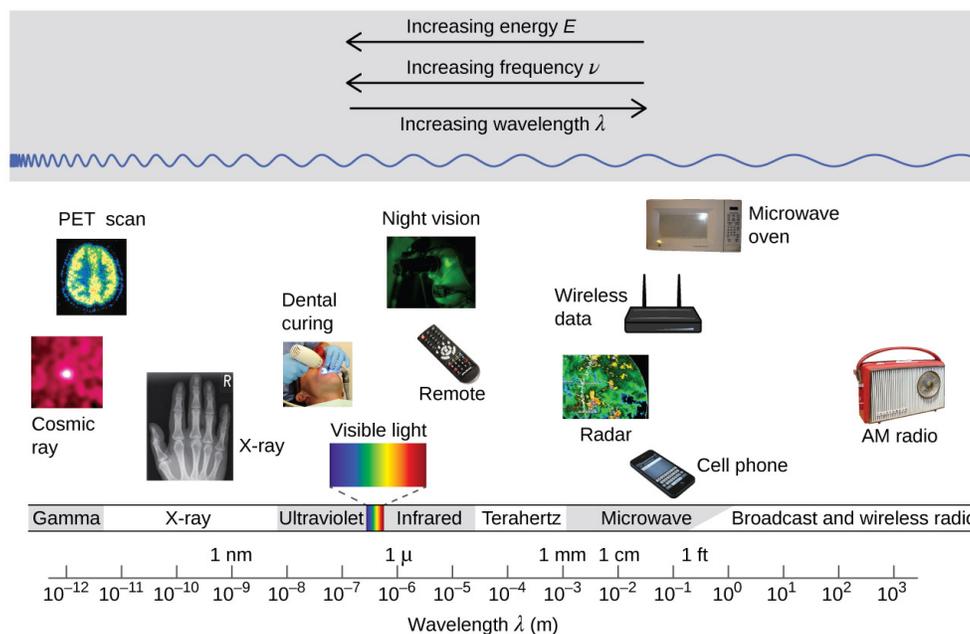
Figure 3.2.2: Portions of the electromagnetic spectrum are shown in order of decreasing frequency and increasing wavelength. (credit "Cosmic ray": modification of work by NASA; credit "PET scan": modification of work by the National Institute of Health; credit "X-ray": modification of work by Dr. Jochen Lengerke; credit "Dental curing": modification of work by the Department of the Navy; credit "Night vision": modification of work by the Department of the Army; credit "Remote": modification of work by Emilian Robert Vicol; credit "Cell phone": modification of work by Brett Jordan; credit "Microwave oven": modification of work by Billy Mabray; credit "Ultrasound": modification of work by Jane Whitney; credit "AM radio": modification of work by Dave Clausen)

✔ Example 3.2.1: Determining the Frequency and Wavelength of Radiation

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

Solution

We can rearrange the Equation $c = \lambda \nu$ to solve for the frequency:

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

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

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

? Exercise 3.2.1

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

Answer

0.353 m = 35.3 cm

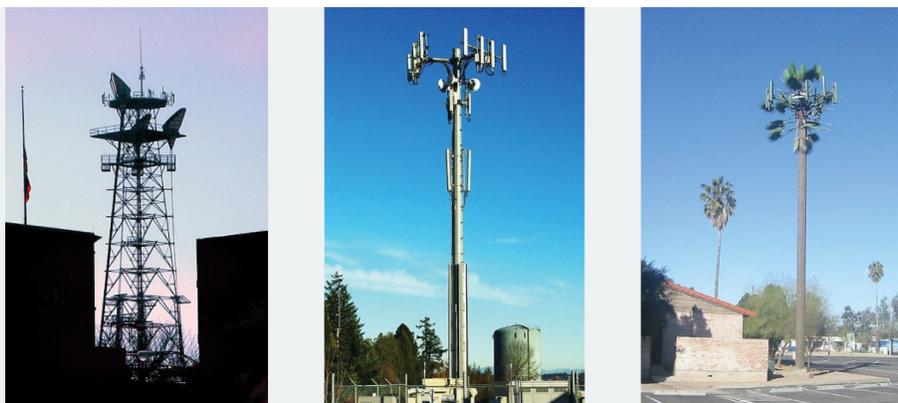### 📌 Chemistry in Everyday Life: Wireless Communication

Figure 3.2.3: Radio and cell towers are typically used to transmit long-wavelength electromagnetic radiation. Increasingly, cell towers are designed to blend in with the landscape, as with the Tucson, Arizona, cell tower (right) disguised as a palm tree. (credit left: modification of work by Sir Mildred Pierce; credit middle: modification of work by M.O. Stevens)

Many valuable technologies operate in the radio (3 kHz-300 GHz) frequency region of the electromagnetic spectrum. At the low frequency (low energy, long wavelength) end of this region are AM (amplitude modulation) radio signals (540-2830 kHz) that can travel long distances. FM (frequency modulation) radio signals are used at higher frequencies (87.5-108.0 MHz). In AM radio, the information is transmitted by varying the amplitude of the wave (Figure 3.2.4). In FM radio, by contrast, the amplitude is constant and the instantaneous frequency varies.
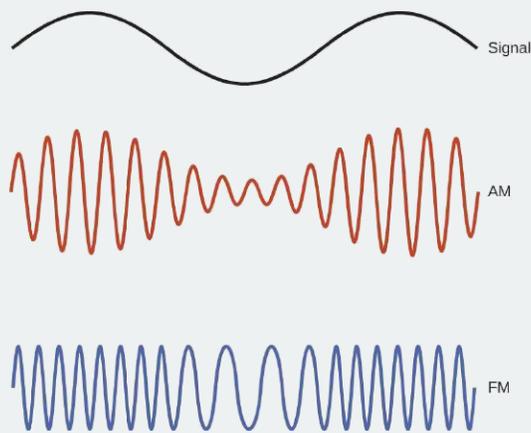

Figure 3.2.4: This schematic depicts how amplitude modulation (AM) and frequency modulation (FM) can be used to transmit a radio wave.

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

One particularly characteristic phenomenon of waves results when two or more waves come into contact: They interfere with each other. Figure 3.2.5 shows the interference patterns that arise when light passes through narrow slits closely spaced about a wavelength apart. The fringe patterns produced depend on the wavelength, with the fringes being more closely spaced for shorter wavelength light passing through a given set of slits. When the light passes through the two slits, each slit effectively acts as a new source, resulting in two closely spaced waves coming into contact at the detector (the camera in this case). The dark regions in Figure 3.2.5 correspond to regions where the peaks for the wave from one slit happen to coincide with the troughs for the wave from the other slit (destructive interference), while the brightest regions correspond to the regions where the peaks for the two waves (or their two troughs) happen to coincide (constructive interference). Likewise, when two stones are tossed close together into a pond, interference patterns are visible in the interactions between the waves produced by the stones. Such interference patterns cannot be explained by particles moving according to the laws of classical mechanics.
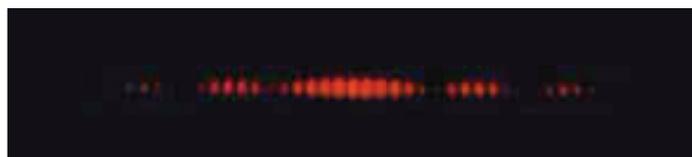
Figure 3.2.5: Interference fringe patterns are shown for light passing through two closely spaced, narrow slits. The spacing of the fringes depends on the wavelength, with the fringes being more closely spaced for the shorter-wavelength blue light. (credit: PASCO)

> ⚑ **Portrait of a Chemist: Dorothy Crowfoot Hodgkin**
>
> X-rays exhibit wavelengths of approximately 0.01–10 nm. Since these wavelengths are comparable to the spaces between atoms in a crystalline solid, X-rays are scattered when they pass through crystals. The scattered rays undergo constructive and destructive interference that creates a specific diffraction pattern that may be measured and used to precisely determine the positions of atoms within the crystal. This phenomenon of X-ray diffraction is the basis for very powerful techniques enabling the determination of molecular structure. One of the pioneers who applied this powerful technology to important biochemical substances was Dorothy Crowfoot Hodgkin.
>
> Born in Cairo, Egypt, in 1910 to British parents, Dorothy's fascination with chemistry was fostered early in her life. At age 11 she was enrolled in a prestigious English grammar school where she was one of just two girls allowed to study chemistry. On her 16th birthday, her mother, Molly, gifted her a book on X-ray crystallography, which had a profound impact on the trajectory of her career. She studied chemistry at Oxford University, graduating with first-class honors in 1932 and directly entering Cambridge University to pursue a doctoral degree. At Cambridge, Dorothy recognized the promise of X-ray crystallography for protein structure determinations, conducting research that earned her a PhD in 1937. Over the course of a very productive career, Dr. Hodgkin was credited with determining structures for several important biomolecules, including cholesterol iodide, penicillin, and vitamin B12. In recognition of her achievements in the use of X-ray techniques to elucidate the structures of biochemical substances, she was awarded the 1964 Nobel Prize in Chemistry. In 1969, she led a team of scientists who deduced the structure of insulin, facilitating the mass production of this hormone and greatly advancing the treatment of diabetic patients worldwide. Dr. Hodgkin continued working with the international scientific community, earning numerous distinctions and awards prior to her death in 1993.

Not all waves are travelling waves. Standing waves (also known as stationary waves) remain constrained within some region of space. As we shall see, standing waves play an important role in our understanding of the electronic structure of atoms and molecules. The simplest example of a standing wave is a one-dimensional wave associated with a vibrating string that is held fixed at its two end points. Figure 3.2.6 shows the four lowest-energy standing waves (the fundamental wave and the lowest three harmonics) for a vibrating string at a particular amplitude. Although the string's motion lies mostly within a plane, the wave itself is considered to be one dimensional, since it lies along the length of the string. The motion of string segments in a direction perpendicular to the string length generates the waves and so the amplitude of the waves is visible as the maximum displacement of the curves seen in Figure 3.2.6. The key observation from the figure is *that only those waves having an integer number, n, of half-wavelengths between the end points can form*. A system with fixed end points such as this restricts the number and type of the possible waveforms. This is an example of **quantization**, in which only discrete values from a more general set of continuous values of some property are observed. Another important observation is that the harmonic waves (those waves displaying more than one-half wavelength) all have one or more points between the two end points that are not in motion. These special points are **nodes**. The energies of the standing waves with a given amplitude in a vibrating string increase with the number of half-wavelengths n. Since the number of nodes is $n-1$, the energy can also be said to depend on the number of nodes, generally increasing as the number of nodes increases.
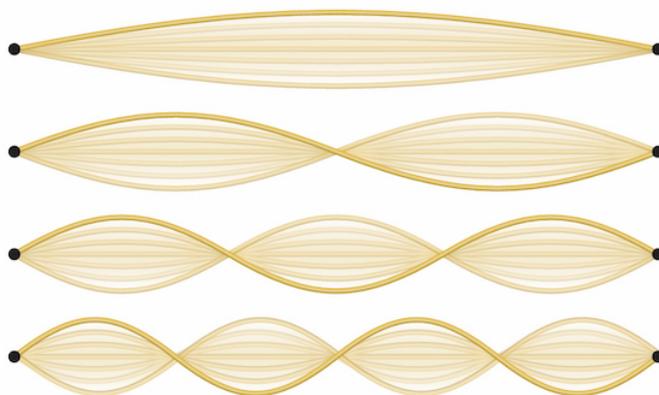
Figure 3.2.6: A vibrating string shows some one-dimensional standing waves. Since the two end points of the string are held fixed, only waves having an integer number of half-wavelengths can form. The points on the string between the end points that are not moving are called the nodes.

An example of two-dimensional standing waves is shown in Figure 3.2.7, which shows the vibrational patterns on a flat surface. Although the vibrational amplitudes cannot be seen like they could in the vibrating string, the nodes have been made visible by sprinkling the drum surface with a powder that collects on the areas of the surface that have minimal displacement. For one-dimensional standing waves, the nodes were points on the line, but for two-dimensional standing waves, the nodes are lines on the surface (for three-dimensional standing waves, the nodes are two-dimensional surfaces within the three-dimensional volume).
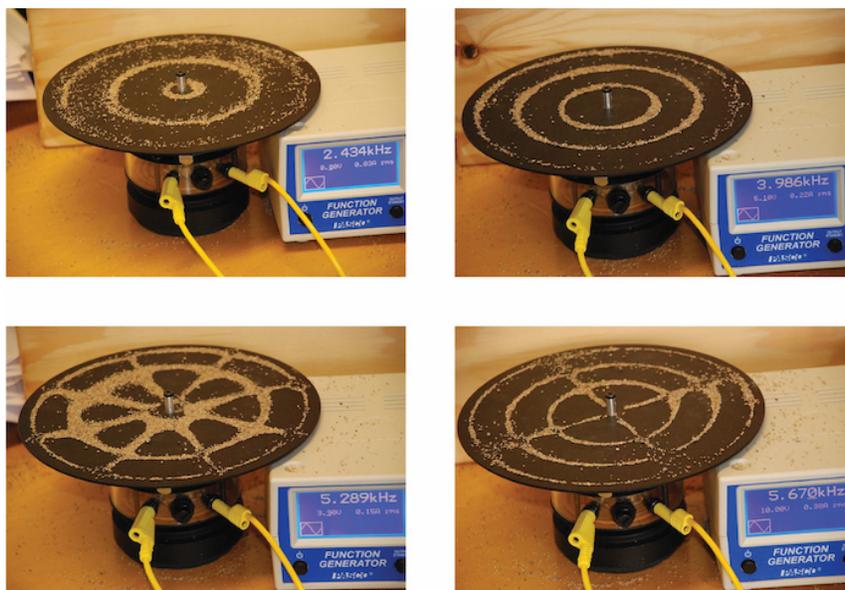

Figure 3.2.7: Two-dimensional standing waves can be visualized on a vibrating surface. The surface has been sprinkled with a powder that collects near the nodal lines. There are two types of nodes visible: radial nodes (circles) and angular nodes (radii).

📌 Link to Learning

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

Blackbody Radiation and the Ultraviolet Catastrophe

The last few decades of the nineteenth century witnessed intense research activity in commercializing newly discovered electric lighting. This required obtaining a better understanding of the distributions of light emitted from various sources being considered. Artificial lighting is usually designed to mimic natural sunlight within the limitations of the underlying technology. Such lighting consists of a range of broadly distributed frequencies that form a **continuous spectrum**. Figure 3.2.8 shows the wavelength distribution for sunlight. The most intense radiation is in the visible region, with the intensity dropping off rapidly for shorter wavelength ultraviolet (UV) light, and more slowly for longer wavelength infrared (IR) light.
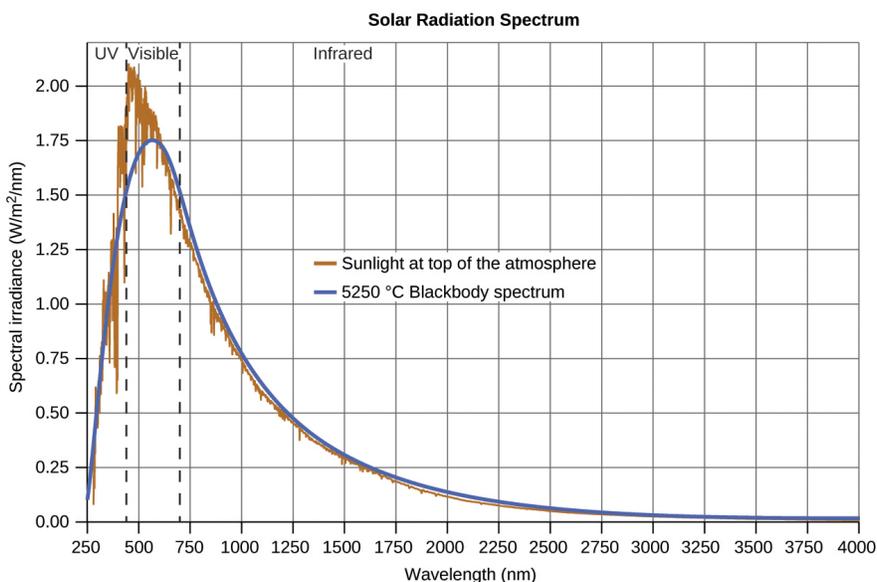
Figure $3.2.8$: The spectral distribution (light intensity vs. wavelength) of sunlight reaches the Earth's atmosphere as UV light, visible light, and IR light. The unabsorbed sunlight at the top of the atmosphere has a distribution that approximately matches the theoretical distribution of a blackbody at 5250 °C, represented by the blue curve. (credit: modification of work by American Society for Testing and Materials (ASTM) Terrestrial Reference Spectra for Photovoltaic Performance Evaluation)

In Figure $3.2.8$, the solar distribution is compared to a representative distribution, called a **blackbody spectrum**, that corresponds to a temperature of 5250 °C. The blackbody spectrum matches the solar spectrum quite well. A blackbody is a convenient, ideal emitter that approximates the behavior of many materials when heated. It is "ideal" in the same sense that an ideal gas is a convenient, simple representation of real gases that works well, provided that the pressure is not too high nor the temperature too low. A good approximation of a blackbody that can be used to observe blackbody radiation is a metal oven that can be heated to very high temperatures. The oven has a small hole allowing for the light being emitted within the oven to be observed with a spectrometer so that the wavelengths and their intensities can be measured. Figure $3.2.9$ shows the resulting curves for some representative temperatures. Each distribution depends only on a single parameter: the temperature. The maxima in the blackbody curves, $\lambda_{\max}$, shift to shorter wavelengths as the temperature increases, reflecting the observation that metals being heated to high temperatures begin to glow a darker red that becomes brighter as the temperature increases, eventually becoming white hot at very high temperatures as the intensities of all of the visible wavelengths become appreciable. This common observation was at the heart of the first paradox that showed the fundamental limitations of classical physics that we will examine.Physicists derived mathematical expressions for the blackbody curves using well-accepted concepts from the theories of classical mechanics and classical electromagnetism. The theoretical expressions as functions of temperature fit the observed experimental blackbody curves well at longer wavelengths, but showed significant discrepancies at shorter wavelengths. Not only did the theoretical curves not show a peak, they absurdly showed the intensity becoming infinitely large as the wavelength became smaller, which would imply that everyday objects at room temperature should be emitting large amounts of UV light. This became known as the "ultraviolet catastrophe" because no one could find any problems with the theoretical treatment that could lead to such unrealistic short-wavelength behavior. Finally, around 1900, Max Planck derived a theoretical expression for blackbody radiation that fit the experimental observations exactly (within experimental error). Planck developed his theoretical treatment by extending the earlier work that had been based on the premise that the atoms composing the oven vibrated at increasing frequencies (or decreasing wavelengths) as the temperature increased, with these vibrations being the source of the emitted electromagnetic radiation. But where the earlier treatments had allowed the vibrating atoms to have any energy values obtained from a continuous set of energies (perfectly reasonable, according to classical physics), Planck found that by restricting the vibrational energies to discrete values for each frequency, he could derive an expression for blackbody radiation that correctly had the intensity dropping rapidly for the short wavelengths in the UV region.

$$E = nh\nu, n = 1, 2, 3, \ldots \tag{3.2.1}$$

The quantity h is a constant now known as **Planck's constant**, in his honor. Although Planck was pleased he had resolved the blackbody radiation paradox, he was disturbed that to do so, he needed to assume the vibrating atoms required quantized energies,

which he was unable to explain. The value of Planck's constant is very small, 6.626 10^{-34} joule seconds (J s), which helps explain why energy quantization had not been observed previously in macroscopic phenomena.
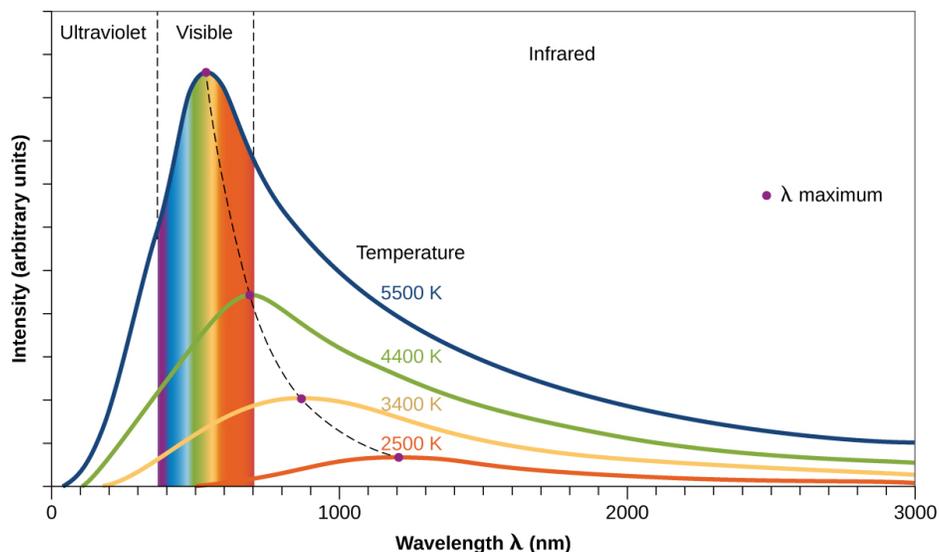

Figure 3.2.9: Blackbody spectral distribution curves are shown for some representative temperatures.

The Photoelectric Effect

The next paradox in the classical theory to be resolved concerned the photoelectric effect (Figure 3.2.10). It had been observed that electrons could be ejected from the clean surface of a metal when light having a frequency greater than some threshold frequency was shone on it. Surprisingly, the kinetic energy of the ejected electrons did not depend on the brightness of the light, but increased with increasing frequency of the light. Since the electrons in the metal had a certain amount of binding energy keeping them there, the incident light needed to have more energy to free the electrons. According to classical wave theory, a wave's energy depends on its intensity (which depends on its amplitude), not its frequency. One part of these observations was that the number of electrons ejected within in a given time period was seen to increase as the brightness increased. In 1905, Albert Einstein was able to resolve the paradox by incorporating Planck's quantization findings into the discredited particle view of light (Einstein actually won his Nobel prize for this work, and not for his theories of relativity for which he is most famous).

Einstein argued that the quantized energies that Planck had postulated in his treatment of blackbody radiation could be applied to the light in the photoelectric effect so that the light striking the metal surface should not be viewed as a wave, but instead as a stream of particles (later called **photons**) whose energy depended on their frequency, according to Planck's formula (Equation 3.2.1), $E = h\nu$ (or, in terms of wavelength using $c = \nu\lambda$, $E = \frac{hc}{\lambda}$). Electrons were ejected when hit by photons having sufficient energy (a frequency greater than the threshold). The greater the frequency, the greater the kinetic energy imparted to the escaping electrons by the collisions. Einstein also argued that the light intensity did not depend on the amplitude of the incoming wave, but instead corresponded to the number of photons striking the surface within a given time period. This explains why the number of ejected electrons increased with increasing brightness, since the greater the number of incoming photons, the greater the likelihood that they would collide with some of the electrons.
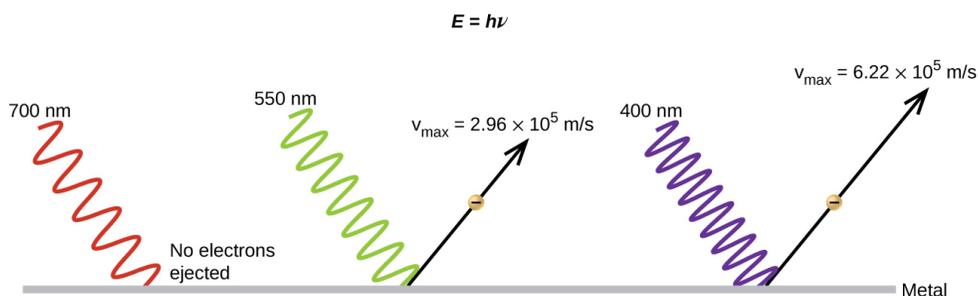

Figure 3.2.10: Photons with low frequencies do not have enough energy to cause electrons to be ejected via the photoelectric effect. For any frequency of light above the threshold frequency, the kinetic energy of an ejected electron will increase linearly with the energy of the incoming photon.

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

> ✔ Example 3.2.2: Calculating the Energy of Radiation
>
> When we see light from a neon sign, we are observing radiation from excited neon atoms. If this radiation has a wavelength of 640 nm, what is the energy of the photon being emitted?
>
> **Solution**
>
> We use the part of Planck's equation that includes the wavelength, λ, and convert units of nanometers to meters so that the units of λ and c are the same.
>
> $$E = \frac{hc}{\lambda}$$
>
> $$= \frac{\left(6.626 \times 10^{-34} \text{ J} \cdot \text{s}\right)\left(2.998 \times 10^8 \text{ m} \cdot \text{s}^{-1}\right)}{(640 \text{ nm})\left(\frac{1 \text{ m}}{10^9 \text{ nm}}\right)}$$
>
> $$= 3.10 \times 10^{-19} J$$

> ? Exercise 3.2.2
>
> The microwaves in an oven are of a specific frequency that will heat the water molecules contained in food. (This is why most plastics and glass do not become hot in a microwave oven-they do not contain water molecules.) This frequency is about 3 10^9 Hz. What is the energy of one photon in these microwaves?
>
> **Answer**
>
> 2 10^{-24} J

> 📌 Link to Learning
>
> Use this simulation program to experiment with the photoelectric effect to see how intensity, frequency, type of metal, and other factors influence the ejected photons.

> ✔ Example 3.2.3: Photoelectric Effect
>
> Identify which of the following statements are false and, where necessary, change the italicized word or phrase to make them true, consistent with Einstein's explanation of the photoelectric effect.
>
> a. Increasing the brightness of incoming light *increases* the kinetic energy of the ejected electrons.
> b. Increasing the *wavelength* of incoming light increases the kinetic energy of the ejected electrons.
> c. Increasing the brightness of incoming light *increases* the number of ejected electrons.
> d. Increasing the *frequency* of incoming light can increase the number of ejected electrons.
>
> **Solution**
> a. False. Increasing the brightness of incoming light *has no effect* on the kinetic energy of the ejected electrons. Only energy, not the number or amplitude, of the photons influences the kinetic energy of the electrons.
> b. False. Increasing the *frequency* of incoming light increases the kinetic energy of the ejected electrons. Frequency is proportional to energy and inversely proportional to wavelength. Frequencies above the threshold value transfer the excess energy into the kinetic energy of the electrons.
> c. True. Because the number of collisions with photons increases with brighter light, the number of ejected electrons increases.

d. True with regard to the threshold energy binding the electrons to the metal. Below this threshold, electrons are not emitted and above it they are. Once over the threshold value, further increasing the frequency does not increase the number of ejected electrons

> **? Exercise 3.2.3**
>
> Calculate the threshold energy in kJ/mol of electrons in aluminum, given that the lowest frequency photon for which the photoelectric effect is observed is 9.87 10^{14} Hz.
>
> **Answer**
>
> 394 kJ/mol

Line Spectra

Another paradox within the classical electromagnetic theory that scientists in the late nineteenth century struggled with concerned the light emitted from atoms and molecules. When solids, liquids, or condensed gases are heated sufficiently, they radiate some of the excess energy as light. Photons produced in this manner have a range of energies, and thereby produce a continuous spectrum in which an unbroken series of wavelengths is present. Most of the light generated from stars (including our sun) is produced in this fashion. You can see all the visible wavelengths of light present in sunlight by using a prism to separate them. As can be seen in Figure 3.2.8: , sunlight also contains UV light (shorter wavelengths) and IR light (longer wavelengths) that can be detected using instruments but that are invisible to the human eye. Incandescent (glowing) solids such as tungsten filaments in incandescent lights also give off light that contains all wavelengths of visible light. These continuous spectra can often be approximated by blackbody radiation curves at some appropriate temperature, such as those shown in Figure 3.2.9.

In contrast to continuous spectra, light can also occur as discrete or **line spectra** having very narrow line widths interspersed throughout the spectral regions such as those shown in Figure 3.2.12 Exciting a gas at low partial pressure using an electrical current, or heating it, will produce line spectra. Fluorescent light bulbs and neon signs operate in this way (Figure 3.2.11). Each element displays its own characteristic set of lines, as do molecules, although their spectra are generally much more complicated.

Figure 3.2.11: Neon signs operate by exciting a gas at low partial pressure using an electrical current. This sign shows the elaborate artistic effects that can be achieved. (credit: Dave Shaver)

Each emission line consists of a single wavelength of light, which implies that the light emitted by a gas consists of a set of discrete energies. For example, when an electric discharge passes through a tube containing hydrogen gas at low pressure, the H_2 molecules are broken apart into separate H atoms and we see a blue-pink color. Passing the light through a prism produces a line spectrum, indicating that this light is composed of photons of four visible wavelengths, as shown in Figure 3.2.12
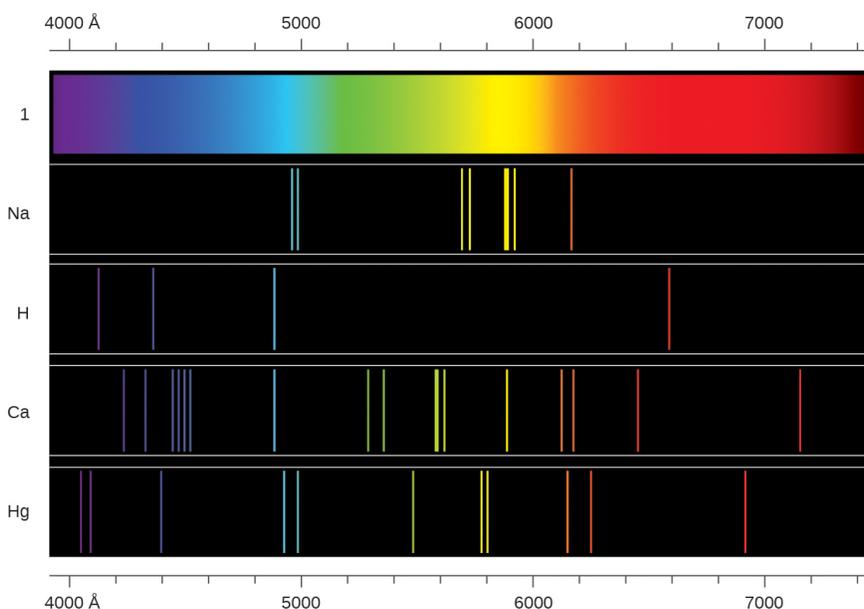
Figure 3.2.12: Compare the two types of emission spectra: continuous spectrum of white light (top) and the line spectra of the light from excited sodium, hydrogen, calcium, and mercury atoms.

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

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

Other discrete lines for the hydrogen atom were found in the UV and IR regions. Johannes Rydberg generalized Balmer's work and developed an empirical formula that predicted all of hydrogen's emission lines, not just those restricted to the visible range, where n_1 and n_2 are integers, $n_1 < n_2$, and R_∞ is the **Rydberg constan**t ($1.097 \ 10^7 \ \text{m}^{-1} = 2.18 \times 10^{-18}$ J).

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

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

3.3: The Bohr Model

> **◑ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Describe the Bohr model of the hydrogen atom
> - Use the Rydberg equation to calculate energies of light emitted or absorbed by hydrogen atoms

Following the work of Ernest Rutherford and his colleagues in the early twentieth century, the picture of atoms consisting of tiny dense nuclei surrounded by lighter and even tinier electrons continually moving about the nucleus was well established. This picture was called the planetary model, since it pictured the atom as a miniature "solar system" with the electrons orbiting the nucleus like planets orbiting the sun. The simplest atom is hydrogen, consisting of a single proton as the nucleus about which a single electron moves. The electrostatic force attracting the electron to the proton depends only on the distance between the two particles. This classical mechanics description of the atom is incomplete, however, since an electron moving in an elliptical orbit would be accelerating (by changing direction) and, according to classical electromagnetism, it should continuously emit electromagnetic radiation. This loss in orbital energy should result in the electron's orbit getting continually smaller until it spirals into the nucleus, implying that atoms are inherently unstable.

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

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

In this equation, h is Planck's constant and E_i and E_f are the initial and final orbital energies, respectively. The absolute value of the energy difference is used, since frequencies and wavelengths are always positive. Instead of allowing for continuous values of energy, Bohr assumed the energies of these electron orbitals were quantized:

$$E_n = -\frac{k}{n^2}, n = 1, 2, 3, \ldots$$

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

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

or

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

which is identical to the Rydberg equation in which

$$R_\infty = \frac{k}{hc}$$

Therefore, we can also conclude:

$$\Delta E = R_\infty \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{3.3.1}$$

where R_∞ = 2.179 10^{-18} J

When Bohr calculated his theoretical value for the Rydberg constant, R_∞, and compared it with the experimentally accepted value, he got excellent agreement. Since the Rydberg constant was one of the most precisely measured constants at that time, this level of agreement was astonishing and meant that Bohr's model was taken seriously, despite the many assumptions that Bohr needed to derive it.
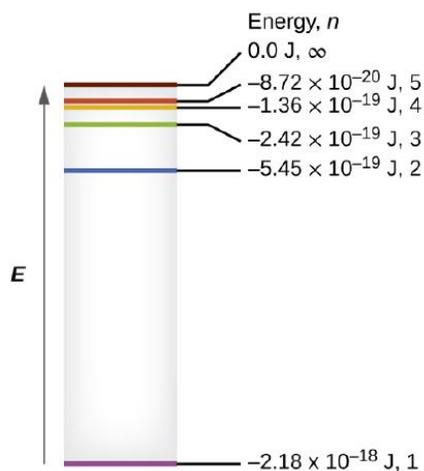

Figure 3.3.1: Quantum numbers and energy levels in a hydrogen atom. The more negative the calculated value, the lower the energy.

The lowest few energy levels are shown in Figure 3.3.1. One of the fundamental laws of physics is that matter is most stable with the lowest possible energy. Thus, the electron in a hydrogen atom usually moves in the $n = 1$ orbit, the orbit in which it has the lowest energy. When the electron is in this lowest energy orbit, the atom is said to be in its ground electronic state (or simply ground state). If the atom receives energy from an outside source, it is possible for the electron to move to an orbit with a higher n value and the atom is now in an excited electronic state (or simply an excited state) with a higher energy. When an electron transitions from an excited state (higher energy orbit) to a less excited state, or ground state, the difference in energy is emitted as a photon. Similarly, if a photon is absorbed by an atom, the energy of the photon moves an electron from a lower energy orbit up to a more excited one. We can relate the energy of electrons in atoms to what we learned previously about energy. The law of conservation of energy says that we can neither create nor destroy energy. Thus, if a certain amount of external energy is required to excite an electron from one energy level to another, that same amount of energy will be liberated when the electron returns to its initial state (Figure 3.3.2).
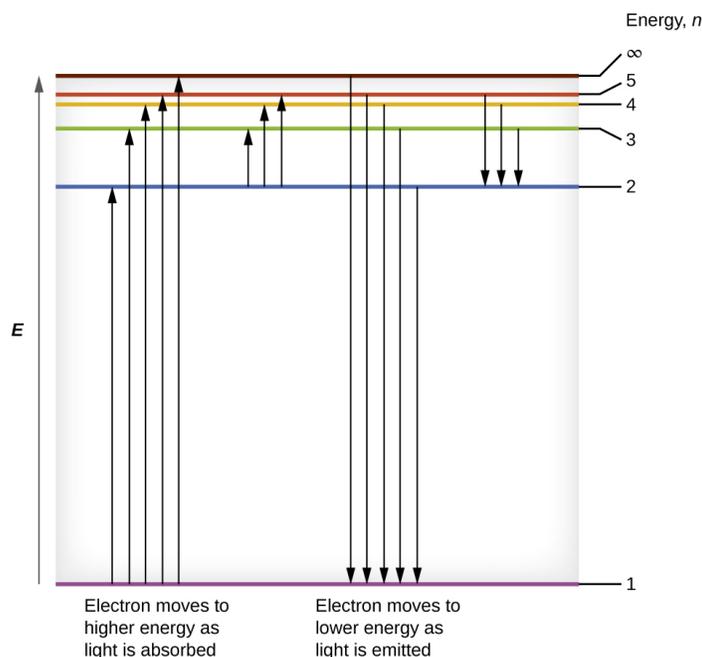
Energy, n

Figure 3.3.2: The horizontal lines show the relative energy of orbits in the Bohr model of the hydrogen atom, and the vertical arrows depict the energy of photons absorbed (left) or emitted (right) as electrons move between these orbits.

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

$$E_n = -\frac{kZ^2}{n^2} \tag{3.3.2}$$

The sizes of the circular orbits for hydrogen-like atoms are given in terms of their radii by the following expression, in which \(a_0\) is a constant called the **Bohr radius**, with a value of 5.292 10^{-11} m:

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

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

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

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

✔ **Example 3.3.1: Calculating the Energy of an Electron in a Bohr Orbit**

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

Solution

The energy of the electron is given by Equation 3.3.2:

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

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

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

? **Exercise 3.3.1**

The electron in Figure 3.3.2 is promoted even further to an orbit with $n = 6$. What is its new energy?

Answer

$-6.053 \ 10^{-20}$ J

✔ **Example 3.3.2: Calculating the Energy and Wavelength of Electron Transitions in a One–electron (Bohr) System**

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

Solution

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

$$\Delta E = E_1 - E_2$$

$$= 2.179 \times 10^{-18} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

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

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

$$= 7.566 \times 10^{-20} J$$

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

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

$$= \left(6.626 \times 10^{-34} \ \text{J} \cancel{s} \right) \times \frac{2.998 \times 10^8 \ \text{m} \ \cancel{s}^{-1}}{7.566 \times 10^{-20} \ \cancel{J}}$$

$$= 2.626 \times 10^{-6} \ \text{m}$$

> From the illustration of the electromagnetic spectrum in Electromagnetic Energy, we can see that this wavelength is found in the infrared portion of the electromagnetic spectrum.

> **? Exercise 3.3.2**
>
> What is the energy in joules and the wavelength in meters of the photon produced when an electron falls from the $n = 5$ to the $n = 3$ level in a He^+ ion ($Z = 2$ for He^+)?
>
> **Answer**
>
> 6.198×10^{-19} J; 3.205×10^{-7} m

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

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

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

3.4: Development of Quantum Theory

> ### ◑ Learning Objectives
>
> By the end of this section, you will be able to:
>
> - Extend the concept of wave–particle duality that was observed in electromagnetic radiation to matter as well
> - Understand the general idea of the quantum mechanical description of electrons in an atom, and that it uses the notion of three-dimensional wave functions, or orbitals, that define the distribution of probability to find an electron in a particular part of space
> - List and describe traits of the four quantum numbers that form the basis for completely specifying the state of an electron in an atom

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

Behavior in the Microscopic World

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

When waves interact with each other, they show interference patterns that are not displayed by macroscopic particles such as the billiard ball. For example, interacting waves on the surface of water can produce interference patterns similar to those shown on Figure 3.4.1. This is a case of wave behavior on the macroscopic scale, and it is clear that particles and waves are very different phenomena in the macroscopic realm.

Figure 3.4.1: An interference pattern on the water surface is formed by interacting waves. The waves are caused by reflection of water from the rocks. (credit: modification of work by Sukanto Debnath)

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

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

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

This is called the **de Broglie wavelength**. Unlike the other values of λ discussed in this chapter, the de Broglie wavelength is a characteristic of particles and other bodies, not electromagnetic radiation (note that this equation involves velocity [v, m/s], not frequency [ν, Hz]. Although these two symbols appear nearly identical, they mean very different things). Where Bohr had postulated the electron as being a particle orbiting the nucleus in quantized orbits, de Broglie argued that Bohr's assumption of quantization can be explained if the electron is considered not as a particle, but rather as a circular standing wave such that only an integer number of wavelengths could fit exactly within the orbit (Figure 3.4.2).
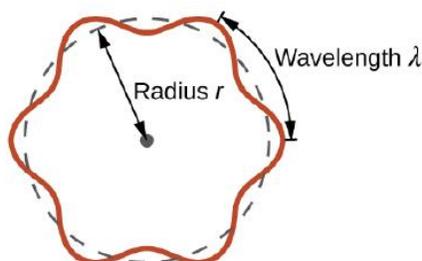
Figure 3.4.2: If an electron is viewed as a wave circling around the nucleus, an integer number of wavelengths must fit into the orbit for this standing wave behavior to be possible.

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

$$2\pi r = n\lambda, \qquad n = 1, 2, 3, \ldots$$

Shortly after de Broglie proposed the wave nature of matter, two scientists at Bell Laboratories, C. J. Davisson and L. H. Germer, demonstrated experimentally that electrons can exhibit wavelike behavior by showing an interference pattern for electrons travelling through a regular atomic pattern in a crystal. The regularly spaced atomic layers served as slits, as used in other interference experiments. Since the spacing between the layers serving as slits needs to be similar in size to the wavelength of the tested wave for an interference pattern to form, Davisson and Germer used a crystalline nickel target for their "slits," since the spacing of the atoms within the lattice was approximately the same as the de Broglie wavelengths of the electrons that they used. Figure 3.4.3 shows an interference pattern. It is strikingly similar to the interference patterns for light shown in Electromagnetic Energy for light passing through two closely spaced, narrow slits. The wave–particle duality of matter can be seen in Figure 3.4.3 by observing what happens if electron collisions are recorded over a long period of time. Initially, when only a few electrons have been recorded, they show clear particle-like behavior, having arrived in small localized packets that appear to be random. As more and more electrons arrived and were recorded, a clear interference pattern that is the hallmark of wavelike behavior emerged. Thus, it appears that while electrons are small localized particles, their motion does not follow the equations of motion implied by classical mechanics, but instead it is governed by some type of a wave equation. Thus the wave–particle duality first observed with photons is actually a fundamental behavior intrinsic to all quantum particles.
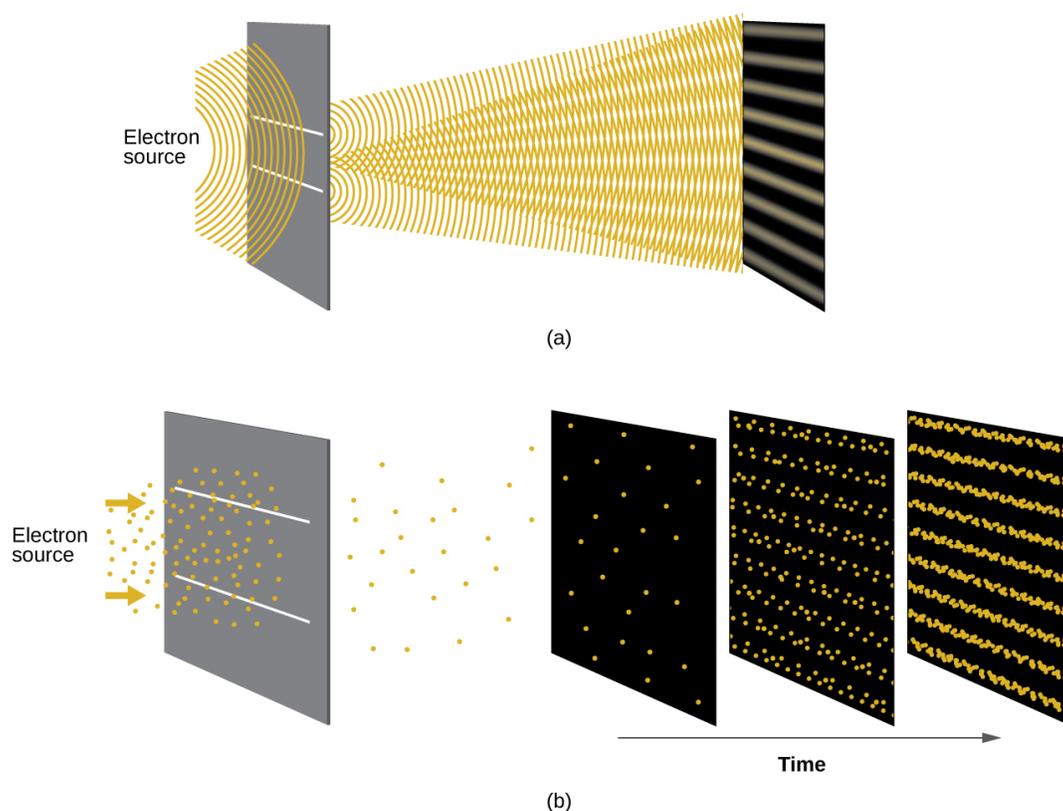
Figure 3.4.3: (a) The interference pattern for electrons passing through very closely spaced slits demonstrates that quantum particles such as electrons can exhibit wavelike behavior. (b) The experimental results illustrated here demonstrate the wave–particle duality in electrons.

📌 Link to Learning

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

✔ Example 3.4.1: Calculating the Wavelength of a Particle

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

Solution

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

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

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

$$= 7.274 \times 10^{-11} m$$

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

? Exercise 3.4.1

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

Answer

1.9 10^{-34} m.

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

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

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

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

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

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

It should be noted that Heisenberg's uncertainty principle is not just limited to uncertainties in position and momentum, but it also links other dynamical variables. For example, when an atom absorbs a photon and makes a transition from one energy state to another, the uncertainty in the energy and the uncertainty in the time required for the transition are similarly related, as:

$$\Delta E \Delta t \geq \frac{\hbar}{2}$$

Heisenberg's principle imposes ultimate limits on what is knowable in science. The uncertainty principle can be shown to be a consequence of wave–particle duality, which lies at the heart of what distinguishes modern quantum theory from classical mechanics.

📌 Link to Learning

Read this article that describes a recent macroscopic demonstration of the uncertainty principle applied to microscopic objects.

The Quantum–Mechanical Model of an Atom

Shortly after de Broglie published his ideas that the electron in a hydrogen atom could be better thought of as being a circular standing wave instead of a particle moving in quantized circular orbits, Erwin Schrödinger extended de Broglie's work by deriving what is today known as the Schrödinger equation. When Schrödinger applied his equation to hydrogen-like atoms, he was able to

reproduce Bohr's expression for the energy and, thus, the Rydberg formula governing hydrogen spectra. Schrödinger described electrons as three-dimensional stationary waves, or **wavefunctions**, represented by the Greek letter psi, ψ. A few years later, Max Born proposed an interpretation of the wavefunction ψ that is still accepted today: Electrons are still particles, and so the waves represented by ψ are not physical waves but, instead, are complex probability amplitudes. The square of the magnitude of a wavefunction $|\psi|^2$ describes the probability of the quantum particle being present near a certain location in space. This means that wavefunctions can be used to determine the distribution of the electron's density with respect to the nucleus in an atom. In the most general form, the Schrödinger equation can be written as:

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

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

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

> 📌 Link to Learning
>
> You may also have heard of Schrödinger because of his famous thought experiment. This story explains the concepts of superposition and entanglement as related to a cat in a box with poison.

Understanding Quantum Theory of Electrons in Atoms

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

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

The energy levels are labeled with an n value, where $n = 1, 2, 3, \ldots$. Generally speaking, the energy of an electron in an atom is greater for greater values of n. This number, n, is referred to as the principal quantum number. The principal quantum number defines the location of the energy level. It is essentially the same concept as the n in the Bohr atom description. Another name for the principal quantum number is the shell number. The shells of an atom can be thought of concentric circles radiating out from the nucleus. The electrons that belong to a specific shell are most likely to be found within the corresponding circular area. The further we proceed from the nucleus, the higher the shell number, and so the higher the energy level (Figure 3.4.4). The positively charged protons in the nucleus stabilize the electronic orbitals by electrostatic attraction between the positive charges of the protons and the negative charges of the electrons. So the further away the electron is from the nucleus, the greater the energy it has.
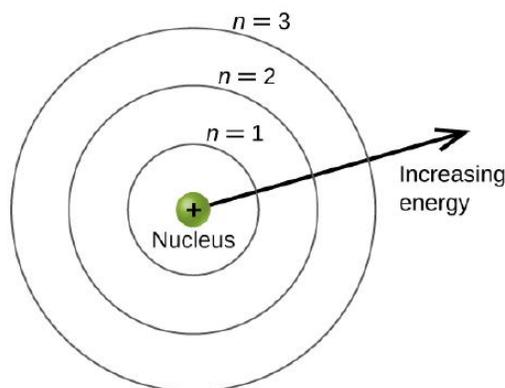

Figure 3.4.4: Different shells are numbered by principal quantum numbers.

This quantum mechanical model for where electrons reside in an atom can be used to look at electronic transitions, the events when an electron moves from one energy level to another. If the transition is to a higher energy level, energy is absorbed, and the energy

change has a positive value. To obtain the amount of energy necessary for the transition to a higher energy level, a photon is absorbed by the atom. A transition to a lower energy level involves a release of energy, and the energy change is negative. This process is accompanied by emission of a photon by the atom. The following equation summarizes these relationships and is based on the hydrogen atom:

$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

$$= -2.18 \times 10^{-18} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) J$$

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

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

Another quantum number is l, the **secondary (angular momentum) quantum number**. It is an integer that may take the values, $l = 0, 1, 2, \ldots, n-1$. This means that an orbital with $n = 1$ can have only one value of l, $l = 0$, whereas $n = 2$ permits $l = 0$ and $l = 1$, and so on. Whereas the principal quantum number, n, defines the general size and energy of the orbital, the secondary quantum number l specifies the shape of the orbital. Orbitals with the same value of l define a **subshell**.

Orbitals with $l = 0$ are called s orbitals and they make up the s subshells. The value $l = 1$ corresponds to the p orbitals. For a given n, p orbitals constitute a p subshell (e.g., 3p if n = 3). The orbitals with $l = 2$ are called the **d orbitals**, followed by the *f-, g-, and h*-orbitals for l = 3, 4, and 5.

There are certain distances from the nucleus at which the probability density of finding an electron located at a particular orbital is zero. In other words, the value of the wavefunction ψ is zero at this distance for this orbital. Such a value of radius r is called a **radial node**. The number of radial nodes in an orbital is $n-l-1$.
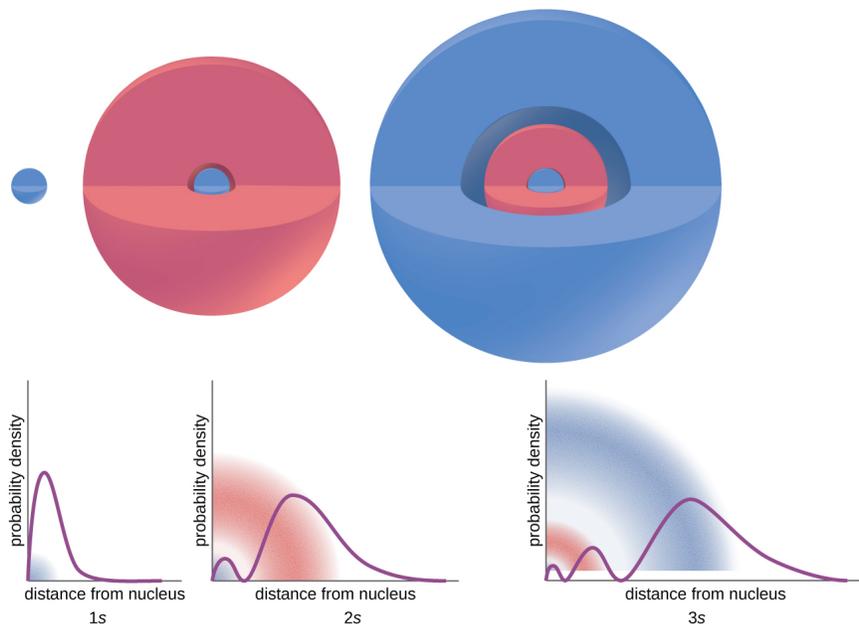
Figure 3.4.5: The graphs show the probability (*y* axis) of finding an electron for the 1*s*, 2*s*, 3*s* orbitals as a function of distance from the nucleus.

Consider the examples in Figure 3.4.5. The orbitals depicted are of the *s* type, thus $l = 0$ for all of them. It can be seen from the graphs of the probability densities that there are $1 - 0 - 1 = 0$ places where the density is zero (nodes) for 1*s* (*n* = 1), $2 - 0 - 1 = 1$ node for 2*s*, and $3 - 0 - 1 = 2$ nodes for the 3*s* orbitals.

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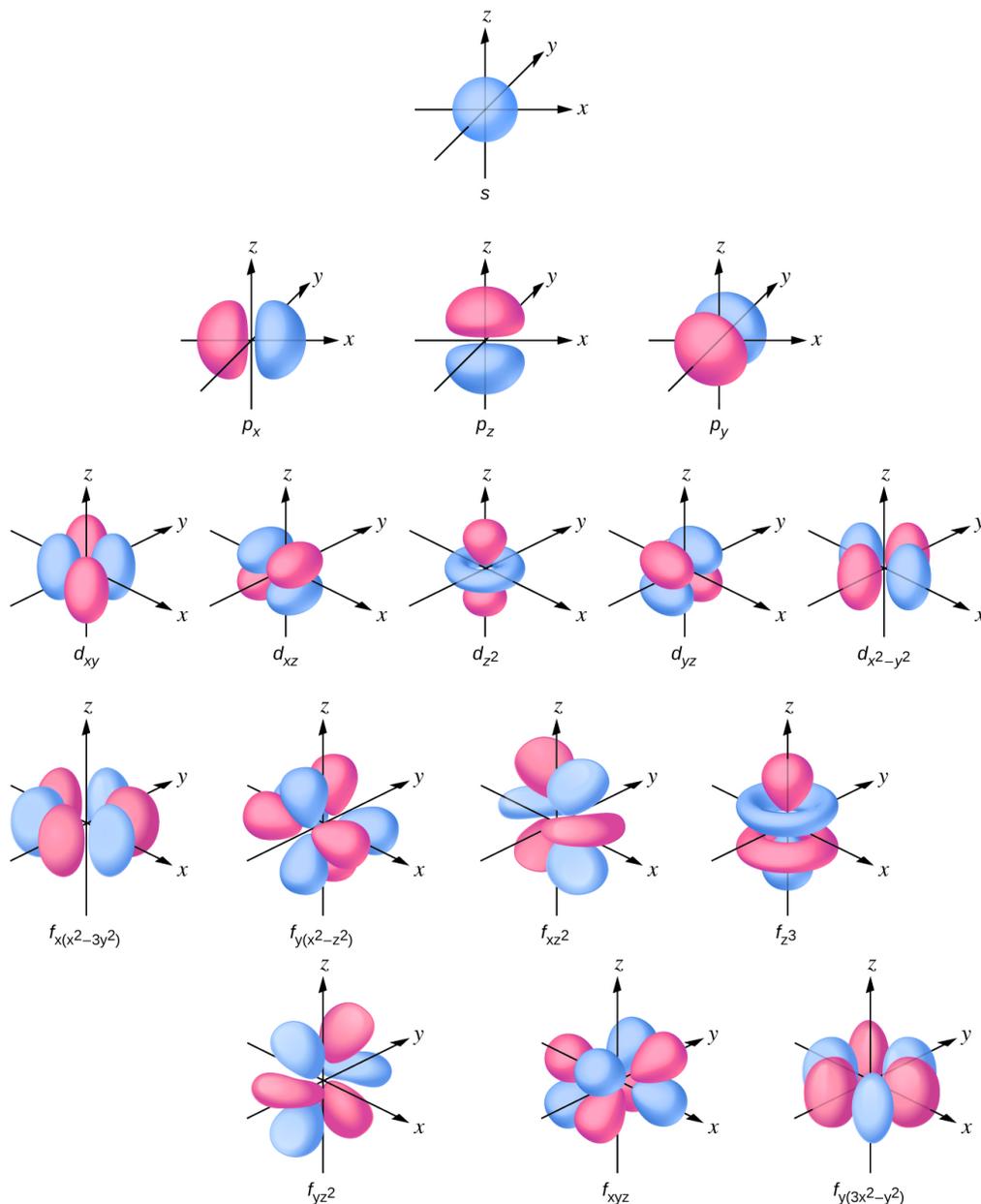

Figure 3.4.6: Shapes of *s*, *p*, *d*, and *f* orbitals.

The **magnetic quantum number**, m_l, specifies the relative spatial orientation of a particular orbital. Generally speaking, m_l are rangeed from $-l$ to $+l$, i.e.

$$-l, -(l-1), \ldots, 0, \ldots, (l-1), l\backslash).$$

The total number of possible orbitals with the same value of l (that is, in the same subshell) is $2l+1$. Thus, there is one s-orbital in an s subshell ($l=0$), there are three p-orbitals in a p subshell ($l=1$), five d-orbitals in a d subshell (l = 2), seven f-orbitals in an f subshell ($l=3$), and so forth. The principal quantum number defines the general value of the electronic energy. The angular momentum quantum number determines the shape of the orbital. And the magnetic quantum number specifies orientation of the orbital in space, as can be seen in Figure 3.4.6.

Figure 3.4.7 illustrates the energy levels for various orbitals. The number before the orbital name (such as 2*s*, 3*p*, and so forth) stands for the principal quantum number, n. The letter in the orbital name defines the subshell with a specific angular momentum

quantum number $l = 0$ for s orbitals, 1 for p orbitals, 2 for d orbitals. Finally, there are more than one possible orbitals for $l \geq 1$, each corresponding to a specific value of m_l. In the case of a hydrogen atom or a one-electron ion (such as He$^+$, Li^{2+}, and so on), energies of all the orbitals with the same n are the same. This is called a degeneracy, and the energy levels for the same principal quantum number, n, are called degenerate orbitals. However, in atoms with more than one electron, this degeneracy is eliminated by the electron–electron interactions, and orbitals that belong to different subshells have different energies, as shown on Figure 3.4.7. Orbitals within the same subshell are still degenerate and have the same energy.
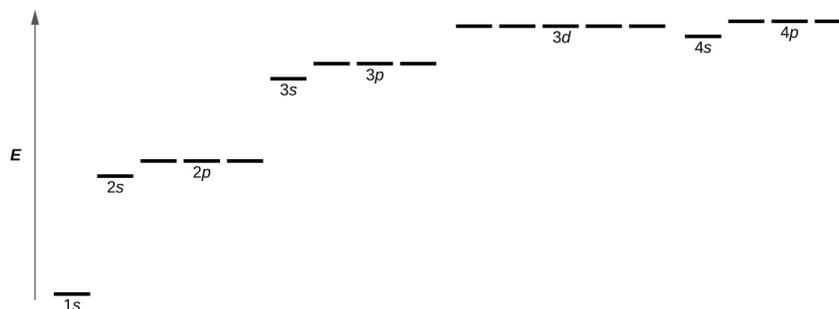
Figure 3.4.7: The chart shows the energies of electron orbitals in a multi-electron atom.

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

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

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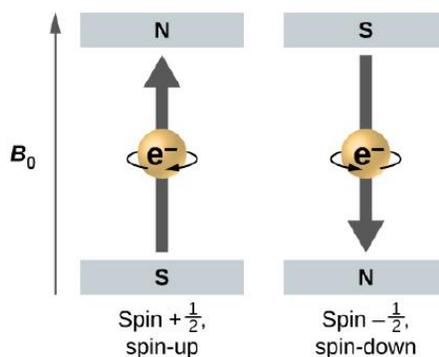

Figure 3.4.8: Electrons with spin values in an external magnetic field.

Figure 3.4.8 illustrates this phenomenon. An electron acts like a tiny magnet. Its moment is directed up (in the positive direction of the z axis) for the $m_s = +1/2$ spin quantum number and down (in the negative z direction) for the spin quantum number of $m_s = -1/2$. A magnet has a lower energy if its magnetic moment is aligned with the external magnetic field (the left electron on

Figure 3.4.8) and a higher energy for the magnetic moment being opposite to the applied field. This is why an electron with $m_s = +1/2$ has a slightly lower energy in an external field in the positive z direction, and an electron with $m_s = -1/2$ has a slightly higher energy in the same field. This is true even for an electron occupying the same orbital in an atom. A spectral line corresponding to a transition for electrons from the same orbital but with different spin quantum numbers has two possible values of energy; thus, the line in the spectrum will show a fine structure splitting.

The Pauli Exclusion Principle

An electron in an atom is completely described by four quantum numbers: n, l, m_l, and m_s. The first three quantum numbers define the orbital and the fourth quantum number describes the intrinsic electron property called spin. An Austrian physicist Wolfgang Pauli formulated a general principle that gives the last piece of information that we need to understand the general behavior of electrons in atoms. The **Pauli exclusion principle** can be formulated as follows: No two electrons in the same atom can have exactly the same set of all the four quantum numbers. What this means is that two electrons can share the same orbital (the same set of the quantum numbers n, l, and m_l) only if their spin quantum numbers m_s have different values. Since the spin quantum number can only have two values no more than two electrons can occupy the same orbital (and if two electrons are located in the same orbital, they must have opposite spins). Therefore, any atomic orbital can be populated by only zero, one, or two electrons. The properties and meaning of the quantum numbers of electrons in atoms are briefly summarized in Table 3.4.1.

Table 3.4.1: Quantum Numbers, Their Properties, and Significance

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

---

✔ **Example 3.4.2: Working with Shells and Subshells**

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

Solution

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

? **Exercise 3.4.2**

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

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

Answer

a. 3p
b. 5f

c. 2s

✔ Example 3.4.3: Maximum Number of Electrons

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

Solution

a. When $n = 2$, there are four orbitals (a single 2s orbital, and three orbitals labeled 2p). These four orbitals can contain eight electrons.
b. When $n = 2$, there are four orbitals (a single 2s orbital, and three orbitals labeled 2p). These four orbitals can contain eight electrons.
   When $n = 5$, there are five subshells of orbitals that we need to sum:

$$
\begin{array}{r}
1 \text{ orbital labeled 5s} \\
3 \text{ orbitals labeled 5p} \\
5 \text{ orbitals labeled 5d} \\
7 \text{ orbitals labeled 5f} \\
+ \quad 9 \text{ orbitals labeled 5g} \\
\hline
25 \text{ orbitals total}
\end{array}
$$

   Again, each orbital holds two electrons, so 50 electrons can fit in this shell.
c. The number of orbitals in any shell n will equal n^2. There can be up to two electrons in each orbital, so the maximum number of electrons will be $2 \times n^2$.

? Exercise 3.4.3

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

Answer

$n = 4$

✔ Example 3.4.4: Working with Quantum Numbers

Complete the following table for atomic orbitals:

Orbital	n	l	m_l degeneracy	Radial nodes (#)
4f				
	4	1		
	7		7	3
5d				

Solution

The table can be completed using the following rules:

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

Orbital	n	l	m_l degeneracy	Radial nodes (#)
4f	4	3	7	0
4p	4	1	3	2
7f	7	3	7	3
5d	5	2	5	2

? Exercise 3.4.1

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

Answer

The five degenerate $3d$ orbitals

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3.5: Electronic Structure of Atoms (Electron Configurations)

> ◑ **Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Derive the predicted ground-state electron configurations of atoms
> - Identify and explain exceptions to predicted electron configurations for atoms and ions
> - Relate electron configurations to element classifications in the periodic table

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

Orbital Energies and Atomic Structure

The energy of atomic orbitals increases as the principal quantum number, n, increases. In any atom with two or more electrons, the repulsion between the electrons makes energies of subshells with different values of l differ so that the energy of the orbitals increases within a shell in the order $s < p < d < f$. Figure 3.5.1: depicts how these two trends in increasing energy relate. The 1s orbital at the bottom of the diagram is the orbital with electrons of lowest energy. The energy increases as we move up to the 2s and then 2p, 3s, and 3p orbitals, showing that the increasing n value has more influence on energy than the increasing l value for small atoms. However, this pattern does not hold for larger atoms. The 3d orbital is higher in energy than the 4s orbital. Such overlaps continue to occur frequently as we move up the chart.
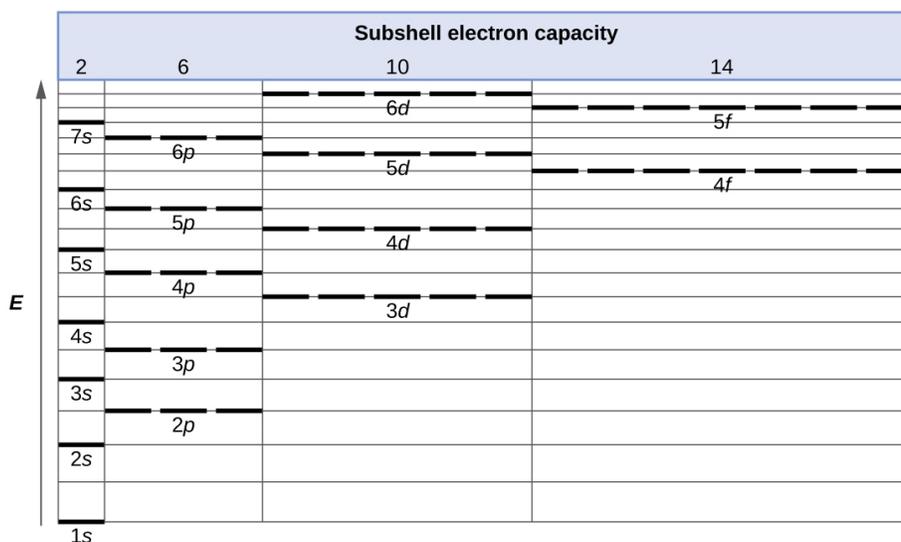
Figure 3.5.1: Generalized energy-level diagram for atomic orbitals in an atom with two or more electrons (not to scale).

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

The arrangement of electrons in the orbitals of an atom is called the **electron configuration** of the atom. We describe an electron configuration with a symbol that contains three pieces of information (Figure $3.5.2$):

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

For example, the notation $2p^4$ (read "two–p–four") indicates four electrons in a p subshell ($l = 1$) with a principal quantum number (n) of 2. The notation $3d^8$ (read "three–d–eight") indicates eight electrons in the d subshell (i.e., $l = 2$) of the principal shell for which $n = 3$.
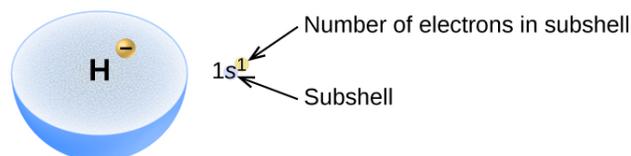
Figure $3.5.2$: The diagram of an electron configuration specifies the subshell (n and l value, with letter symbol) and superscript number of electrons.

The Aufbau Principle

To determine the electron configuration for any particular atom, we can "build" the structures in the order of atomic numbers. Beginning with hydrogen, and continuing across the periods of the periodic table, we add one proton at a time to the nucleus and one electron to the proper subshell until we have described the electron configurations of all the elements. This procedure is called the **Aufbau principle**, from the German word *Aufbau* ("to build up"). Each added electron occupies the subshell of lowest energy available (in the order shown in Figure $3.5.1$), subject to the limitations imposed by the allowed quantum numbers according to the Pauli exclusion principle. Electrons enter higher-energy subshells only after lower-energy subshells have been filled to capacity. Figure $3.5.3$ illustrates the traditional way to remember the filling order for atomic orbitals.
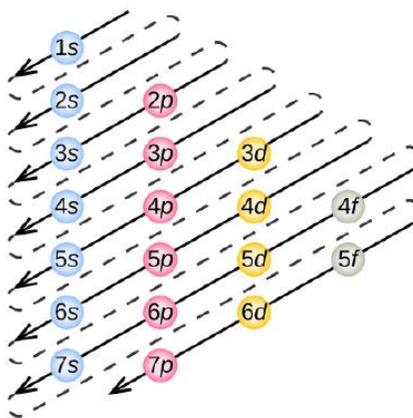
Figure $3.5.3$: This diagram depicts the energy order for atomic orbitals and is useful for deriving ground-state electron configurations.

Since the arrangement of the periodic table is based on the electron configurations, Figure $3.5.4$ provides an alternative method for determining the electron configuration. The filling order simply begins at hydrogen and includes each subshell as you proceed in increasing Z order. For example, after filling the $3p$ block up to Ar, we see the orbital will be 4s (K, Ca), followed by the $3d$ orbitals.

Electron Configuration Table

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 1 (1s)																	He 2 (1s)
2	Li 1 (2s)	Be 2											B 1	C 2	N 3	O 4	F 5	Ne 6 (2p)
3	Na 1 (3s)	Mg 2											Al 1	Si 2	P 3	S 4	Cl 5	Ar 6 (3p)
4	K 1 (4s)	Ca 2	Sc 1	Ti 2	V 3	Cr 4	Mn 5	Fe 6	Co 7	Ni 8	Cu 9	Zn 10 (3d)	Ga 1	Ge 2	As 3	Se 4	Br 5	Kr 6 (4p)
5	Rb 1 (5s)	Sr 2	Y 1	Zr 2	Nb 3	Mo 4	Tc 5	Ru 6	Rh 7	Pd 8	Ag 9	Cd 10 (4d)	In 1	Sn 2	Sb 3	Te 4	I 5	Xe 6 (5p)
6	Cs 1 (6s)	Ba 2	La *1	Hf 2	Ta 3	W 4	Re 5	Os 6	Ir 7	Pt 8	Au 9	Hg 10 (5d)	Tl 1	Pb 2	Bi 3	Po 4	At 5	Rn 6 (6p)
7	Fr 1 (7s)	Ra 2	Ac **1	Rf 2	Db 3	Sg 4	Bh 5	Hs 6	Mt	Ds	Rg	Cn (6d)	Nh	Fl	Mc	Lv	Ts	Og

Legend:
- Name → H
- Electrons → 1
- Subshell → 1s

Figure 3.5.4: This partial periodic table shows electron configurations for the valence subshells of atoms. By "building up" from hydrogen, this table can be used to determine the electron configuration for atoms of most elements in the periodic table. (Electron configurations of the lanthanides and actinides are not accurately predicted by this simple approach. See Figure 3.5.6:

We will now construct the ground-state electron configuration and orbital diagram for a selection of atoms in the first and second periods of the periodic table. **Orbital diagrams** are pictorial representations of the electron configuration, showing the individual orbitals and the pairing arrangement of electrons. We start with a single hydrogen atom (atomic number 1), which consists of one proton and one electron. Referring to Figure 3.5.3 or Figure 3.5.4, we would expect to find the electron in the $1s$ orbital. By convention, the $m_s = +\frac{1}{2}$ value is usually filled first. The electron configuration and the orbital diagram are:

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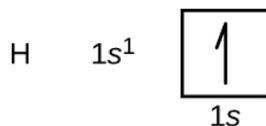
Following hydrogen is the noble gas helium, which has an atomic number of 2. The helium atom contains two protons and two electrons. The first electron has the same four quantum numbers as the hydrogen atom electron ($n = 1$, $l = 0$, $m_{-l} = 0$), $m_s = +\frac{1}{2}$. The second electron also goes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

$$\text{He} \qquad 1s^2 \qquad \boxed{\uparrow\downarrow} \\ \qquad\qquad\qquad\quad 1s$$
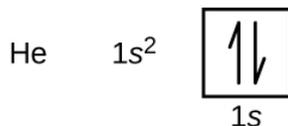
The $n = 1$ shell is completely filled in a helium atom.

The next atom is the alkali metal lithium with an atomic number of 3. The first two electrons in lithium fill the $1s$ orbital and have the same sets of four quantum numbers as the two electrons in helium. The remaining electron must occupy the orbital of next lowest energy, the $2s$ orbital (Figure 3.5.3 or Figure 3.5.4). Thus, the electron configuration and orbital diagram of lithium are:

Li $1s^2 2s^1$
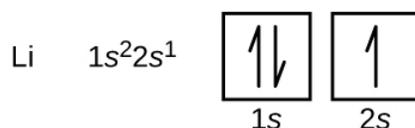
An atom of the alkaline earth metal beryllium, with an atomic number of 4, contains four protons in the nucleus and four electrons surrounding the nucleus. The fourth electron fills the remaining space in the 2s orbital.

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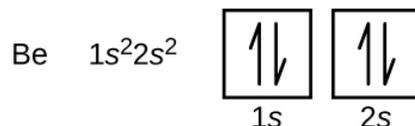
An atom of boron (atomic number 5) contains five electrons. The $n = 1$ shell is filled with two electrons and three electrons will occupy the $n = 2$ shell. Because any s subshell can contain only two electrons, the fifth electron must occupy the next energy level, which will be a $2p$ orbital. There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

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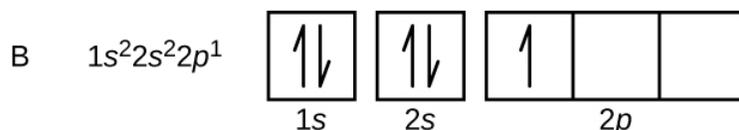
Carbon (atomic number 6) has six electrons. Four of them fill the 1s and 2s orbitals. The remaining two electrons occupy the $2p$ subshell. We now have a choice of filling one of the $2p$ orbitals and pairing the electrons or of leaving the electrons unpaired in two different, but degenerate, p orbitals.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

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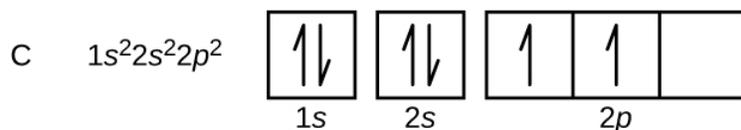
Nitrogen (atomic number 7) fills the 1s and 2s subshells and has one electron in each of the three $2p$ orbitals, in accordance with Hund's rule. These three electrons have unpaired spins. Oxygen (atomic number 8) has a pair of electrons in any one of the $2p$ orbitals (the electrons have opposite spins)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

N $1s^22s^22p^3$

| ⇅ | ⇅ | ↑ | ↑ | ↑ |

1s   2s   2p

O $1s^22s^22p^4$

| ⇅ | ⇅ | ⇅ | ↑ | ↑ |

1s   2s   2p

F $1s^22s^22p^5$

| ⇅ | ⇅ | ⇅ | ⇅ | ↑ |

1s   2s   2p

Ne $1s^22s^22p^6$

| ⇅ | ⇅ | ⇅ | ⇅ | ⇅ |

1s   2s   2p
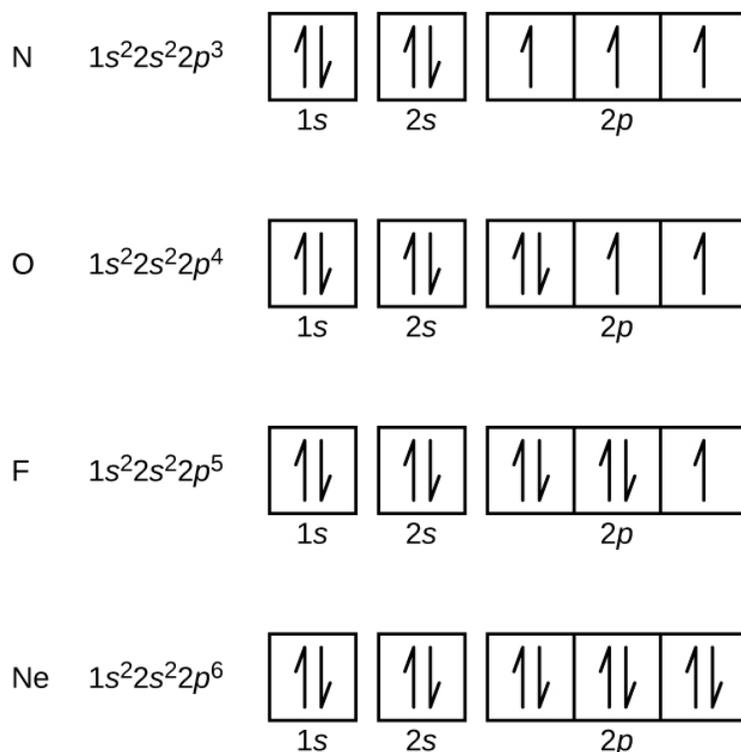
The alkali metal sodium (atomic number 11) has one more electron than the neon atom. This electron must go into the lowest-energy subshell available, the 3s orbital, giving a $1s^22s^22p^63s^1$ configuration. The electrons occupying the outermost shell orbital(s) (highest value of n) are called **valence electrons**, and those occupying the inner shell orbitals are called **core electrons** (Figure 3.5.5). Since the core electron shells correspond to noble gas electron configurations, we can abbreviate electron configurations by writing the noble gas that matches the core electron configuration, along with the valence electrons in a condensed format. For our sodium example, the symbol [Ne] represents core electrons, ($1s^22s^22p^6$) and our abbreviated or condensed configuration is [Ne]$3s^1$.

Na $1s^22s^22p^63s^1$ Abbreviation [Ne]$3s^1$

Core electrons   Valence electron

Figure 3.5.5: A core-abbreviated electron configuration (right) replaces the core electrons with the noble gas symbol whose configuration matches the core electron configuration of the other element.

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

$$Li : [He]2s^1$$
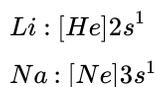
$$Na : [Ne]3s^1$$

The alkaline earth metal magnesium (atomic number 12), with its 12 electrons in a [Ne]$3s^2$ configuration, is analogous to its family member beryllium, [He]$2s^2$. Both atoms have a filled s subshell outside their filled inner shells. Aluminum (atomic number 13), with 13 electrons and the electron configuration [Ne]$3s^23p^1$, is analogous to its family member boron, [He]$2s^22p^1$.

The electron configurations of silicon (14 electrons), phosphorus (15 electrons), sulfur (16 electrons), chlorine (17 electrons), and argon (18 electrons) are analogous in the electron configurations of their outer shells to their corresponding family members carbon, nitrogen, oxygen, fluorine, and neon, respectively, except that the principal quantum number of the outer shell of the heavier elements has increased by one to n = 3. Figure 3.5.6 shows the lowest energy, or ground-state, electron configuration for these elements as well as that for atoms of each of the known elements.

Electron Configuration Table

Figure: Periodic table showing outer-shell electron configuration of each element

Group →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H $1s^1$																	2 He $1s^2$
2	3 Li $2s^1$	4 Be $2s^2$											5 B $2s^22p^1$	6 C $2s^22p^2$	7 N $2s^22p^3$	8 O $2s^22p^4$	9 F $2s^22p^5$	10 Ne $2s^22p^6$
3	11 Na $3s^1$	12 Mg $3s^2$											13 Al $3s^23p^1$	14 Si $3s^23p^2$	15 P $3s^23p^3$	16 S $3s^23p^4$	17 Cl $3s^23p^5$	18 Ar $3s^23p^6$
4	19 K $4s^1$	20 Ca $4s^2$	21 Sc $4s^23d^1$	22 Ti $4s^23d^2$	23 V $4s^23d^3$	24 Cr $4s^13d^5$	25 Mn $4s^23d^5$	26 Fe $4s^23d^6$	27 Co $4s^23d^7$	28 Ni $4s^23d^8$	29 Cu $4s^13d^{10}$	30 Zn $4s^23d^{10}$	31 Ga $4s^23d^{10}4p^1$	32 Ge $4s^23d^{10}4p^2$	33 As $4s^23d^{10}4p^3$	34 Se $4s^23d^{10}4p^4$	35 Br $4s^23d^{10}4p^5$	36 Kr $4s^23d^{10}4p^6$
5	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $5s^24d^1$	40 Zr $5s^24d^2$	41 Nb $5s^14d^4$	42 Mo $5s^14d^5$	43 Tc $5s^14d^6$	44 Ru $5s^14d^7$	45 Rh $5s^14d^8$	46 Pd $4d^{10}$	47 Ag $5s^14d^{10}$	48 Cd $5s^24d^{10}$	49 In $5s^24d^{10}5p^1$	50 Sn $5s^24d^{10}5p^2$	51 Sb $5s^24d^{10}5p^3$	52 Te $5s^24d^{10}5p^4$	53 I $5s^24d^{10}5p^5$	54 Xe $5s^24d^{10}5p^6$
6	55 Cs $6s^1$	56 Ba $6s^2$	57 La* $6s^25d^1$	72 Hf $6s^24f^{14}5d^2$	73 Ta $6s^24f^{14}5d^3$	74 W $6s^24f^{14}5d^4$	75 Re $6s^24f^{14}5d^5$	76 Os $6s^24f^{14}5d^6$	77 Ir $6s^24f^{14}5d^7$	78 Pt $6s^14f^{14}5d^9$	79 Au $6s^14f^{14}5d^{10}$	80 Hg $6s^24f^{14}5d^{10}$	81 Tl $6s^24f^{14}5d^{10}6p^1$	82 Pb $6s^24f^{14}5d^{10}6p^2$	83 Bi $6s^24f^{14}5d^{10}6p^3$	84 Po $6s^24f^{14}5d^{10}6p^4$	85 At $6s^24f^{14}5d^{10}6p^5$	86 Rn $6s^24f^{14}5d^{10}6p^6$
7	87 Fr $7s^1$	88 Ra $7s^2$	89 Ac** $7s^26d^1$	104 Rf $7s^25f^{14}6d^2$	105 Db $7s^25f^{14}6d^3$	106 Sg $7s^25f^{14}6d^4$	107 Bh $7s^25f^{14}6d^5$	108 Hs $7s^25f^{14}6d^6$	109 Mt $7s^25f^{14}6d^7$	110 Ds $7s^25f^{14}6d^8$	111 Rg $7s^25f^{14}6d^9$	112 Cn $7s^25f^{14}6d^{10}$	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

* Lanthanides:

58 Ce $6s^24f^2$	59 Pr $6s^24f^3$	60 Nd $6s^24f^4$	61 Pm $6s^24f^5$	62 Sm $6s^24f^6$	63 Eu $6s^24f^7$	64 Gd $6s^24f^75d^1$	65 Tb $6s^24f^9$	66 Dy $6s^24f^{10}$	67 Ho $6s^24f^{11}$	68 Er $6s^24f^{12}$	69 Tm $6s^24f^{13}$	70 Yb $6s^24f^{14}$	71 Lu $6s^24f^{14}5d^1$

** Actinides:

90 Th $7s^26d^2$	91 Pa $7s^25f^26d^1$	92 U $7s^25f^36d^1$	93 Np $7s^25f^46d^1$	94 Pu $7s^25f^6$	95 Am $7s^25f^7$	96 Cm $7s^25f^76d^1$	97 Bk $7s^25f^86d^1$	98 Cf $7s^25f^{10}$	99 Es $7s^25f^{11}$	100 Fm $7s^25f^{12}$	101 Md $7s^25f^{13}$	102 No $7s^25f^{14}$	103 Lr $7s^25f^{14}6d^1$

Key (element cell diagram):
- Atomic number → 1
- Name → H
- Outer electron configuration → $1s^1$
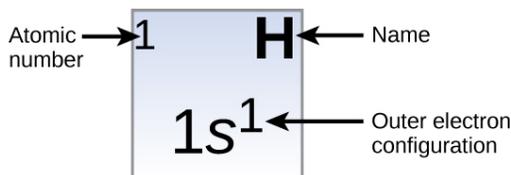
Figure 3.5.6: This version of the periodic table shows the outer-shell electron configuration of each element. Note that down each group, the configuration is often similar.

When we come to the next element in the periodic table, the alkali metal potassium (atomic number 19), we might expect that we would begin to add electrons to the 3d subshell. However, all available chemical and physical evidence indicates that potassium is like lithium and sodium, and that the next electron is not added to the 3d level but is, instead, added to the 4s level (Figure 3.5.6). As discussed previously, the 3d orbital with no radial nodes is higher in energy because it is less penetrating and more shielded from the nucleus than the 4s, which has three radial nodes. Thus, potassium has an electron configuration of [Ar]$4s^1$. Hence, potassium corresponds to Li and Na in its valence shell configuration. The next electron is added to complete the 4s subshell and calcium has an electron configuration of [Ar]$4s^2$. This gives calcium an outer-shell electron configuration corresponding to that of beryllium and magnesium.

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

> ✔ Example 3.5.1: Quantum Numbers and Electron Configurations
>
> What is the electron configuration and orbital diagram for a phosphorus atom? What are the four quantum numbers for the last electron added?

Solution

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

$$P \quad 1s^2 2s^2 2p^6 3s^2 3p^3$$
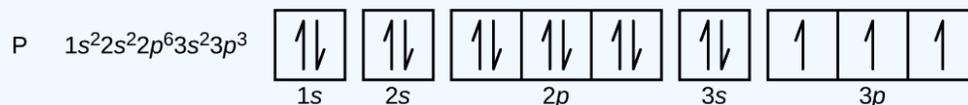
The last electron added is a 3p electron. Therefore, $n = 3$ and, for a p-type orbital, $l = 1$. The m_l value could be –1, 0, or +1. The three p orbitals are degenerate, so any of these m_l values is correct. For unpaired electrons, convention assigns the value of $+\frac{1}{2}$ for the spin quantum number; thus, $m_s = +\frac{1}{2}$

? Exercise 3.5.1

Identify the atoms from the electron configurations given:

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

Answer

   a. Mn
   b. Xe

The periodic table can be a powerful tool in predicting the electron configuration of an element. However, we do find exceptions to the order of filling of orbitals that are shown in Figure 3.5.3 or Figure 3.5.4. For instance, the electron configurations (shown in Figure 3.5.6) of the transition metals chromium (Cr; atomic number 24) and copper (Cu; atomic number 29), among others, are not those we would expect. In general, such exceptions involve subshells with very similar energy, and small effects can lead to changes in the order of filling.

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

Electron Configurations and the Periodic Table

As described earlier, the periodic table arranges atoms based on increasing atomic number so that elements with the same chemical properties recur periodically. When their electron configurations are added to the table (Figure 3.5.6), we also see a periodic recurrence of similar electron configurations in the outer shells of these elements. Because they are in the outer shells of an atom, valence electrons play the most important role in chemical reactions. The outer electrons have the highest energy of the electrons in an atom and are more easily lost or shared than the core electrons. Valence electrons are also the determining factor in some physical properties of the elements.

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

It is important to remember that the periodic table was developed on the basis of the chemical behavior of the elements, well before any idea of their atomic structure was available. Now we can understand why the periodic table has the arrangement it has—the

arrangement puts elements whose atoms have the same number of valence electrons in the same group. This arrangement is emphasized in Figure 3.5.6: , which shows in periodic-table form the electron configuration of the last subshell to be filled by the Aufbau principle. The colored sections of Figure 3.5.6: show the three categories of elements classified by the orbitals being filled: main group, transition, and inner transition elements. These classifications determine which orbitals are counted in the **valence shell**, or highest energy level orbitals of an atom.

1. **Main group elements** (sometimes called **representative elements**) are those in which the last electron added enters an *s* or a *p* orbital in the outermost shell, shown in blue and red in Figure 3.5.6. This category includes all the nonmetallic elements, as well as many metals and the metalloids. The valence electrons for main group elements are those with the highest *n* level. For example, gallium (Ga, atomic number 31) has the electron configuration [Ar]$\underline{4s^2}3d^{10}\underline{4p^1}$, which contains three valence electrons (underlined). The completely filled *d* orbitals count as core, not valence, electrons.

2. **Transition elements or transition metals**. These are metallic elements in which the last electron added enters a *d* orbital. The valence electrons (those added after the last noble gas configuration) in these elements include the *ns* and $(n-1)$ *d* electrons. The official IUPAC definition of transition elements specifies those with partially filled *d* orbitals. Thus, the elements with completely filled orbitals (Zn, Cd, Hg, as well as Cu, Ag, and Au in Figure 3.5.6) are not technically transition elements. However, the term is frequently used to refer to the entire *d* block (colored yellow in Figure 3.5.6), and we will adopt this usage in this textbook.

3. **Inner transition elements** are metallic elements in which the last electron added occupies an *f* orbital. They are shown in green in Figure 3.5.6. The valence shells of the inner transition elements consist of the $(n-2)f$, the $(n-1)d$, and the *ns* subshells. There are two inner transition series:
   a. The lanthanide series: lanthanum (La) through lutetium (Lu)
   b. The actinide series: actinium (Ac) through lawrencium (Lr)

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

Electron Configurations of Ions

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

> ✔ Example 3.5.2: Predicting Electron Configurations of Ions
>
> What is the electron configuration of:
>
> a. Na^+
> b. P^{3-}
> c. Al^{2+}
> d. Fe^{2+}
> e. Sm^{3+}
>
> **Solution**
>
> First, write out the electron configuration for each parent atom. We have chosen to show the full, unabbreviated configurations to provide more practice for students who want it, but listing the core-abbreviated electron configurations is also acceptable.
>
> Next, determine whether an electron is gained or lost. Remember electrons are negatively charged, so ions with a positive charge have *lost* an electron. For main group elements, the last orbital gains or loses the electron. For transition metals, the last *s* orbital loses an electron before the *d* orbitals.
>
> a. Na: $1s^22s^22p^63s^1$. Sodium cation loses one electron, so Na^+: $1s^22s^22p^63s^1 = Na^+$: $1s^22s^22p^6$.
> b. P: $1s^22s^22p^63s^23p^3$. Phosphorus trianion gains three electrons, so P^{3-}: $1s^22s^22p^63s^23p^6$.
> c. Al: $1s^22s^22p^63s^23p^1$. Aluminum dication loses two electrons Al^{2+}: $1s^22s^22p^63s^23p^1 = Al^{2+}$: $1s^22s^22p^63s^1$.
> d. Fe: $1s^22s^22p^63s^23p^64s^23d^6$. Iron(II) loses two electrons and, since it is a transition metal, they are removed from the 4*s* orbital Fe^{2+}: $1s^22s^22p^63s^23p^64s^23d^6 = 1s^22s^22p^63s^23p^63d^6$.

e. Sm: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^6$. Samarium trication loses three electrons. The first two will be lost from the 6s orbital, and the final one is removed from the $4f$ orbital. Sm^{3+}: $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^66s^24f^6$ = $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^{10}5p^64f^5$.

> **? Exercise 3.5.21**
>
> Which ion with a +2 charge has the electron configuration $1s^22s^22p^63s^23p^64s^23d^{10}4p^64d^5$? Which ion with a +3 charge has this configuration?
>
> **Answer**
>
> Tc^{2+}, Ru^{3+}

3.6: Periodic Variations in Element Properties

> **◐ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Describe and explain the observed trends in atomic size, ionization energy, and electron affinity of the elements

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

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

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

Variation in Covalent Radius

The quantum mechanical picture makes it difficult to establish a definite size of an atom. However, there are several practical ways to define the radius of atoms and, thus, to determine their relative sizes that give roughly similar values. We will use the covalent radius (Figure 3.6.1), which is defined as one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond (this measurement is possible because atoms within molecules still retain much of their atomic identity). We know that as we scan down a group, the principal quantum number, n, increases by one for each element. Thus, the electrons are being added to a region of space that is increasingly distant from the nucleus. Consequently, the size of the atom (and its covalent radius) must increase as we increase the distance of the outermost electrons from the nucleus. This trend is illustrated for the covalent radii of the halogens in Table 3.6.1 and Figure 3.6.1. The trends for the entire periodic table can be seen in Figure 3.6.2.

Table 3.6.1: Covalent Radii of the Halogen Group Elements

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

F radius = $\frac{128\ pm}{2}$ = 64 pm   Cl radius = $\frac{198\ pm}{2}$ = 99 pm   Br radius = $\frac{228\ pm}{2}$ = 114 pm   I radius = $\frac{266\ pm}{2}$ = 133 pm

(a)

(b)

Figure 3.6.1: (a) The radius of an atom is defined as one-half the distance between the nuclei in a molecule consisting of two identical atoms joined by a covalent bond. The atomic radius for the halogens increases down the group as *n* increases. (b) Covalent radii of the elements are shown to scale. The general trend is that radii increase down a group and decrease across a period.
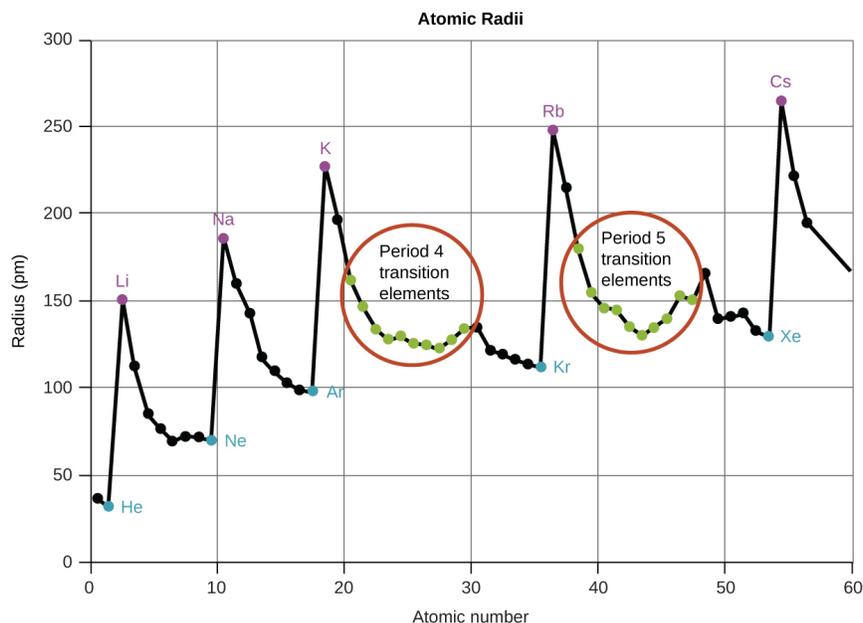
Figure 3.6.2: Within each period, the trend in atomic radius decreases as *Z* increases; for example, from K to Kr. Within each group (e.g., the alkali metals shown in purple), the trend is that atomic radius increases as *Z* increases.

As shown in Figure 3.6.2, as we move across a period from left to right, we generally find that each element has a smaller covalent radius than the element preceding it. This might seem counterintuitive because it implies that atoms with more electrons have a smaller atomic radius. This can be explained with the concept of **effective nuclear charge**, Z_{eff}. This is the pull exerted on a

specific electron by the nucleus, taking into account any electron–electron repulsions. For hydrogen, there is only one electron and so the nuclear charge (Z) and the effective nuclear charge (Z_{eff}) are equal. For all other atoms, the inner electrons partially *shield* the outer electrons from the pull of the nucleus, and thus:

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

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

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

> ✔ **Example 3.6.1: Sorting Atomic Radii**
>
> Predict the order of increasing covalent radius for Ge, Fl, Br, Kr.
>
> **Solution**
> Radius increases as we move down a group, so Ge < Fl (Note: Fl is the symbol for flerovium, element 114, NOT fluorine). Radius decreases as we move across a period, so Kr < Br < Ge. Putting the trends together, we obtain Kr < Br < Ge < Fl.

> ? **Exercise 3.6.1**
>
> Give an example of an atom whose size is smaller than fluorine.
>
> **Answer**
>   Ne or He

Variation in Ionic Radii

Ionic radius is the measure used to describe the size of an ion. A cation always has fewer electrons and the same number of protons as the parent atom; it is smaller than the atom from which it is derived (Figure 3.6.3). For example, the covalent radius of an aluminum atom ($1s^2 2s^2 2p^6 3s^2 3p^1$) is 118 pm, whereas the ionic radius of an Al^{3+} ($1s^2 2s^2 2p^6$) is 68 pm. As electrons are removed from the outer valence shell, the remaining core electrons occupying smaller shells experience a greater effective nuclear charge Z_{eff} (as discussed) and are drawn even closer to the nucleus.

● Al	118	● S	104
• Al^{3+}	68	● S^{2-}	170

Figure 3.6.3: The radius for a cation is smaller than the parent atom (Al), due to the lost electrons; the radius for an anion is larger than the parent (S), due to the gained electrons.

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

An anion (negative ion) is formed by the addition of one or more electrons to the valence shell of an atom. This results in a greater repulsion among the electrons and a decrease in Z_{eff} per electron. Both effects (the increased number of electrons and the decreased Z_{eff}) cause the radius of an anion to be larger than that of the parent atom (Figure 3.6.3). For example, a sulfur atom ($[Ne]3s^2 3p^4$) has a covalent radius of 104 pm, whereas the ionic radius of the sulfide anion ($[Ne]3s^2 3p^6$) is 170 pm. For consecutive elements proceeding down any group, anions have larger principal quantum numbers and, thus, larger radii.

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

Variation in Ionization Energies

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

$$X(g) \longrightarrow X^+(g) + e^- \qquad IE_1$$
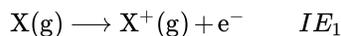
The energy required to remove the second most loosely bound electron is called the second ionization energy (IE_2).

$$X^+(g) \longrightarrow X^{2+}(g) + e^- \qquad IE_2$$
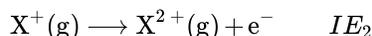
The energy required to remove the third electron is the third ionization energy, and so on. Energy is always required to remove electrons from atoms or ions, so ionization processes are endothermic and IE values are always positive. For larger atoms, the most loosely bound electron is located farther from the nucleus and so is easier to remove. Thus, as size (atomic radius) increases, the ionization energy should decrease. Relating this logic to what we have just learned about radii, we would expect first ionization energies to decrease down a group and to increase across a period.

Figure 3.6.4 graphs the relationship between the first ionization energy and the atomic number of several elements. The values of first ionization energy for the elements are given in Figure 3.6.5. Within a period, the IE_1 generally increases with increasing Z. Down a group, the IE_1 value generally decreases with increasing Z. There are some systematic deviations from this trend, however. Note that the ionization energy of boron (atomic number 5) is less than that of beryllium (atomic number 4) even though the nuclear charge of boron is greater by one proton. This can be explained because the energy of the subshells increases as l increases, due to penetration and shielding (as discussed previously in this chapter). Within any one shell, the s electrons are lower in energy than the p electrons. This means that an s electron is harder to remove from an atom than a p electron in the same shell. The electron removed during the ionization of beryllium ([He]$2s^2$) is an s electron, whereas the electron removed during the ionization of boron ([He]$2s^2 2p^1$) is a p electron; this results in a lower first ionization energy for boron, even though its nuclear charge is greater by one proton. Thus, we see a small deviation from the predicted trend occurring each time a new subshell begins.
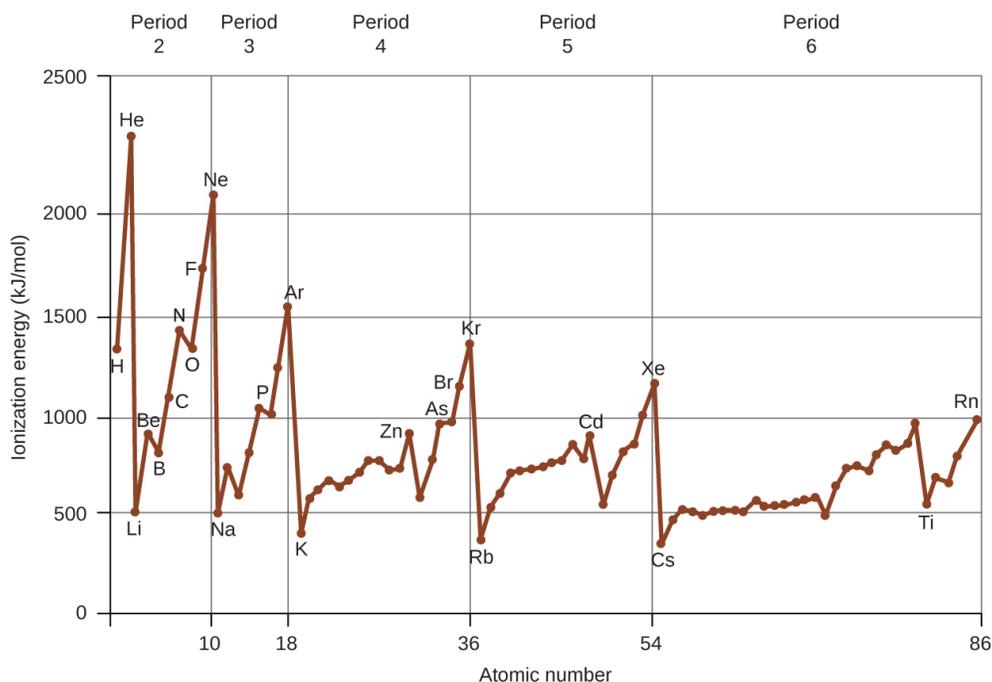
Figure 3.6.4: The first ionization energy of the elements in the first five periods are plotted against their atomic number.

Figure 3.6.5: This version of the periodic table shows the first ionization energy (IE_1), in kJ/mol, of selected elements.

Another deviation occurs as orbitals become more than one-half filled. The first ionization energy for oxygen is slightly less than that for nitrogen, despite the trend in increasing IE_1 values across a period. Looking at the orbital diagram of oxygen, we can see that removing one electron will eliminate the electron–electron repulsion caused by pairing the electrons in the $2p$ orbital and will result in a half-filled orbital (which is energetically favorable). Analogous changes occur in succeeding periods (note the dip for sulfur after phosphorus in Figure 3.6.5).
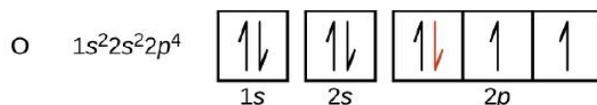
Removing an electron from a cation is more difficult than removing an electron from a neutral atom because of the greater electrostatic attraction to the cation. Likewise, removing an electron from a cation with a higher positive charge is more difficult than removing an electron from an ion with a lower charge. Thus, successive ionization energies for one element always increase. As seen in Table 3.6.2, there is a large increase in the ionization energies for each element. This jump corresponds to removal of the core electrons, which are harder to remove than the valence electrons. For example, Sc and Ga both have three valence electrons, so the rapid increase in ionization energy occurs after the third ionization.

Table 3.6.2: Successive Ionization Energies for Selected Elements (kJ/mol)

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

✔ Example 3.6.2: Ranking Ionization Energies

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

Solution

Removing the $6p^1$ electron from Tl is easier than removing the $3p^1$ electron from Al because the higher n orbital is farther from the nucleus, so $IE_1(Tl) < IE_1(Al)$. Ionizing the third electron from Al ($Al^{2+} \longrightarrow Al^{3+} + e^-$) requires more energy because the cation Al^{2+} exerts a stronger pull on the electron than the neutral Al atom, so $IE_1(Al) < IE_3(Al)$. The second ionization

energy for sodium removes a core electron, which is a much higher energy process than removing valence electrons. Putting this all together, we obtain: $IE_1(Tl) < IE_1(Al) < IE_3(Al) < IE_2(Na)$.

> **? Exercise 3.6.2**
>
> Which has the lowest value for IE_1: O, Po, Pb, or Ba?
>
> **Answer**
>
>   Ba

Variation in Electron Affinities

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

$$X(g) + e^- \longrightarrow X^-(g) \quad EA_1$$
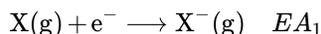
This process can be either endothermic or exothermic, depending on the element. The EA of some of the elements is given in Figure 3.6.6. You can see that many of these elements have negative values of EA, which means that energy is released when the gaseous atom accepts an electron. However, for some elements, energy is required for the atom to become negatively charged and the value of their EA is positive. Just as with ionization energy, subsequent EA values are associated with forming ions with more charge. The second EA is the energy associated with adding an electron to an anion to form a –2 ion, and so on.

As we might predict, it becomes easier to add an electron across a series of atoms as the effective nuclear charge of the atoms increases. We find, as we go from left to right across a period, EAs tend to become more negative. The exceptions found among the elements of group 2 (2A), group 15 (5A), and group 18 (8A) can be understood based on the electronic structure of these groups. The noble gases, group 18 (8A), have a completely filled shell and the incoming electron must be added to a higher n level, which is more difficult to do. Group 2 (2A) has a filled ns subshell, and so the next electron added goes into the higher energy np, so, again, the observed EA value is not as the trend would predict. Finally, group 15 (5A) has a half-filled np subshell and the next electron must be paired with an existing np electron. In all of these cases, the initial relative stability of the electron configuration disrupts the trend in EA.

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

Electron Affinity Values for Selected Elements (kJ/mol)

Period / Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H −72																	He +20*
2	Li −60	Be +240*											B −23	C −123	N 0	O −141	F −322	Ne −30
3	Na −53	Mg +230*											Al −44	Si −120	P −74	S −200	Cl −348	Ar +35*
4	K −48	Ca +150*	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga −40*	Ge −115	As −7	Se −195	Br −324	Kr +40*
5	Rb −46	Sr +160*	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In −40*	Sn −121	Sb −101	Te −190	I −295	Xe +40*
6	Cs −45	Ba +50*	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl −50	Pb −101	Bi −101	Po −170	At −270*	Rn +40*
7	Fr	Ra																

* Calculated value

Figure 3.6.6: This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements.

The properties discussed in this section (size of atoms and ions, effective nuclear charge, ionization energies, and electron affinities) are central to understanding chemical reactivity. For example, because fluorine has an energetically favorable EA and a large energy barrier to ionization (IE), it is much easier to form fluorine anions than cations. Metallic properties including conductivity and malleability (the ability to be formed into sheets) depend on having electrons that can be removed easily. Thus, metallic character increases as we move down a group and decreases across a period in the same trend observed for atomic size because it is easier to remove an electron that is farther away from the nucleus.

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3.7: Key Terms

amplitude | extent of the displacement caused by a wave

atomic orbital | mathematical function that describes the behavior of an electron in an atom (also called the wavefunction)

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

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

Bohr's model of the hydrogen atom | structural model in which an electron moves around the nucleus only in circular orbits, each with a specific allowed radius

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

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

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

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

degenerate orbitals | orbitals that have the same energy

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

electromagnetic radiation | energy transmitted by waves that have an electric-field component and a magnetic-field component

electromagnetic spectrum | range of energies that electromagnetic radiation can comprise, including radio, microwaves, infrared, visible, ultraviolet, X-rays, and gamma rays

electron affinity | energy change associated with addition of an electron to a gaseous atom or ion

electron configuration | listing that identifies the electron occupancy of an atom's shells and subshells

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

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

f orbital | multilobed region of space with high electron density, describes orbitals with $l = 3$

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

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

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

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

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

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

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

ionization energy | energy required to remove an electron from a gaseous atom or ion

isoelectronic | group of ions or atoms that have identical electron configurations

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

magnetic quantum number (m_l) | quantum number signifying the orientation of an atomic orbital around the nucleus

node | any point of a standing wave with zero amplitude

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

p orbital | dumbbell-shaped region of space with high electron density, describes orbitals with $l = 1$

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

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

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

quantization | limitation of some property to specific discrete values, not continuous

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

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

s orbital | spherical region of space with high electron density, describes orbitals with $l = 0$

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

shell | atomic orbitals with the same principal quantum number, n

spin quantum number (m_s) | number specifying the electron spin direction, either or

standing wave | (also, stationary wave) localized wave phenomenon characterized by discrete wavelengths determined by the boundary conditions used to generate the waves; standing waves are inherently quantized

subshell | atomic orbitals with the same values of n and l

valence electrons | electrons in the high energy outer shell(s) of an atom

valence shell | high energy outer shell(s) of an atom

wave | oscillation of a property over time or space; can transport energy from one point to another

wave-particle duality | observation that elementary particles can exhibit both wave-like and particle-like properties

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

wavelength (λ) | distance between two consecutive peaks or troughs in a wave

---

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3.8: Key Equations

$c = \lambda v$
where $h = 6.626 \ 10^{-34}$ J s

3.9: Summary

Light and other forms of electromagnetic radiation move through a vacuum with a constant speed, c, of 2.998 10^8 m s^{-1}. This radiation shows wavelike behavior, which can be characterized by a frequency, v, and a wavelength, λ, such that $c = \lambda v$. Light is an example of a travelling wave. Other important wave phenomena include standing waves, periodic oscillations, and vibrations. Standing waves exhibit quantization, since their wavelengths are limited to discrete integer multiples of some characteristic lengths. Electromagnetic radiation that passes through two closely spaced narrow slits having dimensions roughly similar to the wavelength will show an interference pattern that is a result of constructive and destructive interference of the waves. Electromagnetic radiation also demonstrates properties of particles called photons. The energy of a photon is related to the frequency (or alternatively, the wavelength) of the radiation as $E = hv$ (or), where h is Planck's constant. That light demonstrates both wavelike and particle-like behavior is known as wave-particle duality. All forms of electromagnetic radiation share these properties, although various forms including X-rays, visible light, microwaves, and radio waves interact differently with matter and have very different practical applications. Electromagnetic radiation can be generated by exciting matter to higher energies, such as by heating it. The emitted light can be either continuous (incandescent sources like the sun) or discrete (from specific types of excited atoms). Continuous spectra often have distributions that can be approximated as blackbody radiation at some appropriate temperature. The line spectrum of hydrogen can be obtained by passing the light from an electrified tube of hydrogen gas through a prism. This line spectrum was simple enough that an empirical formula called the Rydberg formula could be derived from the spectrum. Three historically important paradoxes from the late 19th and early 20th centuries that could not be explained within the existing framework of classical mechanics and classical electromagnetism were the blackbody problem, the photoelectric effect, and the discrete spectra of atoms. The resolution of these paradoxes ultimately led to quantum theories that superseded the classical theories.

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

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

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

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

Electrons in the outermost orbitals, called valence electrons, are responsible for most of the chemical behavior of elements. In the periodic table, elements with analogous valence electron configurations usually occur within the same group. There are some exceptions to the predicted filling order, particularly when half-filled or completely filled orbitals can be formed. The periodic table

can be divided into three categories based on the orbital in which the last electron to be added is placed: main group elements (*s* and *p* orbitals), transition elements (*d* orbitals), and inner transition elements (*f* orbitals).

Electron configurations allow us to understand many periodic trends. Covalent radius increases as we move down a group because the *n* level (orbital size) increases. Covalent radius mostly decreases as we move left to right across a period because the effective nuclear charge experienced by the electrons increases, and the electrons are pulled in tighter to the nucleus. Anionic radii are larger than the parent atom, while cationic radii are smaller, because the number of valence electrons has changed while the nuclear charge has remained constant. Ionization energy (the energy associated with forming a cation) decreases down a group and mostly increases across a period because it is easier to remove an electron from a larger, higher energy orbital. Electron affinity (the energy associated with forming an anion) is more favorable (exothermic) when electrons are placed into lower energy orbitals, closer to the nucleus. Therefore, electron affinity becomes increasingly negative as we move left to right across the periodic table and decreases as we move down a group. For both IE and electron affinity data, there are exceptions to the trends when dealing with completely filled or half-filled subshells.

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3.10: Exercises

1.

The light produced by a red neon sign is due to the emission of light by excited neon atoms. Qualitatively describe the spectrum produced by passing light from a neon lamp through a prism.

2.

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

3.

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

4.

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

5.

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

6.

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

7.

A photon of light produced by a surgical laser has an energy of 3.027×10^{-19} J. Calculate the frequency and wavelength of the photon. What is the total energy in 1 mole of photons? What is the color of the emitted light?

8.

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

9.

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

10.

Photons of infrared radiation are responsible for much of the warmth we feel when holding our hands before a fire. These photons will also warm other objects. How many infrared photons with a wavelength of 1.5×10^{-6} m must be absorbed by the water to warm a cup of water (175 g) from 25.0 °C to 40 °C?

11.

One of the radiographic devices used in a dentist's office emits an X-ray of wavelength 2.090×10^{-11} m. What is the energy, in joules, and frequency of this X-ray?

12.

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

13.

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

14.

Answer the following questions about a Blu-ray laser:

a. The laser on a Blu-ray player has a wavelength of 405 nm. In what region of the electromagnetic spectrum is this radiation? What is its frequency?

b. A Blu-ray laser has a power of 5 milliwatts (1 watt = 1 J s^{-1}). How many photons of light are produced by the laser in 1 hour?

c. The ideal resolution of a player using a laser (such as a Blu-ray player), which determines how close together data can be stored on a compact disk, is determined using the following formula: Resolution = 0.60(λ/NA), where λ is the wavelength of the laser and NA is the numerical aperture. Numerical aperture is a measure of the size of the spot of light on the disk; the larger the NA, the smaller the spot. In a typical Blu-ray system, NA = 0.95. If the 405-nm laser is used in a Blu-ray player, what is the closest that information can be stored on a Blu-ray disk?

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

15.

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

16.

Why is the electron in a Bohr hydrogen atom bound less tightly when it has a quantum number of 3 than when it has a quantum number of 1?

17.

What does it mean to say that the energy of the electrons in an atom is quantized?

18.

Using the Bohr model, determine the energy, in joules, necessary to ionize a ground-state hydrogen atom. Show your calculations.

19.

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

20.

Using the Bohr model, determine the lowest possible energy, in joules, for the electron in the Li^{2+} ion.

21.

Using the Bohr model, determine the lowest possible energy for the electron in the He$^+$ ion.

22.

Using the Bohr model, determine the energy of an electron with $n = 6$ in a hydrogen atom.

23.

Using the Bohr model, determine the energy of an electron with $n = 8$ in a hydrogen atom.

24.

How far from the nucleus in angstroms (1 angstrom = 1 10^{-10} m) is the electron in a hydrogen atom if it has an energy of –8.72 10^{-20} J?

25.

What is the radius, in angstroms, of the orbital of an electron with $n = 8$ in a hydrogen atom?

26.

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

27.

Using the Bohr model, determine the energy in joules of the photon produced when an electron in a Li²⁺ ion moves from the orbit with $n = 2$ to the orbit with $n = 1$.

28.

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

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

29.

How are the Bohr model and the Rutherford model of the atom similar? How are they different?

30.

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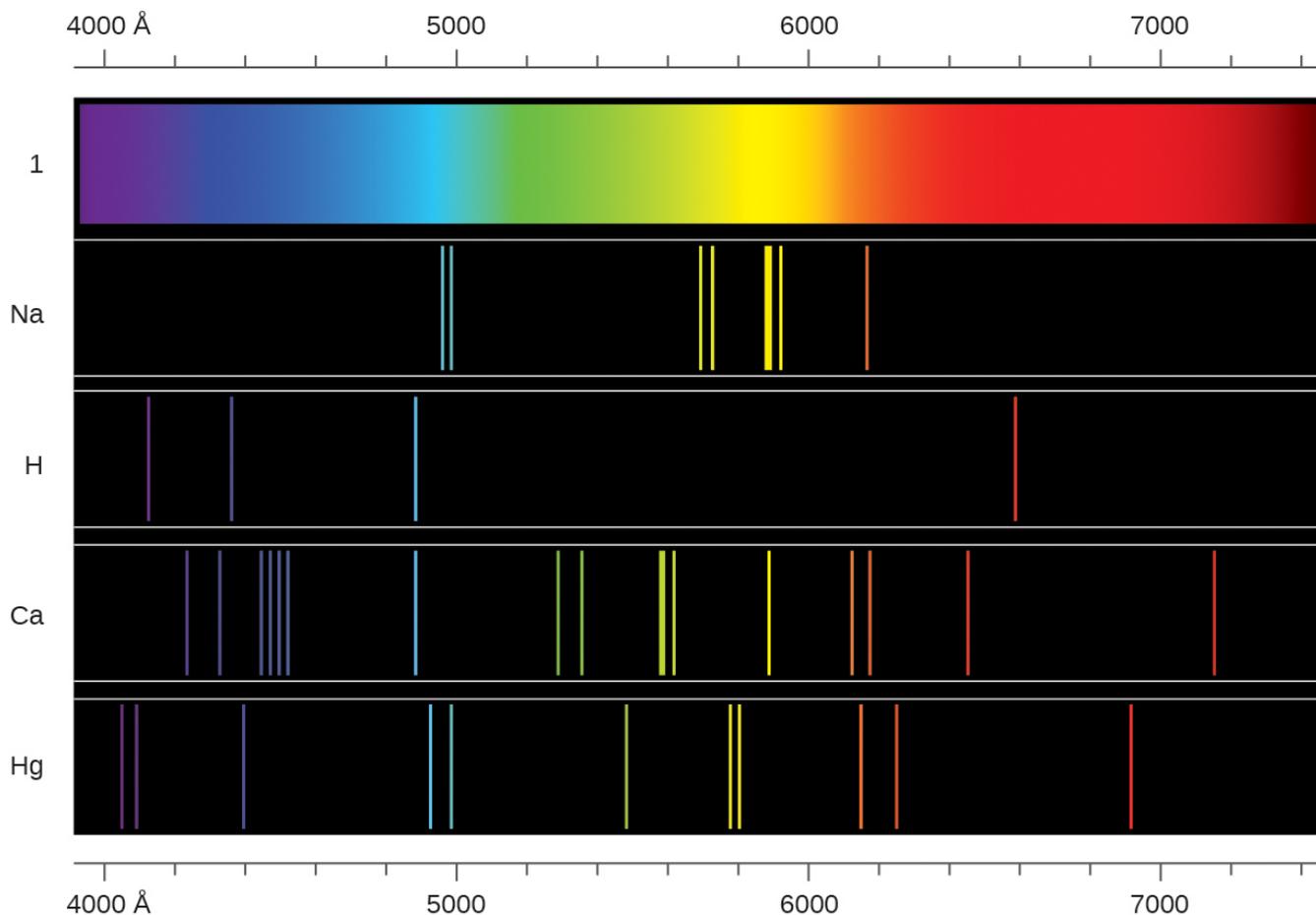
What causes the lines in these spectra? Why are the colors of the lines different? Suggest a reason for the observation that the spectrum of calcium is more complicated than the spectrum of hydrogen.

31.

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

32.

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

33.

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

34.

Answer the following questions:

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

35.

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

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

36.

Which of the subshells described in the previous question contain degenerate orbitals? How many degenerate orbitals are in each?

37.

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

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

38.

Which of the subshells described in the previous question contain degenerate orbitals? How many degenerate orbitals are in each?

39.

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

40.

Sketch the p_x and d_{xz} orbitals. Be sure to show and label the coordinates.

41.

Consider the orbitals shown here in outline.

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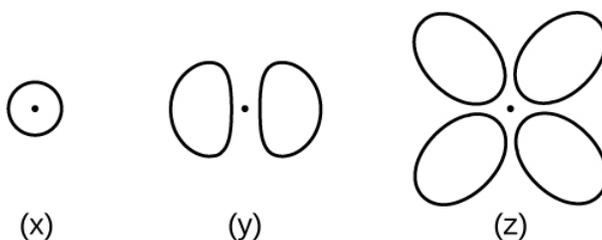
a. What is the maximum number of electrons contained in an orbital of type (x)? Of type (y)? Of type (z)?
b. How many orbitals of type (x) are found in a shell with $n = 2$? How many of type (y)? How many of type (z)?
c. Write a set of quantum numbers for an electron in an orbital of type (x) in a shell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

42.

State the Heisenberg uncertainty principle. Describe briefly what the principle implies.

43.

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

44.

Which of the following equations describe particle-like behavior? Which describe wavelike behavior? Do any involve both types of behavior? Describe the reasons for your choices.

  a. $c = \lambda v$
  b. $E = mv^2/2$
  c. $E = hv$
  d. $\lambda = h/mv$

45.

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

46.

Read the labels of several commercial products and identify monatomic ions of at least four transition elements contained in the products. Write the complete electron configurations of these cations.

47.

Read the labels of several commercial products and identify monatomic ions of at least six main group elements contained in the products. Write the complete electron configurations of these cations and anions.

48.

Using complete subshell notation (not abbreviations, $1s^2 2s^2 2p^6$, and so forth), predict the electron configuration of each of the following atoms:

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

49.

Using complete subshell notation ($1s^2 2s^2 2p^6$, and so forth), predict the electron configuration of each of the following atoms:

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

50.

Is $1s^2 2s^2 2p^6$ the symbol for a macroscopic property or a microscopic property of an element? Explain your answer.

51.

What additional information do we need to answer the question "Which ion has the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6$"?

52.

Draw the orbital diagram for the valence shell of each of the following atoms:

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

53.

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

  a. N

  b. Si

  c. Fe

  d. Te

  e. Mo

54.

Using complete subshell notation ($1s^22s^22p^6$, and so forth), predict the electron configurations of the following ions.

  a. N^{3-}

  b. Ca^{2+}

  c. S^-

  d. Cs^{2+}

  e. Cr^{2+}

  f. Gd^{3+}

55.

Which atom has the electron configuration $1s^22s^22p^63s^23p^64s^23d^{10}4p^65s^24d^2$?

56.

Which atom has the electron configuration $1s^22s^22p^63s^23p^63d^74s^2$?

57.

Which ion with a +1 charge has the electron configuration $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$? Which ion with a –2 charge has this configuration?

58.

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

59.

Which of the following has two unpaired electrons?

  a. Mg

  b. Si

  c. S

  d. Both Mg and S

  e. Both Si and S.

60.

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

61.

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

62.

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

63.

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

64.

Write the electron configurations for the following atoms or ions:

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

65.

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

66.

Write a set of quantum numbers for each of the electrons with an n of 3 in a Sc atom.

67.

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

68.

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

69.

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

70.

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

71.

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

72.

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

73.

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

74.

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

75.

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

76.

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

77.

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

78.

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

79.

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

80.

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

81.

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

82.

Of the five elements Al, Cl, I, Na, Rb, which has the most exothermic reaction? (E represents an atom.) What name is given to the energy for the reaction?

$E^+(g)+e^- \longrightarrow E(g)$
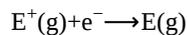
83.

Of the five elements Sn, Si, Sb, O, Te, which has the most endothermic reaction? (E represents an atom.) What name is given to the energy for the reaction?

$E(g) \longrightarrow E^+(g)+e^-$
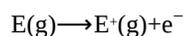
84.

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

85.

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

86.

Explain why Al is a member of group 13 rather than group 3?

4: Chemical Bonding and Molecular Geometry

A chemical bond is an attraction between atoms that allows the formation of chemical substances that contain two or more atoms. The bond is caused by the electrostatic force of attraction between opposite charges, either between electrons and nuclei, or as the result of a dipole attraction. All bonds can be explained by quantum theory, but, in practice, simplification rules allow chemists to predict the strength, directionality, and polarity of bonds. The octet rule and VSEPR theory are two examples. More sophisticated theories are valence bond theory which includes orbital hybridization and resonance, and the linear combination of atomic orbitals molecular orbital method. Electrostatics are used to describe bond polarities and the effects they have on chemical substances.

4.1: Introduction

It has long been known that pure carbon occurs in different forms (allotropes) including graphite and diamonds. But it was not until 1985 that a new form of carbon was recognized: buckminsterfullerene. This molecule was named after the architect and inventor R. Buckminster Fuller (1895–1983), whose signature architectural design was the geodesic dome, characterized by a lattice shell structure supporting a spherical surface. Experimental evidence revealed the formula, C_{60}, and then scientists determined how 60 carbon atoms could form one symmetric, stable molecule. They were guided by bonding theory—the topic of this chapter—which explains how individual atoms connect to form more complex structures.

Figure 4.1.1: Nicknamed "buckyballs," buckminsterfullerene molecules (C_{60}) contain only carbon atoms (left) arranged to form a geometric framework of hexagons and pentagons, similar to the pattern on a soccer ball (center). This molecular structure is named after architect R. Buckminster Fuller, whose innovative designs combined simple geometric shapes to create large, strong structures such as this weather radar dome near Tucson, Arizona (right). (credit middle: modification of work by "Petey21"/Wikimedia Commons; credit right: modification of work by Bill Morrow)

4.2: Ionic Bonding

> 🧠 **Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Explain the formation of cations, anions, and ionic compounds
> - Predict the charge of common metallic and nonmetallic elements, and write their electron configurations

As you have learned, ions are atoms or molecules bearing an electrical charge. A cation (a positive ion) forms when a neutral atom loses one or more electrons from its valence shell, and an anion (a negative ion) forms when a neutral atom gains one or more electrons in its valence shell.

Compounds composed of ions are called ionic compounds (or salts), and their constituent ions are held together by ionic bonds: electrostatic forces of attraction between oppositely charged cations and anions. The properties of ionic compounds shed some light on the nature of ionic bonds. Ionic solids exhibit a crystalline structure and tend to be rigid and brittle; they also tend to have high melting and boiling points, which suggests that ionic bonds are very strong. Ionic solids are also poor conductors of electricity for the same reason—the strength of ionic bonds prevents ions from moving freely in the solid state. Most ionic solids, however, dissolve readily in water. Once dissolved or melted, ionic compounds are excellent conductors of electricity and heat because the ions can move about freely.

Neutral atoms and their associated ions have very different physical and chemical properties. Sodium *atoms* form sodium metal, a soft, silvery-white metal that burns vigorously in air and reacts explosively with water. Chlorine *atoms* form chlorine gas, Cl_2, a yellow-green gas that is extremely corrosive to most metals and very poisonous to animals and plants. The vigorous reaction between the elements sodium and chlorine forms the white, crystalline compound sodium chloride, common table salt, which contains sodium *cations* and chloride *anions* (Figure 4.2.1). The compound composed of these ions exhibits properties entirely different from the properties of the elements sodium and chlorine. Chlorine is poisonous, but sodium chloride is essential to life; sodium atoms react vigorously with water, but sodium chloride simply dissolves in water.

| (a) | (b) | (c) |

Figure 4.2.1: (a) Sodium is a soft metal that must be stored in mineral oil to prevent reaction with air or water. (b) Chlorine is a pale yellow-green gas. (c) When combined, they form white crystals of sodium chloride (table salt). (credit a: modification of work by "Jurii"/Wikimedia Commons)

The Formation of Ionic Compounds

Binary ionic compounds are composed of just two elements: a metal (which forms the cations) and a nonmetal (which forms the anions). For example, NaCl is a binary ionic compound. We can think about the formation of such compounds in terms of the periodic properties of the elements. Many metallic elements have relatively low ionization potentials and lose electrons easily. These elements lie to the left in a period or near the bottom of a group on the periodic table. Nonmetal atoms have relatively high electron affinities and thus readily gain electrons lost by metal atoms, thereby filling their valence shells. Nonmetallic elements are found in the upper-right corner of the periodic table.

As all substances must be electrically neutral, the total number of positive charges on the cations of an ionic compound must equal the total number of negative charges on its anions. The formula of an ionic compound represents the simplest ratio of the numbers of ions necessary to give identical numbers of positive and negative charges. For example, the formula for aluminum oxide, Al_2O_3,

indicates that this ionic compound contains two aluminum cations, Al^{3+}, for every three oxide anions, O^{2-} [thus, $(2 +3) + (3 -2) = 0$].

It is important to note, however, that the formula for an ionic compound does *not* represent the physical arrangement of its ions. It is incorrect to refer to a sodium chloride (NaCl) "molecule" because there is not a single ionic bond, per se, between any specific pair of sodium and chloride ions. The attractive forces between ions are isotropic—the same in all directions—meaning that any particular ion is equally attracted to all of the nearby ions of opposite charge. This results in the ions arranging themselves into a tightly bound, three-dimensional lattice structure. Sodium chloride, for example, consists of a regular arrangement of equal numbers of Na^+ cations and Cl^- anions (Figure 4.2.2).
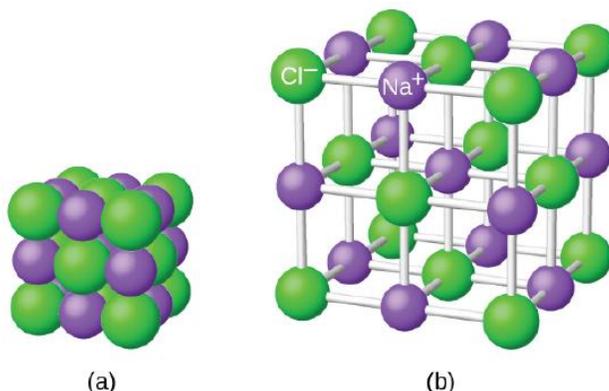
Figure 4.2.2: The atoms in sodium chloride (common table salt) are arranged to (a) maximize opposite charges interacting. The smaller spheres represent sodium ions, the larger ones represent chloride ions. In the expanded view (b), the geometry can be seen more clearly. Note that each ion is "bonded" to all of the surrounding ions—six in this case.

The strong electrostatic attraction between Na^+ and Cl^- ions holds them tightly together in solid NaCl. It requires 769 kJ of energy to dissociate one mole of solid NaCl into separate gaseous Na^+ and Cl^- ions:

$$NaCl(s) \longrightarrow Na^+(g) + Cl^-(g) \qquad \Delta H = 769 \, kJ$$

Electronic Structures of Cations

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

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

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

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

configurations, the outermost *s* electrons are the first to be lost when these atoms ionize. When the inner transition metals form ions, they usually have a 3+ charge, resulting from the loss of their outermost *s* electrons and a *d* or *f* electron.

> ✔ Example 4.2.1: Determining the Electronic Structures of Cations
>
> There are at least 14 elements categorized as "essential trace elements" for the human body. They are called "essential" because they are required for healthy bodily functions, "trace" because they are required only in small amounts, and "elements" in spite of the fact that they are really ions. Two of these essential trace elements, chromium and zinc, are required as Cr^{3+} and Zn^{2+}. Write the electron configurations of these cations.
>
> **Solution**
>
> First, write the electron configuration for the neutral atoms:
>
> > Zn: $[Ar]3d^{10}4s^2$
> >
> > Cr: $[Ar]3d^54s^1$
>
> Next, remove electrons from the highest energy orbital. For the transition metals, electrons are removed from the *s* orbital first and then from the *d* orbital. For the *p*-block elements, electrons are removed from the *p* orbitals and then from the *s* orbital. Zinc is a member of group 12, so it should have a charge of 2+, and thus loses only the two electrons in its *s* orbital. Chromium is a transition element and should lose its *s* electrons and then its *d* electrons when forming a cation. Thus, we find the following electron configurations of the ions:
>
> > Zn^{2+}: $[Ar]3d^{10}$
> >
> > Cr^{3+}: $[Ar]3d^3$

> ❓ Exercise 4.2.1
>
> Potassium and magnesium are required in our diet. Write the electron configurations of the ions expected from these elements.
>
> **Answer**
>
> > K^+: [Ar], Mg^{2+}: [Ne]

Electronic Structures of Anions

Most monatomic anions form when a neutral nonmetal atom gains enough electrons to completely fill its outer *s* and *p* orbitals, thereby reaching the electron configuration of the next noble gas. Thus, it is simple to determine the charge on such a negative ion: The charge is equal to the number of electrons that must be gained to fill the *s* and *p* orbitals of the parent atom. Oxygen, for example, has the electron configuration $1s^22s^22p^4$, whereas the oxygen anion has the electron configuration of the noble gas neon (Ne), $1s^22s^22p^6$. The two additional electrons required to fill the valence orbitals give the oxide ion the charge of 2– (O^{2-}).

> ✔ Example 4.2.1: Determining the Electronic Structure of Anions
>
> Selenium and iodine are two essential trace elements that form anions. Write the electron configurations of the anions.
>
> **Solution**
>
> > Se^{2-}: $[Ar]3d^{10}4s^24p^6$
> >
> > I^-: $[Kr]4d^{10}5s^25p^6$
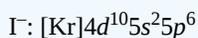
> ❓ Exercise 4.2.2
>
> Write the electron configurations of a phosphorus atom and its negative ion. Give the charge on the anion.
>
> **Answer**
>
> > P: $[Ne]3s^23p^3$; P^{3-}: $[Ne]3s^23p^6$
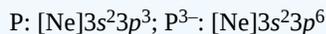
4.3: Covalent Bonding

> **Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Describe the formation of covalent bonds
> - Define electronegativity and assess the polarity of covalent bonds

Ionic bonding results from the electrostatic attraction of oppositely charged ions that are typically produced by the transfer of electrons between metallic and nonmetallic atoms. A different type of bonding results from the mutual attraction of atoms for a "shared" pair of electrons. Such bonds are called covalent bonds. Covalent bonds are formed between two atoms when both have similar tendencies to attract electrons to themselves (i.e., when both atoms have identical or fairly similar ionization energies and electron affinities). For example, two hydrogen atoms bond covalently to form an H_2 molecule; each hydrogen atom in the H_2 molecule has two electrons stabilizing it, giving each atom the same number of valence electrons as the noble gas He.

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

Formation of Covalent Bonds

Nonmetal atoms frequently form covalent bonds with other nonmetal atoms. For example, the hydrogen molecule, H_2, contains a covalent bond between its two hydrogen atoms. Figure 4.3.1 illustrates why this bond is formed. Starting on the far right, we have two separate hydrogen atoms with a particular potential energy, indicated by the red line. Along the *x*-axis is the distance between the two atoms. As the two atoms approach each other (moving left along the *x*-axis), their valence orbitals (1*s*) begin to overlap. The single electrons on each hydrogen atom then interact with both atomic nuclei, occupying the space around both atoms. The strong attraction of each shared electron to both nuclei stabilizes the system, and the potential energy decreases as the bond distance decreases. If the atoms continue to approach each other, the positive charges in the two nuclei begin to repel each other, and the potential energy increases. The bond length is determined by the distance at which the lowest potential energy is achieved.
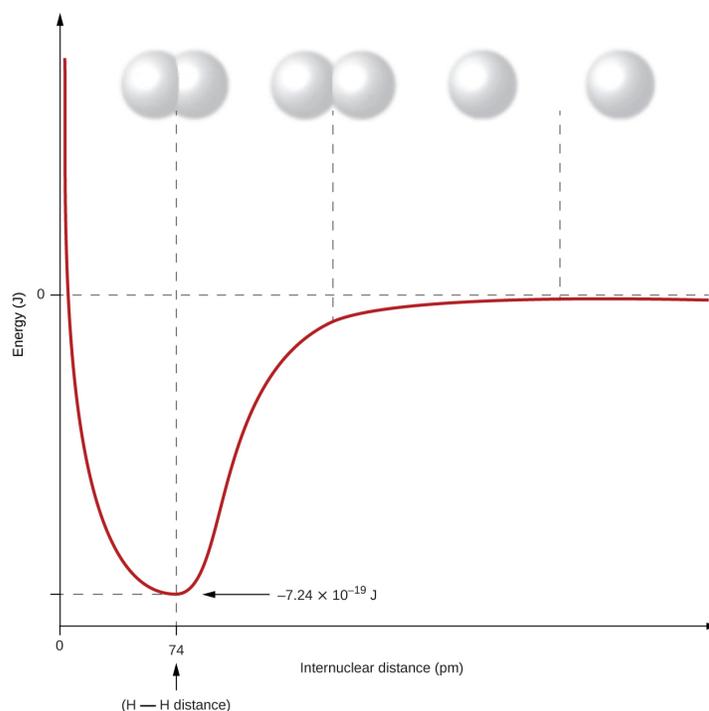
Figure 4.3.1: The potential energy of two separate hydrogen atoms (right) decreases as they approach each other, and the single electrons on each atom are shared to form a covalent bond. The bond length is the internuclear distance at which the lowest potential energy is achieved.

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

$$H_2(g) \longrightarrow 2\,H(g) \quad \Delta H = 436\,kJ$$
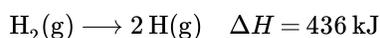
Conversely, the same amount of energy is released when one mole of H_2 molecules forms from two moles of H atoms:

$$2\,H(g) \longrightarrow H_2(g) \quad \Delta H = -436\,kJ$$
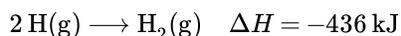
Pure vs. Polar Covalent Bonds

If the atoms that form a covalent bond are identical, as in H_2, Cl_2, and other diatomic molecules, then the electrons in the bond must be shared equally. We refer to this as a pure covalent bond. Electrons shared in pure covalent bonds have an equal probability of being near each nucleus.

In the case of Cl_2, each atom starts off with seven valence electrons, and each Cl shares one electron with the other, forming one covalent bond:

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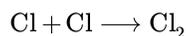
The total number of electrons around each individual atom consists of six nonbonding electrons and two shared (i.e., bonding) electrons for eight total electrons, matching the number of valence electrons in the noble gas argon. Since the bonding atoms are identical, Cl_2 also features a pure covalent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

When the atoms linked by a covalent bond are different, the bonding electrons are shared, but no longer equally. Instead, the bonding electrons are more attracted to one atom than the other, giving rise to a shift of electron density toward that atom. This unequal distribution of electrons is known as a polar covalent bond, characterized by a partial positive charge on one atom and a partial negative charge on the other. The atom that attracts the electrons more strongly acquires the partial negative charge and vice versa. For example, the electrons in the H–Cl bond of a hydrogen chloride molecule spend more time near the chlorine atom than near the hydrogen atom. Thus, in an HCl molecule, the chlorine atom carries a partial negative charge and the hydrogen atom has a partial positive charge. Figure 4.3.2 shows the distribution of electrons in the H–Cl bond. Note that the shaded area around Cl is

much larger than it is around H. Compare this to Figure 4.3.1, which shows the even distribution of electrons in the H_2 nonpolar bond.

We sometimes designate the positive and negative atoms in a polar covalent bond using a lowercase Greek letter "delta," δ, with a plus sign or minus sign to indicate whether the atom has a partial positive charge (δ+) or a partial negative charge (δ–). This symbolism is shown for the H–Cl molecule in Figure 4.3.2.
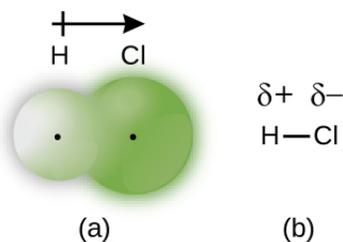
Figure 4.3.2: (a) The distribution of electron density in the HCl molecule is uneven. The electron density is greater around the chlorine nucleus. The small, black dots indicate the location of the hydrogen and chlorine nuclei in the molecule. (b) Symbols δ+ and δ– indicate the polarity of the H–Cl bond.

Electronegativity

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

Figure 4.3.3 shows the electronegativity values of the elements as proposed by one of the most famous chemists of the twentieth century: Linus Pauling (Figure 4.3.4). In general, electronegativity increases from left to right across a period in the periodic table and decreases down a group. Thus, the nonmetals, which lie in the upper right, tend to have the highest electronegativities, with fluorine the most electronegative element of all (EN = 4.0). Metals tend to be less electronegative elements, and the group 1 metals have the lowest electronegativities. Note that noble gases are excluded from this figure because these atoms usually do not share electrons with others atoms since they have a full valence shell. (While noble gas compounds such as XeO_2 do exist, they can only be formed under extreme conditions, and thus they do not fit neatly into the general model of electronegativity.)
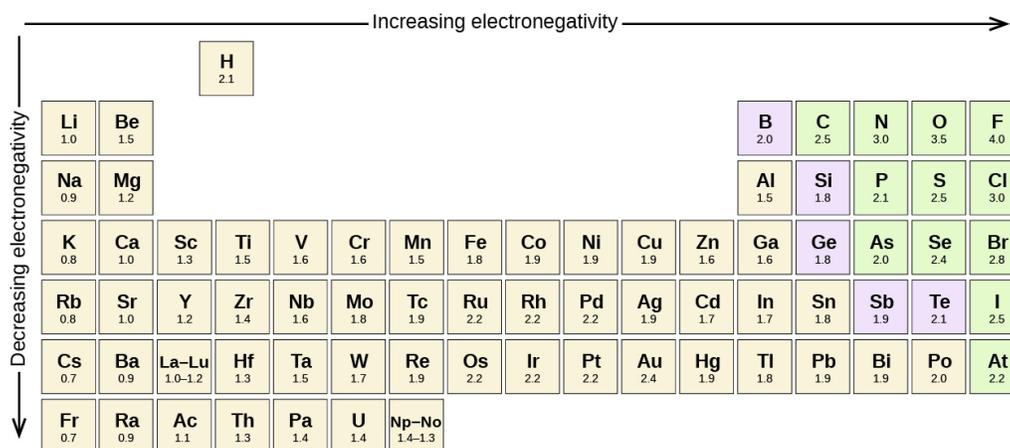
Figure 4.3.3: The electronegativity values derived by Pauling follow predictable periodic trends, with the higher electronegativities toward the upper right of the periodic table.

Electronegativity versus Electron Affinity

We must be careful not to confuse electronegativity and electron affinity. The electron affinity of an element is a measurable physical quantity, namely, the energy released or absorbed when an isolated gas-phase atom acquires an electron, measured in kJ/mol. Electronegativity, on the other hand, describes how tightly an atom attracts electrons in a bond. It is a dimensionless

quantity that is calculated, not measured. Pauling derived the first electronegativity values by comparing the amounts of energy required to break different types of bonds. He chose an arbitrary relative scale ranging from 0 to 4.

> **📌 Portrait of a Chemist: Linus Pauling**
>
> Linus Pauling, shown in Figure 4.3.4, is the only person to have received two unshared (individual) Nobel Prizes: one for chemistry in 1954 for his work on the nature of chemical bonds and one for peace in 1962 for his opposition to weapons of mass destruction. He developed many of the theories and concepts that are foundational to our current understanding of chemistry, including electronegativity and resonance structures.
>
>
>
> Figure 4.3.4: Linus Pauling (1901–1994) made many important contributions to the field of chemistry. He was also a prominent activist, publicizing issues related to health and nuclear weapons.
>
> Pauling also contributed to many other fields besides chemistry. His research on sickle cell anemia revealed the cause of the disease—the presence of a genetically inherited abnormal protein in the blood—and paved the way for the field of molecular genetics. His work was also pivotal in curbing the testing of nuclear weapons; he proved that radioactive fallout from nuclear testing posed a public health risk.
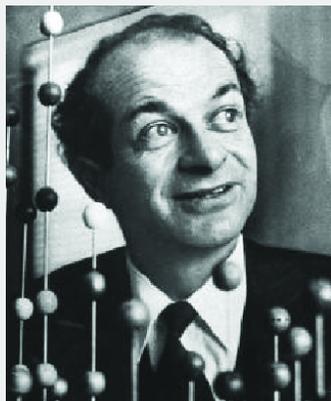
Electronegativity and Bond Type

The absolute value of the difference in electronegativity (ΔEN) of two bonded atoms provides a rough measure of the polarity to be expected in the bond and, thus, the bond type. When the difference is very small or zero, the bond is covalent and nonpolar. When it is large, the bond is polar covalent or ionic. The absolute values of the electronegativity differences between the atoms in the bonds H–H, H–Cl, and Na–Cl are 0 (nonpolar), 0.9 (polar covalent), and 2.1 (ionic), respectively. The degree to which electrons are shared between atoms varies from completely equal (pure covalent bonding) to not at all (ionic bonding). Figure 4.3.5 shows the relationship between electronegativity difference and bond type.

Bond Type	Electronegativity Difference
pure covalent	< 0.4
polar covalent	between 0.4 and 1.8
ionic	> 1.8
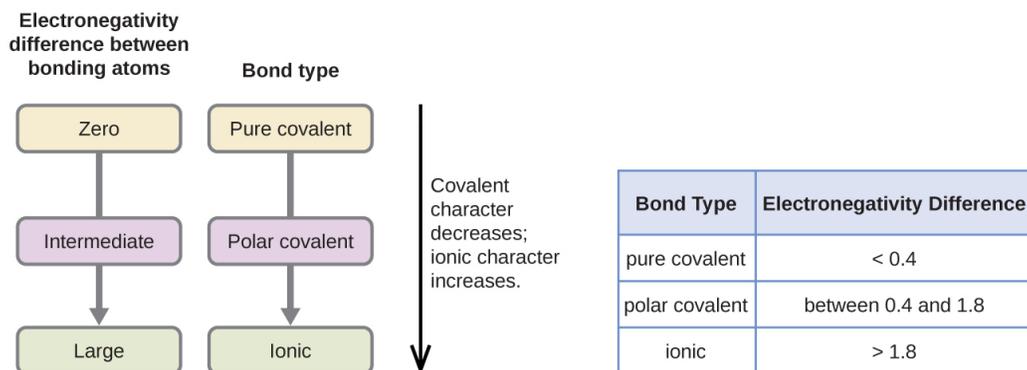
Figure 4.3.5: As the electronegativity difference increases between two atoms, the bond becomes more ionic.

A rough approximation of the electronegativity differences associated with covalent, polar covalent, and ionic bonds is shown in Figure 4.3.5. This table is just a general guide, however, with many exceptions. For example, the H and F atoms in HF have an electronegativity difference of 1.9, and the N and H atoms in NH_3 a difference of 0.9, yet both of these compounds form bonds that are considered polar covalent. Likewise, the Na and Cl atoms in NaCl have an electronegativity difference of 2.1, and the Mn and I atoms in MnI_2 have a difference of 1.0, yet both of these substances form ionic compounds.

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

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

---

✔ Example 4.3.1: Electronegativity and Bond Polarity

Bond polarities play an important role in determining the structure of proteins. Using the electronegativity values in Figure 4.3.3, arrange the following covalent bonds—all commonly found in amino acids—in order of increasing polarity. Then designate the positive and negative atoms using the symbols δ+ and δ–:

$$C–H, C–N, C–O, N–H, O–H, S–H$$

Solution

The polarity of these bonds increases as the absolute value of the electronegativity difference increases. The atom with the δ– designation is the more electronegative of the two. Table 4.3.1 shows these bonds in order of increasing polarity.

Table 4.3.1: Bond Polarity and Electronegativity Difference

Bond	ΔEN	Polarity
C–H	0.4	
S–H	0.4	
C–N	0.5	
N–H	0.9	
C–O	1.0	
O–H	1.4	

? Exercise 4.3.1

Silicones are polymeric compounds containing, among others, the following types of covalent bonds: Si–O, Si–C, C–H, and C–C. Using the electronegativity values in Figure 4.3.3, arrange the bonds in order of increasing polarity and designate the positive and negative atoms using the symbols δ+ and δ–.

Answer

Bond	Electronegativity Difference	Polarity
C–C	0.0	nonpolar
C–H	0.4	
Si–C	0.7	
Si–O	1.7	

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4.4: Lewis Symbols and Structures

> ◆ **Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Write Lewis symbols for neutral atoms and ions
> - Draw Lewis structures depicting the bonding in simple molecules

Thus far in this chapter, we have discussed the various types of bonds that form between atoms and/or ions. In all cases, these bonds involve the sharing or transfer of valence shell electrons between atoms. In this section, we will explore the typical method for depicting valence shell electrons and chemical bonds, namely Lewis symbols and Lewis structures.

Lewis Symbols

We use Lewis symbols to describe valence electron configurations of atoms and monatomic ions. A Lewis symbol consists of an elemental symbol surrounded by one dot for each of its valence electrons:

$$\cdot Ca \cdot$$

Figure 4.4.1: shows the Lewis symbols for the elements of the third period of the periodic table.

Atoms	Electronic Configuration	Lewis Symbol
sodium	$[Ne]3s^1$	Na $\cdot$
magnesium	$[Ne]3s^2$	$\cdot$ Mg $\cdot$
aluminum	$[Ne]3s^2 3p^1$	$\cdot \overset{\cdot}{Al} \cdot$
silicon	$[Ne]3s^2 3p^2$	$\cdot \overset{\cdot}{Si} \cdot$
phosphorus	$[Ne]3s^2 3p^3$	$\cdot \overset{\cdot \cdot}{\underset{\cdot}{P}} \cdot$
sulfur	$[Ne]3s^2 3p^4$	$: \overset{\cdot \cdot}{\underset{\cdot}{S}} \cdot$
chlorine	$[Ne]3s^2 3p^5$	$: \overset{\cdot \cdot}{\underset{\cdot \cdot}{Cl}} \cdot$
argon	$[Ne]3s^2 3p^6$	$: \overset{\cdot \cdot}{\underset{\cdot \cdot}{Ar}} :$

Figure 4.4.1: Lewis symbols illustrating the number of valence electrons for each element in the third period of the periodic table.

Lewis symbols can also be used to illustrate the formation of cations from atoms, as shown here for sodium and calcium:

Na $\cdot$ $\longrightarrow$ Na$^+$ + e$^-$

sodium atom → sodium cation

$\cdot$ Ca $\cdot$ $\longrightarrow$ Ca^{2+} + 2e$^-$

calcium atom → calcium cation

Likewise, they can be used to show the formation of anions from atoms, as shown here for chlorine and sulfur:

$: \overset{\cdot \cdot}{\underset{\cdot \cdot}{Cl}} \cdot$ + e$^-$ $\longrightarrow$ $: \overset{\cdot \cdot}{\underset{\cdot \cdot}{Cl}} :$ $^-$

chlorine atom → chlorine anion

$: \overset{\cdot \cdot}{\underset{\cdot}{S}} \cdot$ + 2e$^-$ $\longrightarrow$ $: \overset{\cdot \cdot}{\underset{\cdot \cdot}{S}} :$ $^{2-}$

sulfur atom → sulfide anion

Figure 4.4.2 demonstrates the use of Lewis symbols to show the transfer of electrons during the formation of ionic compounds.

Metal		Nonmetal		Ionic Compound
Na ·	+	:Cl·	⟶	Na⁺ [:Cl:]⁻
sodium atom		chlorine atom		sodium chloride (sodium ion and chloride ion)
· Mg ·	+	:O·	⟶	Mg²⁺ [:O:]²⁻
magnesium atom		oxygen atom		magnesium oxide (magnesium ion and oxide ion)
· Ca ·	+	2 :F·	⟶	Ca²⁺ [:F:]⁻₂
calcium atom		fluorine atoms		calcium fluoride (calcium ion and two fluoride ions)

Figure 4.4.2: Cations are formed when atoms lose electrons, represented by fewer Lewis dots, whereas anions are formed by atoms gaining electrons. The total number of electrons does not change.

Lewis Structures

We also use Lewis symbols to indicate the formation of covalent bonds, which are shown in Lewis structures, drawings that describe the bonding in molecules and polyatomic ions. For example, when two chlorine atoms form a chlorine molecule, they share one pair of electrons:

:Cl· + ·Cl: ⟶ :Cl:Cl:

chlorine atoms → chlorine molecule

The Lewis structure indicates that each Cl atom has three pairs of electrons that are not used in bonding (called lone pairs) and one shared pair of electrons (written between the atoms). A dash (or line) is sometimes used to indicate a shared pair of electrons:

H—H   :Cl—Cl:

A single shared pair of electrons is called a single bond. Each Cl atom interacts with eight valence electrons: the six in the lone pairs and the two in the single bond.

The Octet Rule

The other halogen molecules (F_2, Br_2, I_2, and At_2) form bonds like those in the chlorine molecule: one single bond between atoms and three lone pairs of electrons per atom. This allows each halogen atom to have a noble gas electron configuration. The tendency of main group atoms to form enough bonds to obtain eight valence electrons is known as the octet rule.

The number of bonds that an atom can form can often be predicted from the number of electrons needed to reach an octet (eight valence electrons); this is especially true of the nonmetals of the second period of the periodic table (C, N, O, and F). For example, each atom of a group 14 element has four electrons in its outermost shell and therefore requires four more electrons to reach an octet. These four electrons can be gained by forming four covalent bonds, as illustrated here for carbon in CCl_4 (carbon tetrachloride) and silicon in SiH_4 (silane). Because hydrogen only needs two electrons to fill its valence shell, it is an exception to the octet rule. The transition elements and inner transition elements also do not follow the octet rule:

carbon tetrachloride

silane

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

ammonia   Water   hydrogen fluoride

Double and Triple Bonds

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

formaldehyde   ethylene

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

carbon monoxide   cyanide ion

Writing Lewis Structures with the Octet Rule

For very simple molecules and molecular ions, we can write the Lewis structures by merely pairing up the unpaired electrons on the constituent atoms. See these examples:

For more complicated molecules and molecular ions, it is helpful to follow the step-by-step procedure outlined here.

> **📌 Writing Lewis Structures**
>
> 1. Determine the total number of valence (outer shell) electrons. For cations, subtract one electron for each positive charge. For anions, add one electron for each negative charge.
> 2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom. (Generally, the least electronegative element should be placed in the center.) Connect each atom to the central atom with a single bond (one electron pair).
> 3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen), completing an octet around each atom.
> 4. Place all remaining electrons on the central atom.
> 5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

Let us determine the Lewis structures of SiH_4, CHO_2^-, NO^+, and OF_2 as examples in following this procedure:

1. Determine the total number of valence (outer shell) electrons in the molecule or ion.
   - For a molecule, we add the number of valence electrons on each atom in the molecule:

$$SiH_4$$

$$
\begin{array}{rl}
\text{Si: 4 valence electrons/atom} \times \text{ 1 atom} & = 4 \\
+ \quad \text{H : 1 valence electron/atom} \times \text{ 4 atoms} & = 4 \\
\hline
\text{total valence electrons} & = 8
\end{array}
$$

   - For a *negative ion*, such as CHO_2^-, we add the number of valence electrons on the atoms to the number of negative charges on the ion (one electron is gained for each single negative charge):

$$CHO_2^-$$

$$
\begin{array}{rl}
\text{C: 4 valence electrons/atom} \times \text{ 1 atom} & = 4 \\
\text{H: 1 valence electron/atom} \times \text{ 1 atoms} & = 1 \\
\text{O: 6 valence electron/atom} \times \text{ 2 atoms} & = 12 \\
+ \quad \text{1 electron} & = 1 \\
\hline
\text{total valence electrons} & = 18
\end{array}
$$

   - For a *positive ion*, such as NO^+, we add the number of valence electrons on the atoms in the ion and then subtract the number of positive charges on the ion (one electron is lost for each single positive charge) from the total number of valence electrons:

$$NO^+$$

$$
\begin{array}{rl}
\text{N: 5 valence electrons/atom} \times \text{ 1 atom} & = 5 \\
\text{O: 6 valence electron/atom} \times \text{ 1 atoms} & = 6 \\
+ \quad \text{e: -1 electron (positive charge)} \times \text{ 1 electron} & = -1 \\
\hline
\text{total valence electrons} & = 10
\end{array}
$$

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

$$OF_2$$

$$O: \text{6 valence electrons/atom} \times \text{1 atom} = 6$$
$$+ \quad F: \text{7 valence electron/atom} \times \text{2 atoms} = 14$$
$$\overline{\text{total valence electrons} = 20}$$

2. Draw a skeleton structure of the molecule or ion, arranging the atoms around a central atom and connecting each atom to the central atom with a single (one electron pair) bond. (Note that we denote ions with brackets around the structure, indicating the charge outside the brackets:)
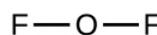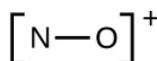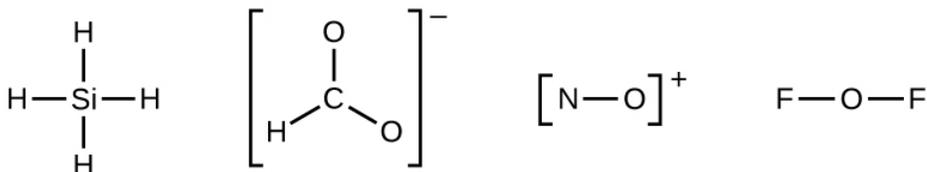
When several arrangements of atoms are possible, as for CHO_2^-, we must use experimental evidence to choose the correct one. In general, the less electronegative elements are more likely to be central atoms. In CHO_2^-, the less electronegative carbon atom occupies the central position with the oxygen and hydrogen atoms surrounding it. Other examples include P in $POCl_3$, S in SO_2, and Cl in ClO_4^-. An exception is that hydrogen is almost never a central atom. As the most electronegative element, fluorine also cannot be a central atom.

3. Distribute the remaining electrons as lone pairs on the terminal atoms (except hydrogen) to complete their valence shells with an octet of electrons.

   ○ There are no remaining electrons on SiH_4, so it is unchanged:
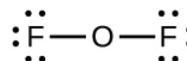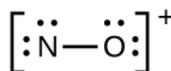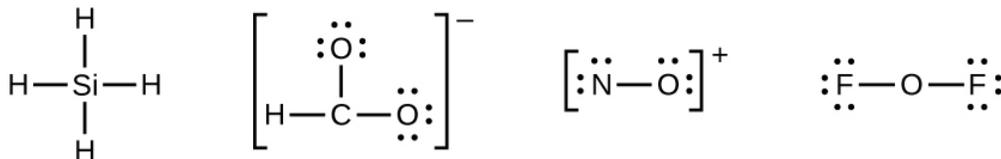
4. Place all remaining electrons on the central atom.

   ○ For SiH_4, CHO_2^-, and NO^+, there are no remaining electrons; we already placed all of the electrons determined in Step 1.
   ○ For OF_2, we had 16 electrons remaining in Step 3, and we placed 12, leaving 4 to be placed on the central atom:
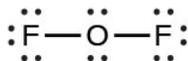
5. Rearrange the electrons of the outer atoms to make multiple bonds with the central atom in order to obtain octets wherever possible.

   ○ SiH_4: Si already has an octet, so nothing needs to be done.
   ○ $CHO2^-$: We have distributed the valence electrons as lone pairs on the oxygen atoms, but the carbon atom lacks an octet:

   gives

   ○ NO^+: For this ion, we added eight valence electrons, but neither atom has an octet. We cannot add any more electrons since we have already used the total that we found in Step 1, so we must move electrons to form a multiple bond:

$$\left[:\overset{..}{N} - \overset{..}{O}: \right]^{+} \quad \text{gives} \quad \left[:\overset{..}{N} = \overset{..}{O}: \right]^{+}$$

This still does not produce an octet, so we must move another pair, forming a triple bond:

$$\left[:N \equiv O: \right]^{+}$$

- In OF_2, each atom has an octet as drawn, so nothing changes.

✔ Example 4.4.1: Writing Lewis Structures

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

Solution

Step 1. *Calculate the number of valence electrons.*

HCN: $(1 \times 1) + (4 \times 1) + (5 \times 1) = 10$
H_3CCH_3: $(1 \times 3) + (2 \times 4) + (1 \times 3) = 14$
HCCH: $(1 \times 1) + (2 \times 4) + (1 \times 1) = 10$
NH_3: $(5 \times 1) + (3 \times 1) = 8$

Step 2 *Draw a skeleton and connect the atoms with single bonds.* Remember that H is never a central atom:

Step 3. *Where needed, distribute electrons to the terminal atoms:*

HCN: six electrons placed on N
H_3CCH_3: no electrons remain
HCCH: no terminal atoms capable of accepting electrons
NH_3: no terminal atoms capable of accepting electrons

Step 4. *Where needed, place remaining electrons on the central atom:*

HCN: no electrons remain
H₃CCH₃: no electrons remain
HCCH: four electrons placed on carbon
NH₃: two electrons placed on nitrogen

Step 5. *Where needed, rearrange electrons to form multiple bonds in order to obtain an octet on each atom:*

HCN: form two more C–N bonds
H₃CCH₃: all atoms have the correct number of electrons
HCCH: form a triple bond between the two carbon atoms
NH₃: all atoms have the correct number of electrons
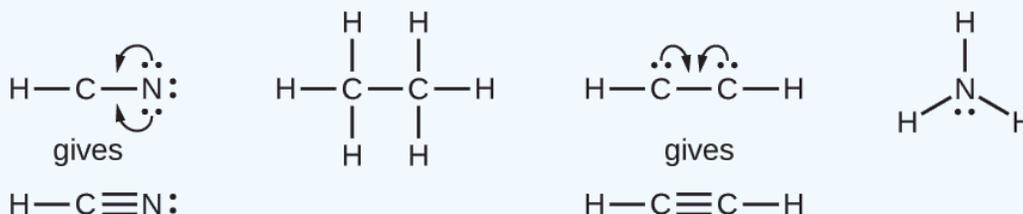
? Exercise 4.4.1

Both carbon monoxide, CO, and carbon dioxide, CO_2, are products of the combustion of fossil fuels. Both of these gases also cause problems: CO is toxic and CO_2 has been implicated in global climate change. What are the Lewis structures of these two molecules?

Answer

📌 How Sciences Interconnect: Fullerene Chemistry

Carbon, in various forms and compounds, has been known since prehistoric times, . Soot has been used as a pigment (often called carbon black) for thousands of years. Charcoal, high in carbon content, has likewise been critical to human development. Carbon is the key additive to iron in the steelmaking process, and diamonds have a unique place in both culture and industry. With all this usage came significant study, particularly with the emergence of organic chemistry. And even with all the known forms and functions of the element, scientists began to uncover the potential for even more varied and extensive carbon structures.

As early as the 1960s, chemists began to observe complex carbon structures, but they had little evidence to support their concepts, or their work did not make it into the mainstream. Eiji Osawa predicted a spherical form based on observations of a similar structure, but his work was not widely known outside Japan. In a similar manner, the most comprehensive advance was likely computational chemist Elena Galpern's, who in 1973 predicted a highly stable, 60-carbon molecule; her work was also isolated to her native Russia. Still later, Harold Kroto, working with Canadian radio astronomers, sought to uncover the nature of long carbon chains that had been discovered in interstellar space.

Kroto sought to use a machine developed by Richard Smalley's team at Rice University to learn more about these structures. Together with Robert Curl, who had introduced them, and three graduate students—James Heath, Sean O'Brien, and Yuan Liu —they performed an intensive series of experiments that led to a major discovery.

In 1996, the Nobel Prize in Chemistry was awarded to Richard Smalley (Figure 4.4.3), Robert Curl, and Harold Kroto for their work in discovering a new form of carbon, the C_{60} buckminsterfullerene molecule. An entire class of compounds, including spheres and tubes of various shapes, were discovered based on C_{60}. This type of molecule, called a fullerene, shows promise in a variety of applications. Because of their size and shape, fullerenes can encapsulate other molecules, so they have shown

potential in various applications from hydrogen storage to targeted drug delivery systems. They also possess unique electronic and optical properties that have been put to good use in solar powered devices and chemical sensors.
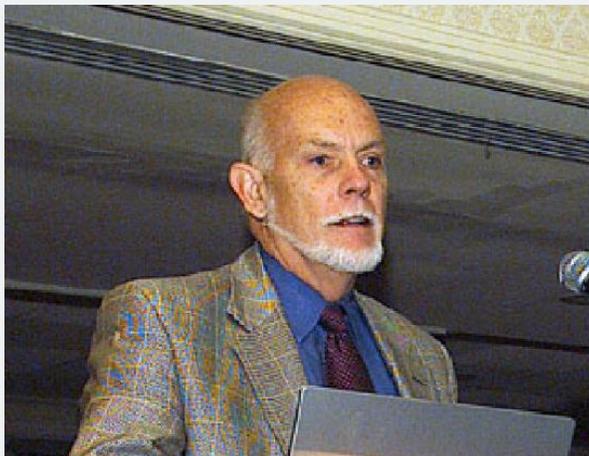
Figure 4.4.3: Richard Smalley (1943–2005), a professor of physics, chemistry, and astronomy at Rice University, was one of the leading advocates for fullerene chemistry. Upon his death in 2005, the US Senate honored him as the "Father of Nanotechnology." (credit: United States Department of Energy)

Exceptions to the Octet Rule

Many covalent molecules have central atoms that do not have eight electrons in their Lewis structures. These molecules fall into three categories:

- Odd-electron molecules have an odd number of valence electrons, and therefore have an unpaired electron.
- Electron-deficient molecules have a central atom that has fewer electrons than needed for a noble gas configuration.
- Hypervalent molecules have a central atom that has more electrons than needed for a noble gas configuration.

Odd-electron Molecules

We call molecules that contain an odd number of electrons free radicals. Nitric oxide, NO, is an example of an odd-electron molecule; it is produced in internal combustion engines when oxygen and nitrogen react at high temperatures.

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

1. *Determine the total number of valence (outer shell) electrons*. The sum of the valence electrons is 5 (from N) + 6 (from O) = 11. The odd number immediately tells us that we have a free radical, so we know that not every atom can have eight electrons in its valence shell.
2. *Draw a skeleton structure of the molecule*. We can easily draw a skeleton with an N–O single bond:
   N–O
3. *Distribute the remaining electrons as lone pairs on the terminal atoms*. In this case, there is no central atom, so we distribute the electrons around both atoms. We give eight electrons to the more electronegative atom in these situations; thus oxygen has the filled valence shell:

$$\ddot{:N} \!-\! \ddot{\underset{..}{O}} \!:$$
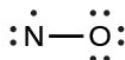
4. *Place all remaining electrons on the central atom*. Since there are no remaining electrons, this step does not apply.
5. *Rearrange the electrons to make multiple bonds with the central atom in order to obtain octets wherever possible*. We know that an odd-electron molecule cannot have an octet for every atom, but we want to get each atom as close to an octet as possible. In this case, nitrogen has only five electrons around it. To move closer to an octet for nitrogen, we take one of the lone pairs from oxygen and use it to form a NO double bond. (We cannot take another lone pair of electrons on oxygen and form a triple bond because nitrogen would then have nine electrons:)

$$\dot{:N} \!=\! \ddot{\underset{..}{O}} \!:$$

Electron-deficient Molecules

We will also encounter a few molecules that contain central atoms that do not have a filled valence shell. Generally, these are molecules with central atoms from groups 2 and 13, outer atoms that are hydrogen, or other atoms that do not form multiple bonds. For example, in the Lewis structures of beryllium dihydride, BeH_2, and boron trifluoride, BF_3, the beryllium and boron atoms each have only four and six electrons, respectively. It is possible to draw a structure with a double bond between a boron atom and a fluorine atom in BF_3, satisfying the octet rule, but experimental evidence indicates the bond lengths are closer to that expected for B–F single bonds. This suggests the best Lewis structure has three B–F single bonds and an electron deficient boron. The reactivity of the compound is also consistent with an electron deficient boron. However, the B–F bonds are slightly shorter than what is actually expected for B–F single bonds, indicating that some double bond character is found in the actual molecule.
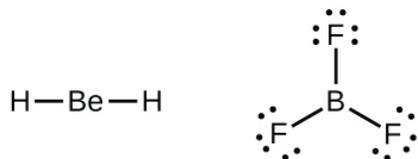
An atom like the boron atom in BF_3, which does not have eight electrons, is very reactive. It readily combines with a molecule containing an atom with a lone pair of electrons. For example, NH_3 reacts with BF_3 because the lone pair on nitrogen can be shared with the boron atom:
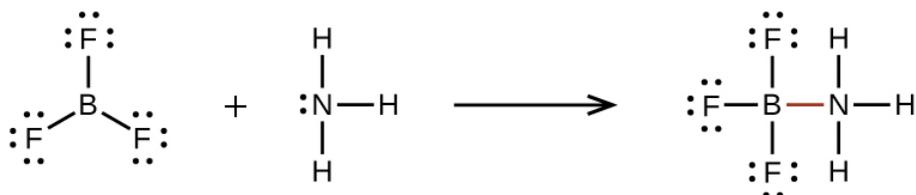
Hypervalent Molecules

Elements in the second period of the periodic table ($n = 2$) can accommodate only eight electrons in their valence shell orbitals because they have only four valence orbitals (one 2s and three 2p orbitals). Elements in the third and higher periods ($n \geq 3$) have more than four valence orbitals and can share more than four pairs of electrons with other atoms because they have empty d orbitals in the same shell. Molecules formed from these elements are sometimes called hypervalent molecules. Figure 4.4.4 shows the Lewis structures for two hypervalent molecules, PCl_5 and SF_6.
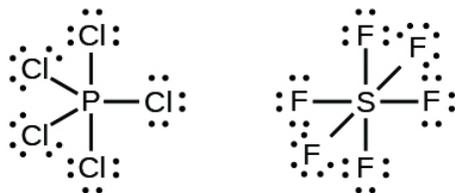
Figure 4.4.4: In PCl_5, the central atom phosphorus shares five pairs of electrons. In SF_6, sulfur shares six pairs of electrons.

In some hypervalent molecules, such as IF_5 and XeF_4, some of the electrons in the outer shell of the central atom are lone pairs:
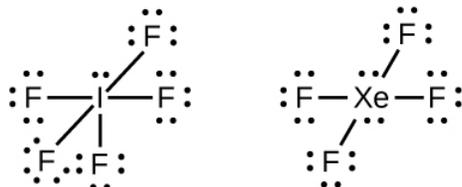
When we write the Lewis structures for these molecules, we find that we have electrons left over after filling the valence shells of the outer atoms with eight electrons. These additional electrons must be assigned to the central atom.

✔ **Example 4.4.2: Writing Lewis Structures - Octet Rule Violations**

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

Solution

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

Step 1. Calculate the number of valence electrons:

XeF_2: 8 + (2 × 7) = 22
XeF_6: 8 + (6 × 7) = 50

Step 2. Draw a skeleton joining the atoms by single bonds. Xenon will be the central atom because fluorine cannot be a central atom:
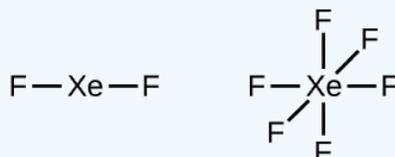
Step 3. Distribute the remaining electrons.

XeF_2: We place three lone pairs of electrons around each F atom, accounting for 12 electrons and giving each F atom 8 electrons. Thus, six electrons (three lone pairs) remain. These lone pairs must be placed on the Xe atom. This is acceptable because Xe atoms have empty valence shell *d* orbitals and can accommodate more than eight electrons. The Lewis structure of XeF_2 shows two bonding pairs and three lone pairs of electrons around the Xe atom:

XeF_6: We place three lone pairs of electrons around each F atom, accounting for 36 electrons. Two electrons remain, and this lone pair is placed on the Xe atom:
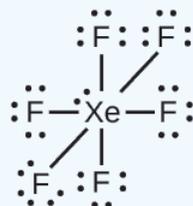
? **Exercise 4.4.2: Interhalogens**

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

Answer
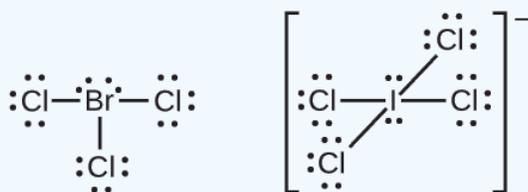
4.5: Formal Charges and Resonance

> 🧠 **Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Compute formal charges for atoms in any Lewis structure
> - Use formal charges to identify the most reasonable Lewis structure for a given molecule
> - Explain the concept of resonance and draw Lewis structures representing resonance forms for a given molecule

In the previous section, we discussed how to write Lewis structures for molecules and polyatomic ions. As we have seen, however, in some cases, there is seemingly more than one valid structure for a molecule. We can use the concept of formal charges to help us predict the most appropriate Lewis structure when more than one is reasonable.

Calculating Formal Charge

The formal charge of an atom in a molecule is the *hypothetical* charge the atom would have if we could redistribute the electrons in the bonds evenly between the atoms. Another way of saying this is that formal charge results when we take the number of valence electrons of a neutral atom, subtract the nonbonding electrons, and then subtract the number of bonds connected to that atom in the Lewis structure.

Thus, we calculate formal charge as follows:

$$\text{formal charge } = \text{\# valence shell electrons (free atom)} - \text{\# lone pair electrons} - \frac{1}{2}\text{\# bonding electrons}$$

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

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

> ✔ **Example 4.5.1: Calculating Formal Charge from Lewis Structures**
>
> Assign formal charges to each atom in the interhalogen ion
>
> **Solution**
> Step 1. *We divide the bonding electron pairs equally for all I–Cl bonds:*
>
>
>
> Step 2. *We assign lone pairs of electrons to their atoms.* Each Cl atom now has seven electrons assigned to it, and the I atom has eight.
>
> Step 3. *Subtract this number from the number of valence electrons for the neutral atom:*
>
>   I: 7 – 8 = –1
>   Cl: 7 – 7 = 0
>
> The sum of the formal charges of all the atoms equals –1, which is identical to the charge of the ion (–1).
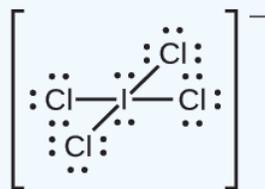
? Exercise 4.5.1

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

$$:C\!\equiv\!O:$$

Answer

   C −1, O +1

✔ Example 4.5.2: Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen molecule $BrCl_3$.

Solution

Step 1. *Assign one of the electrons in each Br–Cl bond to the Br atom and one to the Cl atom in that bond:*
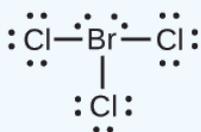
Step 2. *Assign the lone pairs to their atom.* Now each Cl atom has seven electrons and the Br atom has seven electrons.

Step 3. *Subtract this number from the number of valence electrons for the neutral atom.* This gives the formal charge:

   Br: 7 − 7 = 0
   Cl: 7 − 7 = 0

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

? Exercise 4.5.2

Determine the formal charge for each atom in NCl_3.

Answer

   N: 0; all three Cl atoms: 0
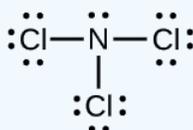
Using Formal Charge to Predict Molecular Structure

The arrangement of atoms in a molecule or ion is called its **molecular structure**. In many cases, following the steps for writing Lewis structures may lead to more than one possible molecular structure—different multiple bond and lone-pair electron placements or different arrangements of atoms, for instance. A few guidelines involving formal charge can be helpful in deciding which of the possible structures is most likely for a particular molecule or ion:

1. A molecular structure in which all formal charges are zero is preferable to one in which some formal charges are not zero.
2. If the Lewis structure must have nonzero formal charges, the arrangement with the smallest nonzero formal charges is preferable.
3. Lewis structures are preferable when adjacent formal charges are zero or of the opposite sign.
4. When we must choose among several Lewis structures with similar distributions of formal charges, the structure with the negative formal charges on the more electronegative atoms is preferable.

To see how these guidelines apply, let us consider some possible structures for carbon dioxide, CO_2. We know from our previous discussion that the less electronegative atom typically occupies the central position, but formal charges allow us to understand *why* this occurs. We can draw three possibilities for the structure: carbon in the center and double bonds, carbon in the center with a single and triple bond, and oxygen in the center with double bonds:

$$\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}{=}C{=}\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} \qquad :O{\equiv}C{-}\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}: \qquad \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}{=}O{=}\overset{\cdot\cdot}{\underset{\cdot\cdot}{C}} \qquad \text{Structure}$$

$$\quad 0 \quad\; 0 \quad\; 0 \qquad\quad +1 \quad 0 \quad -1 \qquad\; 0 \quad +2 \quad -2 \quad \text{Formal charge}$$
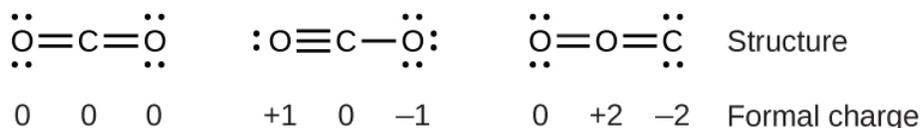
Comparing the three formal charges, we can definitively identify the structure on the left as preferable because it has only formal charges of zero (Guideline 1).

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

$$\text{Structure} \qquad \left[\overset{\cdot\cdot}{:}N{=}C{=}\overset{\cdot\cdot}{S}:\right]^- \qquad \left[\overset{\cdot\cdot}{:}C{=}N{=}\overset{\cdot\cdot}{S}:\right]^- \qquad \left[\overset{\cdot\cdot}{:}C{=}S{=}\overset{\cdot\cdot}{N}:\right]^-$$

$$\text{Formal charge} \quad -1 \quad\; 0 \quad\; 0 \qquad\qquad -2 \quad +1 \quad\; 0 \qquad\qquad -2 \quad +2 \quad -1$$
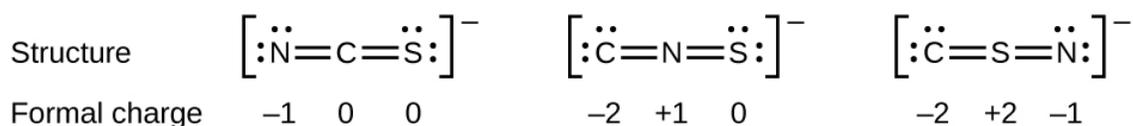
Note that the sum of the formal charges in each case is equal to the charge of the ion (–1). However, the first arrangement of atoms is preferred because it has the lowest number of atoms with nonzero formal charges (Guideline 2). Also, it places the least electronegative atom in the center, and the negative charge on the more electronegative element (Guideline 4).

✔ Example 4.5.3: Using Formal Charge to Determine Molecular Structure

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

$$:N{\equiv}N{-}\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}: \quad \text{or} \quad \overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}{=}O{=}\overset{\cdot\cdot}{\underset{\cdot\cdot}{N}}$$
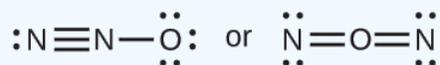
Solution
Determining formal charge yields the following:

$$:N{\equiv}N{=}\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}: \qquad :\overset{\cdot\cdot}{N}{=}O{=}\overset{\cdot\cdot}{N}:$$

$$\quad 0 \quad +1 \quad -1 \qquad\quad -1 \quad +2 \quad -1$$
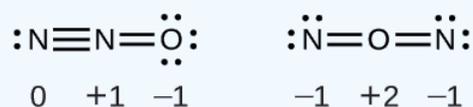
The structure with a terminal oxygen atom best satisfies the criteria for the most stable distribution of formal charge:

$$:N{\equiv}N{-}\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}:$$
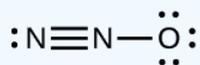
The number of atoms with formal charges are minimized (Guideline 2), there is no formal charge with a magnitude greater than one (Guideline 2), the negative formal charge is on the more electronegative element (Guideline 4), and the less electronegative atom is in the center position.

? Exercise 4.5.3

Which is the most likely molecular structure for the nitrite ion?

$$\left[:\ddot{N}=\ddot{O}-\ddot{O}: \right]^{-} \quad \text{or} \quad \left[:\ddot{O}=\ddot{N}-\ddot{O}: \right]^{-}$$
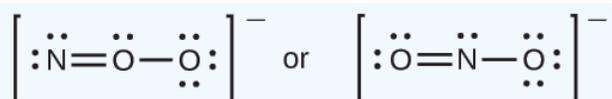
Answer

ONO⁻

Resonance

Notice that the more likely structure for the nitrite anion in Example 4.5.3 may actually be drawn in two different ways, distinguished by the locations of the N-O and N=O bonds:

$$\left[:\ddot{O}-\ddot{N}=\ddot{O} \right]^{-} \qquad \left[\ddot{O}=\ddot{N}-\ddot{O}: \right]^{-}$$

If nitrite ions do indeed contain a single and a double bond, we would expect for the two bond lengths to be different. A double bond between two atoms is shorter (and stronger) than a single bond between the same two atoms. Experiments show, however, that both N–O bonds in have the same strength and length, and are identical in all other properties.

It is not possible to write a single Lewis structure for in which nitrogen has an octet and both bonds are equivalent. Instead, we use the concept of **resonance**: if two or more Lewis structures with the same arrangement of atoms can be written for a molecule or ion, the actual distribution of electrons is an *average* of that shown by the various Lewis structures. The actual distribution of electrons in each of the nitrogen-oxygen bonds in is the average of a double bond and a single bond. We call the individual Lewis structures **resonance forms**. The actual electronic structure of the molecule (the average of the resonance forms) is called a **resonance hybrid** of the individual resonance forms. A double-headed arrow between Lewis structures indicates that they are resonance forms.

$$\left[:\ddot{O}-\ddot{N}=\ddot{O} \right]^{-} \longleftrightarrow \left[\ddot{O}=\ddot{N}-\ddot{O}: \right]^{-}$$

We should remember that a molecule described as a resonance hybrid *never* possesses an electronic structure described by either resonance form. It does not fluctuate between resonance forms; rather, the actual electronic structure is *always* the average of that shown by all resonance forms. George Wheland, one of the pioneers of resonance theory, used a historical analogy to describe the relationship between resonance forms and resonance hybrids. A medieval traveler, having never before seen a rhinoceros, described it as a hybrid of a dragon and a unicorn because it had many properties in common with both. Just as a rhinoceros is neither a dragon sometimes nor a unicorn at other times, a resonance hybrid is neither of its resonance forms at any given time. Like a rhinoceros, it is a real entity that experimental evidence has shown to exist. It has some characteristics in common with its resonance forms, but the resonance forms themselves are convenient, imaginary images (like the unicorn and the dragon).

The carbonate anion, provides a second example of resonance:

$$\left[\begin{matrix} :\ddot{O}: \\ \| \\ \ddot{O}\!=\!\!C\!\!-\!\ddot{O}: \end{matrix} \right]^{2-} \longleftrightarrow \left[\begin{matrix} :\ddot{O}: \\ | \\ :\ddot{O}\!-\!C\!\!=\!\!\ddot{O} \end{matrix} \right]^{2-} \longleftrightarrow \left[\begin{matrix} :O: \\ \| \\ :\ddot{O}\!-\!C\!\!-\!\ddot{O}: \end{matrix} \right]^{2-}$$
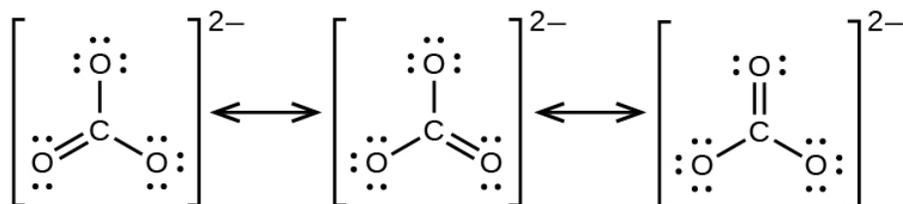
One oxygen atom must have a double bond to carbon to complete the octet on the central atom. All oxygen atoms, however, are equivalent, and the double bond could form from any one of the three atoms. This gives rise to three resonance forms of the carbonate ion. Because we can write three identical resonance structures, we know that the actual arrangement of electrons in the carbonate ion is the average of the three structures. Again, experiments show that all three C–O bonds are exactly the same.

4.6: Strengths of Ionic and Covalent Bonds

> **◑ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Describe the energetics of covalent and ionic bond formation and breakage
> - Use the Born-Haber cycle to compute lattice energies for ionic compounds
> - Use average covalent bond energies to estimate enthalpies of reaction

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

Bond Strength: Covalent Bonds

Stable molecules exist because covalent bonds hold the atoms together. We measure the strength of a covalent bond by the energy required to break it, that is, the energy necessary to separate the bonded atoms. Separating any pair of bonded atoms requires energy. The stronger a bond, the greater the energy required to break it.

The energy required to break a specific covalent bond in one mole of gaseous molecules is called the **bond energy** or the **bond dissociation energy**. The bond energy for a diatomic molecule, D_{X-Y}, is defined as the **standard enthalpy change** for the endothermic reaction:

$$XY(g) \longrightarrow X(g) + Y(g) \qquad D_{\text{X}-\text{Y}} = \Delta H°$$

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

$$H_2(g) \longrightarrow 2\,H(g) \qquad D_{H-H} = \Delta H° = 436\,\text{kJ}$$

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

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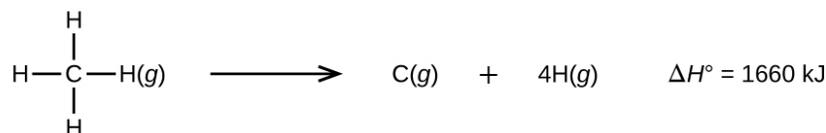
The average C$-$H bond energy, D_{C-H}, is 1660/4 = 415 kJ/mol because there are four moles of C$-$H bonds broken per mole of the reaction. Although the four C$-$H bonds are equivalent in the original molecule, they do not each require the same energy to break; once the first bond is broken (which requires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

The strength of a bond between two atoms increases as the number of electron pairs in the bond increases. Generally, as the bond strength increases, the bond length decreases. Thus, we find that triple bonds are stronger and shorter than double bonds between the same two atoms; likewise, double bonds are stronger and shorter than single bonds between the same two atoms. Average bond energies for some common bonds appear in Table 4.6.1, and a comparison of bond lengths and bond strengths for some common bonds appears in Table 4.6.2. When one atom bonds to various atoms in a group, the bond strength typically decreases as we move down the group. For example, C$-$F is 439 kJ/mol, C$-$Cl is 330 kJ/mol, and C$-$Br is 275 kJ/mol.

Table 4.6.1: Bond Energies (kJ/mol)

Bond	Bond Energy	Bond	Bond Energy	Bond	Bond Energy
H–H	436	C–S	260	F–Cl	255
H–C	415	C–Cl	330	F–Br	235
H–N	390	C–Br	275	Si–Si	230

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

Table 4.6.2: Average Bond Lengths and Bond Energies for Some Common Bonds

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

We can use bond energies to calculate approximate enthalpy changes for reactions where enthalpies of formation are not available. Calculations of this type will also tell us whether a reaction is exothermic or endothermic. An exothermic reaction (ΔH negative, heat produced) results when the bonds in the products are stronger than the bonds in the reactants. An endothermic reaction (ΔH positive, heat absorbed) results when the bonds in the products are weaker than those in the reactants.

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

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

In this expression, the symbol $\sum$ means "the sum of" and D represents the bond energy in kilojoules per mole, which is always a positive number. The bond energy is obtained from a table (like Table 4.6.2) and will depend on whether the particular bond is a single, double, or triple bond. Thus, in calculating enthalpies in this manner, it is important that we consider the bonding in all reactants and products. Because D values are typically averages for one type of bond in many different molecules, this calculation provides a rough estimate, not an exact value, for the enthalpy of reaction.

Consider the following reaction:

$$\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \longrightarrow 2\,\text{HCl}(\text{g})$$

or

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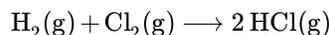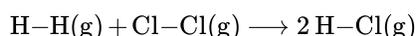
To form two moles of HCl, one mole of H–H bonds and one mole of Cl–Cl bonds must be broken. The energy required to break these bonds is the sum of the bond energy of the H–H bond (436 kJ/mol) and the Cl–Cl bond (243 kJ/mol). During the reaction, two moles of H–Cl bonds are formed (bond energy = 432 kJ/mol),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

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

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

✔ **Example 4.6.1: Using Bond Energies to Calculate Approximate Enthalpy Changes**

Methanol, CH_3OH, may be an excellent alternative fuel. The high-temperature reaction of steam and carbon produces a mixture of the gases carbon monoxide, CO, and hydrogen, H_2, from which methanol can be produced. Using the bond energies in Table 4.6.2, calculate the approximate enthalpy change, ΔH, for the reaction here:

$$\text{CO}(\text{g}) + 2\,\text{H}_2(\text{g}) \longrightarrow \text{CH}_3\text{OH}(\text{g})$$
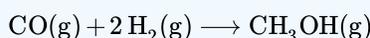
Solution

First, we need to write the Lewis structures of the reactants and the products:
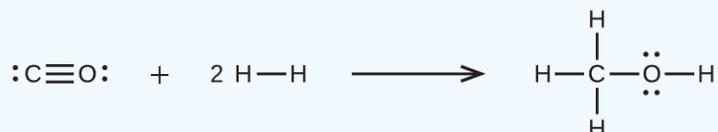
From this, we see that ΔH for this reaction involves the energy required to break a C–O triple bond and two H–H single bonds, as well as the energy produced by the formation of three C–H single bonds, a C–O single bond, and an O–H single bond. We can express this as follows:

$$\begin{aligned}
\Delta H &= \Sigma D_{\text{bonds broken}} - \Sigma D_{\text{bonds formed}} \\
&= [D_{C\equiv O} + 2\,(D_{H-H})] - [3\,(D_{C-H}) + D_{C-O} + D_{O-H}]
\end{aligned}$$

Using the bond energy values in Table 4.6.2, we obtain:

$$\Delta H = [1080 + 2(436)] - [3(415) + 350 + 464]$$
$$= -107 kJ$$

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

$$\Delta H = \left[\Delta H_f^\circ CH_3OH(g)\right] - \left[\Delta H_f^\circ CO(g) + 2 \times \Delta H_f^\circ H_2\right]$$
$$= [-201.0] - [-110.52 + 2 \times 0]$$
$$= -90.5 kJ$$

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

? Exercise 4.6.1

Ethyl alcohol, CH_3CH_2OH, was one of the first organic chemicals deliberately synthesized by humans. It has many uses in industry, and it is the alcohol contained in alcoholic beverages. It can be obtained by the fermentation of sugar or synthesized by the hydration of ethylene in the following reaction:
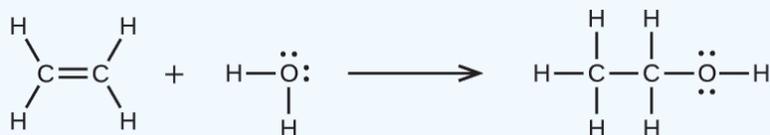
Using the bond energies in Table 4.6.2, calculate an approximate enthalpy change, ΔH, for this reaction.

Answer

–35 kJ

Ionic Bond Strength and Lattice Energy

An ionic compound is stable because of the electrostatic attraction between its positive and negative ions. The lattice energy of a compound is a measure of the strength of this attraction. The **lattice energy** ($\Delta H_{lattice}$) of an ionic compound is defined as the energy required to separate one mole of the solid into its component gaseous ions. For the ionic solid MX, the lattice energy is the enthalpy change of the process:

$$MX(s) \longrightarrow M^{n+}(g) + X^{n-}(g) \quad \Delta H_{\text{lattice}}$$
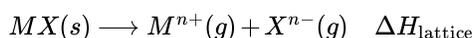
Note that we are using the convention where the ionic solid is separated into ions, so our lattice energies will be *endothermic* (positive values). Some texts use the equivalent but opposite convention, defining lattice energy as the energy released when separate ions combine to form a lattice and giving negative (exothermic) values. Thus, if you are looking up lattice energies in another reference, be certain to check which definition is being used. In both cases, a larger magnitude for lattice energy indicates a more stable ionic compound. For sodium chloride, $\Delta H_{\text{lattice}}$ = 769 kJ. Thus, it requires 769 kJ to separate one mole of solid NaCl into gaseous Na^+ and Cl^- ions. When one mole each of gaseous Na^+ and Cl^- ions form solid NaCl, 769 kJ of heat is released.

The lattice energy $\Delta H_{\text{lattice}}$ of an ionic crystal can be expressed by the following equation (derived from Coulomb's law, governing the forces between electric charges):

$$\Delta H_{\text{lattice}} = \frac{C\,(Z^+)\,(Z^-)}{R_0}$$

in which C is a constant that depends on the type of crystal structure; Z^+ and Z^- are the charges on the ions; and R_0 is the interionic distance (the sum of the radii of the positive and negative ions). Thus, the lattice energy of an ionic crystal increases rapidly as the charges of the ions increase and the sizes of the ions decrease. When all other parameters are kept constant, doubling the charge of both the cation and anion quadruples the lattice energy. For example, the lattice energy of LiF (Z^+ and Z^- = 1) is 1023 kJ/mol, whereas that of MgO (Z^+ and Z^- = 2) is 3900 kJ/mol (R_0 is nearly the same—about 200 pm for both compounds).

Different interatomic distances produce different lattice energies. For example, we can compare the lattice energy of MgF_2 (2957 kJ/mol) to that of MgI_2 (2327 kJ/mol) to observe the effect on lattice energy of the smaller ionic size of F^- as compared to I^-.

> ✔ **Example 4.6.2: Lattice Energy Comparisons**
>
> The precious gem ruby is aluminum oxide, Al_2O_3, containing traces of Cr^{3+}. The compound Al_2Se_3 is used in the fabrication of some semiconductor devices. Which has the larger lattice energy, Al_2O_3 or Al_2Se_3?
>
> **Solution**
>
> In these two ionic compounds, the charges Z^+ and Z^- are the same, so the difference in lattice energy will depend upon R_o. The O^{2-} ion is smaller than the Se^{2-} ion. Thus, Al_2O_3 would have a shorter interionic distance than Al_2Se_3, and Al_2O_3 would have the larger lattice energy.

> ? **Exercise 4.6.1**
>
> Zinc oxide, ZnO, is a very effective sunscreen. How would the lattice energy of ZnO compare to that of NaCl?
>
> **Answer**
>
> > ZnO would have the larger lattice energy because the Z values of both the cation and the anion in ZnO are greater, and the interionic distance of ZnO is smaller than that of NaCl.

The Born-Haber Cycle

It is not possible to measure lattice energies directly. However, the lattice energy can be calculated using the equation given in the previous section or by using a thermochemical cycle. The **Born-Haber cycle** is an application of Hess's law that breaks down the formation of an ionic solid into a series of individual steps:

- ΔH_f° the standard enthalpy of formation of the compound
- IE, the ionization energy of the metal
- EA, the electron affinity of the nonmetal
- ΔH_s° the enthalpy of sublimation of the metal
- D, the bond dissociation energy of the nonmetal
- $\Delta H_{lattice}$, the lattice energy of the compound

Figure 4.6.1: diagrams the Born-Haber cycle for the formation of solid cesium fluoride.
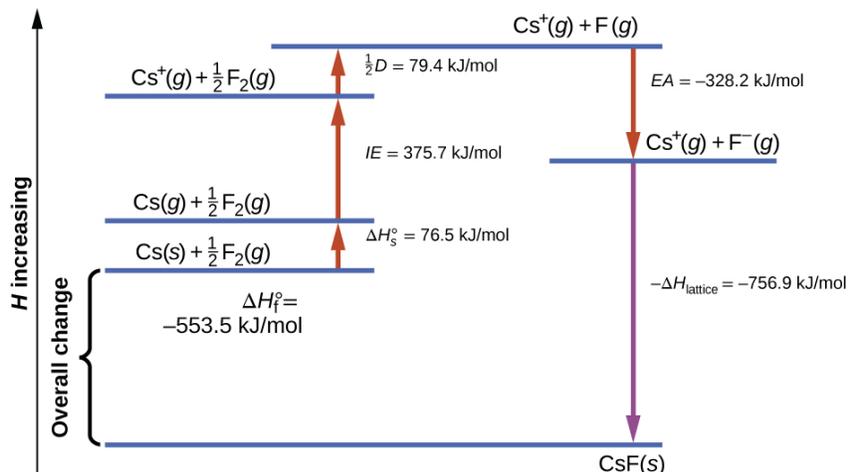
Figure 4.6.1: The Born-Haber cycle shows the relative energies of each step involved in the formation of an ionic solid from the necessary elements in their reference states.

We begin with the elements in their most common states, $Cs(s)$ and $F_2(g)$. The represents the conversion of solid cesium into a gas, and then the ionization energy converts the gaseous cesium atoms into cations. In the next step, we account for the energy required to break the F–F bond to produce fluorine atoms. Converting one mole of fluorine atoms into fluoride ions is an

exothermic process, so this step gives off energy (the electron affinity) and is shown as decreasing along the *y*-axis. We now have one mole of Cs cations and one mole of F anions. These ions combine to produce solid cesium fluoride. The enthalpy change in this step is the negative of the lattice energy, so it is also an exothermic quantity. The total energy involved in this conversion is equal to the experimentally determined enthalpy of formation, ΔH_f° of the compound from its elements. In this case, the overall change is exothermic.

Hess's law can also be used to show the relationship between the enthalpies of the individual steps and the enthalpy of formation. Table 4.6.3 shows this for fluoride, CsF.

<div align="center">Table 4.6.3</div>

Enthalpy of sublimation of $Cs(s)$	$Cs(s) \longrightarrow Cs(g)$	$\Delta H = \Delta H_s^\circ = 76.5\,\mathrm{kJ/mol}$
One-half of the bond energy of F_2	$\frac{1}{2}F_2(g) \longrightarrow F(g)$	$\Delta H = \frac{1}{2}D = 79.4\,\mathrm{kJ/mol}$
Ionization energy of $Cs(g)$	$Cs(g) \longrightarrow Cs^+(g) + e^-$	$\Delta H = IE = 375.7\,\mathrm{kJ/mol}$
Electron affinity of F	$F(g) + e^- \longrightarrow F^-(g)$	$\Delta H = EA = -328.2\,\mathrm{kJ/mol}$
Negative of the lattice energy of $CsF(s)$	$Cs^+(g) + F^-(g) \longrightarrow CsF(s)$	$\Delta H = -\Delta H_\mathrm{lattice} = ?$
Enthalpy of formation of $CsF(s)$, add steps 1–5	$\Delta H = \Delta H_f^\circ = \Delta H_s^\circ + \frac{1}{2}D + IE + (EA) + (-\Delta H_\mathrm{lattice})$ $Cs(s) + \frac{1}{2}F_2(g) \longrightarrow CsF(s)$	$\Delta H = -553.5\,\mathrm{kJ/mol}$

Thus, the lattice energy can be calculated from other values. For cesium fluoride, using this data, the lattice energy is:

$$\Delta H_\mathrm{lattice} = 76.5 + 79.4 + 375.7 + (-328.2) - (-553.5) = 756.9\,\mathrm{kJ/mol}$$

The Born-Haber cycle may also be used to calculate any one of the other quantities in the equation for lattice energy, provided that the remainder is known. For example, if the relevant enthalpy of sublimation ΔH_s°, ionization energy (IE), bond dissociation enthalpy (D), lattice energy $\Delta H_\mathrm{lattice}$, and standard enthalpy of formation are known, the Born-Haber cycle can be used to determine the electron affinity of an atom.

Lattice energies calculated for ionic compounds are typically much higher than bond dissociation energies measured for covalent bonds. Whereas lattice energies typically fall in the range of 600–4000 kJ/mol (some even higher), covalent bond dissociation energies are typically between 150–400 kJ/mol for single bonds. Keep in mind, however, that these are not directly comparable values. For ionic compounds, lattice energies are associated with many interactions, as cations and anions pack together in an extended lattice. For covalent bonds, the bond dissociation energy is associated with the interaction of just two atoms.

4.7: Molecular Structure and Polarity

> ◀▶ **Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Predict the structures of small molecules using valence shell electron pair repulsion (VSEPR) theory
> - Explain the concepts of polar covalent bonds and molecular polarity
> - Assess the polarity of a molecule based on its bonding and structure

Thus far, we have used two-dimensional Lewis structures to represent molecules. However, molecular structure is actually three-dimensional, and it is important to be able to describe molecular bonds in terms of their distances, angles, and relative arrangements in space (Figure $4.7.1$). A bond angle is the angle between any two bonds that include a common atom, usually measured in degrees. A bond distance (or bond length) is the distance between the nuclei of two bonded atoms along the straight line joining the nuclei. Bond distances are measured in Ångstroms (1 Å = 10^{-10} m) or picometers (1 pm = 10^{-12} m, 100 pm = 1 Å).
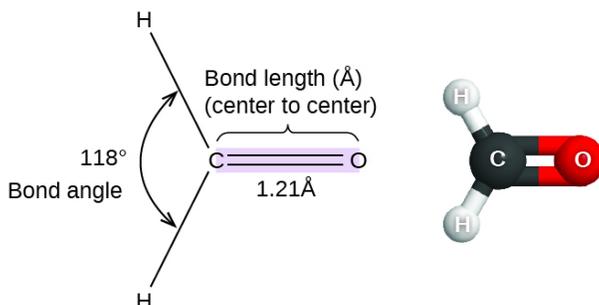
Figure $4.7.1$: Bond distances (lengths) and angles are shown for the formaldehyde molecule, H_2CO.

VSEPR Theory

Valence shell electron-pair repulsion theory (VSEPR theory) enables us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule from an examination of the number of bonds and lone electron pairs in its Lewis structure. The VSEPR model assumes that electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them. The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs. The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.

VSEPR theory predicts the arrangement of electron pairs around each central atom and, usually, the correct arrangement of atoms in a molecule. We should understand, however, that the theory only considers electron-pair repulsions. Other interactions, such as nuclear-nuclear repulsions and nuclear-electron attractions, are also involved in the final arrangement that atoms adopt in a particular molecular structure.

As a simple example of VSEPR theory, let us predict the structure of a gaseous BeF_2 molecule. The Lewis structure of BeF_2 (Figure $4.7.2$) shows only two electron pairs around the central beryllium atom. With two bonds and no lone pairs of electrons on the central atom, the bonds are as far apart as possible, and the electrostatic repulsion between these regions of high electron density is reduced to a minimum when they are on opposite sides of the central atom. The bond angle is 180° (Figure $4.7.2$).
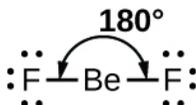
Figure $4.7.2$: The BeF_2 molecule adopts a linear structure in which the two bonds are as far apart as possible, on opposite sides of the Be atom.

Figure $4.7.3$ illustrates this and other electron-pair geometries that minimize the repulsions among regions of high electron density (bonds and/or lone pairs). Two regions of electron density around a central atom in a molecule form a linear geometry; three regions form a trigonal planar geometry; four regions form a tetrahedral geometry; five regions form a trigonal bipyramidal geometry; and six regions form an octahedral geometry.

Number of regions	Two regions of high electron density (bonds and/or unshared pairs)	Three regions of high electron density (bonds and/or unshared pairs)	Four regions of high electron density (bonds and/or unshared pairs)	Five regions of high electron density (bonds and/or unshared pairs)	Six regions of high electron density (bonds and/or unshared pairs)
Spatial arrangement	180°	120°	109.5°	90° / 120°	90° / 90°
Line-dash-wedge notation	H—Be—H	H-B(H)(H)	H-C(H)(H)(H)	F-P(F)(F)(F)(F)	F-S(F)(F)(F)(F)(F)
Electron region geometry	Linear; 180° angle	Trigonal planar; all angles 120°	Tetrahedral; all angles 109.5°	Trigonal bipyramidal; angles of 90° or 120° An attached atom may be equatorial (in the plane of the triangle) or axial (above or below the plane of the triangle).	Octahedral; all angles 90° or 180°
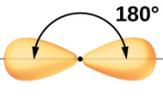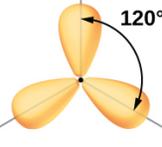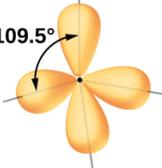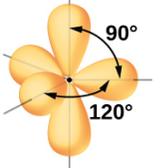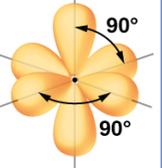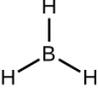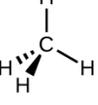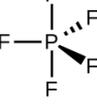
Figure 4.7.3: The basic electron-pair geometries predicted by VSEPR theory maximize the space around any region of electron density (bonds or lone pairs).

Electron-pair Geometry versus Molecular Structure

It is important to note that electron-pair geometry around a central atom is *not* the same thing as its molecular structure. The electron-pair geometries shown in Figure 4.7.3 describe all regions where electrons are located, bonds as well as lone pairs. Molecular structure describes the location of the *atoms*, not the electrons.

We differentiate between these two situations by naming the geometry that includes *all* electron pairs the electron-pair geometry. The structure that includes only the placement of the atoms in the molecule is called the molecular structure. The electron-pair geometries will be the same as the molecular structures when there are no lone electron pairs around the central atom, but they will be different when there are lone pairs present on the central atom.
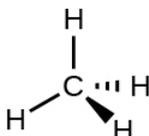
Figure 4.7.4: The molecular structure of the methane molecule, CH_4, is shown with a tetrahedral arrangement of the hydrogen atoms. VSEPR structures like this one are often drawn using the wedge and dash notation, in which solid lines represent bonds in the plane of the page, solid wedges represent bonds coming up out of the plane, and dashed lines represent bonds going down into the plane.

For example, the methane molecule, CH_4, which is the major component of natural gas, has four bonding pairs of electrons around the central carbon atom; the electron-pair geometry is tetrahedral, as is the molecular structure (Figure 4.7.4). On the other hand,

the ammonia molecule, NH_3, also has four electron pairs associated with the nitrogen atom, and thus has a tetrahedral electron-pair geometry. One of these regions, however, is a lone pair, which is not included in the molecular structure, and this lone pair influences the shape of the molecule (Figure 4.7.5).
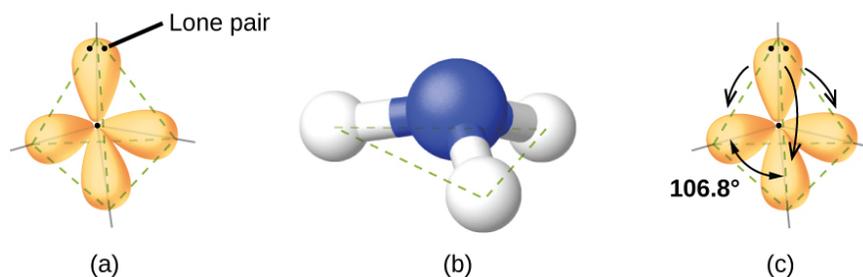
Figure 4.7.5: (a) The electron-pair geometry for the ammonia molecule is tetrahedral with one lone pair and three single bonds. (b) The trigonal pyramidal molecular structure is determined from the electron-pair geometry. (c) The actual bond angles deviate slightly from the idealized angles because the lone pair takes up a larger region of space than do the single bonds, causing the HNH angle to be slightly smaller than 109.5°.

As seen in Figure 4.7.5, small distortions from the ideal angles in Figure 4.7.3 can result from differences in repulsion between various regions of electron density. VSEPR theory predicts these distortions by establishing an order of repulsions and an order of the amount of space occupied by different kinds of electron pairs. The order of electron-pair repulsions from greatest to least repulsion is:

$$\text{lone pair-lone pair} > \text{lone pair-bonding pair} > \text{bonding pair-bonding pair}$$

This order of repulsions determines the amount of space occupied by different regions of electrons. A lone pair of electrons occupies a larger region of space than the electrons in a triple bond; in turn, electrons in a triple bond occupy more space than those in a double bond, and so on. The order of sizes from largest to smallest is:

$$\text{lone pair} > \text{triple bond} > \text{double bond} > \text{single bond}$$
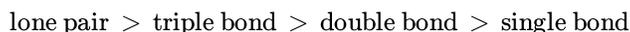
Consider formaldehyde, H_2CO, which is used as a preservative for biological and anatomical specimens (Figure 4.7.1). This molecule has regions of high electron density that consist of two single bonds and one double bond. The basic geometry is trigonal planar with 120° bond angles, but we see that the double bond causes slightly larger angles (121°), and the angle between the single bonds is slightly smaller (118°).

In the ammonia molecule, the three hydrogen atoms attached to the central nitrogen are not arranged in a flat, trigonal planar molecular structure, but rather in a three-dimensional trigonal pyramid (Figure 4.7.5) with the nitrogen atom at the apex and the three hydrogen atoms forming the base. The ideal bond angles in a trigonal pyramid are based on the tetrahedral electron pair geometry. Again, there are slight deviations from the ideal because lone pairs occupy larger regions of space than do bonding electrons. The H–N–H bond angles in NH_3 are slightly smaller than the 109.5° angle in a regular tetrahedron (Figure 4.7.3) because the lone pair-bonding pair repulsion is greater than the bonding pair-bonding pair repulsion (Figure 4.7.5). Figure 4.7.6 illustrates the ideal molecular structures, which are predicted based on the electron-pair geometries for various combinations of lone pairs and bonding pairs.

Number of electron regions	Electron region geometries: 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	**180°** X—E—X Linear				
3	**120°** Trigonal planar	**<120°** Bent or angular			
4	**109°** Tetrahedral	**<109°** Trigonal pyramid	**<<109°** Bent or angular		
5	**120° / 90°** Trigonal bipyramid	**<90° / <120°** Sawhorse or seesaw	**<90°** T-shape	**180°** Linear	
6	**90°** Octahedral	**<90°** Square pyramid	**90°** Square planar	**<90°** T-shape	**180°** Linear

Figure 4.7.6: The molecular structures are identical to the electron-pair geometries when there are no lone pairs present (first column). For a particular number of electron pairs (row), the molecular structures for one or more lone pairs are determined based on modifications of the corresponding electron-pair geometry.

According to VSEPR theory, the terminal atom locations (Xs in Figure 4.7.6) are equivalent within the linear, trigonal planar, and tetrahedral electron-pair geometries (the first three rows of the table). It does not matter which X is replaced with a lone pair because the molecules can be rotated to convert positions. For trigonal bipyramidal electron-pair geometries, however, there are two distinct X positions, as shown in Figure 4.7.7 an axial position (if we hold a model of a trigonal bipyramid by the two axial positions, we have an axis around which we can rotate the model) and an equatorial position (three positions form an equator around the middle of the molecule). As shown in Figure 4.7.6, the axial position is surrounded by bond angles of 90°, whereas the equatorial position has more space available because of the 120° bond angles. In a trigonal bipyramidal electron-pair geometry, lone pairs always occupy equatorial positions because these more spacious positions can more easily accommodate the larger lone pairs.

Theoretically, we can come up with three possible arrangements for the three bonds and two lone pairs for the ClF_3 molecule (Figure 4.7.7). The stable structure is the one that puts the lone pairs in equatorial locations, giving a T-shaped molecular structure.
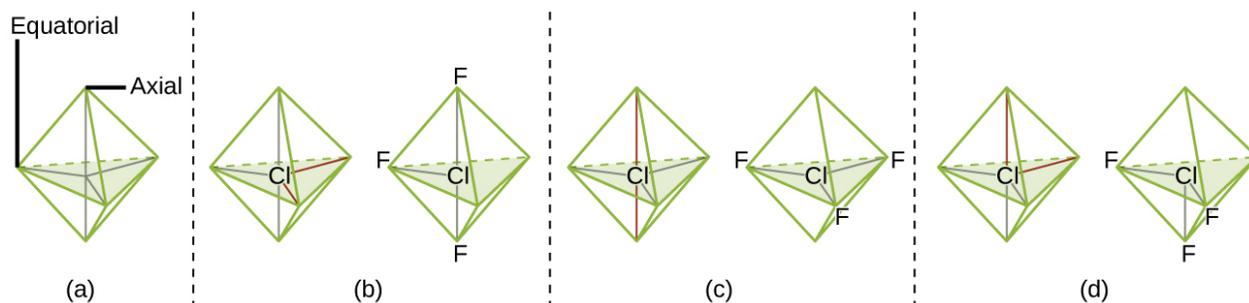
Figure 4.7.7: (a) In a trigonal bipyramid, the two axial positions are located directly across from one another, whereas the three equatorial positions are located in a triangular arrangement. (b–d) The two lone pairs (red lines) in ClF_3 have several possible arrangements, but the T-shaped molecular structure (b) is the one actually observed, consistent with the larger lone pairs both occupying equatorial positions.

When a central atom has two lone electron pairs and four bonding regions, we have an octahedral electron-pair geometry. The two lone pairs are on opposite sides of the octahedron (180° apart), giving a square planar molecular structure that minimizes lone pair-lone pair repulsions (Figure 4.7.6).

Predicting Electron Pair Geometry and Molecular Structure

The following procedure uses VSEPR theory to determine the electron pair geometries and the molecular structures:

1. Write the Lewis structure of the molecule or polyatomic ion.
2. Count the number of regions of electron density (lone pairs and bonds) around the central atom. A single, double, or triple bond counts as one region of electron density.
3. Identify the electron-pair geometry based on the number of regions of electron density: linear, trigonal planar, tetrahedral, trigonal bipyramidal, or octahedral (Figure 4.7.6, first column).
4. Use the number of lone pairs to determine the molecular structure (Figure 4.7.6). If more than one arrangement of lone pairs and chemical bonds is possible, choose the one that will minimize repulsions, remembering that lone pairs occupy more space than multiple bonds, which occupy more space than single bonds. In trigonal bipyramidal arrangements, repulsion is minimized when every lone pair is in an equatorial position. In an octahedral arrangement with two lone pairs, repulsion is minimized when the lone pairs are on opposite sides of the central atom.

The following examples illustrate the use of VSEPR theory to predict the molecular structure of molecules or ions that have no lone pairs of electrons. In this case, the molecular structure is identical to the electron pair geometry.

> ✔ **Example 4.7.1: Predicting Electron-pair Geometry and Molecular Structure: CO_2 and BCl_3**
>
> Predict the electron-pair geometry and molecular structure for each of the following:
>
> a. carbon dioxide, CO_2, a molecule produced by the combustion of fossil fuels
> b. boron trichloride, BCl_3, an important industrial chemical
>
> **Solution**
>
> (a) We write the Lewis structure of CO_2 as:
>
>
>
> This shows us two regions of high electron density around the carbon atom—each double bond counts as one region, and there are no lone pairs on the carbon atom. Using VSEPR theory, we predict that the two regions of electron density arrange themselves on opposite sides of the central atom with a bond angle of 180°. The electron-pair geometry and molecular structure are identical, and CO_2 molecules are linear.
>
> (b) We write the Lewis structure of BCl_3 as:
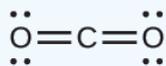
$$:\overset{\displaystyle ..}{\underset{\displaystyle ..}{Cl}}:$$

$$:\overset{..}{\underset{..}{Cl}}-B-\overset{..}{\underset{..}{Cl}}:$$
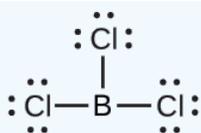
Thus we see that BCl$_3$ contains three bonds, and there are no lone pairs of electrons on boron. The arrangement of three regions of high electron density gives a trigonal planar electron-pair geometry. The B–Cl bonds lie in a plane with 120° angles between them. BCl$_3$ also has a trigonal planar molecular structure (Figure 4.7.8).
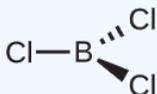
Figure 4.7.8:

The electron-pair geometry and molecular structure of BCl$_3$ are both trigonal planar. Note that the VSEPR geometry indicates the correct bond angles (120°), unlike the Lewis structure shown above.

? Exercise 4.7.1

Carbonate, is a common polyatomic ion found in various materials from eggshells to antacids. What are the electron-pair geometry and molecular structure of this polyatomic ion?

Answer

The electron-pair geometry is trigonal planar and the molecular structure is trigonal planar. Due to resonance, all three C–O bonds are identical. Whether they are single, double, or an average of the two, each bond counts as one region of electron density.

✔ Example 4.7.2: Predicting Electron-pair Geometry and Molecular Structure: Ammonium

Two of the top 50 chemicals produced in the United States, ammonium nitrate and ammonium sulfate, both used as fertilizers, contain the ammonium ion. Predict the electron-pair geometry and molecular structure of the cation.

Solution

We write the Lewis structure of as:
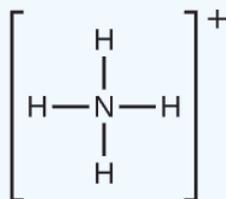
We can see that NH$_4^+$ contains four bonds from the nitrogen atom to hydrogen atoms and no lone pairs. We expect the four regions of high electron density to arrange themselves so that they point to the corners of a tetrahedron with the central nitrogen atom in the middle (Figure 4.7.6). Therefore, the electron pair geometry of Figure 4.7.9.
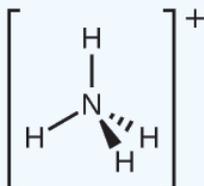
Figure 4.7.9: The ammonium ion displays a tetrahedral electron-pair geometry as well as a tetrahedral molecular structure.

? Exercise 4.7.2

Identify a molecule with trigonal bipyramidal molecular structure.

Answer

Any molecule with five electron pairs around the central atoms including no lone pairs will be trigonal bipyramidal. PF_5 is a common example.

The next several examples illustrate the effect of lone pairs of electrons on molecular structure.

✔ Example 4.7.3: Predicting Electron-pair Geometry and Molecular Structure: Lone Pairs on the Central Atom

Predict the electron-pair geometry and molecular structure of a water molecule.

Solution

The Lewis structure of H_2O indicates that there are four regions of high electron density around the oxygen atom: two lone pairs and two chemical bonds:
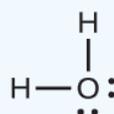
We predict that these four regions are arranged in a tetrahedral fashion (Figure 4.7.10), as indicated in Figure 4.7.6. Thus, the electron-pair geometry is tetrahedral and the molecular structure is bent with an angle slightly less than 109.5°. In fact, the bond angle is 104.5°.
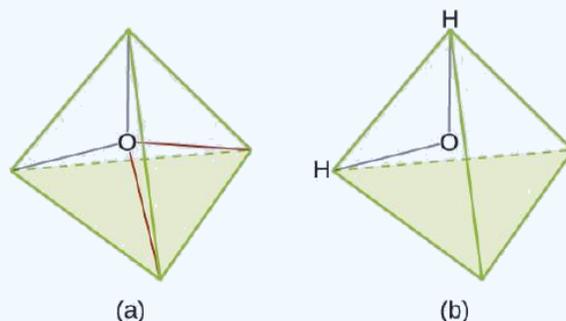
Figure 4.7.10: (a) H_2O has four regions of electron density around the central atom, so it has a tetrahedral electron-pair geometry. (b) Two of the electron regions are lone pairs, so the molecular structure is bent.

? Exercise 4.7.3

The hydronium ion, H_3O^+, forms when acids are dissolved in water. Predict the electron-pair geometry and molecular structure of this cation.

Answer

electron pair geometry: tetrahedral; molecular structure: trigonal pyramidal

✔ Example 4.7.4: Predicting Electron-pair Geometry and Molecular Structure: SF_4

Sulfur tetrafluoride, SF_4, is extremely valuable for the preparation of fluorine-containing compounds used as herbicides (i.e., SF_4 is used as a fluorinating agent). Predict the electron-pair geometry and molecular structure of a SF_4 molecule.

Solution

The Lewis structure of SF_4 indicates five regions of electron density around the sulfur atom: one lone pair and four bonding pairs:
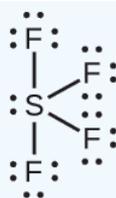
We expect these five regions to adopt a trigonal bipyramidal electron-pair geometry. To minimize lone pair repulsions, the lone pair occupies one of the equatorial positions. The molecular structure (Figure 4.7.11) is that of a seesaw (Figure 4.7.6).

(a)   (b)
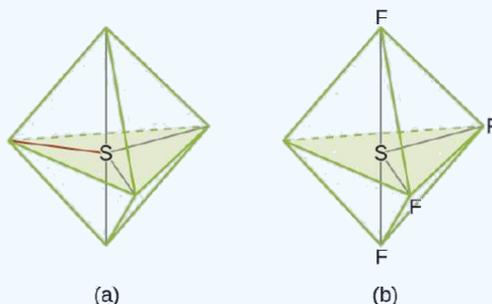
Figure 4.7.11: (a) SF4 has a trigonal bipyramidal arrangement of the five regions of electron density. (b) One of the regions is a lone pair, which results in a seesaw-shaped molecular structure.

? Exercise 4.7.4

Predict the electron pair geometry and molecular structure for molecules of XeF_2.

Answer

The electron-pair geometry is trigonal bipyramidal. The molecular structure is linear.

✔ Example 4.7.5: Predicting Electron-pair Geometry and Molecular Structure: XeF_4

Of all the noble gases, xenon is the most reactive, frequently reacting with elements such as oxygen and fluorine. Predict the electron-pair geometry and molecular structure of the XeF_4 molecule.

Solution

The Lewis structure of XeF_4 indicates six regions of high electron density around the xenon atom: two lone pairs and four bonds:
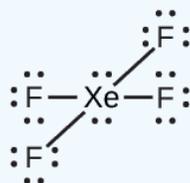
These six regions adopt an octahedral arrangement (Figure 4.7.6), which is the electron-pair geometry. To minimize repulsions, the lone pairs should be on opposite sides of the central atom (Figure 4.7.12). The five atoms are all in the same plane and have a square planar molecular structure.
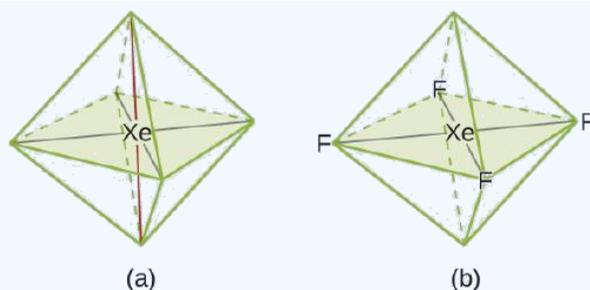
Figure 4.7.12: (a) XeF_4 adopts an octahedral arrangement with two lone pairs (red lines) and four bonds in the electron-pair geometry. (b) The molecular structure is square planar with the lone pairs directly across from one another.

> **? Exercise 4.7.5**
>
> In a certain molecule, the central atom has three lone pairs and two bonds. What will the electron pair geometry and molecular structure be?
>
> **Answer**
>
> electron pair geometry: trigonal bipyramidal; molecular structure: linear

Molecular Structure for Multicenter Molecules

When a molecule or polyatomic ion has only one central atom, the molecular structure completely describes the shape of the molecule. Larger molecules do not have a single central atom, but are connected by a chain of interior atoms that each possess a "local" geometry. The way these local structures are oriented with respect to each other also influences the molecular shape, but such considerations are largely beyond the scope of this introductory discussion. For our purposes, we will only focus on determining the local structures.

> **✔ Example 4.7.6: Predicting Structure in Multicenter Molecules**
>
> The Lewis structure for the simplest amino acid, glycine, $H_2NCH_2CO_2H$, is shown here. Predict the local geometry for the nitrogen atom, the two carbon atoms, and the oxygen atom with a hydrogen atom attached:
>
>
>
> **Solution**
>
>
>
> Consider each central atom independently. The electron-pair geometries:
>
> - nitrogen—four regions of electron density; tetrahedral
> - carbon ($\underline{C}H_2$)—four regions of electron density; tetrahedral
> - carbon ($\underline{C}O_2$)—three regions of electron density; trigonal planar
> - oxygen ($\underline{O}H$)—four regions of electron density; tetrahedral
>
> The local structures:
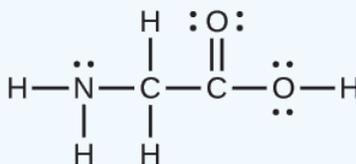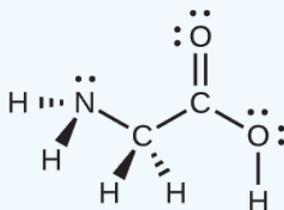
- nitrogen—three bonds, one lone pair; trigonal pyramidal
- carbon ($\underline{C}H_2$)—four bonds, no lone pairs; tetrahedral
- carbon ($\underline{C}O_2$)—three bonds (double bond counts as one bond), no lone pairs; trigonal planar
- oxygen ($\underline{O}H$)—two bonds, two lone pairs; bent (109°)

? Exercise 4.7.6

Another amino acid is alanine, which has the Lewis structure shown here. Predict the electron-pair geometry and local structure of the nitrogen atom, the three carbon atoms, and the oxygen atom with hydrogen attached:
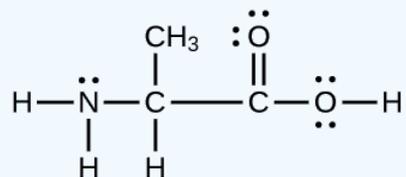
Answer

electron-pair geometries: nitrogen—tetrahedral; carbon ($\underline{C}H$)—tetrahedral; carbon ($\underline{C}H_3$)—tetrahedral; carbon ($\underline{C}O_2$)—trigonal planar; oxygen ($\underline{O}H$)—tetrahedral; local structures: nitrogen—trigonal pyramidal; carbon ($\underline{C}H$)—tetrahedral; carbon ($\underline{C}H_3$)—tetrahedral; carbon ($\underline{C}O_2$)—trigonal planar; oxygen ($\underline{O}H$)—bent (109°)

📌 Link to Learning

The molecular shape simulator lets you build various molecules and practice naming their electron-pair geometries and molecular structures.

✔ Example 4.7.7: Molecular Simulation

Using molecular shape simulator allows us to control whether bond angles and/or lone pairs are displayed by checking or unchecking the boxes under "Options" on the right. We can also use the "Name" checkboxes at bottom-left to display or hide the electron pair geometry (called "electron geometry" in the simulator) and/or molecular structure (called "molecular shape" in the simulator).

Build the molecule HCN in the simulator based on the following Lewis structure:

$$H-C\equiv N$$
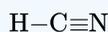
Click on each bond type or lone pair at right to add that group to the central atom. Once you have the complete molecule, rotate it to examine the predicted molecular structure. What molecular structure is this?

Solution

The molecular structure is linear.

? Exercise 4.7.7

Build a more complex molecule in the simulator. Identify the electron-group geometry, molecular structure, and bond angles. Then try to find a chemical formula that would match the structure you have drawn.

Answer

Answers will vary. For example, an atom with four single bonds, a double bond, and a lone pair has an octahedral electron-group geometry and a square pyramidal molecular structure. $XeOF_4$ is a molecule that adopts this structure.

Molecular Polarity and Dipole Moment

As discussed previously, polar covalent bonds connect two atoms with differing electronegativities, leaving one atom with a partial positive charge (δ+) and the other atom with a partial negative charge (δ–), as the electrons are pulled toward the more electronegative atom. This separation of charge gives rise to a bond dipole moment. The magnitude of a bond dipole moment is represented by the Greek letter mu (μ) and is given by the formula shown here, where Q is the magnitude of the partial charges (determined by the electronegativity difference) and r is the distance between the charges:

$$\mu = Qr$$

This bond moment can be represented as a vector, a quantity having both direction and magnitude (Figure 4.7.13). Dipole vectors are shown as arrows pointing along the bond from the less electronegative atom toward the more electronegative atom. A small plus sign is drawn on the less electronegative end to indicate the partially positive end of the bond. The length of the arrow is proportional to the magnitude of the electronegativity difference between the two atoms.
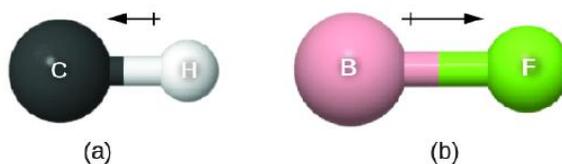
Figure 4.7.13: (a) There is a small difference in electronegativity between C and H, represented as a short vector. (b) The electronegativity difference between B and F is much larger, so the vector representing the bond moment is much longer.

A whole molecule may also have a separation of charge, depending on its molecular structure and the polarity of each of its bonds. If such a charge separation exists, the molecule is said to be a polar molecule (or dipole); otherwise the molecule is said to be nonpolar. The dipole moment measures the extent of net charge separation in the molecule as a whole. We determine the dipole moment by adding the bond moments in three-dimensional space, taking into account the molecular structure.

For diatomic molecules, there is only one bond, so its bond dipole moment determines the molecular polarity. Homonuclear diatomic molecules such as Br_2 and N_2 have no difference in electronegativity, so their dipole moment is zero. For heteronuclear molecules such as CO, there is a small dipole moment. For HF, there is a larger dipole moment because there is a larger difference in electronegativity.

When a molecule contains more than one bond, the geometry must be taken into account. If the bonds in a molecule are arranged such that their bond moments cancel (vector sum equals zero), then the molecule is nonpolar. This is the situation in CO_2 (Figure 4.7.14). Each of the bonds is polar, but the molecule as a whole is nonpolar. From the Lewis structure, and using VSEPR theory, we determine that the CO_2 molecule is linear with polar C=O bonds on opposite sides of the carbon atom. The bond moments cancel because they are pointed in opposite directions. In the case of the water molecule (Figure 4.7.14), the Lewis structure again shows that there are two bonds to a central atom, and the electronegativity difference again shows that each of these bonds has a nonzero bond moment. In this case, however, the molecular structure is bent because of the lone pairs on O, and the two bond moments do not cancel. Therefore, water does have a net dipole moment and is a polar molecule (dipole).
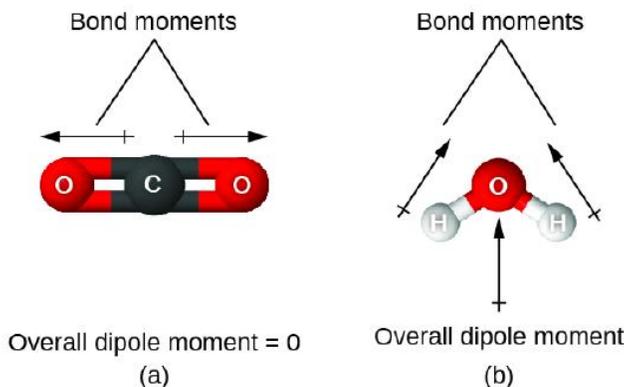
Figure 4.7.14: The overall dipole moment of a molecule depends on the individual bond dipole moments and how they are arranged. (a) Each CO bond has a bond dipole moment, but they point in opposite directions so that the net CO_2 molecule is nonpolar. (b) In contrast, water is polar because the OH bond moments do not cancel out.

The OCS molecule has a structure similar to CO_2, but a sulfur atom has replaced one of the oxygen atoms. To determine if this molecule is polar, we draw the molecular structure. VSEPR theory predicts a linear molecule:
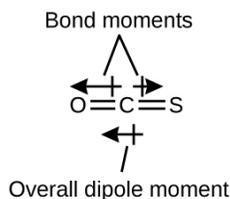
The C-O bond is considerably polar. Although C and S have very similar electronegativity values, S is slightly more electronegative than C, and so the C-S bond is just slightly polar. Because oxygen is more electronegative than sulfur, the oxygen end of the molecule is the negative end.

Chloromethane, CH_3Cl, is a tetrahedral molecule with three slightly polar C-H bonds and a more polar C-Cl bond. The relative electronegativities of the bonded atoms is H < C < Cl, and so the bond moments all point toward the Cl end of the molecule and sum to yield a considerable dipole moment (the molecules are relatively polar).
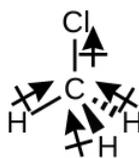
For molecules of high symmetry such as BF_3 (trigonal planar), CH_4 (tetrahedral), PF_5 (trigonal bipyramidal), and SF_6 (octahedral), all the bonds are of identical polarity (same bond moment) and they are oriented in geometries that yield nonpolar molecules (dipole moment is zero). Molecules of less geometric symmetry, however, may be polar even when all bond moments are identical. For these molecules, the directions of the equal bond moments are such that they sum to give a nonzero dipole moment and a polar molecule. Examples of such molecules include hydrogen sulfide, H_2S (nonlinear), and ammonia, NH_3 (trigonal pyramidal).
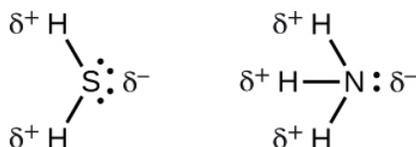
To summarize, to be polar, a molecule must:

1. Contain at least one polar covalent bond.
2. Have a molecular structure such that the sum of the vectors of each bond dipole moment does not cancel.

Properties of Polar Molecules

Polar molecules tend to align when placed in an electric field with the positive end of the molecule oriented toward the negative plate and the negative end toward the positive plate (Figure 4.7.15). We can use an electrically charged object to attract polar molecules, but nonpolar molecules are not attracted. Also, polar solvents are better at dissolving polar substances, and nonpolar solvents are better at dissolving nonpolar substances.
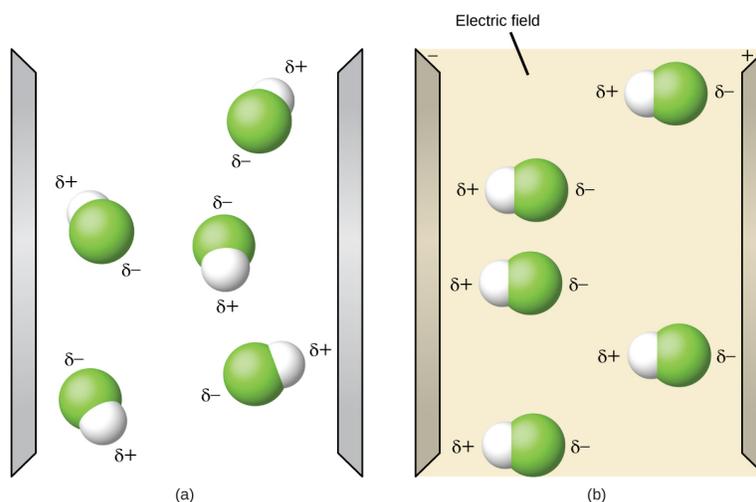
Figure 4.7.15: (a) Molecules are always randomly distributed in the liquid state in the absence of an electric field. (b) When an electric field is applied, polar molecules like HF will align to the dipoles with the field direction.

📌 Link to Learning

The molecule polarity simulation provides many ways to explore dipole moments of bonds and molecules.

✔ Example 4.7.8: Polarity Simulations

Open the molecule polarity simulation and select the "Three Atoms" tab at the top. This should display a molecule ABC with three electronegativity adjustors. You can display or hide the bond moments, molecular dipoles, and partial charges at the right. Turning on the Electric Field will show whether the molecule moves when exposed to a field, similar to Figure 4.7.15.

Use the electronegativity controls to determine how the molecular dipole will look for the starting bent molecule if:

a. A and C are very electronegative and B is in the middle of the range.
b. A is very electronegative, and B and C are not.

Solution
a. Molecular dipole moment points immediately between A and C.
b. Molecular dipole moment points along the A–B bond, toward A.

❓ Exercise 4.7.8

Determine the partial charges that will give the largest possible bond dipoles.

Answer

The largest bond moments will occur with the largest partial charges. The two solutions above represent how unevenly the electrons are shared in the bond. The bond moments will be maximized when the electronegativity difference is greatest. The controls for A and C should be set to one extreme, and B should be set to the opposite extreme. Although the magnitude of the bond moment will not change based on whether B is the most electronegative or the least, the direction of the bond moment will.

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4.8: Key Terms

axial position | location in a trigonal bipyramidal geometry in which there is another atom at a 180° angle and the equatorial positions are at a 90° angle

bond angle | angle between any two covalent bonds that share a common atom

bond dipole moment | separation of charge in a bond that depends on the difference in electronegativity and the bond distance represented by partial charges or a vector

bond distance | (also, bond length) distance between the nuclei of two bonded atoms

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

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

Born-Haber cycle | thermochemical cycle relating the various energetic steps involved in the formation of an ionic solid from the relevant elements

covalent bond | bond formed when electrons are shared between atoms

dipole moment | property of a molecule that describes the separation of charge determined by the sum of the individual bond moments based on the molecular structure

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

electron-pair geometry | arrangement around a central atom of all regions of electron density (bonds, lone pairs, or unpaired electrons)

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

equatorial position | one of the three positions in a trigonal bipyramidal geometry with 120° angles between them; the axial positions are located at a 90° angle

formal charge | charge that would result on an atom by taking the number of valence electrons on the neutral atom and subtracting the nonbonding electrons and the number of bonds (one-half of the bonding electrons)

free radical | molecule that contains an odd number of electrons

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

inert pair effect | tendency of heavy atoms to form ions in which their valence s electrons are not lost

ionic bond | strong electrostatic force of attraction between cations and anions in an ionic compound

lattice energy ($\Delta H_{lattice}$) | energy required to separate one mole of an ionic solid into its component gaseous ions

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

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

linear | shape in which two outside groups are placed on opposite sides of a central atom

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

molecular structure | arrangement of atoms in a molecule or ion

molecular structure | structure that includes only the placement of the atoms in the molecule

octahedral | shape in which six outside groups are placed around a central atom such that a three-dimensional shape is generated with four groups forming a square and the other two forming the apex of two pyramids, one above and one below the square plane

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

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

polar molecule | (also, dipole) molecule with an overall dipole moment

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

resonance | situation in which one Lewis structure is insufficient to describe the bonding in a molecule and the average of multiple structures is observed

resonance forms | two or more Lewis structures that have the same arrangement of atoms but different arrangements of electrons

resonance hybrid | average of the resonance forms shown by the individual Lewis structures

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

tetrahedral | shape in which four outside groups are placed around a central atom such that a three-dimensional shape is generated with four corners and 109.5° angles between each pair and the central atom

trigonal bipyramidal | shape in which five outside groups are placed around a central atom such that three form a flat triangle with 120° angles between each pair and the central atom, and the other two form the apex of two pyramids, one above and one below the triangular plane

trigonal planar | shape in which three outside groups are placed in a flat triangle around a central atom with 120° angles between each pair and the central atom

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

valence shell electron-pair repulsion theory (VSEPR) | theory used to predict the bond angles in a molecule based on positioning regions of high electron density as far apart as possible to minimize electrostatic repulsion

vector | quantity having magnitude and direction

4.9: Key Equations

Bond energy for a diatomic molecule:
Enthalpy change: $\Delta H = \Sigma D_{bonds\ broken} - \Sigma D_{bonds\ formed}$
Lattice energy for a solid MX:
Lattice energy for an ionic crystal:

4.10: Summary

Atoms gain or lose electrons to form ions with particularly stable electron configurations. The charges of cations formed by the representative metals may be determined readily because, with few exceptions, the electronic structures of these ions have either a noble gas configuration or a completely filled electron shell. The charges of anions formed by the nonmetals may also be readily determined because these ions form when nonmetal atoms gain enough electrons to fill their valence shells.

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

Valence electronic structures can be visualized by drawing Lewis symbols (for atoms and monatomic ions) and Lewis structures (for molecules and polyatomic ions). Lone pairs, unpaired electrons, and single, double, or triple bonds are used to indicate where the valence electrons are located around each atom in a Lewis structure. Most structures—especially those containing second row elements—obey the octet rule, in which every atom (except H) is surrounded by eight electrons. Exceptions to the octet rule occur for odd-electron molecules (free radicals), electron-deficient molecules, and hypervalent molecules.

In a Lewis structure, formal charges can be assigned to each atom by treating each bond as if one-half of the electrons are assigned to each atom. These hypothetical formal charges are a guide to determining the most appropriate Lewis structure. A structure in which the formal charges are as close to zero as possible is preferred. Resonance occurs in cases where two or more Lewis structures with identical arrangements of atoms but different distributions of electrons can be written. The actual distribution of electrons (the resonance hybrid) is an average of the distribution indicated by the individual Lewis structures (the resonance forms).

The strength of a covalent bond is measured by its bond dissociation energy, that is, the amount of energy required to break that particular bond in a mole of molecules. Multiple bonds are stronger than single bonds between the same atoms. The enthalpy of a reaction can be estimated based on the energy input required to break bonds and the energy released when new bonds are formed. For ionic bonds, the lattice energy is the energy required to separate one mole of a compound into its gas phase ions. Lattice energy increases for ions with higher charges and shorter distances between ions. Lattice energies are often calculated using the Born-Haber cycle, a thermochemical cycle including all of the energetic steps involved in converting elements into an ionic compound.

VSEPR theory predicts the three-dimensional arrangement of atoms in a molecule. It states that valence electrons will assume an electron-pair geometry that minimizes repulsions between areas of high electron density (bonds and/or lone pairs). Molecular structure, which refers only to the placement of atoms in a molecule and not the electrons, is equivalent to electron-pair geometry only when there are no lone electron pairs around the central atom. A dipole moment measures a separation of charge. For one bond, the bond dipole moment is determined by the difference in electronegativity between the two atoms. For a molecule, the overall dipole moment is determined by both the individual bond moments and how these dipoles are arranged in the molecular structure. Polar molecules (those with an appreciable dipole moment) interact with electric fields, whereas nonpolar molecules do not.

4.11: Exercises

1.

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

2.

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

3.

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

4.

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

5.

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

(a) P

(b) Mg

(c) Al

(d) O

(e) Cl

(f) Cs

6.

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

(a) I

(b) Sr

(c) K

(d) N

(e) S

(f) In

7.

Write the electron configuration for each of the following ions

(a) As^{3-}

(b) I^-

(c) Be^{2+}

(d) Cd^{2+}

(e) O^{2-}

(f) Ga^{3+}

(g) Li^+

(h) N^{3-}

(i) Sn^{2+}

(j) Co^{2+}

(k) Fe^{2+}

(l) As^{3+}

8.

Write the electron configuration for the monatomic ions formed from the following elements (which form the greatest concentration of monatomic ions in seawater):

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

9.

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

(a) Al

(b) Br

(c) Sr

(d) Li

(e) As

(f) S

10.

From the labels of several commercial products, prepare a list of six ionic compounds in the products. For each compound, write the formula. (You may need to look up some formulas in a suitable reference.)

11.

Why is it incorrect to speak of a molecule of solid NaCl?

12.

What information can you use to predict whether a bond between two atoms is covalent or ionic?

13.

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

(a) Cl_2CO

(b) MnO

(c) NCl_3

(d) $CoBr_2$

(e) K_2S

(f) CO

(g) CaF_2

(h) HI

(i) CaO

(j) IBr

(k) CO_2

14.

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

15.

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

(a) Br or Cl

(b) N or O

(c) S or O

(d) P or S

(e) Si or N

(f) Ba or P

(g) N or K

16.

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

(a) N or P

(b) N or Ge

(c) S or F

(d) Cl or S

(e) H or C

(f) Se or P

(g) C or Si

17.

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

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

18.

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

a. As, H, N, P, Sb
b. Cl, H, P, S, Si
c. Br, Cl, Ge, H, Sr
d. Ca, H, K, N, Si
e. Cl, Cs, Ge, H, Sr

19.

Which atoms can bond to sulfur so as to produce a positive partial charge on the sulfur atom?

20.

Which is the most polar bond?

a. C–C
b. C–H

c. N–H

d. O–H

e. Se–H

21.

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

(a) HF or HCl

(b) NO or CO

(c) SH or OH

(d) PCl or SCl

(e) CH or NH

(f) SO or PO

(g) CN or NN

22.

Which of the following molecules or ions contain polar bonds?

(a) O_3

(b) S_8

(c) O_2^{2-}

(d) NO_3^-

(e) CO_2

(f) H_2S

(g) BH_4^-

23.

Write the Lewis symbols for each of the following ions:

(a) As^{3-}

(b) I^-

(c) Be^{2+}

(d) O^{2-}

(e) Ga^{3+}

(f) Li^+

(g) N^{3-}

24.

Many monatomic ions are found in seawater, including the ions formed from the following list of elements. Write the Lewis symbols for the monatomic ions formed from the following elements:

a. Cl

b. Na

c. Mg

d. Ca

e. K

f. Br

g. Sr

h. F

25.

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

(a) As^{3-}

(b) I^-

(c) Be^{2+}

(d) O^{2-}

(e) Ga^{3+}

(f) Li^+

(g) N^{3-}

26.

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

(a)

$$\left[M^{2+}\right]\left[:\!\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}\!:\right]^{2-}$$

(b)

$$\left[M^{3+}\right]\left[:\!\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}\!:\right]_3^{-}$$

(c)

$$\left[M^{+}\right]_2\left[:\!\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}\!:\right]^{2-}$$

(d)

$$\left[M^{3+}\right]_2\left[:\!\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}\!:\right]_3^{2-}$$
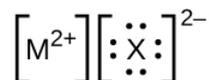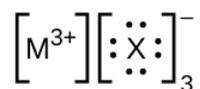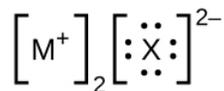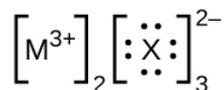
27.

Write the Lewis structure for the diatomic molecule P_2, an unstable form of phosphorus found in high-temperature phosphorus vapor.

28.

Write Lewis structures for the following:

(a) H_2

(b) HBr

(c) PCl_3

(d) SF_2

(e) H_2CCH_2

(f) HNNH

(g) H_2CNH

(h) NO^-

(i) N_2

(j) CO

(k) CN^-

29.

Write Lewis structures for the following:

(a) O_2

(b) H_2CO

(c) AsF_3

(d) ClNO

(e) $SiCl_4$

(f) H_3O^+

(g) NH_4^+

(h) BF_4^-

(i) HCCH

(j) ClCN

(k) C_2^{2+}

30.

Write Lewis structures for the following:

  a. ClF_3
  b. PCl_5
  c. BF_3
  d. PF_6^-

31.

Write Lewis structures for the following:

  a. SeF_6
  b. XeF_4
  c. SCl_3^+
  d. Cl_2BBCl_2 (contains a B–B bond)

32.

Write Lewis structures for:

  a. PO_4^{3-}
  b. ICl_4^-
  c. SO_3^{2-}
  d. HONO

33.

Correct the following statement: "The bonds in solid $PbCl_2$ are ionic; the bond in a HCl molecule is covalent. Thus, all of the valence electrons in $PbCl_2$ are located on the Cl^- ions, and all of the valence electrons in a HCl molecule are shared between the H and Cl atoms."

34.

Write Lewis structures for the following molecules or ions:

  a. SbH_3

b. XeF_2

c. Se_8 (a cyclic molecule with a ring of eight Se atoms)

35.

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

36.

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

37.

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

38.

Identify the atoms that correspond to each of the following electron configurations. Then, write the Lewis symbol for the common ion formed from each atom:

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

39.

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

(a) the amino acid serine:
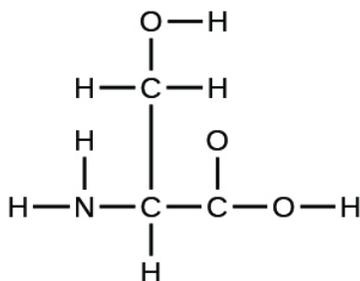
(b) urea:
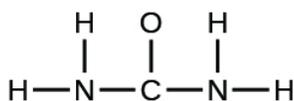
(c) pyruvic acid:
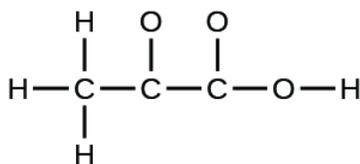
(d) uracil:
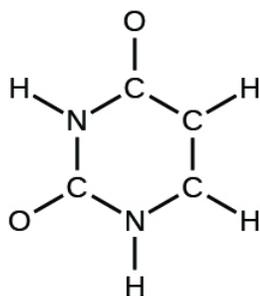
(e) carbonic acid:
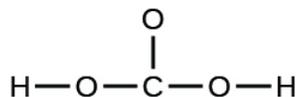
40.

A compound with a molar mass of about 28 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

41.

A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen by mass. Write the Lewis structure for a molecule of the compound.

42.

Two arrangements of atoms are possible for a compound with a molar mass of about 45 g/mol that contains 52.2% C, 13.1% H, and 34.7% O by mass. Write the Lewis structures for the two molecules.

43.

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

44.

Write resonance forms that describe the distribution of electrons in each of these molecules or ions.

   a. selenium dioxide, OSeO
   b. nitrate ion,
   c. nitric acid, HNO_3 (N is bonded to an OH group and two O atoms)
   d. benzene, C_6H_6:
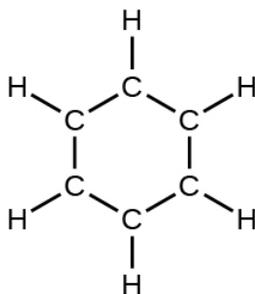
(e) the formate ion:
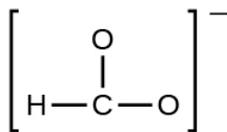
45.

Write resonance forms that describe the distribution of electrons in each of these molecules or ions.

a. sulfur dioxide, SO_2
b. carbonate ion,
c. hydrogen carbonate ion, (C is bonded to an OH group and two O atoms)
d. pyridine:
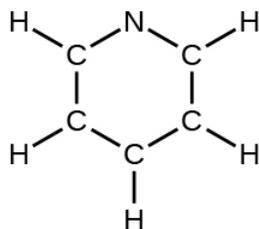
(e) the allyl ion:
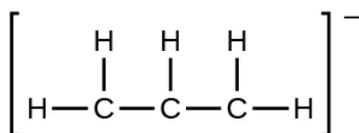
46.

Write the resonance forms of ozone, O_3, the component of the upper atmosphere that protects the Earth from ultraviolet radiation.

47.

Sodium nitrite, which has been used to preserve bacon and other meats, is an ionic compound. Write the resonance forms of the nitrite ion,

48.

In terms of the bonds present, explain why acetic acid, CH_3CO_2H, contains two distinct types of carbon-oxygen bonds, whereas the acetate ion, formed by loss of a hydrogen ion from acetic acid, only contains one type of carbon-oxygen bond. The skeleton structures of these species are shown:
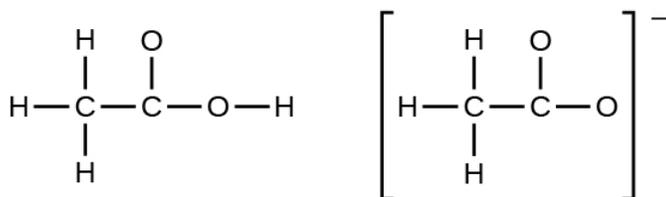
49.

Write the Lewis structures for the following, and include resonance structures where appropriate. Indicate which has the strongest carbon-oxygen bond.

a. CO_2
b. CO

50.

Toothpastes containing sodium hydrogen carbonate (sodium bicarbonate) and hydrogen peroxide are widely used. Write Lewis structures for the hydrogen carbonate ion and hydrogen peroxide molecule, with resonance forms where appropriate.

51.

Determine the formal charge of each element in the following:

a. HCl
b. CF_4

c. PCl_3
d. PF_5

<mark>52.</mark>

Determine the formal charge of each element in the following:

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

53.

Calculate the formal charge of chlorine in the molecules Cl_2, $BeCl_2$, and ClF_5.

54.

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

a. F_2CO
b. NO^-
c. BF_4-
d. $SnCl_3-$
e. H_2CCH_2
f. ClF_3
g. SeF_6
h. PO_4^{3-}

55.

Draw all possible resonance structures for each of these compounds. Determine the formal charge on each atom in each of the resonance structures:

a. O_3
b. SO_2
c. NO_2^-
d. NO_3^-

56.

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

57.

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

58.

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

59.

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

<mark>60.</mark>

Iodine forms a series of fluorides (listed here). Write Lewis structures for each of the four compounds and determine the formal charge of the iodine atom in each molecule:

a. IF
b. IF_3

c. IF$_5$

d. IF$_7$

61.

Write the Lewis structure and chemical formula of the compound with a molar mass of about 70 g/mol that contains 19.7% nitrogen and 80.3% fluorine by mass, and determine the formal charge of the atoms in this compound.

62.

Which of the following structures would we expect for nitrous acid? Determine the formal charges:
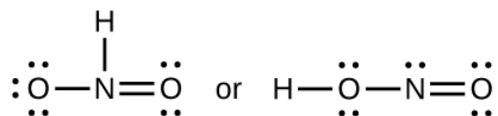
63.

Sulfuric acid is the industrial chemical produced in greatest quantity worldwide. About 90 billion pounds are produced each year in the United States alone. Write the Lewis structure for sulfuric acid, H$_2$SO$_4$, which has two oxygen atoms and two OH groups bonded to the sulfur.

64.

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

(a) C–C or C=CC=C

(b) C–N or C≡NC≡N

(c) C≡OC≡O or C=OC=O

(d) H–F or H–Cl

(e) C–H or O–H

(f) C–N or C–O

65.

Using the bond energies in Table 7.2, determine the approximate enthalpy change for each of the following reactions:

(a) H$_2$(g)+Br$_2$(g)⟶2HBr(g)

(b) CH$_4$(g)+I2(g)⟶CH3I(g)+HI(g)

(c) C$_2$H$_4$(g)+3O$_2$(g)⟶2CO$_2$(g)+2H$_2$O(g)

66.

Using the bond energies in Table 7.2, determine the approximate enthalpy change for each of the following reactions:

(a) Cl$_2$(g)+3F$_2$(g)⟶2ClF$_3$(g)

(b) H$_2$C=CH$_2$(g)+H$_2$(g)⟶H$_3$CCH$_3$

(c) 2C$_2$H$_6$(g)+7O$_2$(g)⟶4CO$_2$(g)+6H$_2$O(g)

67.

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

68.

How does the bond energy of HCl(g) differ from the standard enthalpy of formation of HCl(g)?

69.

Using the standard enthalpy of formation data in Appendix G, show how the standard enthalpy of formation of HCl(g) can be used to determine the bond energy.

70.

Using the standard enthalpy of formation data in Appendix G, calculate the bond energy of the carbon-sulfur double bond in CS_2.

71.

Using the standard enthalpy of formation data in Appendix G, determine which bond is stronger: the S–F bond in $SF_4(g)$ or in $SF_6(g)$?

72.

Using the standard enthalpy of formation data in Appendix G, determine which bond is stronger: the P–Cl bond in $PCl_3(g)$ or in $PCl_5(g)$?

73.

Complete the following Lewis structure by adding bonds (not atoms), and then indicate the longest bond:

```
      H   H              H   H
  H   C   C   C   C   C   C   H
      H   H
```

74.

Use the bond energy to calculate an approximate value of ΔH for the following reaction. Which is the more stable form of FNO_2?

$$\ddot{O}=N-\ddot{O}: \longrightarrow \ddot{O}=N-\ddot{O}-\ddot{F}:$$

(with :F: bonded above N in the left structure)

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

  a. The radius of the Ca atom is 197 pm; the radius of the Ca^{2+} ion is 99 pm. Account for the difference.
  b. The lattice energy of CaO(s) is –3460 kJ/mol; the lattice energy of K_2O is –2240 kJ/mol. Account for the difference.
  c. Given these ionization values, explain the difference between Ca and K with regard to their first and second ionization energies.

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

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

76.

The lattice energy of LiF is 1023 kJ/mol, and the Li–F distance is 200.8 pm. NaF crystallizes in the same structure as LiF but with a Na–F distance of 231 pm. Which of the following values most closely approximates the lattice energy of NaF: 510, 890, 1023, 1175, or 4090 kJ/mol? Explain your choice.

77.

For which of the following substances is the least energy required to convert one mole of the solid into separate ions?

  a. MgO

b. SrO

c. KF

d. CsF

e. MgF_2

78.

The reaction of a metal, M, with a halogen, X_2, proceeds by an exothermic reaction as indicated by this equation: For each of the following, indicate which option will make the reaction more exothermic. Explain your answers.

a. a large radius vs. a small radius for M^{+2}

b. a high ionization energy vs. a low ionization energy for M

c. an increasing bond energy for the halogen

d. a decreasing electron affinity for the halogen

e. an increasing size of the anion formed by the halogen

79.

The lattice energy of LiF is 1023 kJ/mol, and the Li–F distance is 201 pm. MgO crystallizes in the same structure as LiF but with a Mg–O distance of 205 pm. Which of the following values most closely approximates the lattice energy of MgO: 256 kJ/mol, 512 kJ/mol, 1023 kJ/mol, 2046 kJ/mol, or 4008 kJ/mol? Explain your choice.

80.

Which compound in each of the following pairs has the larger lattice energy? Note: Mg^{2+} and Li^+ have similar radii; O^{2-} and F^- have similar radii. Explain your choices.

a. MgO or MgSe

b. LiF or MgO

c. Li_2O or LiCl

d. Li_2Se or MgO

81.

Which compound in each of the following pairs has the larger lattice energy? Note: Ba^{2+} and

K^+ have similar radii; S^{2-} and Cl^- have similar radii. Explain your choices.

a. K_2O or Na_2O

b. K_2S or BaS

c. KCl or BaS

d. BaS or $BaCl_2$

82.

Which of the following compounds requires the most energy to convert one mole of the solid into separate ions?

a. MgO

b. SrO

c. KF

d. CsF

e. MgF_2

83.

Which of the following compounds requires the most energy to convert one mole of the solid into separate ions?

a. K_2S

b. K_2O

c. CaS

d. Cs_2S

e. CaO

84.

The lattice energy of KF is 794 kJ/mol, and the interionic distance is 269 pm. The Na–F

distance in NaF, which has the same structure as KF, is 231 pm. Which of the following values is the closest approximation of the lattice energy of NaF: 682 kJ/mol, 794 kJ/mol, 924 kJ/mol, 1588 kJ/mol, or 3175 kJ/mol? Explain your answer.

85.

Explain why the HOH molecule is bent, whereas the HBeH molecule is linear.

86.

What feature of a Lewis structure can be used to tell if a molecule's (or ion's) electron-pair geometry and molecular structure will be identical?

87.

Explain the difference between electron-pair geometry and molecular structure.

88.

Why is the H–N–H angle in NH_3 smaller than the H–C–H bond angle in CH_4? Why is the H–N–H angle in identical to the H–C–H bond angle in CH_4?

89.

Explain how a molecule that contains polar bonds can be nonpolar.

90.

As a general rule, MX_n molecules (where M represents a central atom and X represents terminal atoms; n = 2 − 5) are polar if there is one or more lone pairs of electrons on M. NH_3 (M = N, X = H, n = 3) is an example. There are two molecular structures with lone pairs that are exceptions to this rule. What are they?

91.

Predict the electron pair geometry and the molecular structure of each of the following molecules or ions:

  a. SF_6
  b. PCl_5
  c. BeH_2
  d. CH_3^+

92.

Identify the electron pair geometry and the molecular structure of each of the following molecules or ions:

  a. IF_6^+
  b. CF_4
  c. BF_3
  d. SiF_5^-
  e. $BeCl_2$

93.

What are the electron-pair geometry and the molecular structure of each of the following molecules or ions?

(a) ClF_5

(b) ClO_2^-

(c) $TeCl_4^{2-}$

(d) PCl_3

(e) SeF_4

(f) PH_2^-

94.

Predict the electron pair geometry and the molecular structure of each of the following ions:

(a) H_3O^+

(b) PCl_4^-

(c) $SnCl_3^+$

(d) $BrCl_4^-$

(e) ICl_3

(f) XeF_4

(g) SF_2

95.

Identify the electron pair geometry and the molecular structure of each of the following molecules:

(a) ClNO (N is the central atom)

(b) CS_2

(c) Cl_2CO (C is the central atom)

(d) Cl_2SO (S is the central atom)

(e) SO_2F_2 (S is the central atom)

(f) XeO_2F_2 (Xe is the central atom)

(g) $ClOF_2^+$ (Cl is the central atom)

96.

Predict the electron pair geometry and the molecular structure of each of the following:

(a) IOF_5 (I is the central atom)

(b) $POCl_3$ (P is the central atom)

(c) Cl_2SeO (Se is the central atom)

(d) $ClSO^+$ (S is the central atom)

(e) F_2SO (S is the central atom)

(f) NO_2^-

(g) SiO_4^{4-}

97.

Which of the following molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?

(a) ClF_5

(b) ClO_2^-

(c) $TeCl_4^{2-}$

(d) PCl_3

(e) SeF_4

(f) PH_2^-

(g) XeF_2

98.

Which of these molecules and ions contain polar bonds? Which of these molecules and ions have dipole moments?

(a) H_3O^+

(b) PCl_4^-

(c) $SnCl_3^-$

(d) $BrCl_4^-$

(e) ICl_3

(f) XeF_4

(g) SF_2

99.

Which of the following molecules have dipole moments?

  a. CS_2
  b. SeS_2
  c. CCl_2F_2
  d. PCl_3 (P is the central atom)
  e. $ClNO$ (N is the central atom)

100.

Identify the molecules with a dipole moment:

  a. SF_4
  b. CF_4
  c. Cl_2CCBr_2
  d. CH_3Cl
  e. H_2CO

101.

The molecule XF_3 has a dipole moment. Is X boron or phosphorus?

102.

The molecule XCl_2 has a dipole moment. Is X beryllium or sulfur?

103.

Is the Cl_2BBCl_2 molecule polar or nonpolar?

104.

There are three possible structures for PCl_2F_3 with phosphorus as the central atom. Draw them and discuss how measurements of dipole moments could help distinguish among them.

105.

Describe the molecular structure around the indicated atom or atoms:

  a. (i) each of the carbon atoms in allene, H_2CCCH_2

106.

Draw the Lewis structures and predict the shape of each compound or ion:

  a. CO_2
  b. NO_2^-
  c. SO_3
  d. SO_3^{2-}

107.

A molecule with the formula AB_2, in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion for each shape.

108.

A molecule with the formula AB_3, in which A and B represent different atoms, could have one of three different shapes. Sketch and name the three different shapes that this molecule might have. Give an example of a molecule or ion that has each shape.

109.

Draw the Lewis electron dot structures for these molecules, including resonance structures where appropriate:

   a. $CS_3{}^{2-}$
   b. CS_2
   c. CS
   d. predict the molecular shapes for and CS_2 and explain how you arrived at your predictions

110.

What is the molecular structure of the stable form of FNO_2? (N is the central atom.)

111.

A compound with a molar mass of about 42 g/mol contains 85.7% carbon and 14.3% hydrogen. What is its molecular structure?

112.

Use the simulation to perform the following exercises for a two-atom molecule:

   a. Adjust the electronegativity value so the bond dipole is pointing toward B. Then determine what the electronegativity values must be to switch the dipole so that it points toward A.
   b. With a partial positive charge on A, turn on the electric field and describe what happens.
   c. With a small partial negative charge on A, turn on the electric field and describe what happens.
   d. Reset all, and then with a large partial negative charge on A, turn on the electric field and describe what happens.

113.

Use the simulation to perform the following exercises for a real molecule. You may need to rotate the molecules in three dimensions to see certain dipoles.

   a. Sketch the bond dipoles and molecular dipole (if any) for O_3. Explain your observations.
   b. Look at the bond dipoles for NH_3. Use these dipoles to predict whether N or H is more electronegative.
   c. Predict whether there should be a molecular dipole for NH_3 and, if so, in which direction it will point. Check the molecular dipole box to test your hypothesis.

114.

Use the Molecule Shape simulator to build a molecule. Starting with the central atom, click on the double bond to add one double bond. Then add one single bond and one lone pair. Rotate the molecule to observe the complete geometry. Name the electron group geometry and molecular structure and predict the bond angle. Then click the check boxes at the bottom and right of the simulator to check your answers.

115.

Use the Molecule Shape simulator to explore real molecules. On the Real Molecules tab, select H_2O. Switch between the "real" and "model" modes. Explain the difference observed.

116.

Use the Molecule Shape simulator to explore real molecules. On the Real Molecules tab, select "model" mode and S_2O. What is the model bond angle? Explain whether the "real" bond angle should be larger or smaller than the ideal model angle.

Footnotes

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

5: Advanced Theories of Covalent Bonding

We have examined the basic ideas of bonding, showing that atoms share electrons to form molecules with stable Lewis structures and that we can predict the shapes of those molecules by valence shell electron pair repulsion (VSEPR) theory. These ideas provide an important starting point for understanding chemical bonding. But these models sometimes fall short in their abilities to predict the behavior of real substances. How can we reconcile the geometries of *s*, *p*, and *d* atomic orbitals with molecular shapes that show angles like 120° and 109.5°? Furthermore, we know that electrons and magnetic behavior are related through electromagnetic fields.

5.1: Introduction

We have examined the basic ideas of bonding, showing that atoms share electrons to form molecules with stable Lewis structures and that we can predict the shapes of those molecules by valence shell electron pair repulsion (VSEPR) theory. These ideas provide an important starting point for understanding chemical bonding. But these models sometimes fall short in their abilities to predict the behavior of real substances. How can we reconcile the geometries of s, p, and d atomic orbitals with molecular shapes that show angles like 120° and 109.5°? Furthermore, we know that electrons and magnetic behavior are related through electromagnetic fields. Both N_2 and O_2 have fairly similar Lewis structures that contain lone pairs of electrons.
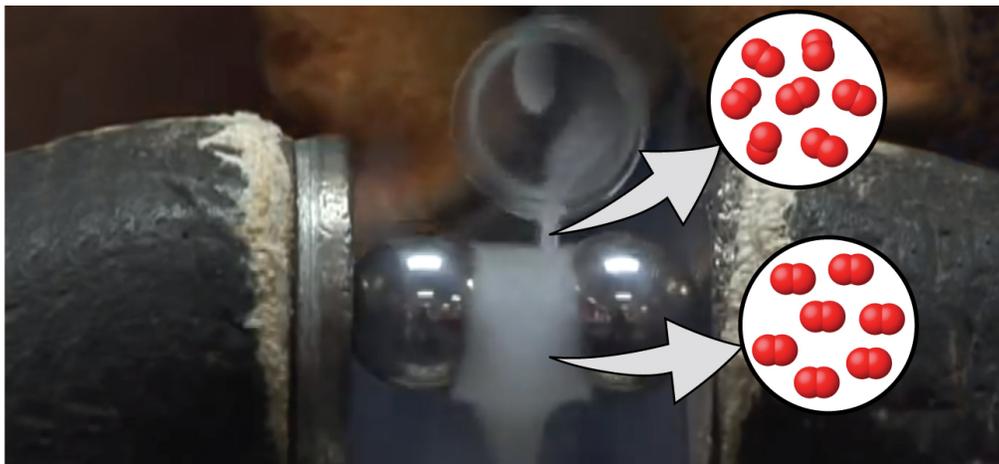
Figure 5.1.1: Oxygen molecules orient randomly most of the time, as shown in the top magnified view. However, when we pour liquid oxygen through a magnet, the molecules line up with the magnetic field, and the attraction allows them to stay suspended between the poles of the magnet where the magnetic field is strongest. Other diatomic molecules (like N_2) flow past the magnet. The detailed explanation of bonding described in this chapter allows us to understand this phenomenon. (credit: modification of work by Jefferson Lab)

Yet oxygen demonstrates very different magnetic behavior than nitrogen. We can pour liquid nitrogen through a magnetic field with no visible interactions, while liquid oxygen (shown in Figure 5.1.1) is attracted to the magnet and floats in the magnetic field. We need to understand the additional concepts of valence bond theory, orbital hybridization, and molecular orbital theory to understand these observations.

5.2: Valence Bond Theory

> **◑ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Describe the formation of covalent bonds in terms of atomic orbital overlap
> - Define and give examples of σ and π bonds

As we know, a scientific theory is a strongly supported explanation for observed natural laws or large bodies of experimental data. For a theory to be accepted, it must explain experimental data and be able to predict behavior. For example, VSEPR theory has gained widespread acceptance because it predicts three-dimensional molecular shapes that are consistent with experimental data collected for thousands of different molecules. However, VSEPR theory does not provide an explanation of chemical bonding.

There are successful theories that describe the electronic structure of atoms. We can use quantum mechanics to predict the specific regions around an atom where electrons are likely to be located: A spherical shape for an *s* orbital, a dumbbell shape for a *p* orbital, and so forth. However, these predictions only describe the orbitals around free atoms. When atoms bond to form molecules, atomic orbitals are not sufficient to describe the regions where electrons will be located in the molecule. A more complete understanding of electron distributions requires a model that can account for the electronic structure of molecules. One popular theory holds that a covalent bond forms when a pair of electrons is shared by two atoms and is simultaneously attracted by the nuclei of both atoms. In the following sections, we will discuss how such bonds are described by valence bond theory and hybridization.

Valence bond theory describes a covalent bond as the overlap of half-filled atomic orbitals (each containing a single electron) that yield a pair of electrons shared between the two bonded atoms. We say that orbitals on two different atoms overlap when a portion of one orbital and a portion of a second orbital occupy the same region of space. According to valence bond theory, a covalent bond results when two conditions are met: (1) an orbital on one atom overlaps an orbital on a second atom and (2) the single electrons in each orbital combine to form an electron pair. The mutual attraction between this negatively charged electron pair and the two atoms' positively charged nuclei serves to physically link the two atoms through a force we define as a covalent bond. The strength of a covalent bond depends on the extent of overlap of the orbitals involved. Orbitals that overlap extensively form bonds that are stronger than those that have less overlap.

The energy of the system depends on how much the orbitals overlap. Figure 5.2.1 illustrates how the sum of the energies of two hydrogen atoms (the colored curve) changes as they approach each other. When the atoms are far apart there is no overlap, and by convention we set the sum of the energies at zero. As the atoms move together, their orbitals begin to overlap. Each electron begins to feel the attraction of the nucleus in the other atom. In addition, the electrons begin to repel each other, as do the nuclei. While the atoms are still widely separated, the attractions are slightly stronger than the repulsions, and the energy of the system decreases. (A bond begins to form.) As the atoms move closer together, the overlap increases, so the attraction of the nuclei for the electrons continues to increase (as do the repulsions among electrons and between the nuclei). At some specific distance between the atoms, which varies depending on the atoms involved, the energy reaches its lowest (most stable) value. This optimum distance between the two bonded nuclei is the bond distance between the two atoms. The bond is stable because at this point, the attractive and repulsive forces combine to create the lowest possible energy configuration. If the distance between the nuclei were to decrease further, the repulsions between nuclei and the repulsions as electrons are confined in closer proximity to each other would become stronger than the attractive forces. The energy of the system would then rise (making the system destabilized), as shown at the far left of Figure 5.2.1.
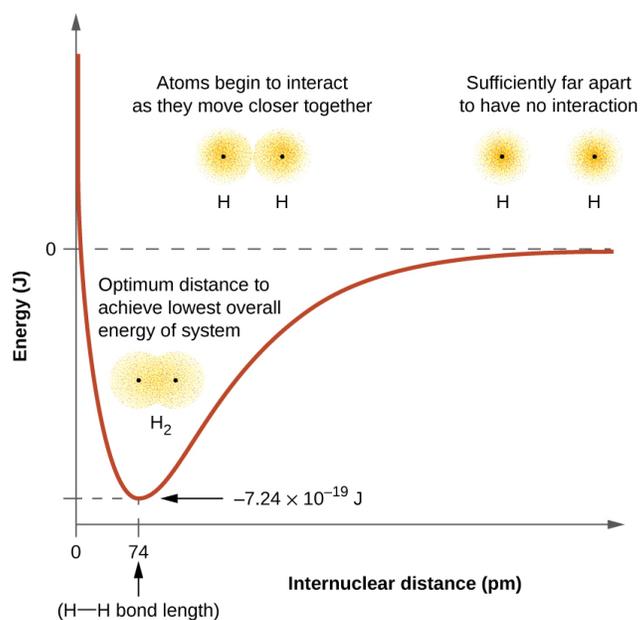
Figure 5.2.1: (a) The interaction of two hydrogen atoms changes as a function of distance. (b) The energy of the system changes as the atoms interact. The lowest (most stable) energy occurs at a distance of 74 pm, which is the bond length observed for the H_2 molecule.

The bond energy is the difference between the energy minimum (which occurs at the bond distance) and the energy of the two separated atoms. This is the quantity of energy released when the bond is formed. Conversely, the same amount of energy is required to break the bond. For the H_2 molecule shown in Figure 5.2.1, at the bond distance of 74 pm the system is 7.24×10^{-19} J lower in energy than the two separated hydrogen atoms. This may seem like a small number. However, we know from our earlier description of thermochemistry that bond energies are often discussed on a per-mole basis. For example, it requires 7.24×10^{-19} J to break one H–H bond, but it takes 4.36×10^5 J to break 1 mole of H–H bonds. A comparison of some bond lengths and energies is shown in Table 5.2.1. We can find many of these bonds in a variety of molecules, and this table provides average values. For example, breaking the first C–H bond in CH_4 requires 439.3 kJ/mol, while breaking the first C–H bond in $H–CH_2C_6H_5$ (a common paint thinner) requires 375.5 kJ/mol.

Table 5.2.1: Representative Bond Energies and Lengths

Bond	Length (pm)	Energy (kJ/mol)	Bond	Length (pm)	Energy (kJ/mol)
H–H	74	436	C–O	140.1	358
H–C	106.8	413	C=O	119.7	745
H–N	101.5	391	C≡O	113.7	1072
H–O	97.5	467	H–Cl	127.5	431
C–C	150.6	347	H–Br	141.4	366
C=C	133.5	614	H–I	160.9	298
C≡C	120.8	839	O–O	148	146
C–N	142.1	305	O=O	120.8	498
C=N	130.0	615	F–F	141.2	159
C≡N	116.1	891	Cl–Cl	198.8	243

In addition to the distance between two orbitals, the orientation of orbitals also affects their overlap (other than for two *s* orbitals, which are spherically symmetric). Greater overlap is possible when orbitals are oriented such that they overlap on a direct line between the two nuclei. Figure 5.2.2 illustrates this for two *p* orbitals from different atoms; the overlap is greater when the orbitals overlap end to end rather than at an angle.
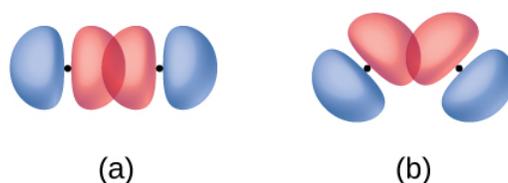
Figure 5.2.2: (a) The overlap of two *p* orbitals is greatest when the orbitals are directed end to end. (b) Any other arrangement results in less overlap. The dots indicate the locations of the nuclei.

The overlap of two *s* orbitals (as in H_2), the overlap of an *s* orbital and a *p* orbital (as in HCl), and the end-to-end overlap of two *p* orbitals (as in Cl_2) all produce sigma bonds (σ bonds), as illustrated in Figure 5.2.3. A σ bond is a covalent bond in which the electron density is concentrated in the region along the internuclear axis; that is, a line between the nuclei would pass through the center of the overlap region. Single bonds in Lewis structures are described as σ bonds in valence bond theory.
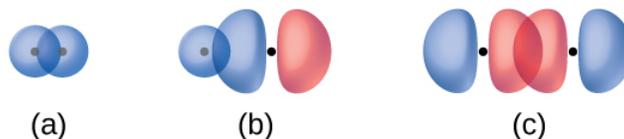
Figure 5.2.3: Sigma (σ) bonds form from the overlap of the following: (a) two *s* orbitals, (b) an *s* orbital and a *p* orbital, and (c) two *p* orbitals. The dots indicate the locations of the nuclei.

A pi bond (π bond) is a type of covalent bond that results from the side-by-side overlap of two *p* orbitals, as illustrated in Figure 5.2.4. In a π bond, the regions of orbital overlap lie on opposite sides of the internuclear axis. Along the axis itself, there is a node, that is, a plane with no probability of finding an electron.
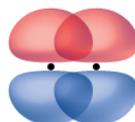
Figure 5.2.4: Pi (π) bonds form from the side-by-side overlap of two *p* orbitals. The dots indicate the location of the nuclei.

While all single bonds are σ bonds, multiple bonds consist of both σ and π bonds. As the Lewis structures below suggest, O_2 contains a double bond, and N_2 contains a triple bond. The double bond consists of one σ bond and one π bond, and the triple bond consists of one σ bond and two π bonds. Between any two atoms, the first bond formed will always be a σ bond, but there can only be one σ bond in any one location. In any multiple bond, there will be one σ bond, and the remaining one or two bonds will be π bonds. These bonds are described in more detail later in this chapter.
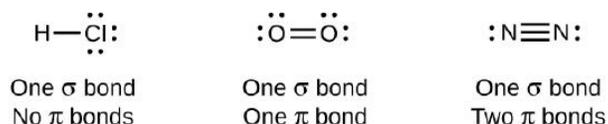
As seen in Figure 5.2.1, an average carbon-carbon single bond is 347 kJ/mol, while in a carbon-carbon double bond, the π bond increases the bond strength by 267 kJ/mol. Adding an additional π bond causes a further increase of 225 kJ/mol. We can see a similar pattern when we compare other σ and π bonds. Thus, each individual π bond is generally weaker than a corresponding σ bond between the same two atoms. In a σ bond, there is a greater degree of orbital overlap than in a π bond.

> ✔ **Example 5.2.1: Counting σ and π Bonds**
>
>
>
> Butadiene, C_4H_6, is used to make synthetic rubber. Identify the number of σ and π bonds contained in this molecule.
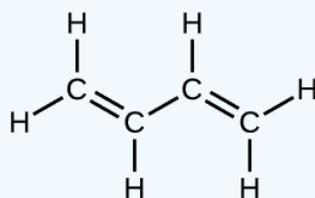
Solution

There are six σ C–H bonds and one σ C–C bond, for a total of seven from the single bonds. There are two double bonds that each have a π bond in addition to the σ bond. This gives a total nine σ and two π bonds overall.

? Exercise 5.2.1

Identify each illustration as depicting a σ or π bond:

a. side-by-side overlap of a 4*p* and a 2*p* orbital
b. end-to-end overlap of a 4*p* and 4*p* orbital
c. end-to-end overlap of a 4*p* and a 2*p* orbital

(a) (b) (c)
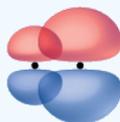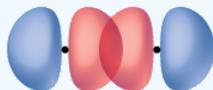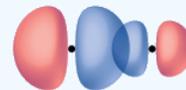
Answer

(a) is a π bond with a node along the axis connecting the nuclei while (b) and (c) are σ bonds that overlap along the axis.

5.3: Hybrid Atomic Orbitals

> **◐ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Explain the concept of atomic orbital hybridization
> - Determine the hybrid orbitals associated with various molecular geometries

Thinking in terms of overlapping atomic orbitals is one way for us to explain how chemical bonds form in diatomic molecules. However, to understand how molecules with more than two atoms form stable bonds, we require a more detailed model. As an example, let us consider the water molecule, in which we have one oxygen atom bonding to two hydrogen atoms. Oxygen has the electron configuration $1s^2 2s^2 2p^4$, with two unpaired electrons (one in each of the two $2p$ orbitals). Valence bond theory would predict that the two O–H bonds form from the overlap of these two $2p$ orbitals with the $1s$ orbitals of the hydrogen atoms. If this were the case, the bond angle would be 90°, as shown in Figure 5.3.1, because p orbitals are perpendicular to each other. Experimental evidence shows that the bond angle is 104.5°, not 90°. The prediction of the valence bond theory model does not match the real-world observations of a water molecule; a different model is needed.
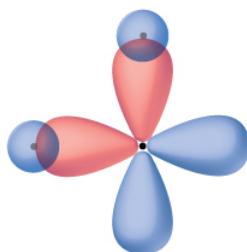
Figure 5.3.1: The hypothetical overlap of two of the $2p$ orbitals on an oxygen atom (red) with the $1s$ orbitals of two hydrogen atoms (blue) would produce a bond angle of 90°. This is not consistent with experimental evidence.[1]

Quantum-mechanical calculations suggest why the observed bond angles in H_2O differ from those predicted by the overlap of the $1s$ orbital of the hydrogen atoms with the $2p$ orbitals of the oxygen atom. The mathematical expression known as the wave function, ψ, contains information about each orbital and the wavelike properties of electrons in an isolated atom. When atoms are bound together in a molecule, the wave functions combine to produce new mathematical descriptions that have different shapes. This process of combining the wave functions for atomic orbitals is called **hybridization** and is mathematically accomplished by the *linear combination of atomic orbitals*, LCAO, (a technique that we will encounter again later). The new orbitals that result are called **hybrid orbitals**. The valence orbitals in an *isolated* oxygen atom are a $2s$ orbital and three $2p$ orbitals. The valence orbitals in an oxygen atom in a water molecule differ; they consist of four equivalent hybrid orbitals that point approximately toward the corners of a tetrahedron (Figure 5.3.2). Consequently, the overlap of the O and H orbitals should result in a tetrahedral bond angle (109.5°). The observed angle of 104.5° is experimental evidence for which quantum-mechanical calculations give a useful explanation: Valence bond theory must include a hybridization component to give accurate predictions.
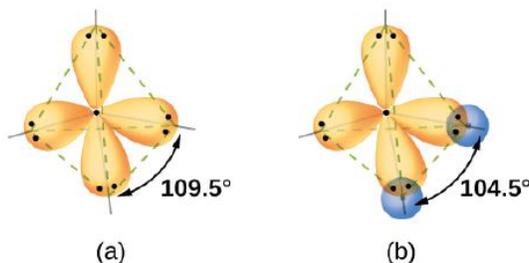
Figure 5.3.2: (a) A water molecule has four regions of electron density, so VSEPR theory predicts a tetrahedral arrangement of hybrid orbitals. (b) Two of the hybrid orbitals on oxygen contain lone pairs, and the other two overlap with the $1s$ orbitals of hydrogen atoms to form the O–H bonds in H_2O. This description is more consistent with the experimental structure.

The following ideas are important in understanding hybridization:

1. Hybrid orbitals do not exist in isolated atoms. They are formed only in covalently bonded atoms.
2. Hybrid orbitals have shapes and orientations that are very different from those of the atomic orbitals in isolated atoms.

3. A set of hybrid orbitals is generated by combining atomic orbitals. The number of hybrid orbitals in a set is equal to the number of atomic orbitals that were combined to produce the set.
4. All orbitals in a set of hybrid orbitals are equivalent in shape and energy.
5. The type of hybrid orbitals formed in a bonded atom depends on its electron-pair geometry as predicted by the VSEPR theory.
6. Hybrid orbitals overlap to form σ bonds. Unhybridized orbitals overlap to form π bonds.

In the following sections, we shall discuss the common types of hybrid orbitals.

sp Hybridization

The beryllium atom in a gaseous $BeCl_2$ molecule is an example of a central atom with no lone pairs of electrons in a linear arrangement of three atoms. There are two regions of valence electron density in the $BeCl_2$ molecule that correspond to the two covalent Be–Cl bonds. To accommodate these two electron domains, two of the Be atom's four valence orbitals will mix to yield two hybrid orbitals. This hybridization process involves mixing of the valence *s* orbital with one of the valence *p* orbitals to yield two equivalent ***sp* hybrid orbitals** that are oriented in a linear geometry (Figure 5.3.3). In this figure, the set of *sp* orbitals appears similar in shape to the original *p* orbital, but there is an important difference. The number of atomic orbitals combined always equals the number of hybrid orbitals formed. The *p* orbital is one orbital that can hold up to two electrons. The *sp* set is two equivalent orbitals that point 180° from each other. The two electrons that were originally in the *s* orbital are now distributed to the two *sp* orbitals, which are half filled. In gaseous $BeCl_2$, these half-filled hybrid orbitals will overlap with orbitals from the chlorine atoms to form two identical σ bonds.
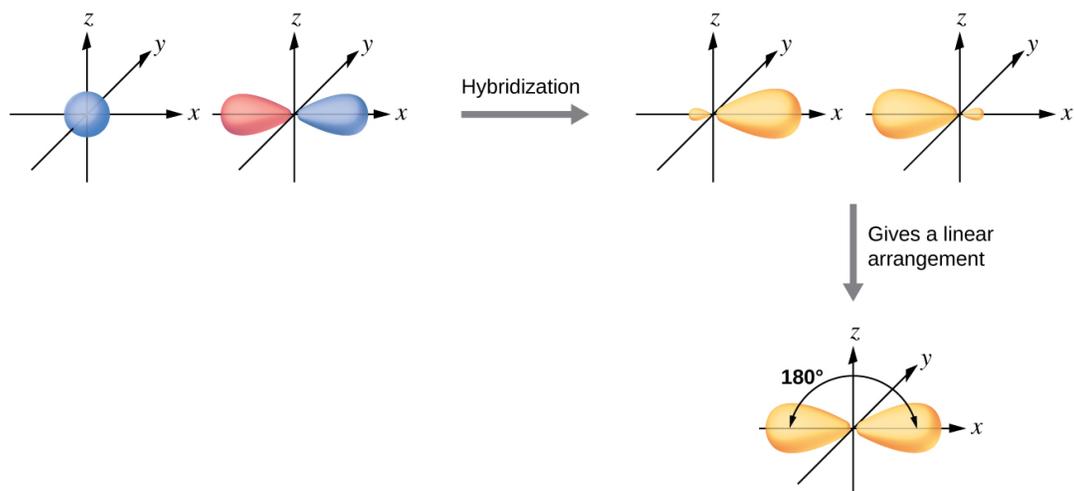
Figure 5.3.3: Hybridization of an *s* orbital (blue) and a *p* orbital (red) of the same atom produces two *sp* hybrid orbitals (yellow). Each hybrid orbital is oriented primarily in just one direction. Note that each *sp* orbital contains one lobe that is significantly larger than the other. The set of two *sp* orbitals are oriented at 180°, which is consistent with the geometry for two domains.

We illustrate the electronic differences in an isolated Be atom and in the bonded Be atom in the orbital energy-level diagram in Figure 5.3.4. These diagrams represent each orbital by a horizontal line (indicating its energy) and each electron by an arrow. Energy increases toward the top of the diagram. We use one upward arrow to indicate one electron in an orbital and two arrows (up and down) to indicate two electrons of opposite spin.
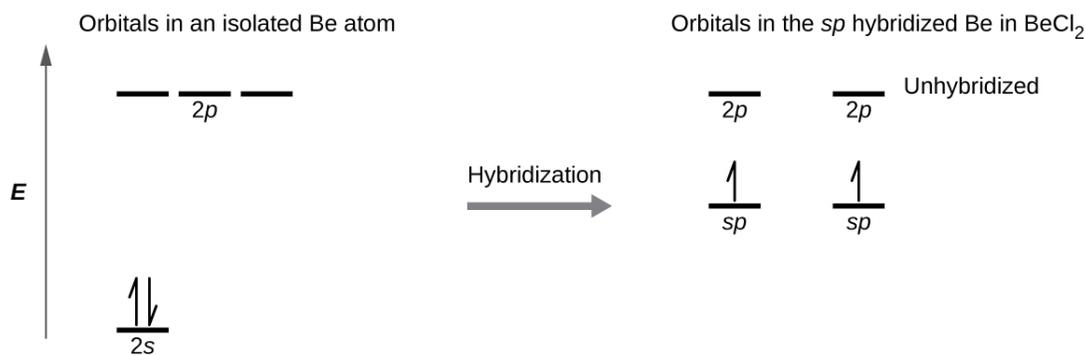
Figure 5.3.4: This orbital energy-level diagram shows the *sp* hybridized orbitals on Be in the linear BeCl$_2$ molecule. Each of the two *sp* hybrid orbitals holds one electron and is thus half filled and available for bonding via overlap with a Cl 3*p* orbital.

When atomic orbitals hybridize, the valence electrons occupy the newly created orbitals. The Be atom had two valence electrons, so each of the *sp* orbitals gets one of these electrons. Each of these electrons pairs up with the unpaired electron on a chlorine atom when a hybrid orbital and a chlorine orbital overlap during the formation of the Be–Cl bonds.

Any central atom surrounded by just two regions of valence electron density in a molecule will exhibit *sp* hybridization. Other examples include the mercury atom in the linear HgCl$_2$ molecule, the zinc atom in Zn(CH$_3$)$_2$, which contains a linear C–Zn–C arrangement, and the carbon atoms in HCCH and CO$_2$.

> 📌 Link to Learning
>
> Check out the University of Wisconsin-Oshkosh website to learn about visualizing hybrid orbitals in three dimensions.

sp^2 Hybridization

The valence orbitals of a central atom surrounded by three regions of electron density consist of a set of three **sp^2 hybrid orbitals** and one unhybridized *p* orbital. This arrangement results from *sp*^{2} hybridization, the mixing of one *s* orbital and two *p* orbitals to produce three identical hybrid orbitals oriented in a trigonal planar geometry (Figure 5.3.5).
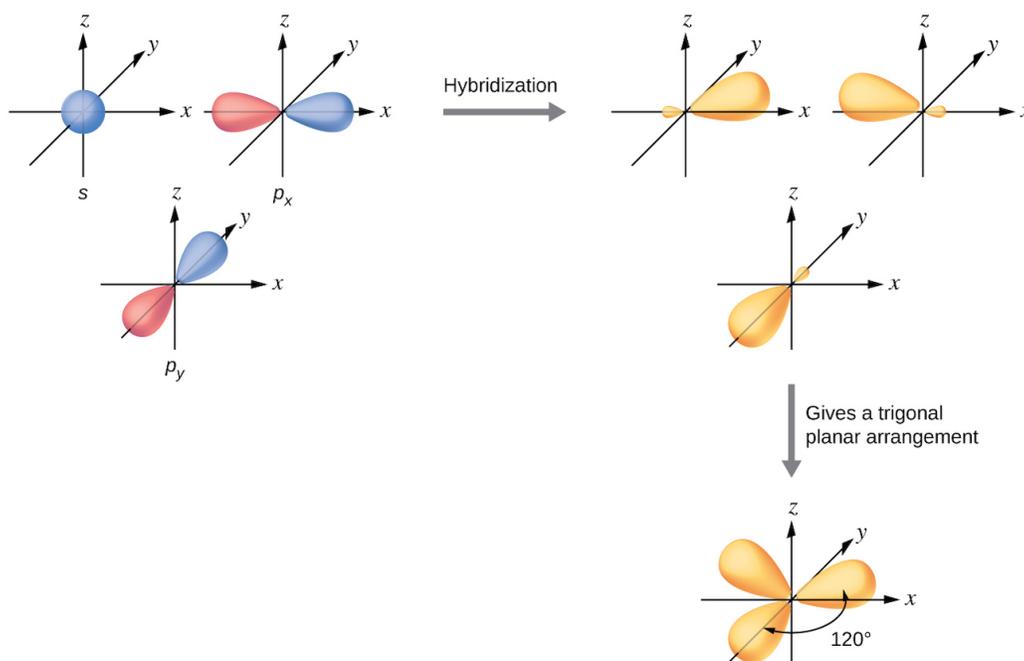
Figure 5.3.5: The hybridization of an *s* orbital (blue) and two *p* orbitals (red) produces three equivalent *sp*^{2} hybridized orbitals (yellow) oriented at 120° with respect to each other. The remaining unhybridized *p* orbital is not shown here, but is located along the z axis.

Although quantum mechanics yields the "plump" orbital lobes as depicted in Figure 5.3.5, sometimes for clarity these orbitals are drawn thinner and without the minor lobes, as in Figure 5.3.6, to avoid obscuring other features of a given illustration. We will use these "thinner" representations whenever the true view is too crowded to easily visualize.

120°
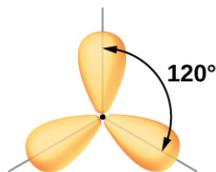
Figure 5.3.6: This alternate way of drawing the trigonal planar sp^2 hybrid orbitals is sometimes used in more crowded figures.

The observed structure of the borane molecule, BH_3, suggests sp^2 hybridization for boron in this compound. The molecule is trigonal planar, and the boron atom is involved in three bonds to hydrogen atoms (Figure 5.3.7). We can illustrate the comparison of orbitals and electron distribution in an isolated boron atom and in the bonded atom in BH_3 as shown in the orbital energy level diagram in Figure 5.3.8. We redistribute the three valence electrons of the boron atom in the three sp^2 hybrid orbitals, and each boron electron pairs with a hydrogen electron when B–H bonds form.
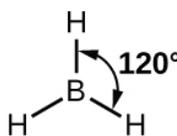
Figure 5.3.7: BH_3 is an electron-deficient molecule with a trigonal planar structure.
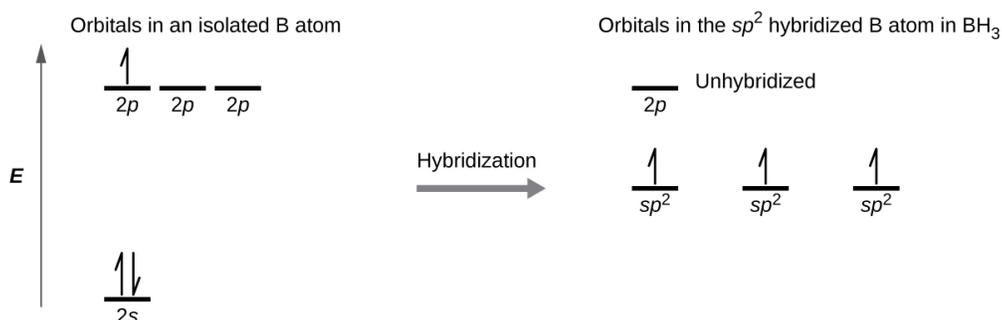
Figure 5.3.8: In an isolated B atom, there are one 2s and three 2p valence orbitals. When boron is in a molecule with three regions of electron density, three of the orbitals hybridize and create a set of three sp^2 orbitals and one unhybridized 2p orbital. The three half-filled hybrid orbitals each overlap with an orbital from a hydrogen atom to form three σ bonds in BH_3.

Any central atom surrounded by three regions of electron density will exhibit sp^2 hybridization. This includes molecules with a lone pair on the central atom, such as ClNO (Figure 5.3.9), or molecules with two single bonds and a double bond connected to the central atom, as in formaldehyde, CH_2O, and ethene, H_2CCH_2.
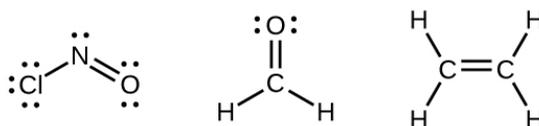
Figure 5.3.9: The central atom(s) in each of the structures shown contain three regions of electron density and are sp^2 hybridized. As we know from the discussion of VSEPR theory, a region of electron density contains all of the electrons that point in one direction. A lone pair, an unpaired electron, a single bond, or a multiple bond would each count as one region of electron density.

sp^3 Hybridization

The valence orbitals of an atom surrounded by a tetrahedral arrangement of bonding pairs and lone pairs consist of a set of four **sp^3 hybrid orbitals**. The hybrids result from the mixing of one s orbital and all three p orbitals that produces four identical sp^3 hybrid orbitals (Figure 5.3.10). Each of these hybrid orbitals points toward a different corner of a tetrahedron.
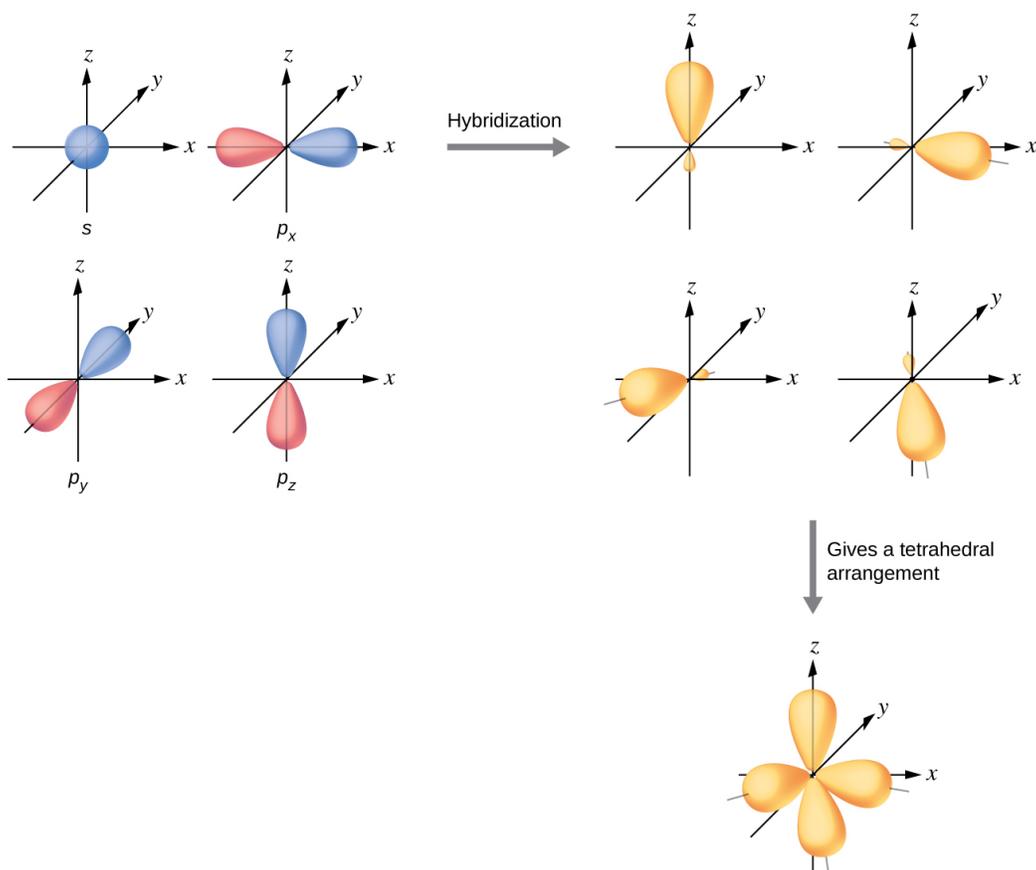
Figure 5.3.10: The hybridization of an *s* orbital (blue) and three *p* orbitals (red) produces four equivalent sp^3 hybridized orbitals (yellow) oriented at 109.5° with respect to each other.

A molecule of methane, CH_4, consists of a carbon atom surrounded by four hydrogen atoms at the corners of a tetrahedron. The carbon atom in methane exhibits sp^3 hybridization. We illustrate the orbitals and electron distribution in an isolated carbon atom and in the bonded atom in CH_4 in Figure 5.3.11. The four valence electrons of the carbon atom are distributed equally in the hybrid orbitals, and each carbon electron pairs with a hydrogen electron when the C–H bonds form.
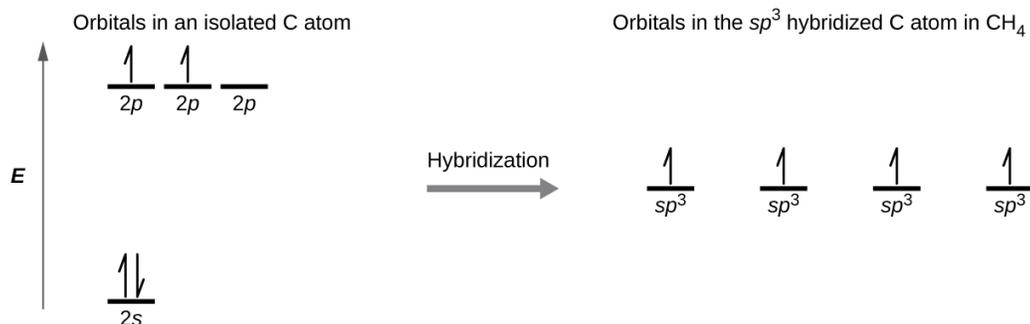
Figure 5.3.11: The four valence atomic orbitals from an isolated carbon atom all hybridize when the carbon bonds in a molecule like CH_4 with four regions of electron density. This creates four equivalent sp^3 hybridized orbitals. Overlap of each of the hybrid orbitals with a hydrogen orbital creates a C–H σ bond.

In a methane molecule, the 1*s* orbital of each of the four hydrogen atoms overlaps with one of the four sp^3 orbitals of the carbon atom to form a sigma (σ) bond. This results in the formation of four strong, equivalent covalent bonds between the carbon atom and each of the hydrogen atoms to produce the methane molecule, CH_4.

The structure of ethane, C_2H_6, is similar to that of methane in that each carbon in ethane has four neighboring atoms arranged at the corners of a tetrahedron—three hydrogen atoms and one carbon atom (Figure 5.3.12). However, in ethane an sp^3 orbital of one carbon atom overlaps end to end with an sp^3 orbital of a second carbon atom to form a σ bond between the two carbon atoms. Each

of the remaining sp^3 hybrid orbitals overlaps with an s orbital of a hydrogen atom to form carbon–hydrogen σ bonds. The structure and overall outline of the bonding orbitals of ethane are shown in Figure 5.3.12. The orientation of the two CH_3 groups is not fixed relative to each other. Experimental evidence shows that rotation around σ bonds occurs easily.

(a) (b)
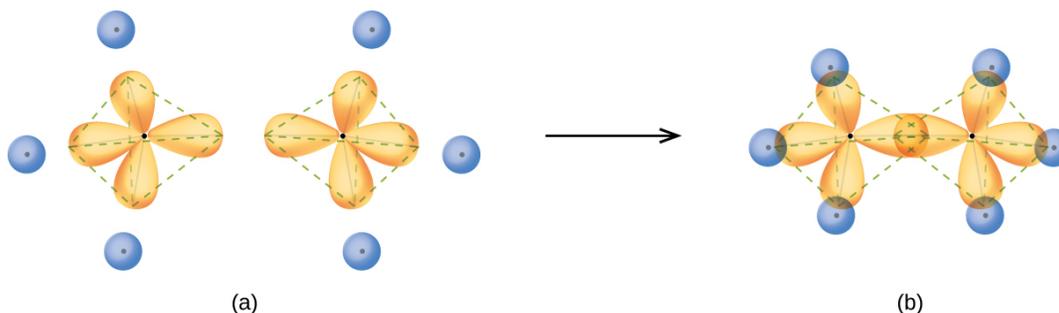
Figure 5.3.12: (a) In the ethane molecule, C_2H_6, each carbon has four sp^3 orbitals. (b) These four orbitals overlap to form seven σ bonds.

An sp^3 hybrid orbital can also hold a lone pair of electrons. For example, the nitrogen atom in ammonia is surrounded by three bonding pairs and a lone pair of electrons directed to the four corners of a tetrahedron. The nitrogen atom is sp^3 hybridized with one hybrid orbital occupied by the lone pair.

The molecular structure of water is consistent with a tetrahedral arrangement of two lone pairs and two bonding pairs of electrons. Thus we say that the oxygen atom is sp^3 hybridized, with two of the hybrid orbitals occupied by lone pairs and two by bonding pairs. Since lone pairs occupy more space than bonding pairs, structures that contain lone pairs have bond angles slightly distorted from the ideal. Perfect tetrahedra have angles of 109.5°, but the observed angles in ammonia (107.3°) and water (104.5°) are slightly smaller. Other examples of sp^3 hybridization include CCl_4, PCl_3, and NCl_3.

sp^3d and sp^3d^2 Hybridization

To describe the five bonding orbitals in a trigonal bipyramidal arrangement, we must use five of the valence shell atomic orbitals (the s orbital, the three p orbitals, and one of the d orbitals), which gives five **sp^3d hybrid orbitals**. With an octahedral arrangement of six hybrid orbitals, we must use six valence shell atomic orbitals (the s orbital, the three p orbitals, and two of the d orbitals in its valence shell), which gives six **sp^3d^2 hybrid orbitals**. These hybridizations are only possible for atoms that have d orbitals in their valence subshells (that is, not those in the first or second period).
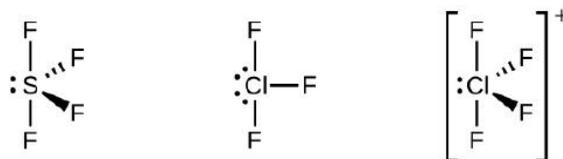
Figure 5.3.13: The three compounds pictured exhibit sp^3d hybridization in the central atom and a trigonal bipyramid form. SF_4 and have one lone pair of electrons on the central atom, and ClF_3 has two lone pairs giving it the T-shape shown.

In a molecule of phosphorus pentachloride, PCl_5, there are five P–Cl bonds (thus five pairs of valence electrons around the phosphorus atom) directed toward the corners of a trigonal bipyramid. We use the 3s orbital, the three 3p orbitals, and one of the 3d orbitals to form the set of five sp^3d hybrid orbitals (Figure 5.3.14) that are involved in the P–Cl bonds. Other atoms that exhibit sp^3d hybridization include the sulfur atom in SF_4 and the chlorine atoms in ClF_3 and in (The electrons on fluorine atoms are omitted for clarity.)
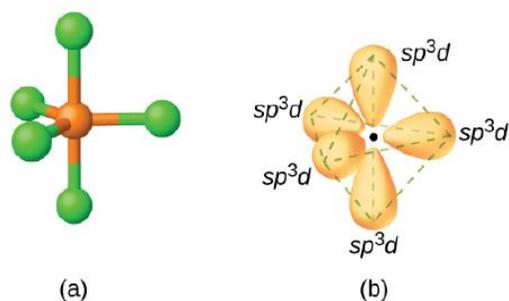
Figure 5.3.14: (a) The five regions of electron density around phosphorus in PCl$_5$ require five hybrid sp^3d orbitals. (b) These orbitals combine to form a trigonal bipyramidal structure with each large lobe of the hybrid orbital pointing at a vertex. As before, there are also small lobes pointing in the opposite direction for each orbital (not shown for clarity).

The sulfur atom in sulfur hexafluoride, SF$_6$, exhibits sp^3d^2 hybridization. A molecule of sulfur hexafluoride has six bonding pairs of electrons connecting six fluorine atoms to a single sulfur atom. There are no lone pairs of electrons on the central atom. To bond six fluorine atoms, the 3s orbital, the three 3p orbitals, and two of the 3d orbitals form six equivalent sp^3d^2 hybrid orbitals, each directed toward a different corner of an octahedron. Other atoms that exhibit sp^3d^2 hybridization include the phosphorus atom in the iodine atom in the interhalogens IF$_5$, and the xenon atom in XeF$_4$.
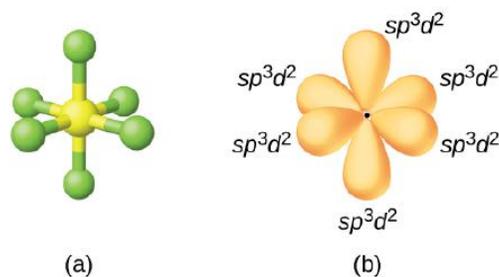
Figure 5.3.15: (a) Sulfur hexafluoride, SF$_6$, has an octahedral structure that requires sp^3d^2 hybridization. (b) The six sp^3d^2 orbitals form an octahedral structure around sulfur. Again, the minor lobe of each orbital is not shown for clarity.

Assignment of Hybrid Orbitals to Central Atoms

The hybridization of an atom is determined based on the number of regions of electron density that surround it. The geometrical arrangements characteristic of the various sets of hybrid orbitals are shown in Figure 5.3.16. These arrangements are identical to those of the electron-pair geometries predicted by VSEPR theory. VSEPR theory predicts the shapes of molecules, and hybrid orbital theory provides an explanation for how those shapes are formed. To find the hybridization of a central atom, we can use the following guidelines:

1. Determine the Lewis structure of the molecule.
2. Determine the number of regions of electron density around an atom using VSEPR theory, in which single bonds, multiple bonds, radicals, and lone pairs each count as one region.
3. Assign the set of hybridized orbitals from Figure 5.3.16 that corresponds to this geometry.

Regions of Electron Density	Arrangement		Hybridization	
2	- - - - - - - - - - - - -	linear	sp	180°
3	(triangle)	trigonal planar	sp^2	120°
4	(tetrahedron)	tetrahedral	sp^3	109.5°
5	(trigonal bipyramid)	trigonal bipyramidal	sp^3d	90° 120°
6	(octahedron)	octahedral	sp^3d^2	90° 90°

Figure 5.3.16: The shapes of hybridized orbital sets are consistent with the electron-pair geometries. For example, an atom surrounded by three regions of electron density is sp^2 hybridized, and the three sp^2 orbitals are arranged in a trigonal planar fashion.

It is important to remember that hybridization was devised to rationalize experimentally observed molecular geometries. The model works well for molecules containing small central atoms, in which the valence electron pairs are close together in space. However, for larger central atoms, the valence-shell electron pairs are farther from the nucleus, and there are fewer repulsions. Their compounds exhibit structures that are often not consistent with VSEPR theory, and hybridized orbitals are not necessary to explain the observed data. For example, we have discussed the H–O–H bond angle in H_2O, 104.5°, which is more consistent with sp^3 hybrid orbitals (109.5°) on the central atom than with $2p$ orbitals (90°). Sulfur is in the same group as oxygen, and H_2S has a similar Lewis structure. However, it has a much smaller bond angle (92.1°), which indicates much less hybridization on sulfur than oxygen. Continuing down the group, tellurium is even larger than sulfur, and for H_2Te, the observed bond angle (90°) is consistent with overlap of the $5p$ orbitals, without invoking hybridization. We invoke hybridization where it is necessary to explain the observed structures.

104.5°   92.1°   90°
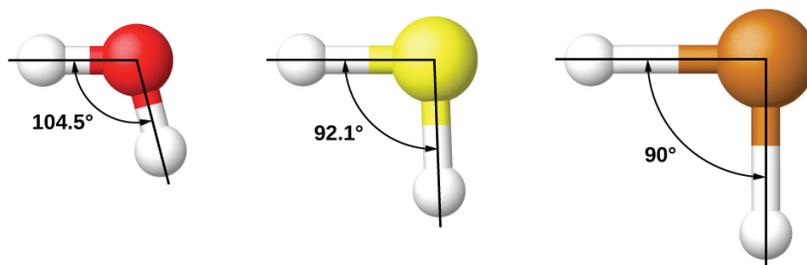
> ✔ **Example 5.3.1: Assigning Hybridization**
>
> Ammonium sulfate is important as a fertilizer. What is the hybridization of the sulfur atom in the sulfate ion,
>
> **Solution**
>
> The Lewis structure of sulfate shows there are four regions of electron density. The hybridization is sp^3.
>
>
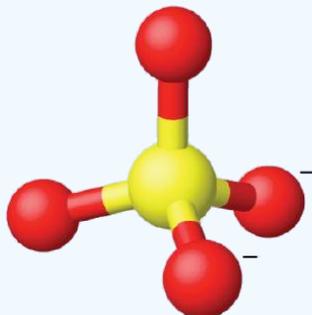
> ❓ **Exercise 5.3.1**
>
> What is the hybridization of the selenium atom in SeF_4?
>
>
>
> **Answer**
>
> The selenium atom is sp^3d hybridized.

> ✔ **Example 5.3.2: Assigning Hybridization**
>
> Urea, $NH_2C(O)NH_2$, is sometimes used as a source of nitrogen in fertilizers. What is the hybridization of the carbon atom in urea?
>
> **Solution**
>
> The Lewis structure of urea is
>
>
>
> The carbon atom is surrounded by three regions of electron density, positioned in a trigonal planar arrangement. The hybridization in a trigonal planar electron pair geometry is sp^2 (Figure $5.3.16$), which is the hybridization of the carbon atom in urea.
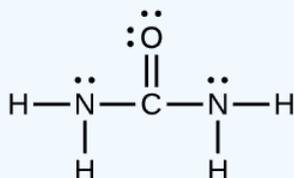
> ❓ **Exercise 5.3.1**
>
> Acetic acid, $H_3CC(O)OH$, is the molecule that gives vinegar its odor and sour taste. What is the hybridization of the two carbon atoms in acetic acid?
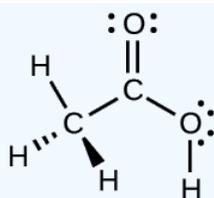
Answer

H$_3$<u>C</u>, *sp^3*; <u>C</u>(O)OH, *sp^2*

Footnotes

- [1]Note that orbitals may sometimes be drawn in an elongated "balloon" shape rather than in a more realistic "plump" shape in order to make the geometry easier to visualize.

5.4: Multiple Bonds

> **◑ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Describe multiple covalent bonding in terms of atomic orbital overlap
> - Relate the concept of resonance to π-bonding and electron delocalization

The hybrid orbital model appears to account well for the geometry of molecules involving single covalent bonds. Is it also capable of describing molecules containing double and triple bonds? We have already discussed that multiple bonds consist of σ and π bonds. Next we can consider how we visualize these components and how they relate to hybrid orbitals. The Lewis structure of ethene, C_2H_4, shows us that each carbon atom is surrounded by one other carbon atom and two hydrogen atoms.
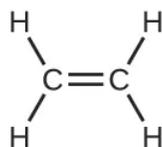
The three bonding regions form a trigonal planar electron-pair geometry. Thus we expect the σ bonds from each carbon atom are formed using a set of sp^2 hybrid orbitals that result from hybridization of two of the $2p$ orbitals and the $2s$ orbital (Figure 5.4.1).
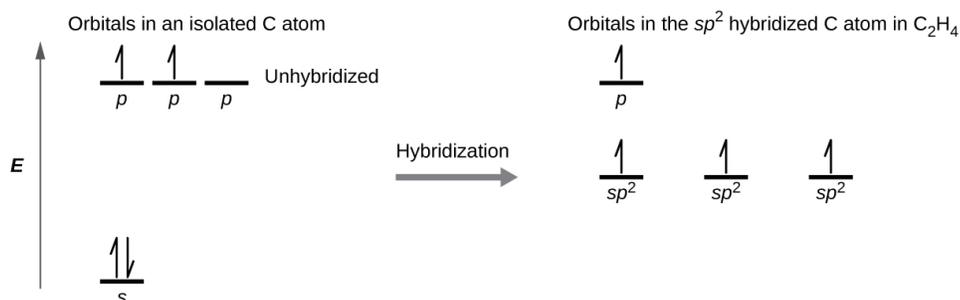
Figure 5.4.1: In ethene, each carbon atom is sp^2 hybridized, and the sp^2 orbitals and the p orbital are singly occupied. The hybrid orbitals overlap to form σ bonds, while the p orbitals on each carbon atom overlap to form a π bond.

These orbitals form the C–H single bonds and the σ bond in the Figure 5.4.2. The π bond in the C=C double bond results from the overlap of the third (remaining) 2p orbital on each carbon atom that is not involved in hybridization. This unhybridized p orbital (lobes shown in red and blue in Figure 5.4.2) is perpendicular to the plane of the sp2 hybrid orbitals. Thus the unhybridized 2p orbitals overlap in a side-by-side fashion, above and below the internuclear axis (Figure 5.4.2) and form a π bond.
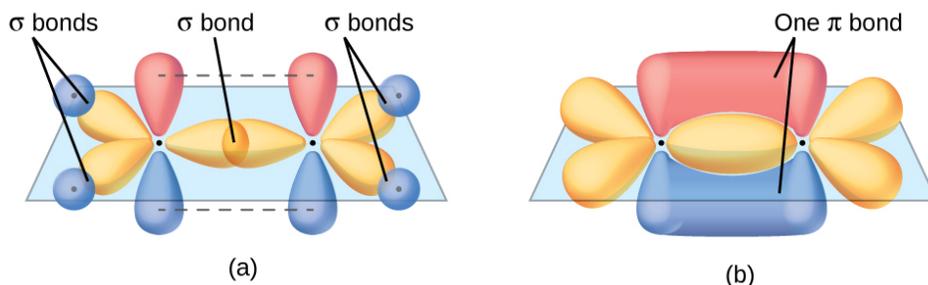
Figure 5.4.2: In the ethene molecule, C_2H_4, there are (a) five σ bonds. One C–C σ bond results from overlap of sp^2 hybrid orbitals on the carbon atom with one sp^2 hybrid orbital on the other carbon atom. Four C–H bonds result from the overlap between the C atoms' sp^2 orbitals with s orbitals on the hydrogen atoms. (b) The π bond is formed by the side-by-side overlap of the two unhybridized p orbitals in the two carbon atoms. The two lobes of the π bond are above and below the plane of the σ system.

In an ethene molecule, the four hydrogen atoms and the two carbon atoms are all in the same plane. If the two planes of sp^2 hybrid orbitals tilted relative to each other, the p orbitals would not be oriented to overlap efficiently to create the π bond. The planar configuration for the ethene molecule occurs because it is the most stable bonding arrangement. This is a significant difference

between σ and π bonds; rotation around single (σ) bonds occurs easily because the end-to-end orbital overlap does not depend on the relative orientation of the orbitals on each atom in the bond. In other words, rotation around the internuclear axis does not change the extent to which the σ bonding orbitals overlap because the bonding electron density is symmetric about the axis. Rotation about the internuclear axis is much more difficult for multiple bonds; however, this would drastically alter the off-axis overlap of the π bonding orbitals, essentially breaking the π bond.

In molecules with *sp* hybrid orbitals, two unhybridized *p* orbitals remain on the atom (Figure 5.4.3). We find this situation in acetylene, $H - C \equiv C - H$ (Figure 5.4.4), The remaining sp orbitals form σ bonds with hydrogen atoms. The two unhybridized *p* orbitals per carbon are positioned such that they overlap side by side and, hence, form two π bonds. The two carbon atoms of acetylene are thus bound together by one σ bond and two π bonds, giving a triple bond.
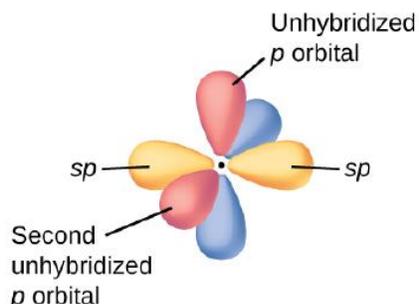
Figure 5.4.3: Diagram of the two linear *sp* hybrid orbitals of a carbon atom, which lie in a straight line, and the two unhybridized *p* orbitals at perpendicular angles.
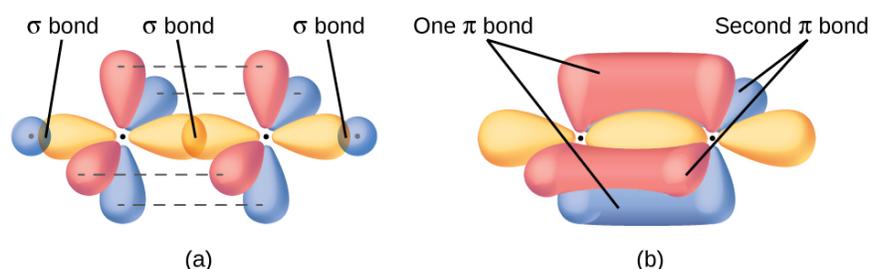
Figure 5.4.4: (a) In the acetylene molecule, C_2H_2, there are two C–H σ bonds and a triple bond involving one C–C σ bond and two C–C π bonds. The dashed lines, each connecting two lobes, indicate the side-by-side overlap of the four unhybridized *p* orbitals. (b) This shows the overall outline of the bonds in C_2H_2. The two lobes of each of the π bonds are positioned across from each other around the line of the C–C σ bond.

Hybridization involves only σ bonds, lone pairs of electrons, and single unpaired electrons (radicals). Structures that account for these features describe the correct hybridization of the atoms. However, many structures also include resonance forms. Remember that resonance forms occur when various arrangements of π bonds are possible. Since the arrangement of π bonds involves only the unhybridized orbitals, resonance does not influence the assignment of hybridization.

For example, molecule benzene has two resonance forms (Figure 5.4.5). We can use either of these forms to determine that each of the carbon atoms is bonded to three other atoms with no lone pairs, so the correct hybridization is sp^2. The electrons in the unhybridized *p* orbitals form π bonds. Neither resonance structure completely describes the electrons in the π bonds. They are not located in one position or the other, but in reality are delocalized throughout the ring. Valence bond theory does not easily address delocalization. Bonding in molecules with resonance forms is better described by molecular orbital theory. (See the next module.)
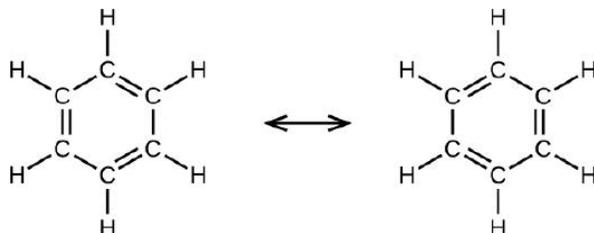
Figure 5.4.5: Each carbon atom in benzene, C_6H_6, is sp^2 hybridized, independently of which resonance form is considered. The electrons in the π bonds are not located in one set of *p* orbitals or the other, but rather delocalized throughout the molecule.

✔ **Example** 5.4.1: Assignment of Hybridization Involving Resonance

Some acid rain results from the reaction of sulfur dioxide with atmospheric water vapor, followed by the formation of sulfuric acid. Sulfur dioxide, SO_2, is a major component of volcanic gases as well as a product of the combustion of sulfur-containing coal. What is the hybridization of the S atom in SO_2?

Solution

The resonance structures of SO_2 are

The sulfur atom is surrounded by two bonds and one lone pair of electrons in either resonance structure. Therefore, the electron-pair geometry is trigonal planar, and the hybridization of the sulfur atom is sp^2.

? **Exercise** 5.4.1

Another acid in acid rain is nitric acid, HNO_3, which is produced by the reaction of nitrogen dioxide, NO_2, with atmospheric water vapor. What is the hybridization of the nitrogen atom in NO_2? (Note: the lone electron on nitrogen occupies a hybridized orbital just as a lone pair would.)

Answer

sp^2

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5.5: Molecular Orbital Theory

> **◐ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - 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:

$$:\ddot{O}=\ddot{O}:$$
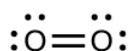
This electronic structure adheres to all the rules governing Lewis theory. There is an O=O double bond, and each oxygen atom has eight electrons around it. However, this picture is at odds with the magnetic behavior of oxygen. By itself, O_2 is not magnetic, but it is attracted to magnetic fields. Thus, 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 $5.5.1$), 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.
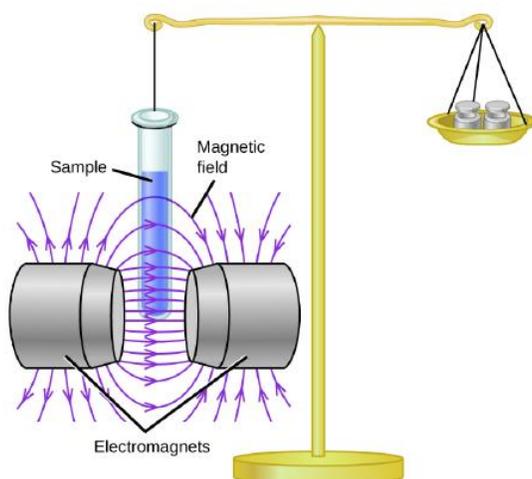
Figure 5.5.1: A Gouy balance compares the mass of a sample in the presence of a magnetic field with the mass with the electromagnet turned off to determine the number of unpaired electrons in a sample.

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.

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.

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 5.5.1 summarizes the main points of the two complementary bonding theories. Both theories provide different, useful ways of describing molecular structure.

Table 5.5.1: 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 5.5.2). 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.
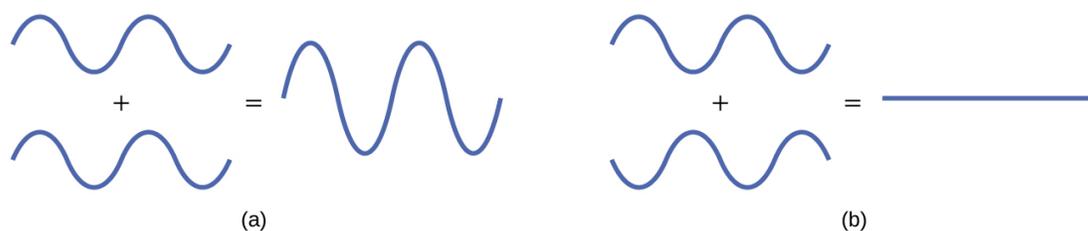
Figure 5.5.2: (a) When in-phase waves combine, constructive interference produces a wave with greater amplitude. (b) When out-of-phase waves combine, destructive interference produces a wave with less (or no) amplitude.

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 5.5.3. 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 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 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.
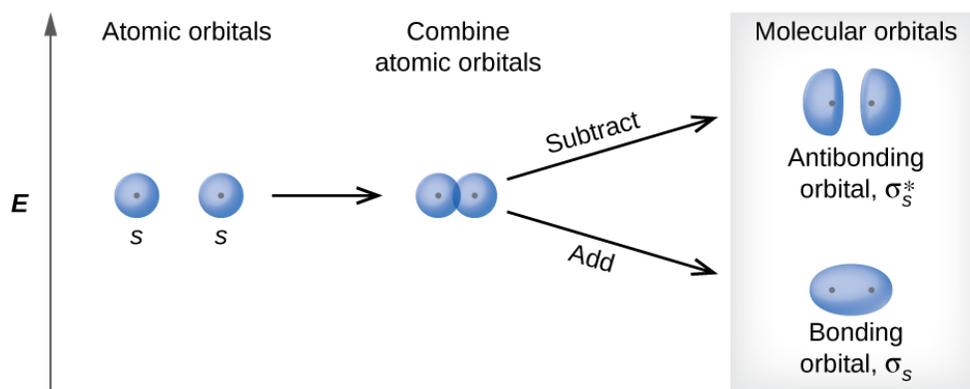
Figure 5.5.3: Sigma (σ) and sigma-star (σ*) molecular orbitals are formed by the combination of two *s* atomic orbitals. The dots ($\cdot$) indicate the locations of nuclei.

> **⚲ Link to Learning**
>
> You can watch animations visualizing the calculated atomic orbitals combining to form various molecular orbitals at the Orbitron website.

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 5.5.4). 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 (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.
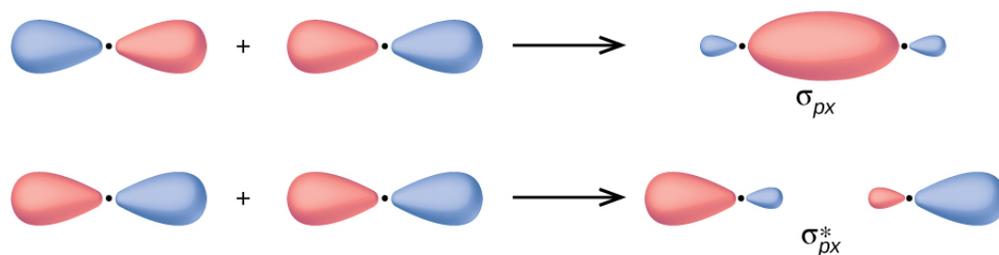
Figure 5.5.4: Combining wave functions of two *p* atomic orbitals along the internuclear axis creates two molecular orbitals, σ_p and σ_p^*.

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 5.5.5. 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.
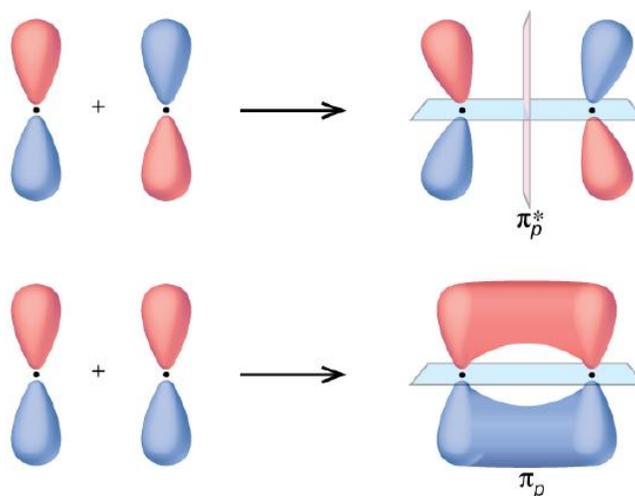
Figure 5.5.5: Side-by-side overlap of each two p orbitals results in the formation of two π molecular orbitals. Combining the out-of-phase orbitals results in an antibonding molecular orbital with two nodes. One contains the internuclear axis, and one is perpendicular to the axis. Combining the in-phase orbitals results in a bonding orbital. There is a node (blue) 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 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 5.5.1: 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.

$3p_x$ and $3p_x$	$3p_x$ and $3p_y$	$3p_y$ and $3p_y$
(a)	(b)	(c)
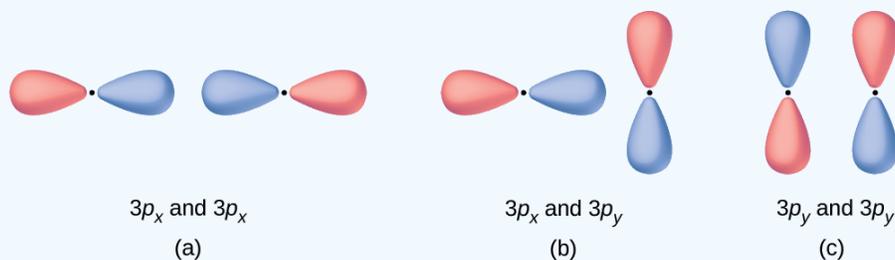
Solution

a. is an in-phase combination, resulting in a σ_{3p} orbital

b. 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. is an out-of-phase combination, resulting in a π_{3p}^* orbital.

? Exercise 5.5.1

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.

📌 Portrait of a Chemist: Walter Kohn: Nobel Laureate

Walter Kohn (Figure 5.5.6) is a theoretical physicist who studies the electronic structure of solids. His work combines the principles of quantum mechanics with advanced mathematical techniques. This technique, called density functional theory, makes it possible to compute properties of molecular orbitals, including their shape and energies. Kohn and mathematician John Pople were awarded the Nobel Prize in Chemistry in 1998 for their contributions to our understanding of electronic structure. Kohn also made significant contributions to the physics of semiconductors.
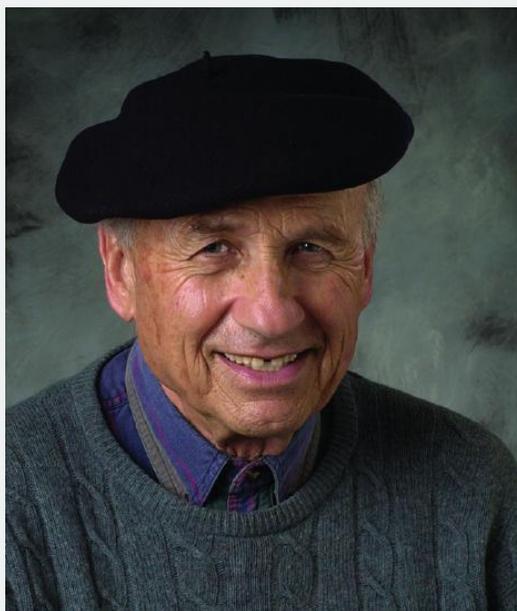
Figure 5.5.6: Walter Kohn developed methods to describe molecular orbitals. (credit: image courtesy of Walter Kohn)

Kohn's biography has been remarkable outside the realm of physical chemistry as well. He was born in Austria, and during World War II he was part of the Kindertransport program that rescued 10,000 children from the Nazi regime. His summer jobs included discovering gold deposits in Canada and helping Polaroid explain how its instant film worked. Dr. Kohn passed away in 2016 at the age of 93.

📌 How Sciences Interconnect: 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 (see Figure 5.5.7). 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.
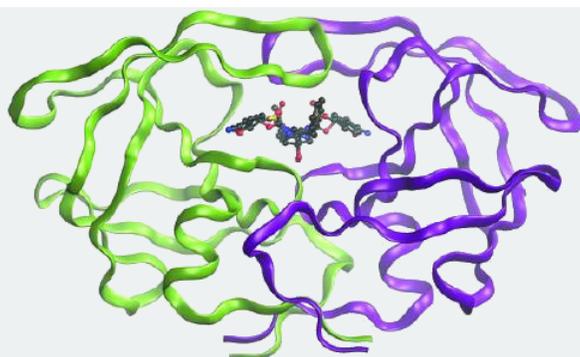
Figure 5.5.7: The molecule shown, HIV-1 protease, is an important target for pharmaceutical research. By designing molecules that bind to this protein, scientists are able to drastically inhibit the progress of the disease.

Molecular Orbital Energy Diagrams

The relative energy levels of atomic and molecular orbitals are typically shown in a molecular orbital diagram (Figure 5.5.8). 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 $2p$ atomic orbitals results in three bonding orbitals (one σ and two π) and three antibonding orbitals (one σ^* and two π^*).

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 5.5.8). 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.
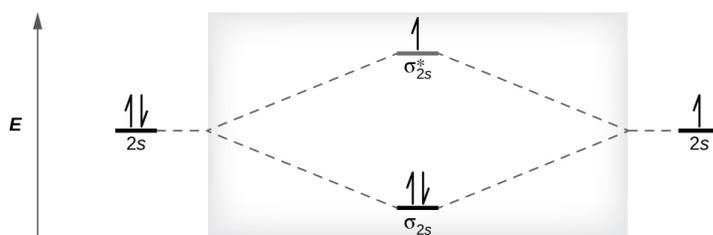
Figure 5.5.8: This is the molecular orbital diagram for the homonuclear diatomic showing the molecular orbitals of the valence shell only. The molecular orbitals are filled in the same manner as atomic orbitals, using the Aufbau principle and Hund's rule.

Bond Order

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

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

In the molecular orbital model, an electron contributes to a bonding interaction if it occupies a bonding orbital and it contributes to an antibonding interaction if it occupies an antibonding orbital. The bond order is calculated by subtracting the destabilizing

(antibonding) electrons from the stabilizing (bonding) electrons. Since a bond consists of two electrons, we divide by two to get the bond order. We can determine bond order with the following equation:

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

The order of a covalent bond is a guide to its strength; a bond between two given atoms becomes stronger as the bond order increases (Table 8.1). 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 1s atomic orbitals.

A molecular orbital can hold two electrons, so both electrons in the H_2 molecule are in the σ1s bonding orbital; the electron configuration is $(\sigma_{1s})^2$. We represent this configuration by a molecular orbital energy diagram (Figure 5.5.9) in which a single upward arrow indicates one electron in an orbital, and two (upward and downward) arrows indicate two electrons of opposite spin.
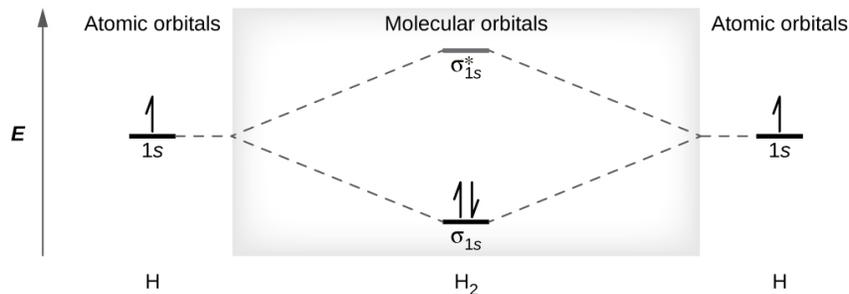
Figure 5.5.9: The molecular orbital energy diagram predicts that H_2 will be a stable molecule with lower energy than the separated atoms.

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

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

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 1s 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

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

A bond order of zero indicates that no bond is formed between two atoms.
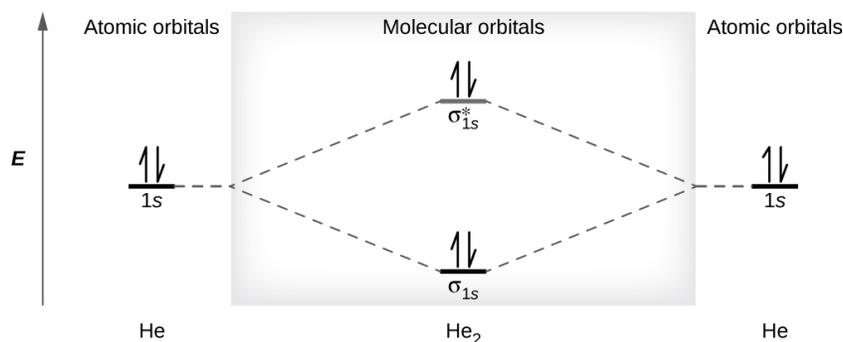
Figure 5.5.10: The molecular orbital energy diagram predicts that He$_2$ will not be a stable molecule, since it has equal numbers of bonding and antibonding electrons.

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 5.5.2).

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.

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 5.5.11. 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.
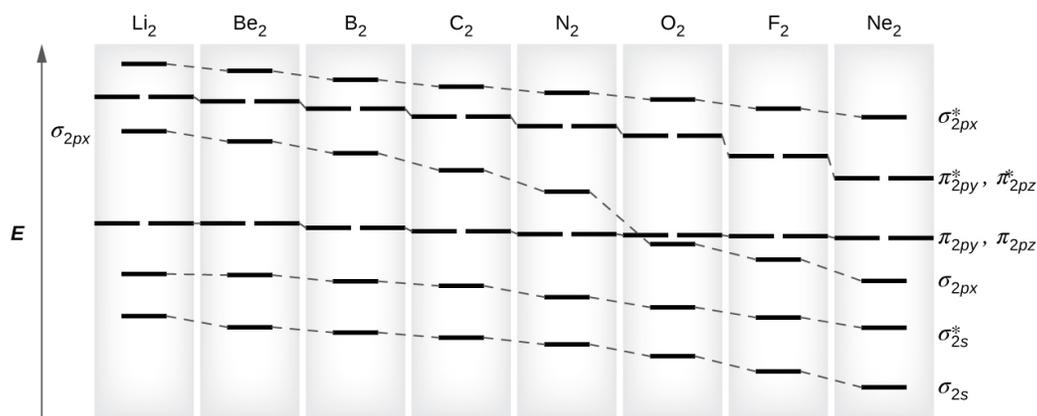
Figure 5.5.11: This shows the MO diagrams for each homonuclear diatomic molecule in the second period. The orbital energies decrease across the period as the effective nuclear charge increases and atomic radius decreases. Between N$_2$ and O$_2$, the order of the orbitals changes.

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 5.5.12). Similarly, the antibonding orbitals also undergo s-p mixing, with the σ_{s*} becoming more stable and the σ_{p*} becoming less stable.
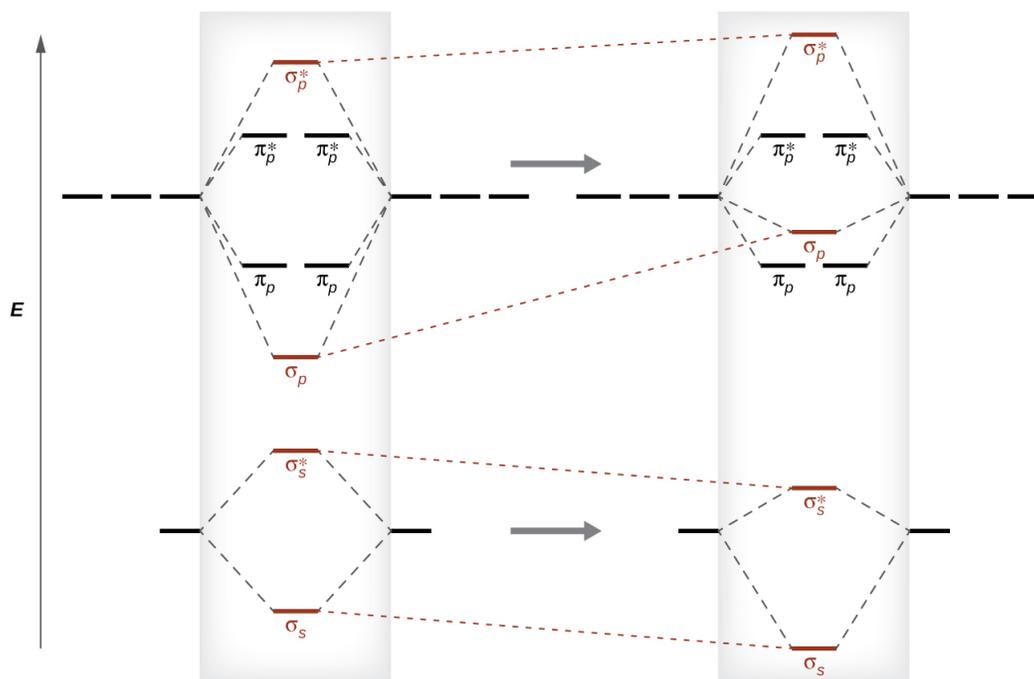
Figure 5.5.12: Without mixing, the MO pattern occurs as expected, with the σ_p orbital lower in energy than the π_p orbitals. When s-p mixing occurs, the orbitals shift as shown, with the σ_p orbital higher in energy than the π_p orbitals.

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_2 exhibit negligible s-p mixing (not sufficient to change the energy ordering), and their MO diagrams follow the normal pattern, as shown in Figure 5.5.11. 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 5.5.11: , 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 5.5.2, Be_2 and Ne_2 molecules would have a bond order of 0, and these molecules do not exist.

Table 5.5.2: Electron Configuration and Bond Order for Molecular Orbitals in Homonuclear Diatomic Molecules of Period Two Elements

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

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 $5.5.2$ with a bond order greater than zero are also known.

The O2 molecule has enough electrons to half fill the $\left(\pi^*_{2py}, \pi^*_{2pz} \right)$ level. We expect the two electrons that occupy these two degenerate orbitals to be unpaired, and this molecular electronic configuration for O2 is in accord with the fact that the oxygen molecule has two unpaired electrons (Figure 8.40). 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.

📌 How Sciences Interconnect: Band Theory

When two identical atomic orbitals on different atoms combine, two molecular orbitals result (see Figure $5.5.3$). 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 $5.5.13$ shows the bands for three important classes of materials: insulators, semiconductors, and conductors.
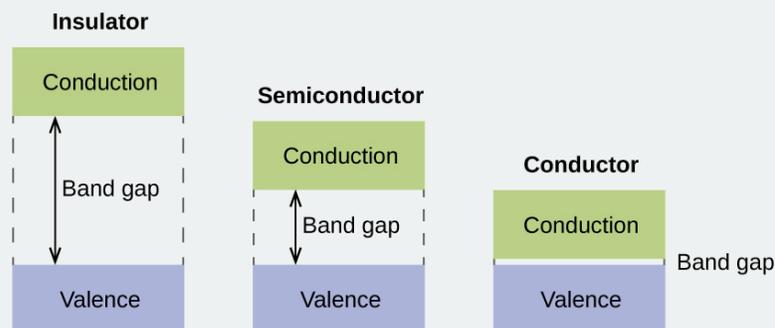
Figure 5.5.13: Molecular orbitals in solids are so closely spaced that they are described as bands. The valence band is lower in energy and the conduction band is higher in energy. The type of solid is determined by the size of the "band gap" between the valence and conduction bands. Only a very small 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 5.5.2: 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 5.5.11. Each oxygen atom contributes six electrons, so the diagram appears as shown in Figure 5.5.14.
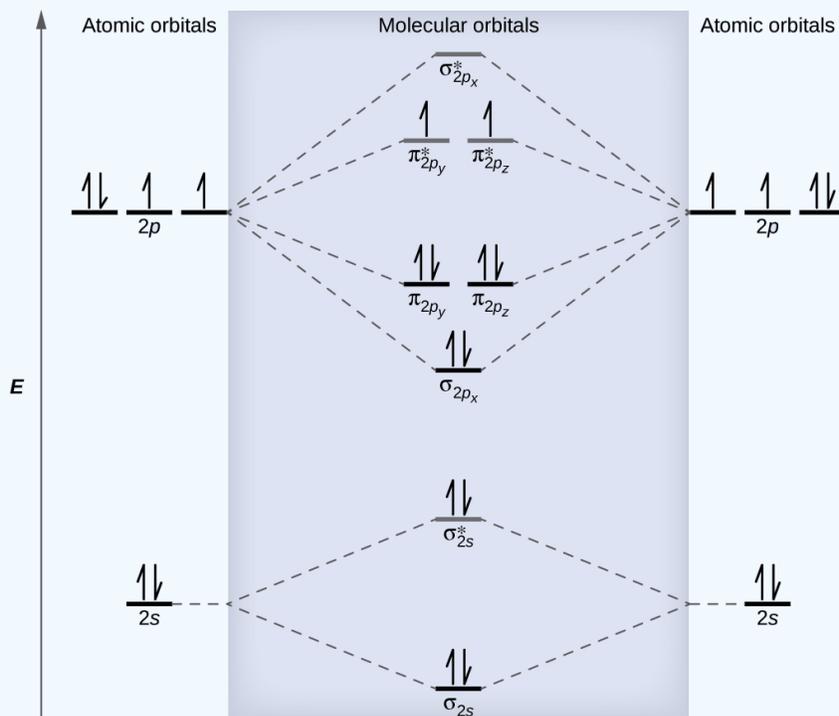
Figure 5.5.14: The molecular orbital energy diagram for O_2 predicts two unpaired electrons.

We calculate the bond order as

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

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

? Exercise 5.5.2

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 5.5.3: 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 $\left(\sigma_{2s}\right)^2\left(\sigma_{2s}^*\right)^2\left(\pi_{2py}, \pi_{2pz}\right)^4\left(\sigma_{2px}\right)^2$. Since this has six more bonding electrons than antibonding, the bond order will be 3, and the ion should be stable.

? Exercise $5.5.3$

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

Answer

two, paramagnetic

📌 Link to Learning

Creating molecular orbital diagrams for molecules with more than two atoms relies on the same basic ideas as the diatomic examples presented here. However, with more atoms, computers are required to calculate how the atomic orbitals combine. See three-dimensional drawings of the molecular orbitals for $\mathrm{C}_6\mathrm{H}_6$.

5.5.1: MO Diagrams for Heterodiatomic Molecules

Skills to Develop

- Construct MO diagrams for simple diatomic compounds

What's Different if we have 2 Elements?

If the elements are different, the main thing is that the AOs won't have the same initial energy. If they don't have the same energy, then the splitting will be smaller. Also, the bonding MO will have a higher % of the lower energy AO and the anti-bonding MO will have a higher % of the higher energy MO. This is exactly the same as saying that it will make a polar covalent bond. The electrons will usually be in the bonding MO, not the anti-bonding MO. The bonding MO has more of the lower energy AO, so the electrons will spend more time next to the atom with lower AOs, which is the same as the more electronegative atom. The bigger the difference in electronegativity/AO energy, the smaller the splitting and the more the bonding MO looks like the AO of the electronegative atom. When the difference is really big, the bond becomes completely ionic, and the "bonding MO" basically is the lower energy AO.

Example 5.5.1.1: CO

This diagram is based on calculations and comparison to experiments. (But it is not drawn exactly, just approximately.) It would be hard to guess all the details, especially about the sp-mixing and the shapes and sizes of MOs. Notice that the bonding orbitals are bigger on the oxygen and the antibonding orbitals are bigger on the carbon. We will talk more about the consequences of this later.

MO diagram for CO.
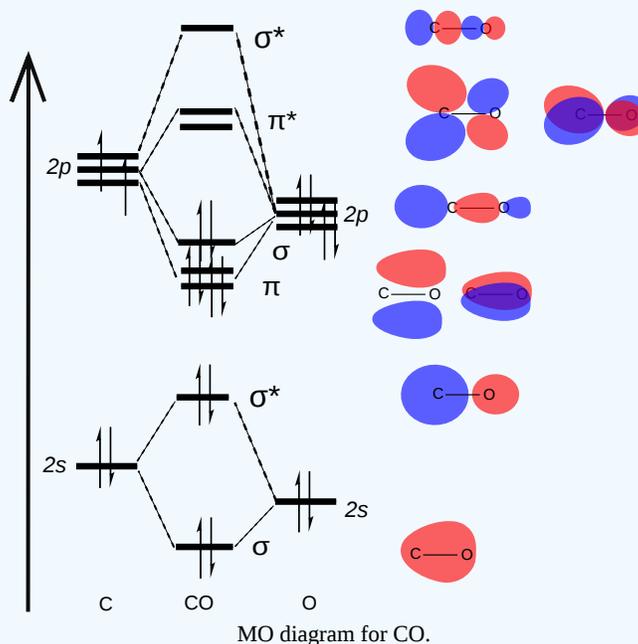
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5.5.2: MO Diagrams for Water and Nitrate Ion

Skills to Develop

- Construct MO diagrams for simple non-linear molecules and/or compounds

Non-linear Molecules

If you take an Inorganic Chemistry class, you'll learn ways to make MO diagrams for more complicated, non-linear molecules. Here we won't really explain these methods, just show some results. First we'll look at an MO diagram for water, because it's pretty simple and water is very important. Then we'll look at the π MOs for the nitrate ion, so we can see the difference between MO theory and valence bond theory.

Example 5.5.2.1: Water

This diagram is based on calculations and comparison to experiments. (But it is not drawn exactly, just approximately.) It would be hard to guess all the details, especially about the sp-mixing and the shapes and sizes of MOs. Notice that the bonding orbitals are bigger on the oxygen and the antibonding orbitals are bigger on the hydrogen. This produces the polarity that makes water a good solvent, because there is more electron density on the O and less electron density on the H.

We start by making the same H AO combinations we used for H_2 and also for BeH_2. Then we do sp-mixing on O, making one orbital pointed toward the H atoms and one pointed away (which will be mostly non-bonding, like a lone pair). Then we make bonding and anti-bonding combinations of H and O orbitals that match.

MO diagram for water.
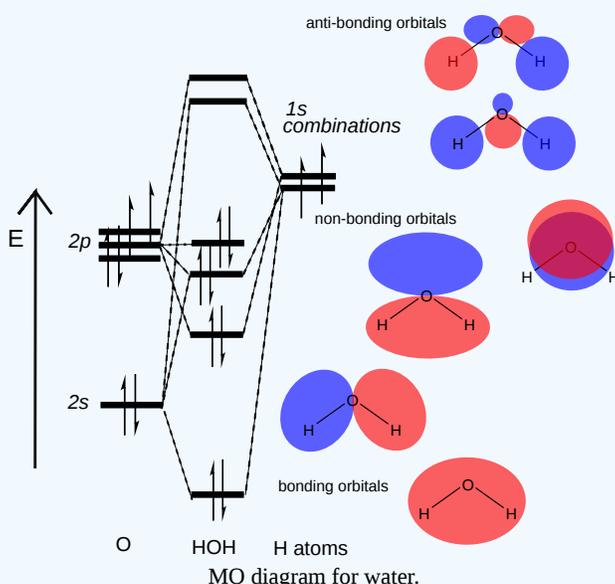
Example 5.5.2.2: Nitrate ion π MOs

In the section on multiple bonds using Valence Bond Theory, we talked about nitrate ion (NO_3^-), which has 1 π bond shared over 4 atoms (3 different resonance structures). That might have seemed kind of weird, so let's look at it again using MO theory, which treats resonance much more naturally. Let's just think about the 4 $2p_z$ orbitals, on 1 N and 3 O atoms. These orbitals point out of the plane of the molecule and will be used to make π bonds. First we will make combinations of the oxygen AOs. The combinations are shown in the figure. Don't worry about where these combinations came from too much, because that's a little too advanced for us (you'll see, if you take an Inorganic Chemistry class).
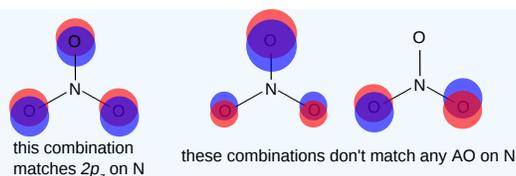
Oxygen π AO combinations for nitrate ion.

You can see that 2 of the combinations don't match the AOs on N, so they will be non-bonding MOs (like 2 lone pairs shared over 3 O atoms). One combination matches the N orbital, so it will make bonding and anti-bonding combinations. There are 6 π electrons in nitrate, so the bonding and non-bonding MOs will be filled. This means there is one π bond shared over the 4 atoms, which is just what valence bond theory says also.

π MO diagram for nitrate ion.
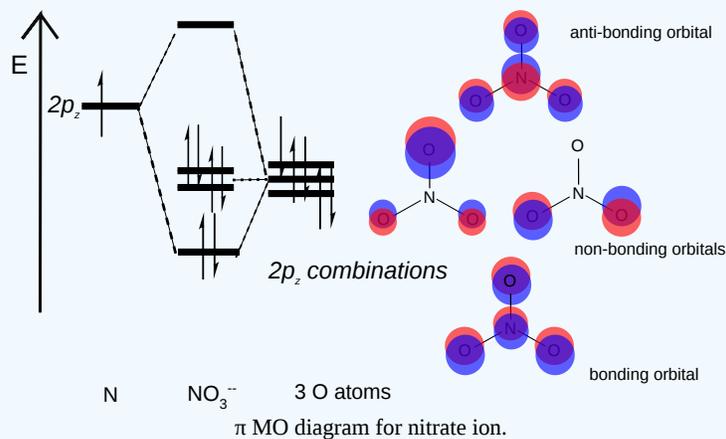
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5.5.3: Types of MOs

> **Skills to Develop**
>
> - Label the parts of an MO diagram

Bonding, Anti-bonding, and Non-bonding MOs

In the previous section, we introduced bonding and anti-bonding MOs. Bonding MOs have more electron density between the nuclei, and lower energy than the atomic orbitals they were made from. Putting electrons in bonding orbitals tends to make a bond between the nuclei, because when the electrons spend time between the nuclei, both nuclei are attracted to the negative charge between them.

Anti-bonding orbitals have less electron density between the nuclei, because they have a node there. They have higher energy than the AOs they were made of. Putting electrons in anti-bonding orbitals tends to break bonds, because with the electrons on the outside, the nuclei repel each other and all the electrons repel each other.

There is a third type of MO: non-bonding MOs. In order to make a bond, orbitals have to have **net overlap**, which means that if you multiply them together and take the integral over the whole molecule, the integral isn't 0. Consider the HF molecule. The H 1s orbital can make a bond with the F 2s or F $2p_z$ orbital. However, there is no net overlap between the H 1s and the F $2p_x$ and $2p_y$. This is shown in the figure. When we multiply Ψ_{1s} times Ψ_{2p}, the top half is + * + = +. The bottom half is + * — = —. Except for the sign, the top half and bottom half are symmetrical, so when we add up the values of $\Psi_{1s}\Psi_{2p}$ everywhere, the top half and bottom half cancel out, and $\int \Psi_{1s}\Psi_{2p} \, dV = 0$. (Note that multiplying the wavefunctions is different from adding them, which would give us the wave interference patterns we saw in hybrids and MOs.) For this reason, the F $2p_x$ and $2p_y$ orbitals in HF are called **non-bonding orbitals**. In contrast, the $2p_z$ orbital does have net overlap with 1s, because $\left|\Psi_{1s}\Psi_{2p}\right|$ on the red side in the figure is bigger than $\left|\Psi_{1s}\Psi_{2p}\right|$ on the blue side.
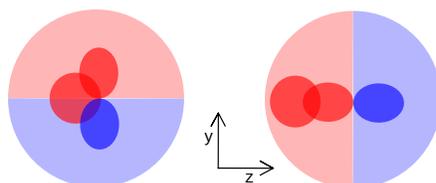
Overlap between an s and p orbital, such as in HF. The s orbital is shown as a small red circle. The p orbital is shown in red and blue, representing the sign (+/—) of the wavefunction. The large circle in light red and light blue shows that the p orbital has a small amplitude over a large area. Left: the 1s and $2p_y$ orbitals have no net overlap. Right: the 1s and $2p_z$ orbitals do have net overlap.

The figure below shows a summary illustration of bonding, non-bonding, and anti-bonding orbitals in HF.
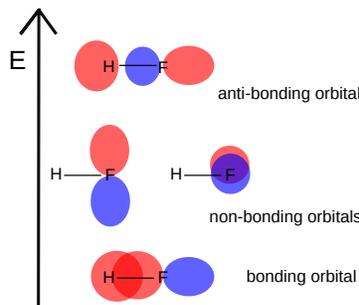
Types of MOs in HF. The sign (+/—) of the wavefunction is shown using red and blue. The MOs are ordered from bottom to top by increasing energy. Electrons in bonding MOs form bonds, electrons in anti-bonding orbitals break bonds, and electrons in non-bonding orbitals don't have any effect on bonding.

σ and π MOs

The bonding and anti-bonding MOs shown above are both σ-type MOs. Recall from the section on multiple bonds that we can classify bonds as σ or π bonds. σ-bonds are symmetrical around the bond (if you rotate them around the bond, they don't change). π-bonds change sign when you rotate them 180° around the bond.

If we think about making MOs for F_2, we can imagine making a bonding and anti-bonding combination of the $2p_z$ orbitals, which point toward each other. This will make a σ-bonding MO and an σ-anti-bonding MO. We can also make σ-type combinations of the 2s orbitals. When we combine the $2p_x$ and $2p_y$ orbitals, these are perpendicular to each other, so they will make π-type bonding and anti-bonding combinations. These are shown below. Note that for both σ combinations and π combinations electron density increases between the nuclei in bonding MOs and decreases between nuclei in anti-bonding MOs.
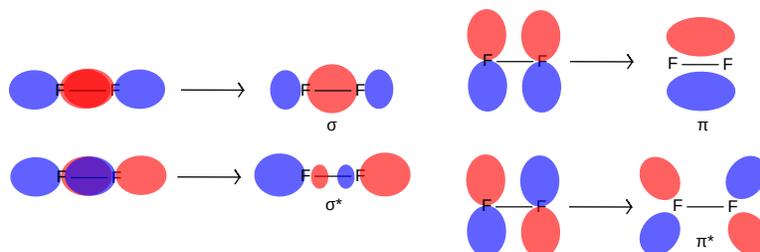
Formation of σ and π bonding and anti-bonding MOs in F_2. The sign (+/—) of the wavefunction is shown using red and blue. Left: σ MOs. Right: π MOs. Top: bonding MOs. Bottom: anti-bonding MOs.

Naming MOs

The easiest way to name and label MOs is using σ and π. Anti-bonding character is shown using a *, such as π* which means a π-type anti-bonding orbital. Each MO in the figure above is labeled in this way. There are other more complicated ways to name MOs, but you won't learn them unless you take Inorganic Chemistry.

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5.5.4: Frontier MOs- An Acid-Base Theory

Skills to Develop

- Distinguish and describe the significance of frontier MOs

Frontier means a border area, between two things (often, between 2 countries). In this case, we are interested in the MOs at the border between occupied and empty. The **frontier MOs** are called the HOMO and the LUMO. HOMO is Highest Occupied MO, the highest-energy MO that has electrons in it. LUMO is Lowest Unoccupied MO, the lowest-energy MO that doesn't have any electrons in it.

Frontier MOs are very important for reactivity. Earlier, we said that most reactions can be called either Lewis acid/base or redox. In a Lewis acid/base reaction, an electron pair from the base is shared with the acid. What this really means is that the base has a HOMO that is pretty high-energy (a lone pair), and the acid has a LUMO that is pretty low energy. (A lone pair in MO theory is an electron pair in a non-bonding MO. A low LUMO usually means an empty valence orbital, like on B or on a cation.) We can make a bonding and anti-bonding combination of the base HOMO and acid LUMO, and that will stabilize the electrons from the base's HOMO, lowering the total energy. This creates a bond between the acid and base.

In a redox reaction, the oxidant has a low LUMO, and the reductant has a high HOMO, but this time the oxidant LUMO is lower than the reductant HOMO, so that the electrons in the reductant HOMO move completely to the oxidant LUMO. Often the energy match is bad, so that no covalent bond forms, just the electron moves. Sometimes a covalent bond forms also. This depends on the AO energies, which depends on the electronegativity, just like you would expect. You can still predict covalent/ionic bonding based on electronegativity.

Diagrams of acid/base, redox, and both reactions.
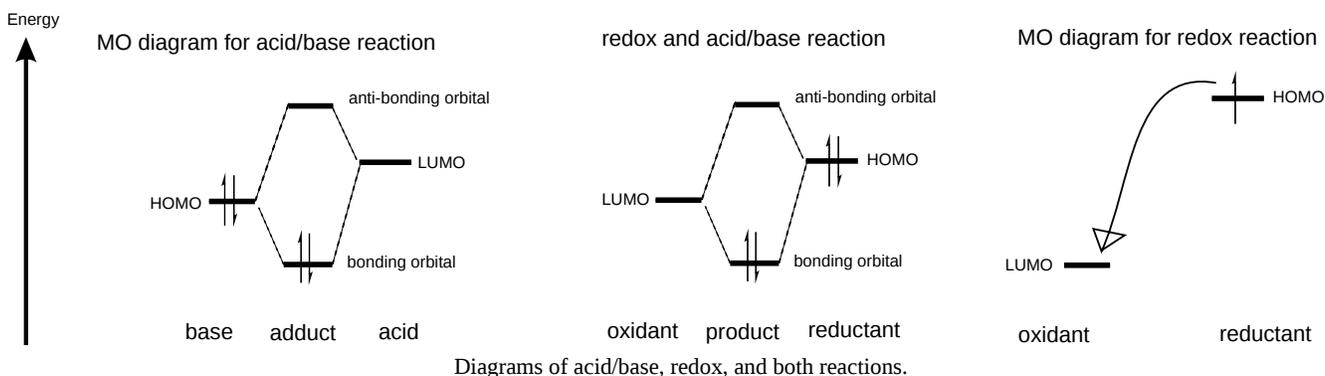
Molecules with low HOMO and high LUMO, a big HOMO-LUMO gap, are not very reactive! Hydrocarbons are a good example (like oil, etc). They do burn easily, but you have to get them hot first. At room temperature, they don't react. This is why if you want to store something reactive like K metal, you probably keep it in a bottle of oil.

Example 5.5.4.1: CO Toxicity

You probably know that CO is toxic (which is why you shouldn't stay in a garage with a car running, because the CO from incomplete combustion can kill you). The reason CO is toxic is because it binds metal ions really tightly. You use Fe(II) ions in your blood to bind O_2 and carry it to your cells. CO binds to the Fe(II) more tightly than O_2, so if you breathe too much CO, your cells won't get any oxygen, because all the Fe(II) in your blood bound CO instead. We can understand how and why CO binds Fe(II) using MO theory. Go back and look at the MO diagram for CO. The HOMO is a slightly-bonding orbital that is mostly on carbon. It is pretty high-energy. The LUMO is a π* orbital that is also mostly on carbon, and it is kind of low-energy because the splitting of π MOs is smaller than σ MOs (because of less overlap). CO has a small gap between the HOMO and LUMO. Fe(II) also has a small gap between HOMO and LUMO, because it has 6 electrons in 3d orbitals. The HOMO is high, because 3d is not so stable, and the LUMO is low, because it is also 3d and not much higher than the HOMO (there is a gap because the other atoms around the Fe(II) in hemoglobin make the d orbitals different energies). So what can happen is that the HOMO on CO makes a σ bond with the LUMO on Fe(II), and the HOMO on Fe(II) makes a π bond with the LUMO on CO. This "multiple bond" between CO and Fe(II) makes CO toxic. And because the HOMO and LUMO of CO are big on carbon, you won't be surprised that the bond is Fe-C=O, not Fe-O=C.
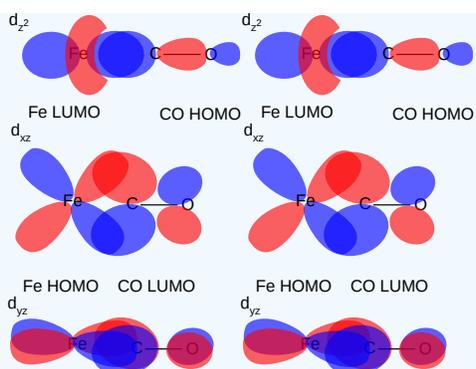
MO interactions between Fe and CO frontier MOs. Top: σ interaction. Bottom: π interactions (2 CO LUMOs, 2 Fe HOMOs, related by 90° rotation)

Contributors and Attributions

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5.6: Key Terms

antibonding orbital | molecular orbital located outside of the region between two nuclei; electrons in an antibonding orbital destabilize the molecule

bond order | number of pairs of electrons between two atoms; it can be found by the number of bonds in a Lewis structure or by the difference between the number of bonding and antibonding electrons divided by two

bonding orbital | molecular orbital located between two nuclei; electrons in a bonding orbital stabilize a molecule

degenerate orbitals | orbitals that have the same energy

diamagnetism | phenomenon in which a material is not magnetic itself but is repelled by a magnetic field; it occurs when there are only paired electrons present

homonuclear diatomic molecule | molecule consisting of two identical atoms

hybrid orbital | orbital created by combining atomic orbitals on a central atom

hybridization | model that describes the changes in the atomic orbitals of an atom when it forms a covalent compound

linear combination of atomic orbitals | technique for combining atomic orbitals to create molecular orbitals

molecular orbital | region of space in which an electron has a high probability of being found in a molecule

molecular orbital diagram | visual representation of the relative energy levels of molecular orbitals

molecular orbital theory | model that describes the behavior of electrons delocalized throughout a molecule in terms of the combination of atomic wave functions

node | plane separating different lobes of orbitals, where the probability of finding an electron is zero

overlap | coexistence of orbitals from two different atoms sharing the same region of space, leading to the formation of a covalent bond

paramagnetism | phenomenon in which a material is not magnetic itself but is attracted to a magnetic field; it occurs when there are unpaired electrons present

pi bond (π bond) | covalent bond formed by side-by-side overlap of atomic orbitals; the electron density is found on opposite sides of the internuclear axis

s-p mixing | change that causes σ_p orbitals to be less stable than π_p orbitals due to the mixing of s and p-based molecular orbitals of similar energies.

sigma bond (σ bond) | covalent bond formed by overlap of atomic orbitals along the internuclear axis

sp **hybrid orbital** | one of a set of two orbitals with a linear arrangement that results from combining one s and one p orbital

sp^2 **hybrid orbital** | one of a set of three orbitals with a trigonal planar arrangement that results from combining one s and two p orbitals

sp^3 **hybrid orbital** | one of a set of four orbitals with a tetrahedral arrangement that results from combining one s and three p orbitals

sp^3*d* **hybrid orbital** | one of a set of five orbitals with a trigonal bipyramidal arrangement that results from combining one s, three p, and one d orbital

sp^3*d*^{2} **hybrid orbital** | one of a set of six orbitals with an octahedral arrangement that results from combining one s, three p, and two d orbitals

valence bond theory | description of bonding that involves atomic orbitals overlapping to form σ or π bonds, within which pairs of electrons are shared

π bonding orbital | molecular orbital formed by side-by-side overlap of atomic orbitals, in which the electron density is found on opposite sides of the internuclear axis

π* bonding orbital | antibonding molecular orbital formed by out of phase side-by-side overlap of atomic orbitals, in which the electron density is found on both sides of the internuclear axis, and there is a node between the nuclei

σ bonding orbital | molecular orbital in which the electron density is found along the axis of the bond

σ* bonding orbital | antibonding molecular orbital formed by out-of-phase overlap of atomic orbital along the axis of the bond, generating a node between the nuclei

---

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5.7: Key Equations

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5.8: Summary

Valence bond theory describes bonding as a consequence of the overlap of two separate atomic orbitals on different atoms that creates a region with one pair of electrons shared between the two atoms. When the orbitals overlap along an axis containing the nuclei, they form a σ bond. When they overlap in a fashion that creates a node along this axis, they form a π bond.

We can use hybrid orbitals, which are mathematical combinations of some or all of the valence atomic orbitals, to describe the electron density around covalently bonded atoms. These hybrid orbitals either form sigma (σ) bonds directed toward other atoms of the molecule or contain lone pairs of electrons. We can determine the type of hybridization around a central atom from the geometry of the regions of electron density about it. Two such regions imply sp hybridization; three, sp^2 hybridization; four, sp^3 hybridization; five, sp^3d hybridization; and six, sp^3d^2 hybridization. Pi (π) bonds are formed from unhybridized atomic orbitals (p or d orbitals).

Multiple bonds consist of a σ bond located along the axis between two atoms and one or two π bonds. The σ bonds are usually formed by the overlap of hybridized atomic orbitals, while the π bonds are formed by the side-by-side overlap of unhybridized orbitals. Resonance occurs when there are multiple unhybridized orbitals with the appropriate alignment to overlap, so the placement of π bonds can vary.

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.

5.9: Exercises

1.

Explain how σ and π bonds are similar and how they are different.

2.

Draw a curve that describes the energy of a system with H and Cl atoms at varying distances. Then, find the minimum energy of this curve two ways.

  a. Use the bond energy found in Table 8.1 to calculate the energy for one single HCl bond (Hint: How many bonds are in a mole?)
  b. Use the enthalpy of reaction and the bond energies for H_2 and Cl_2 to solve for the energy of one mole of HCl bonds.

3.

Explain why bonds occur at specific average bond distances instead of the atoms approaching each other infinitely close.

4.

Use valence bond theory to explain the bonding in F_2, HF, and ClBr. Sketch the overlap of the atomic orbitals involved in the bonds.

5.

Use valence bond theory to explain the bonding in O_2. Sketch the overlap of the atomic orbitals involved in the bonds in O_2.

6.

How many σ and π bonds are present in the molecule HCN?

7.

A friend tells you N_2 has three π bonds due to overlap of the three *p*-orbitals on each N atom. Do you agree?

8.

Draw the Lewis structures for CO_2 and CO, and predict the number of σ and π bonds for each molecule.

  a. CO_2
  b. CO

9.

Why is the concept of hybridization required in valence bond theory?

10.

Give the shape that describes each hybrid orbital set:

  a. sp^2
  b. sp^3d
  c. sp
  d. sp^3d^2

11.

Explain why a carbon atom cannot form five bonds using sp^3d hybrid orbitals.

12.

What is the hybridization of the central atom in each of the following?

  a. BeH_2
  b. SF_6
  c.
  d. PCl_5

13.

A molecule with the formula AB_3 could have one of four different shapes. Give the shape and the hybridization of the central A atom for each.

14.

Methionine, $CH_3SCH_2CH_2CH(NH_2)CO_2H$, is an amino acid found in proteins. The Lewis structure of this compound is shown below. What is the hybridization type of each carbon, oxygen, the nitrogen, and the sulfur?
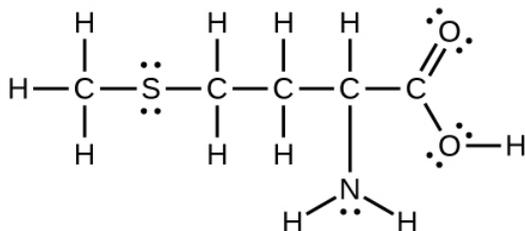
15.

Sulfuric acid is manufactured by a series of reactions represented by the following equations:

Draw a Lewis structure, predict the molecular geometry by VSEPR, and determine the hybridization of sulfur for the following:

a. circular S_8 molecule
b. SO_2 molecule
c. SO_3 molecule
d. H_2SO_4 molecule (the hydrogen atoms are bonded to oxygen atoms)

16.

Two important industrial chemicals, ethene, C_2H_4, and propene, C_3H_6, are produced by the steam (or thermal) cracking process:

For each of the four carbon compounds, do the following:

a. Draw a Lewis structure.
b. Predict the geometry about the carbon atom.
c. Determine the hybridization of each type of carbon atom.

17.

Analysis of a compound indicates that it contains 77.55% Xe and 22.45% F by mass.

a. What is the empirical formula for this compound? *(Assume this is also the molecular formula in responding to the remaining parts of this exercise)*.
b. Write a Lewis structure for the compound.
c. Predict the shape of the molecules of the compound.
d. What hybridization is consistent with the shape you predicted?

18.

Consider nitrous acid, HNO_2 (HONO).

a. Write a Lewis structure.
b. What are the electron pair and molecular geometries of the internal oxygen and nitrogen atoms in the HNO_2 molecule?
c. What is the hybridization on the internal oxygen and nitrogen atoms in HNO_2?

19.

Strike-anywhere matches contain a layer of $KClO_3$ and a layer of P_4S_3. The heat produced by the friction of striking the match causes these two compounds to react vigorously, which sets fire to the wooden stem of the match. $KClO_3$ contains the ion. P_4S_3 is an unusual molecule with the skeletal structure.

a. Write Lewis structures for P_4S_3 and the ion.
b. Describe the geometry about the P atoms, the S atom, and the Cl atom in these species.
c. Assign a hybridization to the P atoms, the S atom, and the Cl atom in these species.
d. Determine the oxidation states and formal charge of the atoms in P_4S_3 and the ion.

20.

Identify the hybridization of each carbon atom in the following molecule. (The arrangement of atoms is given; you need to determine how many bonds connect each pair of atoms.)

```
        H   H               H   H

    H   C   C   C   C   C   C   H

        H   H
```

21.

Write Lewis structures for NF_3 and PF_5. On the basis of hybrid orbitals, explain the fact that NF_3, PF_3, and PF_5 are stable molecules, but NF_5 does not exist.

22.

In addition to NF_3, two other fluoro derivatives of nitrogen are known: N_2F_4 and N_2F_2. What shapes do you predict for these two molecules? What is the hybridization for the nitrogen in each molecule?

23.

The bond energy of a C–C single bond averages 347 kJ mol^{-1}; that of a triple bond averages 839 kJ mol^{-1}. Explain why the triple bond is not three times as strong as a single bond.

24.

For the carbonate ion, draw all of the resonance structures. Identify which orbitals overlap to create each bond.

25.

A useful solvent that will dissolve salts as well as organic compounds is the compound acetonitrile, H_3CCN. It is present in paint strippers.

a. Write the Lewis structure for acetonitrile, and indicate the direction of the dipole moment in the molecule.
b. Identify the hybrid orbitals used by the carbon atoms in the molecule to form σ bonds.
c. Describe the atomic orbitals that form the π bonds in the molecule. Note that it is not necessary to hybridize the nitrogen atom.

26.

For the molecule allene, give the hybridization of each carbon atom. Will the hydrogen atoms be in the same plane or perpendicular planes?

27.

Identify the hybridization of the central atom in each of the following molecules and ions that contain multiple bonds:

a. (f) XeO_2F_2 (Xe is the central atom)

   (g) (Cl is the central atom)

28.

Describe the molecular geometry and hybridization of the N, P, or S atoms in each of the following compounds.

a. H_3PO_4, phosphoric acid, used in cola soft drinks
b. NH_4NO_3, ammonium nitrate, a fertilizer and explosive
c. S_2Cl_2, disulfur dichloride, used in vulcanizing rubber
d. $K_4[O_3POPO_3]$, potassium pyrophosphate, an ingredient in some toothpastes

29.

For each of the following molecules, indicate the hybridization requested and whether or not the electrons will be delocalized:

a. ozone (O_3) central O hybridization
b. carbon dioxide (CO_2) central C hybridization
c. nitrogen dioxide (NO_2) central N hybridization
d. phosphate ion central P hybridization

30.

For each of the following structures, determine the hybridization requested and whether the electrons will be delocalized:

(a) Hybridization of each carbon
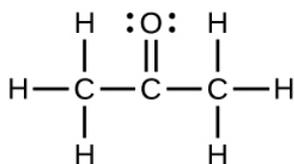
(b) Hybridization of sulfur
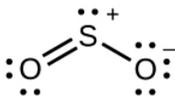
(c) All atoms
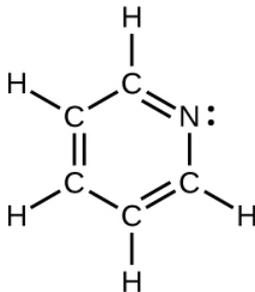
31.

Draw the orbital diagram for carbon in CO_2 showing how many carbon atom electrons are in each orbital.

32.

Sketch the distribution of electron density in the bonding and antibonding molecular orbitals formed from two *s* orbitals and from two *p* orbitals.

33.

How are the following similar, and how do they differ?

a. σ molecular orbitals and π molecular orbitals
b. ψ for an atomic orbital and ψ for a molecular orbital
c. bonding orbitals and antibonding orbitals

34.

If molecular orbitals are created by combining five atomic orbitals from atom A and five atomic orbitals from atom B combine, how many molecular orbitals will result?

35.

Can a molecule with an odd number of electrons ever be diamagnetic? Explain why or why not.

36.

Can a molecule with an even number of electrons ever be paramagnetic? Explain why or why not.

37.

Why are bonding molecular orbitals lower in energy than the parent atomic orbitals?

38.

Calculate the bond order for an ion with this configuration:

39.

Explain why an electron in the bonding molecular orbital in the H_2 molecule has a lower energy than an electron in the $1s$ atomic orbital of either of the separated hydrogen atoms.

40.

Predict the valence electron molecular orbital configurations for the following, and state whether they will be stable or unstable ions.

  a.
  b.
  c.
  d.
  e.
  f.
  g.
  h.

41.

Determine the bond order of each member of the following groups, and determine which member of each group is predicted by the molecular orbital model to have the strongest bond.

  a. H_2,
  b. O_2,
  c. Li_2, Be_2
  d. F_2,
  e. N_2,

42.

For the first ionization energy for an N_2 molecule, what molecular orbital is the electron removed from?

43.

Compare the atomic and molecular orbital diagrams to identify the member of each of the following pairs that has the highest first ionization energy (the most tightly bound electron) in the gas phase:

  a. H and H_2
  b. N and N_2
  c. O and O_2
  d. C and C_2
  e. B and B_2

44.

Which of the period 2 homonuclear diatomic molecules are predicted to be paramagnetic?

45.

A friend tells you that the $2s$ orbital for fluorine starts off at a much lower energy than the $2s$ orbital for lithium, so the resulting σ_{2s} molecular orbital in F_2 is more stable than in Li_2. Do you agree?

46.

True or false: Boron contains $2s^2 2p^1$ valence electrons, so only one p orbital is needed to form molecular orbitals.

47.

What charge would be needed on F_2 to generate an ion with a bond order of 2?

48.

Predict whether the MO diagram for S_2 would show s-p mixing or not.

49.

Explain why is diamagnetic, while which has the same number of valence electrons, is paramagnetic.

50.

Using the MO diagrams, predict the bond order for the stronger bond in each pair:

  a. B_2 or B_2^+
  b. F_2 or F_2^+
  c. O_2 or O_2^{2+}
  d. C_2^+ or C_2^-

51.

Using the MO diagram for CO as guidance, build the MO diagram for NO. Calculate the bond order and indicate LUMO and HOMO. Is CO a diamagnetic or paramagnetic molecule?

52.

Using the MO diagram for H_2O as guidance, build the MO diagram for H_2S. Calculate the bond order and indicate LUMO and HOMO. Is H_2S a diamagnetic or paramagnetic molecule?

53.

Using the MO diagram for NO_3^- as guidance, build the MO diagram for SO_3. Calculate the bond order and indicate LUMO and HOMO. Is SO_3 a diamagnetic or paramagnetic molecule?

CHAPTER OVERVIEW

6: Transition Metals and Coordination Chemistry

Transition metals are defined as those elements that have (or readily form) partially filled d orbitals. These include the d-block (groups 3–11) and f-block element elements. The variety of properties exhibited by transition metals is due to their complex valence shells. Unlike most main group metals where one oxidation state is normally observed, the valence shell structure of transition metals means that they usually occur in several different stable oxidation states. In addition, electron transitions in these elements can correspond with absorption of photons in the visible electromagnetic spectrum, leading to colored compounds. Because of these behaviors, transition metals exhibit a rich and fascinating chemistry.

6.1: Introduction

We have daily contact with many transition metals. Iron occurs everywhere—from the rings in your spiral notebook and the cutlery in your kitchen to automobiles, ships, buildings, and in the hemoglobin in your blood. Titanium is useful in the manufacture of lightweight, durable products such as bicycle frames, artificial hips, and jewelry. Chromium is useful as a protective plating on plumbing fixtures and automotive detailing.

In addition to being used in their pure elemental forms, many compounds containing transition metals have numerous other applications. Silver nitrate is used to create mirrors, zirconium silicate provides friction in automotive brakes, and many important cancer-fighting agents, like the drug cisplatin and related species, are platinum compounds.

Figure 6.1.1: Transition metals often form vibrantly colored complexes. The minerals malachite (green), azurite (blue), and proustite (red) are some examples. (credit left: modification of work by James St. John; credit middle: modification of work by Stephanie Clifford; credit right: modification of work by Terry Wallace)

The variety of properties exhibited by transition metals is due to their complex valence shells. Unlike most main group metals where one oxidation state is normally observed, the valence shell structure of transition metals means that they usually occur in several different stable oxidation states. In addition, electron transitions in these elements can correspond with absorption of photons in the visible electromagnetic spectrum, leading to colored compounds. Because of these behaviors, transition metals exhibit a rich and fascinating chemistry.

6.2: Occurrence, Preparation, and Properties of Transition Metals and Their Compounds

Transition metals are defined as those elements that have (or readily form) partially filled d orbitals. As shown in Figure 6.2.1, the d-block elements in groups 3–11 are transition elements. The f-block elements, also called *inner transition metals* (the lanthanides and actinides), also meet this criterion because the d orbital is partially occupied before the f orbitals. The d orbitals fill with the copper family (group 11); for this reason, the next family (group 12) are technically not transition elements. However, the group 12 elements do display some of the same chemical properties and are commonly included in discussions of transition metals. Some chemists do treat the group 12 elements as transition metals.
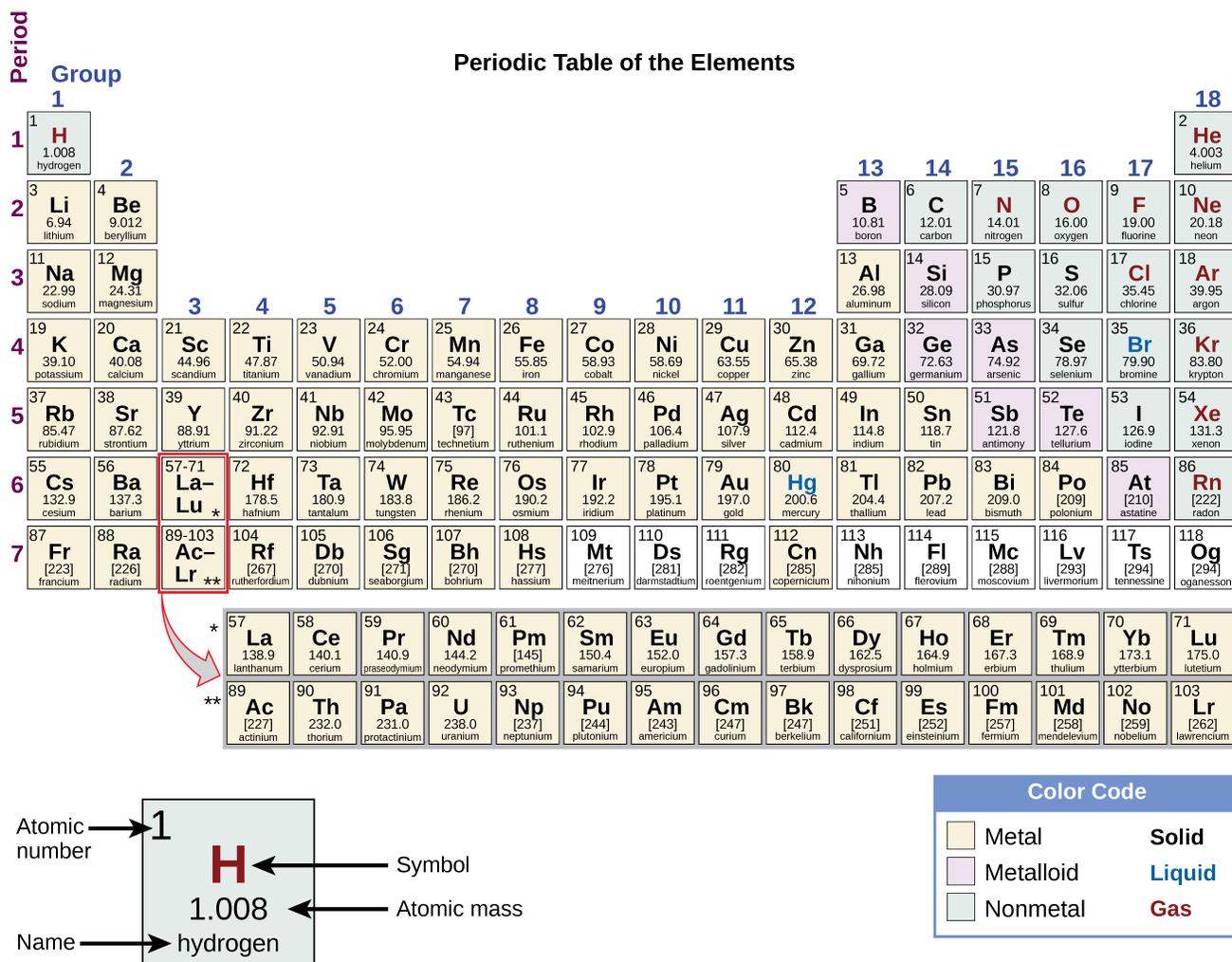
Figure 6.2.1: The transition metals are located in groups 3–11 of the periodic table. The inner transition metals are in the two rows below the body of the table.

The d-block elements are divided into the first transition series (the elements Sc through Cu), the second transition series (the elements Y through Ag), and the third transition series (the element La and the elements Hf through Au). Actinium, Ac, is the first member of the fourth transition series, which also includes Rf through Rg.

The f-block elements are the elements Ce through Lu, which constitute the lanthanide series (or lanthanoid series), and the elements Th through Lr, which constitute the actinide series (or actinoid series). Because lanthanum behaves very much like the lanthanide elements, it is considered a lanthanide element, even though its electron configuration makes it the first member of the third transition series. Similarly, the behavior of actinium means it is part of the actinide series, although its electron configuration makes it the first member of the fourth transition series.

✔ **Example 6.2.1: Valence Electrons in Transition Metals**

Review how to write electron configurations, covered in the chapter on electronic structure and periodic properties of elements. Recall that for the transition and inner transition metals, it is necessary to remove the *s* electrons before the *d* or *f* electrons. Then, for each ion, give the electron configuration:

a. cerium(III)
b. lead(II)
c. Ti^{2+}
d. Am^{3+}
e. Pd^{2+}

For the examples that are transition metals, determine to which series they belong.

Solution

For ions, the *s*-valence electrons are lost prior to the *d* or *f* electrons.

a. $Ce^{3+}[Xe]4f^1$; Ce^{3+} is an inner transition element in the lanthanide series.
b. $Pb^{2+}[Xe]6s^25d^{10}4f^{14}$; the electrons are lost from the *p* orbital. This is a main group element.
c. titanium(II) $[Ar]3d^2$; first transition series
d. americium(III) $[Rn]5f^6$; actinide
e. palladium(II) $[Kr]4d^8$; second transition series

? **Exercise 6.2.1**

Give an example of an ion from the first transition series with no *d* electrons.

Answer

V^{5+} is one possibility. Other examples include Sc^{3+}, Ti^{4+}, Cr^{6+}, and Mn^{7+}.

📌 **Chemistry in Everyday Life: Uses of Lanthanides in Devices**

Lanthanides (elements 57–71) are fairly abundant in the earth's crust, despite their historic characterization as rare earth elements. Thulium, the rarest naturally occurring lanthanoid, is more common in the earth's crust than silver (4.5×10^{-5} % versus 0.79×10^{-5} % by mass). There are 17 rare earth elements, consisting of the 15 lanthanoids plus scandium and yttrium. They are called rare because they were once difficult to extract economically, so it was rare to have a pure sample; due to similar chemical properties, it is difficult to separate any one lanthanide from the others. However, newer separation methods, such as ion exchange resins similar to those found in home water softeners, make the separation of these elements easier and more economical. Most ores that contain these elements have low concentrations of all the rare earth elements mixed together.

The commercial applications of lanthanides are growing rapidly. For example, europium is important in flat screen displays found in computer monitors, cell phones, and televisions. Neodymium is useful in laptop hard drives and in the processes that convert crude oil into gasoline (Figure 6.2.2). Holmium is found in dental and medical equipment. In addition, many alternative energy technologies rely heavily on lanthanoids. Neodymium and dysprosium are key components of hybrid vehicle engines and the magnets used in wind turbines.
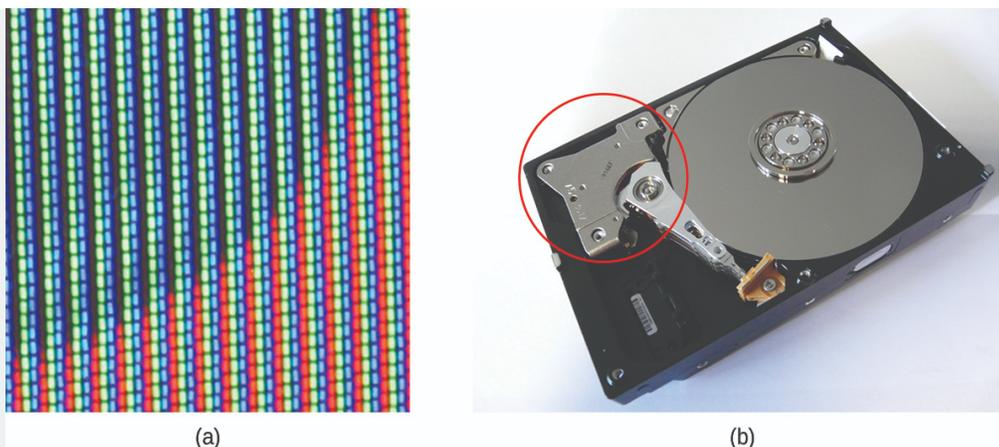
Figure 6.2.2: (a) Europium is used in display screens for televisions, computer monitors, and cell phones. (b) Neodymium magnets are commonly found in computer hard drives. (credit b: modification of work by "KUERT Datenrettung"/Flickr)

As the demand for lanthanide materials has increased faster than supply, prices have also increased. In 2008, dysprosium cost \$110/kg; by 2014, the price had increased to \$470/kg. Increasing the supply of lanthanoid elements is one of the most significant challenges facing the industries that rely on the optical and magnetic properties of these materials.

The transition elements have many properties in common with other metals. They are almost all hard, high-melting solids that conduct heat and electricity well. They readily form alloys and lose electrons to form stable cations. In addition, transition metals form a wide variety of stable **coordination compounds**, in which the central metal atom or ion acts as a Lewis acid and accepts one or more pairs of electrons. Many different molecules and ions can donate lone pairs to the metal center, serving as Lewis bases. In this chapter, we shall focus primarily on the chemical behavior of the elements of the first transition series.

Properties of the Transition Elements

Transition metals demonstrate a wide range of chemical behaviors. As can be seen from their reduction potentials (see Appendix H), some transition metals are strong reducing agents, whereas others have very low reactivity. For example, the lanthanides all form stable 3+ aqueous cations. The driving force for such oxidations is similar to that of alkaline earth metals such as Be or Mg, forming Be^{2+} and Mg^{2+}. On the other hand, materials like platinum and gold have much higher reduction potentials. Their ability to resist oxidation makes them useful materials for constructing circuits and jewelry.

Ions of the lighter d-block elements, such as Cr^{3+}, Fe^{3+}, and Co^{2+}, form colorful hydrated ions that are stable in water. However, ions in the period just below these (Mo^{3+}, Ru^{3+}, and Ir^{2+}) are unstable and react readily with oxygen from the air. The majority of simple, water-stable ions formed by the heavier d-block elements are oxyanions such as MoO_4^- and ReO_4^-.

Ruthenium, osmium, rhodium, iridium, palladium, and platinum are the **platinum metals**. With difficulty, they form simple cations that are stable in water, and, unlike the earlier elements in the second and third transition series, they do not form stable oxyanions.

Both the d- and f-block elements react with nonmetals to form binary compounds; heating is often required. These elements react with halogens to form a variety of halides ranging in oxidation state from 1+ to 6+. On heating, oxygen reacts with all of the transition elements except palladium, platinum, silver, and gold. The oxides of these latter metals can be formed using other reactants, but they decompose upon heating. The f-block elements, the elements of group 3, and the elements of the first transition series except copper react with aqueous solutions of acids, forming hydrogen gas and solutions of the corresponding salts.

Transition metals can form compounds with a wide range of oxidation states. Some of the observed oxidation states of the elements of the first transition series are shown in Figure 6.2.3. As we move from left to right across the first transition series, we see that the number of common oxidation states increases at first to a maximum towards the middle of the table, then decreases. The values in the table are typical values; there are other known values, and it is possible to synthesize new additions. For example, in 2014, researchers were successful in synthesizing a new oxidation state of iridium (9+).

21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
								1+	
		2+	2+	2+	2+	2+	2+	2+	2+
3+	3+	3+	3+	3+	3+	3+	3+	3+	
	4+	4+	4+	4+					
		5+							
			6+	6+	6+				
				7+					

Figure 6.2.3: Transition metals of the first transition series can form compounds with varying oxidation states.

For the elements scandium through manganese (the first half of the first transition series), the highest oxidation state corresponds to the loss of all of the electrons in both the *s* and *d* orbitals of their valence shells. The titanium(IV) ion, for example, is formed when the titanium atom loses its two 3*d* and two 4*s* electrons. These highest oxidation states are the most stable forms of scandium, titanium, and vanadium. However, it is not possible to continue to remove all of the valence electrons from metals as we continue through the series. Iron is known to form oxidation states from 2+ to 6+, with iron(II) and iron(III) being the most common. Most of the elements of the first transition series form ions with a charge of 2+ or 3+ that are stable in water, although those of the early members of the series can be readily oxidized by air.

The elements of the second and third transition series generally are more stable in higher oxidation states than are the elements of the first series. In general, the atomic radius increases down a group, which leads to the ions of the second and third series being larger than are those in the first series. Removing electrons from orbitals that are located farther from the nucleus is easier than removing electrons close to the nucleus. For example, molybdenum and tungsten, members of group 6, are limited mostly to an oxidation state of 6+ in aqueous solution. Chromium, the lightest member of the group, forms stable Cr^{3+} ions in water and, in the absence of air, less stable Cr^{2+} ions. The sulfide with the highest oxidation state for chromium is Cr_2S_3, which contains the Cr^{3+} ion. Molybdenum and tungsten form sulfides in which the metals exhibit oxidation states of 4+ and 6+.

✔ **Example 6.2.2: Activity of the Transition Metals**

Which is the strongest oxidizing agent in acidic solution: dichromate ion, which contains chromium(VI), permanganate ion, which contains manganese(VII), or titanium dioxide, which contains titanium(IV)?

Solution

First, we need to look up the reduction half reactions (in Appendix L) for each oxide in the specified oxidation state:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \quad +1.33V$$
$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + H_2O \quad +1.51V$$
$$TiO_2 + 4H^+ + 2e^- \longrightarrow Ti^{2+} + 2H_2O \quad -0.50V$$
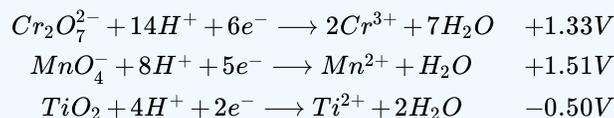
A larger reduction potential means that it is easier to reduce the reactant. Permanganate, with the largest reduction potential, is the strongest oxidizer under these conditions. Dichromate is next, followed by titanium dioxide as the weakest oxidizing agent (the hardest to reduce) of this set.

? **Exercise 6.2.2**

Predict what reaction (if any) will occur between HCl and Co(*s*), and between HBr and Pt(*s*). You will need to use the standard reduction potentials from Appendix L.

Answer

$$Co(s) + 2\,HCl \longrightarrow H_2 + CoCl_2\,(aq)$$

no reaction because Pt(*s*) will not be oxidized by H^+

Preparation of the Transition Elements

Ancient civilizations knew about iron, copper, silver, and gold. The time periods in human history known as the Bronze Age and Iron Age mark the advancements in which societies learned to isolate certain metals and use them to make tools and goods.

Naturally occurring ores of copper, silver, and gold can contain high concentrations of these metals in elemental form (Figure 6.2.4). Iron, on the other hand, occurs on earth almost exclusively in oxidized forms, such as rust (Fe_2O_3). The earliest known iron implements were made from iron meteorites. Surviving iron artifacts dating from approximately 4000 to 2500 BC are rare, but all known examples contain specific alloys of iron and nickel that occur only in extraterrestrial objects, not on earth. It took thousands of years of technological advances before civilizations developed iron **smelting**, the ability to extract a pure element from its naturally occurring ores and for iron tools to become common.
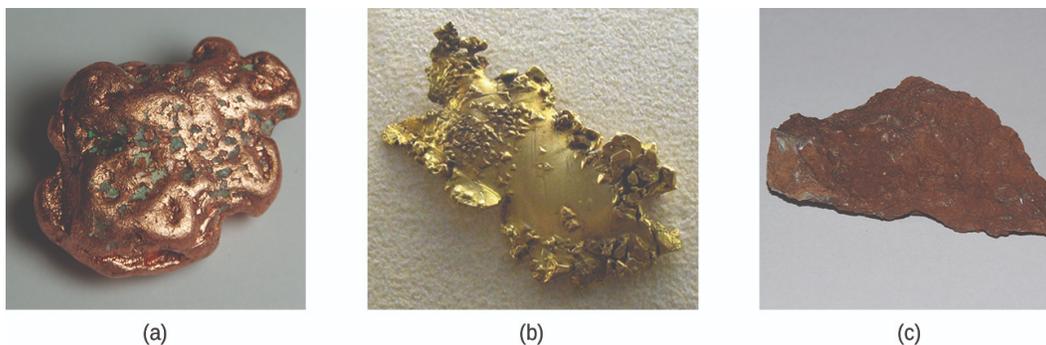
Figure 6.2.4: Transition metals occur in nature in various forms. Examples include (a) a nugget of copper, (b) a deposit of gold, and (c) an ore containing oxidized iron. (credit a: modification of work by http://images-of-elements.com/copper-2.jpg; credit c: modification of work by http://images-of-elements.com/iron-ore.jpg)

Generally, the transition elements are extracted from minerals found in a variety of ores. However, the ease of their recovery varies widely, depending on the concentration of the element in the ore, the identity of the other elements present, and the difficulty of reducing the element to the free metal.

In general, it is not difficult to reduce ions of the *d*-block elements to the free element. Carbon is a sufficiently strong reducing agent in most cases. However, like the ions of the more active main group metals, ions of the *f*-block elements must be isolated by electrolysis or by reduction with an active metal such as calcium.

We shall discuss the processes used for the isolation of iron, copper, and silver because these three processes illustrate the principal means of isolating most of the *d*-block metals. In general, each of these processes involves three principal steps: preliminary treatment, smelting, and refining.

1. Preliminary treatment. In general, there is an initial treatment of the ores to make them suitable for the extraction of the metals. This usually involves crushing or grinding the ore, concentrating the metal-bearing components, and sometimes treating these substances chemically to convert them into compounds that are easier to reduce to the metal.
2. Smelting. The next step is the extraction of the metal in the molten state, a process called smelting, which includes reduction of the metallic compound to the metal. Impurities may be removed by the addition of a compound that forms a slag—a substance with a low melting point that can be readily separated from the molten metal.
3. Refining. The final step in the recovery of a metal is refining the metal. Low boiling metals such as zinc and mercury can be refined by distillation. When fused on an inclined table, low melting metals like tin flow away from higher-melting impurities. Electrolysis is another common method for refining metals.

Isolation of Iron

The early application of iron to the manufacture of tools and weapons was possible because of the wide distribution of iron ores and the ease with which iron compounds in the ores could be reduced by carbon. For a long time, charcoal was the form of carbon used in the reduction process. The production and use of iron became much more widespread about 1620, when coke was introduced as the reducing agent. Coke is a form of carbon formed by heating coal in the absence of air to remove impurities.

The first step in the metallurgy of iron is usually roasting the ore (heating the ore in air) to remove water, decomposing carbonates into oxides, and converting sulfides into oxides. The oxides are then reduced in a blast furnace that is 80–100 feet high and about 25 feet in diameter (Figure 6.2.5) in which the roasted ore, coke, and limestone (impure $CaCO_3$) are introduced continuously into the top. Molten iron and slag are withdrawn at the bottom. The entire stock in a furnace may weigh several hundred tons.
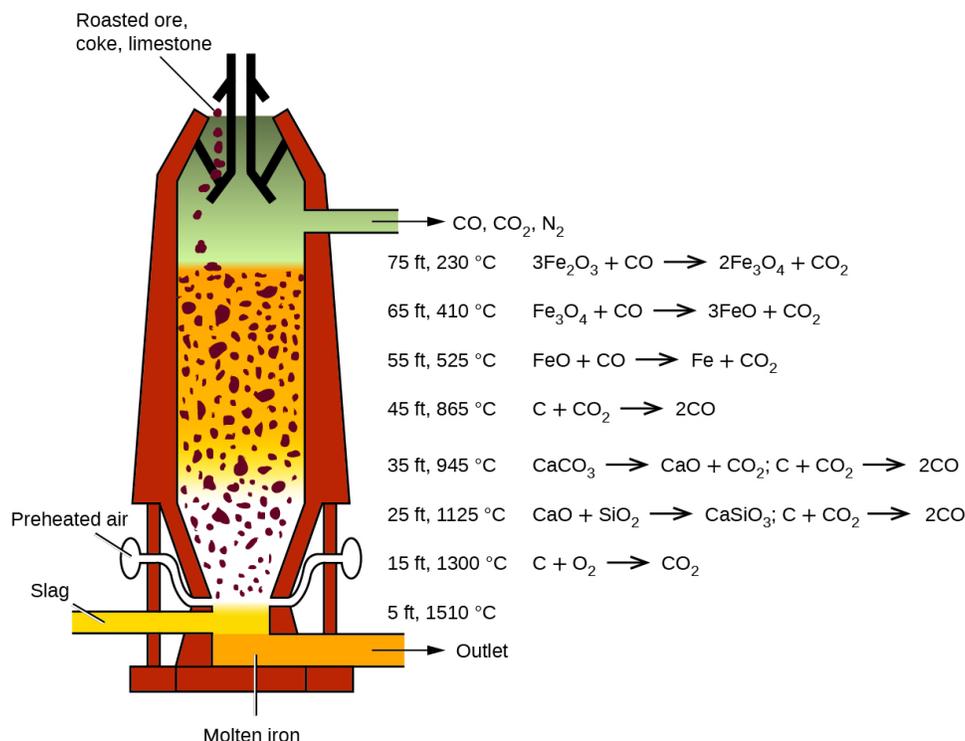
Figure 6.2.5: Within a blast furnace, different reactions occur in different temperature zones. Carbon monoxide is generated in the hotter bottom regions and rises upward to reduce the iron oxides to pure iron through a series of reactions that take place in the upper regions.

Near the bottom of a furnace are nozzles through which preheated air is blown into the furnace. As soon as the air enters, the coke in the region of the nozzles is oxidized to carbon dioxide with the liberation of a great deal of heat. The hot carbon dioxide passes upward through the overlying layer of white-hot coke, where it is reduced to carbon monoxide:

$$CO_2(g) + C(s) \longrightarrow 2\,CO(g)$$
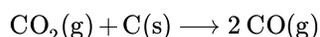
The carbon monoxide serves as the reducing agent in the upper regions of the furnace. The individual reactions are indicated in Figure 6.2.5.

The iron oxides are reduced in the upper region of the furnace. In the middle region, limestone (calcium carbonate) decomposes, and the resulting calcium oxide combines with silica and silicates in the ore to form slag. The slag is mostly calcium silicate and contains most of the commercially unimportant components of the ore:

$$CaO(s) + SiO_2(s) \longrightarrow CaSiO_3(l)$$
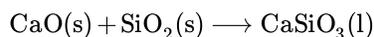
Just below the middle of the furnace, the temperature is high enough to melt both the iron and the slag. They collect in layers at the bottom of the furnace; the less dense slag floats on the iron and protects it from oxidation. Several times a day, the slag and molten iron are withdrawn from the furnace. The iron is transferred to casting machines or to a steelmaking plant (Figure 6.2.6).

Figure 6.2.6: Molten iron is shown being cast as steel. (credit: Clint Budd)

Much of the iron produced is refined and converted into steel. **Steel** is made from iron by removing impurities and adding substances such as manganese, chromium, nickel, tungsten, molybdenum, and vanadium to produce alloys with properties that make the material suitable for specific uses. Most steels also contain small but definite percentages of carbon (0.04%–2.5%). However, a large part of the carbon contained in iron must be removed in the manufacture of steel; otherwise, the excess carbon would make the iron brittle.

> ⏻ Link to Learning
>
> You can watch an animation of steelmaking that walks you through the process.

Isolation of Copper

The most important ores of copper contain copper sulfides (such as covellite, CuS), although copper oxides (such as tenorite, CuO) and copper hydroxycarbonates [such as malachite, $Cu_2(OH)_2CO_3$] are sometimes found. In the production of copper metal, the concentrated sulfide ore is roasted to remove part of the sulfur as sulfur dioxide. The remaining mixture, which consists of Cu_2S, FeS, FeO, and SiO_2, is mixed with limestone, which serves as a flux (a material that aids in the removal of impurities), and heated. Molten slag forms as the iron and silica are removed by Lewis acid-base reactions:

$$CaCO_3(s) + SiO_2(s) \longrightarrow CaSiO_3(l) + CO_2(g)$$
$$FeO(s) + SiO_2(s) \longrightarrow FeSiO_3(l)$$
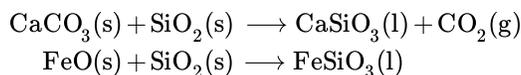
In these reactions, the silicon dioxide behaves as a Lewis acid, which accepts a pair of electrons from the Lewis base (the oxide ion).

Reduction of the Cu_2S that remains after smelting is accomplished by blowing air through the molten material. The air converts part of the Cu_2S into Cu_2O. As soon as copper(I) oxide is formed, it is reduced by the remaining copper(I) sulfide to metallic copper:

$$2\,Cu_2S(l) + 3\,O_2(g) \longrightarrow 2\,Cu_2O(l) + 2\,SO_2(g)$$
$$2\,Cu_2O(l) + Cu_2S(l) \longrightarrow 6\,Cu(l) + SO_2(g)$$
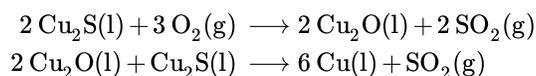
The copper obtained in this way is called blister copper because of its characteristic appearance, which is due to the air blisters it contains (Figure 6.2.7). This impure copper is cast into large plates, which are used as anodes in the electrolytic refining of the metal (which is described in the chapter on electrochemistry).

Figure 6.2.7: Blister copper is obtained during the conversion of copper-containing ore into pure copper. (credit: "Tortie tude"/Wikimedia Commons)

Isolation of Silver

Silver sometimes occurs in large nuggets (Figure 6.2.8) but more frequently in veins and related deposits. At one time, panning was an effective method of isolating both silver and gold nuggets. Due to their low reactivity, these metals, and a few others, occur in deposits as nuggets. The discovery of platinum was due to Spanish explorers in Central America mistaking platinum nuggets for silver. When the metal is not in the form of nuggets, it often useful to employ a process called **hydrometallurgy** to separate silver from its ores. Hydrology involves the separation of a metal from a mixture by first converting it into soluble ions and then extracting and reducing them to precipitate the pure metal. In the presence of air, alkali metal cyanides readily form the soluble dicyanoargentate(I) ion, from silver metal or silver-containing compounds such as Ag_2S and $AgCl$. Representative equations are:

$$
\begin{align*}
&\ce{4 Ag(s) + 8 CN^{-}(aq) + O2(g) + 2 H2O (l) \longrightarrow 4\left[Ag(CN)2 \right]^{-}(aq) + 4 OH^{-}(aq)} \\
&\ce{2 Ag2S(s) + 8 CN^{-}(aq) + O2(g) + 2 H2O(l) \longrightarrow 4\left[Ag(CN)2 \right]^{-}(aq) + 2 S(s) + 4 OH^{-}(aq)} \\
&\ce{AgCl(s) + 2 CN^{-}(aq) \longrightarrow \left[Ag(CN)2 \right]^{-}(aq) + Cl^{-}(aq)}
\end{align*}
$$
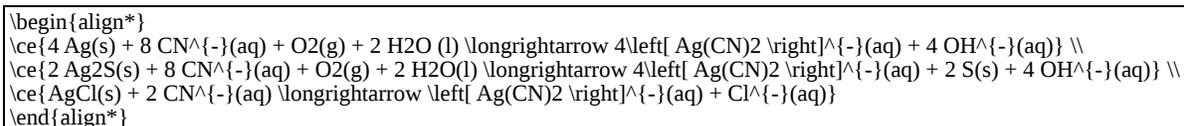
(a)

(b)

Figure 6.2.8: Naturally occurring free silver may be found as nuggets (a) or in veins (b). (credit a: modification of work by "Teravolt"/Wikimedia Commons; credit b: modification of work by James St. John)

The silver is precipitated from the cyanide solution by the addition of either zinc or iron(II) ions, which serves as the reducing agent:

$$
\ce{ 2\left[Ag(CN)2\right]^{-}(aq) + Zn(s) \longrightarrow 2 Ag(s) + \left[Zn(CN)4\right]^{2-}(aq)}
$$
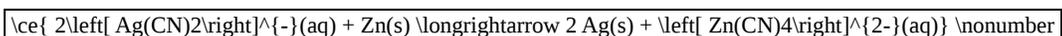
> ✔ **Example 6.2.3: Refining Redox**
>
> One of the steps for refining silver involves converting silver into dicyanoargenate(I) ions:
>
> $$\ce{4 Ag(s) + 8 CN^{-}(aq) + O_2(g) + 2 H_2O(l) \longrightarrow 4 \left[Ag(CN)2 \right]^{-}(aq) + 4 OH^{-}(aq)} \nonumber$$
>
> Explain why oxygen must be present to carry out the reaction. Why does the reaction not occur as:
>
> $$\ce{4 Ag(s) + 8 CN^{-}(aq) \longrightarrow 4\left[Ag(CN)2\right]^{-}(aq)} ? \nonumber$$
>
> **Solution**
>
> The charges, as well as the atoms, must balance in reactions. The silver atom is being oxidized from the 0 oxidation state to the 1+ state. Whenever something loses electrons, something must also gain electrons (be reduced) to balance the equation. Oxygen is a good oxidizing agent for these reactions because it can gain electrons to go from the 0 oxidation state to the 2− state.

> ❓ **Exercise 6.2.3**
>
> During the refining of iron, carbon must be present in the blast furnace. Why is carbon necessary to convert iron oxide into iron?
>
> **Answer**
>
> The carbon is converted into CO, which is the reducing agent that accepts electrons so that iron(III) can be reduced to iron(0).

Transition Metal Compounds

The bonding in the simple compounds of the transition elements ranges from ionic to covalent. In their lower oxidation states, the transition elements form ionic compounds; in their higher oxidation states, they form covalent compounds or polyatomic ions. The variation in oxidation states exhibited by the transition elements gives these compounds a metal-based, oxidation-reduction chemistry. The chemistry of several classes of compounds containing elements of the transition series follows.

Halides

Anhydrous halides of each of the transition elements can be prepared by the direct reaction of the metal with halogens. For example:

$$2\,\mathrm{Fe(s)} + 3\,\mathrm{Cl_2(g)} \longrightarrow 2\,\mathrm{FeCl_3(s)}$$
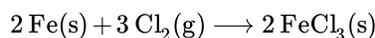
Heating a metal halide with additional metal can be used to form a halide of the metal with a lower oxidation state:

$$\mathrm{Fe(s)} + 2\,\mathrm{FeCl_3(s)} \longrightarrow 3\,\mathrm{FeCl_2(s)}$$
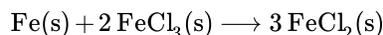
The stoichiometry of the metal halide that results from the reaction of the metal with a halogen is determined by the relative amounts of metal and halogen and by the strength of the halogen as an oxidizing agent. Generally, fluorine forms fluoride-containing metals in their highest oxidation states. The other halogens may not form analogous compounds.

In general, the preparation of stable water solutions of the halides of the metals of the first transition series is by the addition of a hydrohalic acid to carbonates, hydroxides, oxides, or other compounds that contain basic anions. Sample reactions are:

$$\mathrm{NiCO_3(s)} + 2\,\mathrm{HF(aq)} \longrightarrow \mathrm{NiF_2(aq)} + \mathrm{H_2O(l)} + \mathrm{CO_2(g)}$$
$$\mathrm{Co(OH)_2(s)} + 2\,\mathrm{HBr(aq)} \longrightarrow \mathrm{CoBr_2(aq)} + 2\,\mathrm{H_2O(l)}$$
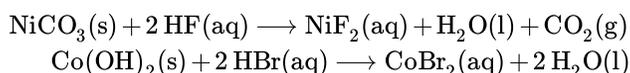
Most of the first transition series metals also dissolve in acids, forming a solution of the salt and hydrogen gas. For example:

$$\mathrm{Cr(s)} + 2\,\mathrm{HCl(aq)} \longrightarrow \mathrm{CrCl_2(aq)} + \mathrm{H_2(g)}$$
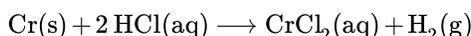
The polarity of bonds with transition metals varies based not only upon the electronegativities of the atoms involved but also upon the oxidation state of the transition metal. Remember that bond polarity is a continuous spectrum with electrons being shared evenly (covalent bonds) at one extreme and electrons being transferred completely (ionic bonds) at the other. No bond is ever 100%

ionic, and the degree to which the electrons are evenly distributed determines many properties of the compound. Transition metal halides with low oxidation numbers form more ionic bonds. For example, titanium(II) chloride and titanium(III) chloride ($TiCl_2$ and $TiCl_3$) have high melting points that are characteristic of ionic compounds, but titanium(IV) chloride ($TiCl_4$) is a volatile liquid, consistent with having covalent titanium-chlorine bonds. All halides of the heavier *d*-block elements have significant covalent characteristics.

The covalent behavior of the transition metals with higher oxidation states is exemplified by the reaction of the metal tetrahalides with water. Like covalent silicon tetrachloride, both the titanium and vanadium tetrahalides react with water to give solutions containing the corresponding hydrohalic acids and the metal oxides:

$$SiCl_4(l) + 2\,H_2O(l) \longrightarrow SiO_2(s) + 4\,HCl(aq)$$
$$TiCl_4(l) + 2\,H_2O(l) \longrightarrow TiO_2(s) + 4\,HCl(aq)$$
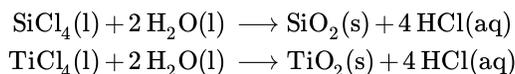
Oxides

As with the halides, the nature of bonding in oxides of the transition elements is determined by the oxidation state of the metal. Oxides with low oxidation states tend to be more ionic, whereas those with higher oxidation states are more covalent. These variations in bonding are because the electronegativities of the elements are not fixed values. The electronegativity of an element increases with increasing oxidation state. Transition metals in low oxidation states have lower electronegativity values than oxygen; therefore, these metal oxides are ionic. Transition metals in very high oxidation states have electronegativity values close to that of oxygen, which leads to these oxides being covalent.

The oxides of the first transition series can be prepared by heating the metals in air. These oxides are Sc_2O_3, TiO_2, V_2O_5, Cr_2O_3, Mn_3O_4, Fe_3O_4, Co_3O_4, NiO, and CuO.

Alternatively, these oxides and other oxides (with the metals in different oxidation states) can be produced by heating the corresponding hydroxides, carbonates, or oxalates in an inert atmosphere. Iron(II) oxide can be prepared by heating iron(II) oxalate, and cobalt(II) oxide is produced by heating cobalt(II) hydroxide:

$$FeC_2O_4(s) \longrightarrow FeO(s) + CO(g) + CO_2(g)$$
$$Co(OH)_2(s) \longrightarrow CoO(s) + H_2O(g)$$
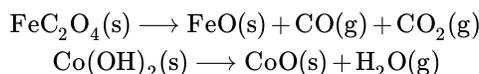
With the exception of CrO_3 and Mn_2O_7, transition metal oxides are not soluble in water. They can react with acids and, in a few cases, with bases. Overall, oxides of transition metals with the lowest oxidation states are basic (and react with acids), the intermediate ones are amphoteric, and the highest oxidation states are primarily acidic. Basic metal oxides at a low oxidation state react with aqueous acids to form solutions of salts and water. Examples include the reaction of cobalt(II) oxide accepting protons from nitric acid, and scandium(III) oxide accepting protons from hydrochloric acid:

$$\begin{align*}
CoO(s) + 2\,HNO_3(aq) &\longrightarrow Co(NO_3)_2(aq) + H_2O(l) \\
Sc_2O_3(s) + 6\,HCl(aq) &\longrightarrow 2\,ScCl_3(aq) + 3\,H_2O(l)
\end{align*}$$
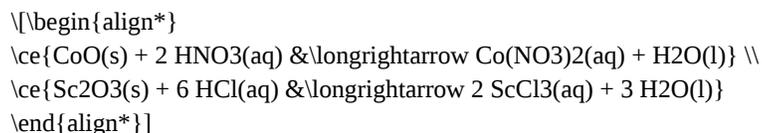
The oxides of metals with oxidation states of 4+ are amphoteric, and most are not soluble in either acids or bases. Vanadium(V) oxide, chromium(VI) oxide, and manganese(VII) oxide are acidic. They react with solutions of hydroxides to form salts of the oxyanions and VO_4^{3-}, CrO_4^{2-}, and MnO_4-. For example, the complete ionic equation for the reaction of chromium(VI) oxide with a strong base is given by:

$$CrO_3(s) + 2\,Na^+(aq) + 2\,OH^-(aq) \longrightarrow 2\,Na^+(aq) + CrO_4^{2-}(aq) + H_2O(l)$$

Chromium(VI) oxide and manganese(VII) oxide react with water to form the acids H_2CrO_4 and $HMnO_4$, respectively.

Hydroxides

When a soluble hydroxide is added to an aqueous solution of a salt of a transition metal of the first transition series, a gelatinous precipitate forms. For example, adding a solution of sodium hydroxide to a solution of cobalt sulfate produces a gelatinous pink or blue precipitate of cobalt(II) hydroxide. The net ionic equation is:

$$Co^{2+}(aq) + 2OH^-(aq) \longrightarrow Co(OH)_2(s)$$
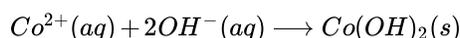
In this and many other cases, these precipitates are hydroxides containing the transition metal ion, hydroxide ions, and water coordinated to the transition metal. In other cases, the precipitates are hydrated oxides composed of the metal ion, oxide ions, and water of hydration:

$$4Fe^{3+}(aq) + 6OH^-(aq) + nH_2O(l) \longrightarrow 2Fe_2O_3 \cdot (n+3)H_2O(s)$$
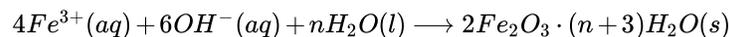
These substances do not contain hydroxide ions. However, both the hydroxides and the hydrated oxides react with acids to form salts and water. When precipitating a metal from solution, it is necessary to avoid an excess of hydroxide ion, as this may lead to complex ion formation as discussed later in this chapter. The precipitated metal hydroxides can be separated for further processing or for waste disposal.

Carbonates

Many of the elements of the first transition series form insoluble carbonates. It is possible to prepare these carbonates by the addition of a soluble carbonate salt to a solution of a transition metal salt. For example, nickel carbonate can be prepared from solutions of nickel nitrate and sodium carbonate according to the following net ionic equation:

$$Ni^{2+}(aq) + CO_3{}^{2-} \longrightarrow NiCO_3(s)$$
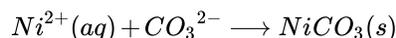
The reactions of the transition metal carbonates are similar to those of the active metal carbonates. They react with acids to form metals salts, carbon dioxide, and water. Upon heating, they decompose, forming the transition metal oxides.

Other Salts

In many respects, the chemical behavior of the elements of the first transition series is very similar to that of the main group metals. In particular, the same types of reactions that are used to prepare salts of the main group metals can be used to prepare simple ionic salts of these elements.

A variety of salts can be prepared from metals that are more active than hydrogen by reaction with the corresponding acids: Scandium metal reacts with hydrobromic acid to form a solution of scandium bromide:

$$2Sc(s) + 6HBr(aq) \longrightarrow 2ScBr_3(aq) + 3H_2(g)$$
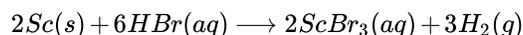
The common compounds that we have just discussed can also be used to prepare salts. The reactions involved include the reactions of oxides, hydroxides, or carbonates with acids. For example:

$$Ni(OH)_2(s) + 2H_3O^+(aq) + 2ClO_4^-(aq) \longrightarrow Ni^{2+}(aq) + 2ClO_4^-(aq) + 4H_2O(l)$$
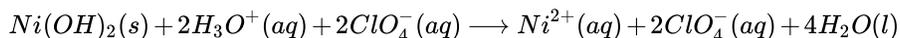
Substitution reactions involving soluble salts may be used to prepare insoluble salts. For example:

$$Ba^{2+}(aq) + 2Cl^-(aq) + 2K^+(aq) + CrO_4^{2-}(aq) \longrightarrow BaCrO_4(s) + 2K^+(aq) + 2Cl^-(aq)$$
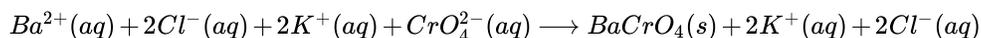
In our discussion of oxides in this section, we have seen that reactions of the covalent oxides of the transition elements with hydroxides form salts that contain oxyanions of the transition elements.

⚑ How Sciences Interconnect: High Temperature Superconductors

A **superconductor** is a substance that conducts electricity with no resistance. This lack of resistance means that there is no energy loss during the transmission of electricity. This would lead to a significant reduction in the cost of electricity.

Most currently used, commercial superconducting materials, such as NbTi and Nb_3Sn, do not become superconducting until they are cooled below 23 K (-250 °C). This requires the use of liquid helium, which has a boiling temperature of 4 K and is expensive and difficult to handle. The cost of liquid helium has deterred the widespread application of superconductors.

One of the most exciting scientific discoveries of the 1980s was the characterization of compounds that exhibit superconductivity at temperatures above 90 K. (Compared to liquid helium, 90 K is a high temperature.) Typical among the high-temperature superconducting materials are oxides containing yttrium (or one of several rare earth elements), barium, and copper in a 1:2:3 ratio. The formula of the ionic yttrium compound is $YBa_2Cu_3O_7$.

The new materials become superconducting at temperatures close to 90 K (Figure 6.2.9), temperatures that can be reached by cooling with liquid nitrogen (boiling temperature of 77 K). Not only are liquid nitrogen-cooled materials easier to handle, but the cooling costs are also about 1000 times lower than for liquid helium.

Further advances during the same period included materials that became superconducting at even higher temperatures and with a wider array of materials. The DuPont team led by Uma Chowdry and Arthur Sleight identified Bismouth-Strontium-Copper-Oxides that became superconducting at temperatures as high as 110 K and, importantly, did not contain rare earth elements. Advances continued through the subsequent decades until, in 2020, a team led by Ranga Dias at University of Rochester announced the development of a room-temperature superconductor, opening doors to widespread applications. More research and development is needed to realize the potential of these materials, but the possibilities are very promising.
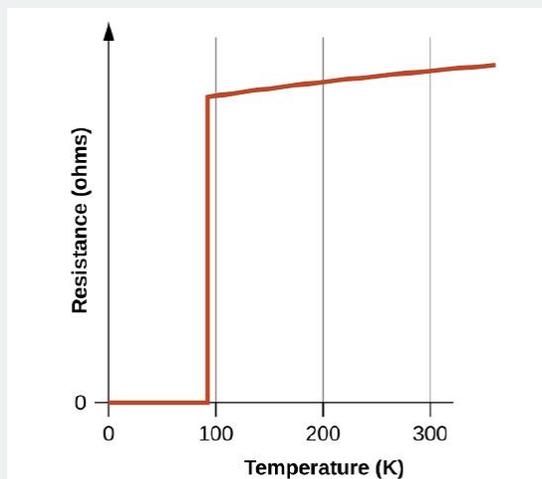
Figure 6.2.9: The resistance of the high-temperature superconductor $YBa_2Cu_3O_7$ varies with temperature. Note how the resistance falls to zero below 92 K, when the substance becomes superconducting.

Although the brittle, fragile nature of these materials presently hampers their commercial applications, they have tremendous potential that researchers are hard at work improving their processes to help realize. Superconducting transmission lines would carry current for hundreds of miles with no loss of power due to resistance in the wires. This could allow generating stations to be located in areas remote from population centers and near the natural resources necessary for power production. The first project demonstrating the viability of high-temperature superconductor power transmission was established in New York in 2008.

Researchers are also working on using this technology to develop other applications, such as smaller and more powerful microchips. In addition, high-temperature superconductors can be used to generate magnetic fields for applications such as medical devices, magnetic levitation trains, and containment fields for nuclear fusion reactors (Figure 6.2.10).

(a)   (b)

Figure 6.2.10: (a) This magnetic levitation train (or maglev) uses superconductor technology to move along its tracks. (b) A magnet can be levitated using a dish like this as a superconductor. (credit a: modification of work by Alex Needham; credit b: modification of work by Kevin Jarrett)

📌 Link to Learning

Watch how a high-temperature superconductor levitates around a magnetic racetrack in the video.

- **19.1: Occurrence, Preparation, and Properties of Transition Metals and Their Compounds** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

6.3: Coordination Chemistry of Transition Metals

> **◑ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - List the defining traits of coordination compounds
> - Describe the structures of complexes containing monodentate and polydentate ligands
> - Use standard nomenclature rules to name coordination compounds
> - Explain and provide examples of geometric and optical isomerism
> - Identify several natural and technological occurrences of coordination compounds

The hemoglobin in your blood, the chlorophyll in green plants, vitamin B-12, and the catalyst used in the manufacture of polyethylene all contain coordination compounds. Ions of the metals, especially the transition metals, are likely to form complexes. Many of these compounds are highly colored (Figure 6.3.1). In the remainder of this chapter, we will consider the structure and bonding of these remarkable compounds.

Figure 6.3.1: Metal ions that contain partially filled d subshell usually form colored complex ions; ions with empty d subshell (d^0) or with filled d subshells (d^{10}) usually form colorless complexes. This figure shows, from left to right, solutions containing $[M(H_2O)_6]^{n+}$ ions with $M = Sc^{3+}(d^0)$, $Cr^{3+}(d^3)$, $Co^{2+}(d^7)$, $Ni^{2+}(d^8)$, $Cu^{2+}(d^9)$, and $Zn^{2+}(d^{10})$. (credit: Sahar Atwa)

Remember that in most main group element compounds, the valence electrons of the isolated atoms combine to form chemical bonds that satisfy the octet rule. For instance, the four valence electrons of carbon overlap with electrons from four hydrogen atoms to form CH_4. The one valence electron leaves sodium and adds to the seven valence electrons of chlorine to form the ionic formula unit NaCl (Figure 6.3.2). Transition metals do not normally bond in this fashion. They primarily form coordinate covalent bonds, a form of the Lewis acid-base interaction in which both of the electrons in the bond are contributed by a donor (Lewis base) to an electron acceptor (Lewis acid). The Lewis acid in coordination complexes, often called a **central metal** ion (or atom), is often a transition metal or inner transition metal, although main group elements can also form **coordination compounds**. The Lewis base donors, called **ligands**, can be a wide variety of chemicals—atoms, molecules, or ions. The only requirement is that they have one or more electron pairs, which can be donated to the central metal. Most often, this involves a **donor atom** with a lone pair of electrons that can form a coordinate bond to the metal.
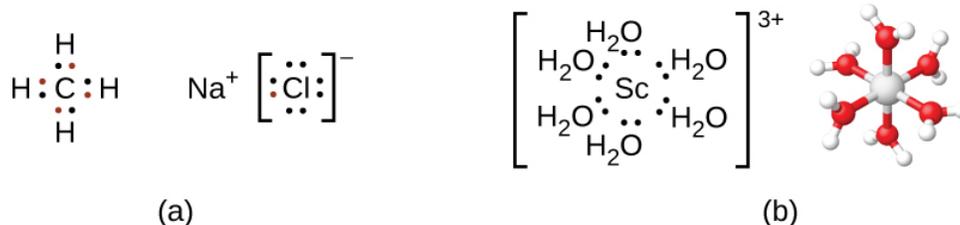
Figure 6.3.2: (a) Covalent bonds involve the sharing of electrons, and ionic bonds involve the transferring of electrons associated with each bonding atom, as indicated by the colored electrons. (b) However, coordinate covalent bonds involve electrons from a Lewis base being donated to a metal center. The lone pairs from six water molecules form bonds to the scandium ion to form an octahedral complex. (Only the donated pairs are shown.)

6.3.1

https://chem.libretexts.org/@go/page/478751

The coordination sphere consists of the central metal ion or atom plus its attached ligands. Brackets in a formula enclose the coordination sphere; species outside the brackets are not part of the coordination sphere. The coordination number of the central metal ion or atom is the number of donor atoms bonded to it. The coordination number for the silver ion in $[Ag(NH_3)_2]^+$ is two (Figure 6.3.3). For the copper(II) ion in $[CuCl_4]^{2-}$, the coordination number is four, whereas for the cobalt(II) ion in $[Co(H_2O)_6]^{2+}$ the coordination number is six. Each of these ligands is monodentate, from the Greek for "one toothed," meaning that they connect with the central metal through only one atom. In this case, the number of ligands and the coordination number are equal.
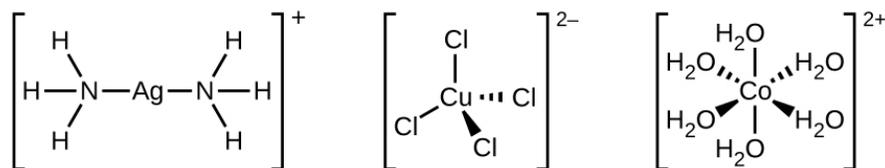
Figure 6.3.3: The complexes (a) $[Ag(NH_3)_2]^+$, (b) $[Cu(Cl)_4]^{2-}$, and (c) $[Co(H_2O)_6]^{2+}$ have coordination numbers of two, four, and six, respectively. The geometries of these complexes are the same as we have seen with VSEPR theory for main group elements: linear, tetrahedral, and octahedral.

Many other ligands coordinate to the metal in more complex fashions. **Bidentate ligands** are those in which two atoms coordinate to the metal center. For example, ethylenediamine (en, $H_2NCH_2CH_2NH_2$) contains two nitrogen atoms, each of which has a lone pair and can serve as a Lewis base (Figure 6.3.4). Both of the atoms can coordinate to a single metal center. In the complex $[Co(en)_3]^{3+}$, there are three bidentate en ligands, and the coordination number of the cobalt(III) ion is six. The most common coordination numbers are two, four, and six, but examples of all coordination numbers from 1 to 15 are known.
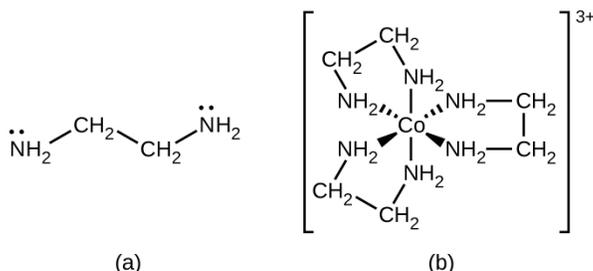
Figure 6.3.4: (a) The ethylenediamine (en) ligand contains two atoms with lone pairs that can coordinate to the metal center. (b) The cobalt(III) complex contains three of these ligands, each forming two bonds to the cobalt ion.

Any ligand that bonds to a central metal ion by more than one donor atom is a **polydentate ligand** (or "many teeth") because it can bite into the metal center with more than one bond. The term **chelate** (pronounced "KEY-late") from the Greek for "claw" is also used to describe this type of interaction. Many polydentate ligands are chelating ligands, and a complex consisting of one or more of these ligands and a central metal is a chelate. A **chelating ligand** is also known as a chelating agent. A chelating ligand holds the metal ion rather like a crab's claw would hold a marble. Figure 6.3.4 showed one example of a chelate. The heme complex in hemoglobin is another important example (Figure 6.3.5). It contains a polydentate ligand with four donor atoms that coordinate to iron.
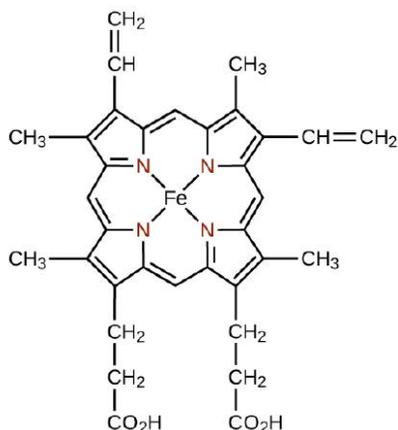
Figure 6.3.5: The single ligand heme contains four nitrogen atoms that coordinate to iron in hemoglobin to form a chelate.

Polydentate ligands are sometimes identified with prefixes that indicate the number of donor atoms in the ligand. As we have seen, ligands with one donor atom, such as NH_3, Cl^-, and H_2O, are monodentate ligands. Ligands with two donor groups are bidentate ligands. Ethylenediamine, $\ce{H2NCH2CH2NH2}$, and the anion of the acid glycine, $NH_2CH_2CO_2^-$ (Figure 6.3.6) are examples of bidentate ligands. Tridentate ligands, tetradentate ligands, pentadentate ligands, and hexadentate ligands contain three, four, five, and six donor atoms, respectively. The ligand in heme (Figure 6.3.5) is a tetradentate ligand.
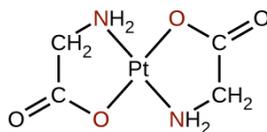
Figure 6.3.6: Each of the anionic ligands shown attaches in a bidentate fashion to platinum(II), with both a nitrogen and oxygen atom coordinating to the metal.

The Naming of Complexes

The nomenclature of the complexes is patterned after a system suggested by Alfred Werner, a Swiss chemist and Nobel laureate, whose outstanding work more than 100 years ago laid the foundation for a clearer understanding of these compounds. The following five rules are used for naming complexes:

1. If a coordination compound is ionic, name the cation first and the anion second, in accordance with the usual nomenclature.
2. Name the ligands first, followed by the central metal. Name the ligands alphabetically. Negative ligands (anions) have names formed by adding -o to the stem name of the group. For examples, see Table 6.3.1. For most neutral ligands, the name of the molecule is used. The four common exceptions are *aqua* (H_2O), *ammine* (NH_3), *carbonyl* (CO), and *nitrosyl* (NO). For example, name [Pt(NH_3)$_2$Cl$_4$] as diamminetetrachloroplatinum(IV).

Table 6.3.1: Examples of Ligands

Ligand	Name
F^-	fluoro
Cl^-	chloro
Br^-	bromo
I^-	iodo
CN^-	cyano
NO_3^-	nitrato
OH^-	hydroxo
O^{2-}	oxo
$C_2O_4^{2-}$	oxalato
CO_3^{2-}	carbonato
NH_3	ammine
H_2O	aquo
CO	carbonyl
ethylenediamine (en)	ethylenediamine
ethylenediaminetetracetate (edta)	ethylenediaminetetracetate

3. If more than one ligand of a given type is present, the number is indicated by the prefixes *di-* (for two), *tri-* (for three), *tetra-* (for four), *penta-* (for five), and *hexa-* (for six). Sometimes, the prefixes *bis-* (for two), *tris-* (for three), and *tetrakis-* (for four) are used when the name of the ligand already includes *di-*, *tri-*, or *tetra-*, or when the ligand name begins with a vowel. For example, the ion bis(bipyridyl)osmium(II) uses bis- to signify that there are two ligands attached to Os, and each bipyridyl ligand contains two pyridine groups (C_5H_4N).

When the complex is either a cation or a neutral molecule, the name of the central metal atom is spelled exactly like the name of the element and is followed by a Roman numeral in parentheses to indicate its oxidation state (Table 6.3.2 and Table 6.3.3). When the complex is an anion, the suffix -ate is added to the stem of the name of the metal, followed by the Roman numeral designation of its oxidation state (Table 6.3.4). Sometimes, the Latin name of the metal is used when the English name is clumsy. For example, *ferrate* is used instead of *ironate*, *plumbate* instead *leadate*, and *stannate* instead of *tinate*. The oxidation state of the metal is determined based on the charges of each ligand and the overall charge of the coordination compound. For example, in $[Cr(H_2O)_4Cl_2]Br$, the coordination sphere (in brackets) has a charge of 1+ to balance the bromide ion. The water ligands are neutral, and the chloride ligands are anionic with a charge of 1− each. To determine the oxidation state of the metal, we set the overall charge equal to the sum of the ligands and the metal: $+1 = −2 + x$, so the oxidation state (x) is equal to 3+.

Table 6.3.2: Examples in Which the Complex Is a Cation

$[Co(NH_3)_6]Cl_3$	hexaamminecobalt(III) chloride
$[Pt(NH_3)_4Cl_2]^{2+}$	tetraamminedichloroplatinum(IV) ion
$[Ag(NH_3)_2]^+$	diamminesilver(I) ion
$[Cr(H_2O)_4Cl_2]Cl$	tetraaquadichlorochromium(III) chloride
$[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$	tris(ethylenediamine)cobalt(III) sulfate

Table 6.3.3: Examples in Which the Complex Is Neutral

$[Pt(NH_3)_2Cl_4]$	diamminetetrachloroplatinum(IV)
$[Ni(H_2NCH_2CH_2NH_2)_2Cl_2]$	dichlorobis(ethylenediamine)nickel(II)

Table 6.3.4: Examples in Which the Complex Is an Anion

$[PtCl_6]^{2-}$	hexachloroplatinate(IV) ion
$Na_2[SnCl_6]$	sodium hexachlorostannate(IV)

📌 Link to Learning

Do you think you understand naming coordination complexes? You can look over more examples and test yourself with online quizzes at the University of Sydney's site.

✔ Example 6.3.1: Coordination Numbers and Oxidation States

Determine the name of the following complexes and give the coordination number of the central metal atom.

 a. $Na_2[PtCl_6]$
 b. $K_3[Fe(C_2O_4)_3]$
 c. $[Co(NH_3)_5Cl]Cl_2$

Solution

(a) There are two Na^+ ions, so the coordination sphere has a negative two charge: $[PtCl_6]^{2-}$. There are six anionic chloride ligands, so $−2 = −6 + x$, and the oxidation state of the platinum is 4+. The name of the complex is sodium hexachloroplatinate(IV), and the coordination number is six.

(b) The coordination sphere has a charge of 3− (based on the potassium) and the oxalate ligands each have a charge of 2−, so the metal oxidation state is given by $−3 = −6 + x$, and this is an iron(III) complex. The name is potassium trisoxalatoferrate(III) (note that tris is used instead of tri because the ligand name starts with a vowel). Because oxalate is a bidentate ligand, this complex has a coordination number of six.

(c) In this example, the coordination sphere has a cationic charge of 2+. The NH_3 ligand is neutral, but the chloro ligand has a charge of 1−. The oxidation state is found by $+2 = −1 + x$ and is 3+, so the complex is pentaamminechlorocobalt(III) chloride and the coordination number is six.

> **?** **Exercise 6.3.1**
>
> The complex potassium dicyanoargenate(I) is used to make antiseptic compounds. Give the formula and coordination number.
>
> **Answer**
>
> $K[Ag(CN)_2]$; coordination number two

The Structures of Complexes

For transition metal complexes, the coordination number determines the geometry around the central metal ion. The most common structures of the complexes in coordination compounds are square planar, tetrahedral, and octahedral, corresponding to coordination numbers of four, four, and six, respectively. Coordination numbers greater than six are less common and yield a variety of structures (see Figure 6.3.7 and Table 6.3.5):

Pentagonal bipyramid   Square antiprism   Dodecahedral
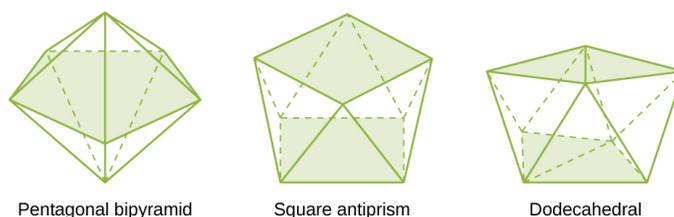
Figure 6.3.7: These are geometries of some complexes with coordination numbers of seven and eight.

Table 6.3.5: Coordination Numbers and Molecular Geometry

Coordination Number	Molecular Geometry	Example
2	linear	$[Ag(NH_3)_2]^+$
3	trigonal planar	$[Cu(CN)_3]^{2-}$
4	tetrahedral(d^0 or d^{10}), low oxidation states for M	$[Zn(CN)_4]^{2-}$
4	square planar (d^8)	$[Ni(CN)_4]^{2-}$
5	trigonal bipyramidal	$[CoCl_5]^{2-}$
5	square pyramidal	$[VO(CN)_4]^{2-}$
6	octahedral	$[CoCl_6]^{3-}$
7	pentagonal bipyramid	$[ZrF_7]^{3-}$
8	square antiprism	$[ReF_8]^{2-}$
8	dodecahedron	$[Mo(CN)_8]^{4-}$
9 and above	more complicated structures	$[ReH_9]^{2-}$

Unlike main group atoms in which both the bonding and nonbonding electrons determine the molecular shape, the nonbonding d-electrons do not change the arrangement of the ligands. Octahedral complexes have a coordination number of six, and the six donor atoms are arranged at the corners of an octahedron around the central metal ion. Examples are shown in Figure 6.3.8. The chloride and nitrate anions in $[Co(H_2O)_6]Cl_2$ and $[Cr(en)_3](NO_3)_3$, and the potassium cations in $K_2[PtCl_6]$, are outside the brackets and are not bonded to the metal ion.
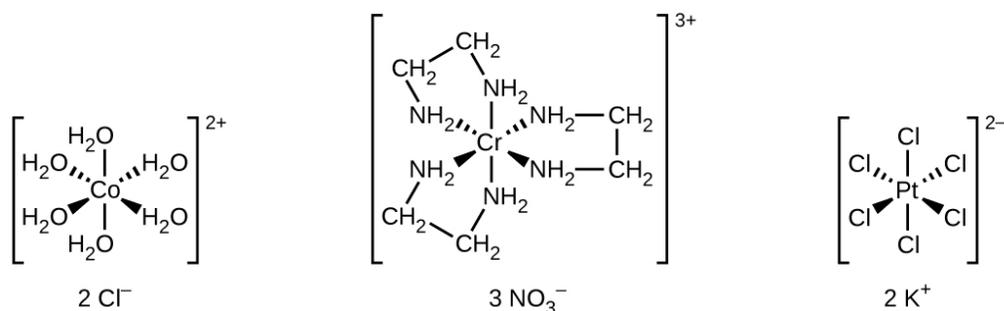
Figure 6.3.8: Many transition metal complexes adopt octahedral geometries, with six donor atoms forming bond angles of 90° about the central atom with adjacent ligands. Note that only ligands within the coordination sphere affect the geometry around the metal center.

For transition metals with a coordination number of four, two different geometries are possible: tetrahedral or square planar. Unlike main group elements, where these geometries can be predicted from VSEPR theory, a more detailed discussion of transition metal orbitals (discussed in the section on Crystal Field Theory) is required to predict which complexes will be tetrahedral and which will be square planar. In tetrahedral complexes such as $[Zn(CN)_4]^{2-}$ (Figure 6.3.9), each of the ligand pairs forms an angle of 109.5°. In square planar complexes, such as $[Pt(NH_3)_2Cl_2]$, each ligand has two other ligands at 90° angles (called the *cis* positions) and one additional ligand at an 180° angle, in the *trans* position.
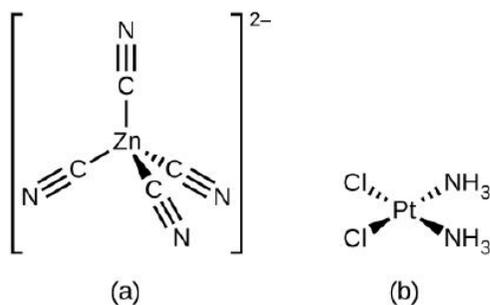
Figure 6.3.9: Transition metals with a coordination number of four can adopt a tetrahedral geometry (a) as in $K_2[Zn(CN)_4]$ or a square planar geometry (b) as shown in $[Pt(NH_3)_2Cl_2]$.

Isomerism in Complexes

Isomers are different chemical species that have the same chemical formula. Transition metal complexes often exist as **geometric isomers**, in which the same atoms are connected through the same types of bonds but with differences in their orientation in space. Coordination complexes with two different ligands in the *cis* and *trans* positions from a ligand of interest form isomers. For example, the octahedral $[Co(NH_3)_4Cl_2]^+$ ion has two isomers. In the *cis* **configuration**, the two chloride ligands are adjacent to each other (Figure 6.3.10). The other isomer, the *trans* **configuration**, has the two chloride ligands directly across from one another.
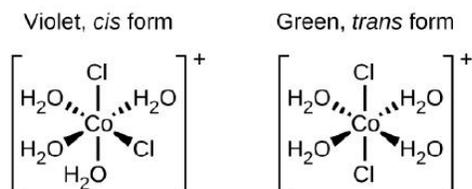
Figure 6.3.10: The *cis* and *trans* isomers of $[Co(H_2O)_4Cl_2]^+$ contain the same ligands attached to the same metal ion, but the spatial arrangement causes these two compounds to have very different properties.

Different geometric isomers of a substance are different chemical compounds. They exhibit different properties, even though they have the same formula. For example, the two isomers of $[Co(NH_3)_4Cl_2]NO_3$ differ in color; the *cis* form is violet, and the *trans* form is green. Furthermore, these isomers have different dipole moments, solubilities, and reactivities. As an example of how the arrangement in space can influence the molecular properties, consider the polarity of the two $[Co(NH_3)_4Cl_2]NO_3$ isomers. Remember that the polarity of a molecule or ion is determined by the bond dipoles (which are due to the difference in electronegativity of the bonding atoms) and their arrangement in space. In one isomer, *cis* chloride ligands cause more electron

density on one side of the molecule than on the other, making it polar. For the *trans* isomer, each ligand is directly across from an identical ligand, so the bond dipoles cancel out, and the molecule is nonpolar.

> ✔ **Example 6.3.2: Geometric Isomers**
>
> Identify which geometric isomer of $[Pt(NH_3)_2Cl_2]$ is shown in Figure 6.3.9. Draw the other geometric isomer and give its full name.
>
> **Solution**
>
> In the Figure 6.3.9, the two chlorine ligands occupy *cis* positions. The other form is shown in Figure 6.3.11. When naming specific isomers, the descriptor is listed in front of the name. Therefore, this complex is *trans*-diamminedichloroplatinum(II).
>
>
>
> Figure 6.3.11: The *trans* isomer of $[Pt(NH_3)_2Cl_2]$ has each ligand directly across from an adjacent ligand.

> ❓ **Exercise 6.3.1**
>
> Draw the ion *trans*-diaqua-*trans*-dibromo-*trans*-dichlorocobalt(II).
>
> **Answer**
>
>
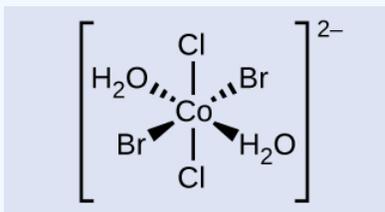
Another important type of isomers are **optical isomers**, or **enantiomers**, in which two objects are exact mirror images of each other but cannot be lined up so that all parts match. This means that optical isomers are nonsuperimposable mirror images. A classic example of this is a pair of hands, in which the right and left hand are mirror images of one another but cannot be superimposed. Optical isomers are very important in organic and biochemistry because living systems often incorporate one specific optical isomer and not the other. Unlike geometric isomers, pairs of optical isomers have identical properties (boiling point, polarity, solubility, etc.). Optical isomers differ only in the way they affect polarized light and how they react with other optical isomers. For coordination complexes, many coordination compounds such as $[M(en)_3]^{n+}$ [in which M^{n+} is a central metal ion such as iron(III) or cobalt(II)] form enantiomers, as shown in Figure 6.3.12. These two isomers will react differently with other optical isomers. For example, DNA helices are optical isomers, and the form that occurs in nature (right-handed DNA) will bind to only one isomer of $[M(en)_3]^{n+}$ and not the other.
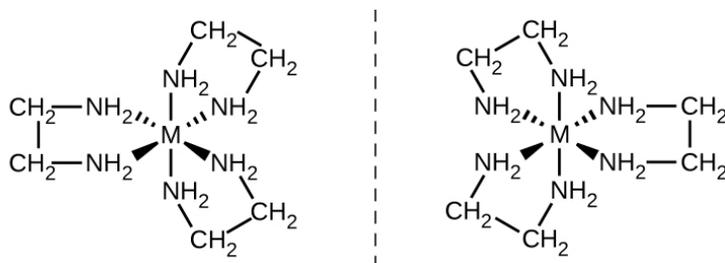
Figure 6.3.12: The complex $[M(en)_3]^{n+}$ (M^{n+} = a metal ion, en = ethylenediamine) has a nonsuperimposable mirror image.

The $[Co(en)_2Cl_2]^+$ ion exhibits geometric isomerism (*cis/trans*), and its *cis* isomer exists as a pair of optical isomers (Figure 6.3.13).

cis form (optical isomers) | *trans* form
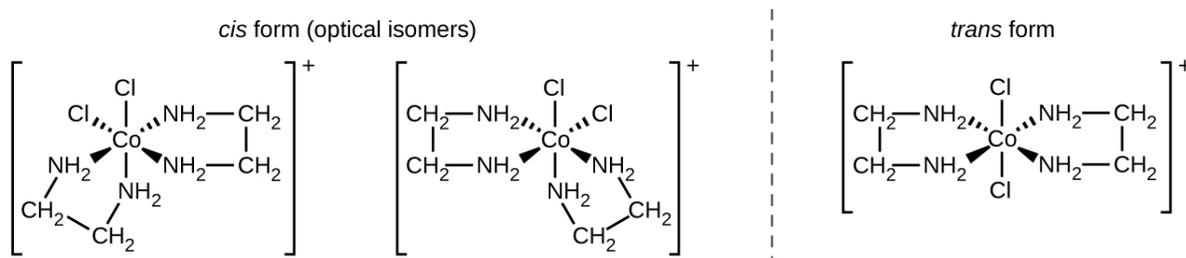
Figure 6.3.13: Three isomeric forms of [Co(en)$_2$Cl$_2$]$^+$ exist. The *trans* isomer, formed when the chlorines are positioned at a 180° angle, has very different properties from the *cis* isomers. The mirror images of the *cis* isomer form a pair of optical isomers, which have identical behavior except when reacting with other enantiomers.

Linkage isomers occur when the coordination compound contains a ligand that can bind to the transition metal center through two different atoms. For example, the CN ligand can bind through the carbon atom (cyano) or through the nitrogen atom (isocyano). Similarly, SCN$^-$ can be bound through the sulfur or nitrogen atom, affording two distinct compounds ([Co(NH$_3$)$_5$SCN]$^{2+}$ or [Co(NH$_3$)$_5$NCS]$^{2+}$).

Ionization isomers (or **coordination isomers**) occur when one anionic ligand in the inner coordination sphere is replaced with the counter ion from the outer coordination sphere. A simple example of two ionization isomers are [CoCl$_6$][Br] and [CoCl$_5$Br][Cl].

Coordination Complexes in Nature and Technology

Chlorophyll, the green pigment in plants, is a complex that contains magnesium (Figure 6.3.14). This is an example of a main group element in a coordination complex. Plants appear green because chlorophyll absorbs red and purple light; the reflected light consequently appears green. The energy resulting from the absorption of light is used in photosynthesis.

(a)   (b)
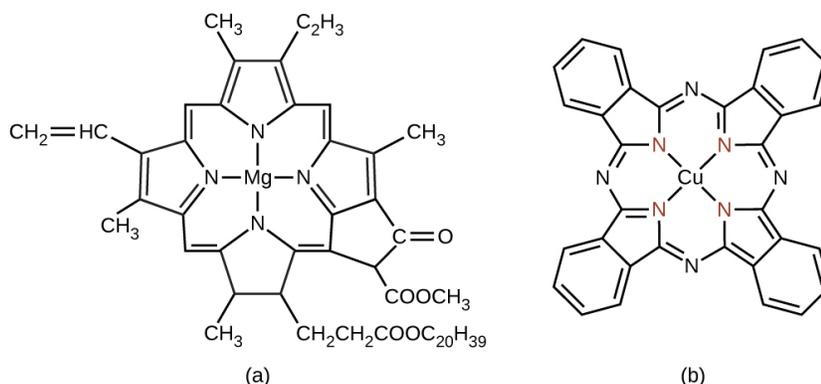
Figure 6.3.14: (a) Chlorophyll comes in several different forms, which all have the same basic structure around the magnesium center. (b) Copper phthalocyanine blue, a square planar copper complex, is present in some blue dyes.

⚓ Chemistry in Everyday Life: Transition Metal Catalysts

One of the most important applications of transition metals is as industrial catalysts. As you recall from the chapter on kinetics, a catalyst increases the rate of reaction by lowering the activation energy and is regenerated in the catalytic cycle. Over 90% of all manufactured products are made with the aid of one or more catalysts. The ability to bind ligands and change oxidation states makes transition metal catalysts well suited for catalytic applications. Vanadium oxide is used to produce 230,000,000 tons of sulfuric acid worldwide each year, which in turn is used to make everything from fertilizers to cans for food. Plastics are made with the aid of transition metal catalysts, along with detergents, fertilizers, paints, and more (see Figure 6.3.15). Very complicated pharmaceuticals are manufactured with catalysts that are selective, reacting with one specific bond out of a large number of possibilities. Catalysts allow processes to be more economical and more environmentally friendly. Developing new catalysts and better understanding of existing systems are important areas of current research.

Figure 6.3.15: (a) Detergents, (b) paints, and (c) fertilizers are all made using transition metal catalysts. (credit a: modification of work by "Mr. Brian"/Flickr; credit b: modification of work by Ewen Roberts; credit c: modification of work by "osseous"/Flickr)

📌 Portrait of a Chemist: Deanna D'Alessandro

Dr. Deanna D'Alessandro develops new metal-containing materials that demonstrate unique electronic, optical, and magnetic properties. Her research combines the fields of fundamental inorganic and physical chemistry with materials engineering. She is working on many different projects that rely on transition metals. For example, one type of compound she is developing captures carbon dioxide waste from power plants and catalytically converts it into useful products (see Figure 6.3.16).
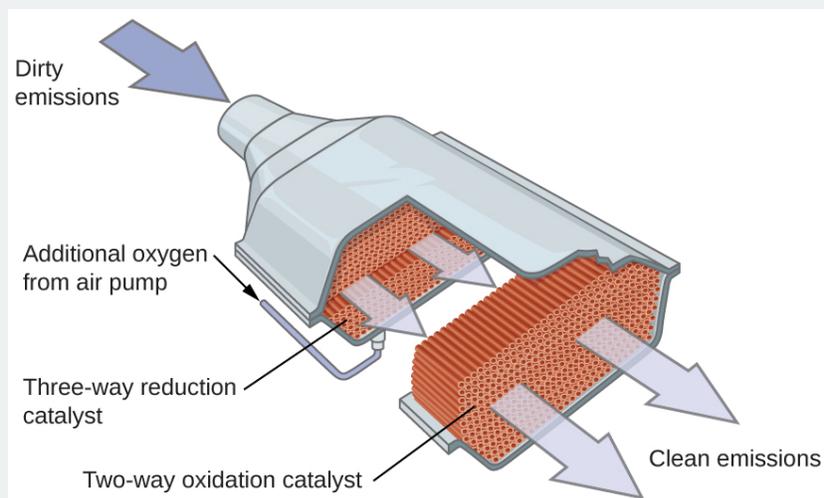
Figure 6.3.16: Catalytic converters change carbon dioxide emissions from power plants into useful products, and, like the one shown here, are also found in cars.

Another project involves the development of porous, sponge-like materials that are "photoactive." The absorption of light causes the pores of the sponge to change size, allowing gas diffusion to be controlled. This has many potential useful applications, from powering cars with hydrogen fuel cells to making better electronics components. Although not a complex, self-darkening sunglasses are an example of a photoactive substance.

Watch this video to learn more about this research and listen to Dr. D'Alessandro (shown in Figure 6.3.17) describe what it is like being a research chemist.

Figure 6.3.17: Dr. Deanna D'Alessandro is a functional materials researcher. Her work combines the inorganic and physical chemistry fields with engineering, working with transition metals to create new systems to power cars and convert energy (credit: image courtesy of Deanna D'Alessandro).

Many other coordination complexes are also brightly colored. The square planar copper(II) complex phthalocyanine blue (from Figure 6.3.14) is one of many complexes used as pigments or dyes. This complex is used in blue ink, blue jeans, and certain blue paints.

The structure of heme (Figure 6.3.18), the iron-containing complex in hemoglobin, is very similar to that in chlorophyll. In hemoglobin, the red heme complex is bonded to a large protein molecule (globin) by the attachment of the protein to the heme ligand. Oxygen molecules are transported by hemoglobin in the blood by being bound to the iron center. When the hemoglobin loses its oxygen, the color changes to a bluish red. Hemoglobin will only transport oxygen if the iron is Fe^{2+}; oxidation of the iron to Fe^{3+} prevents oxygen transport.
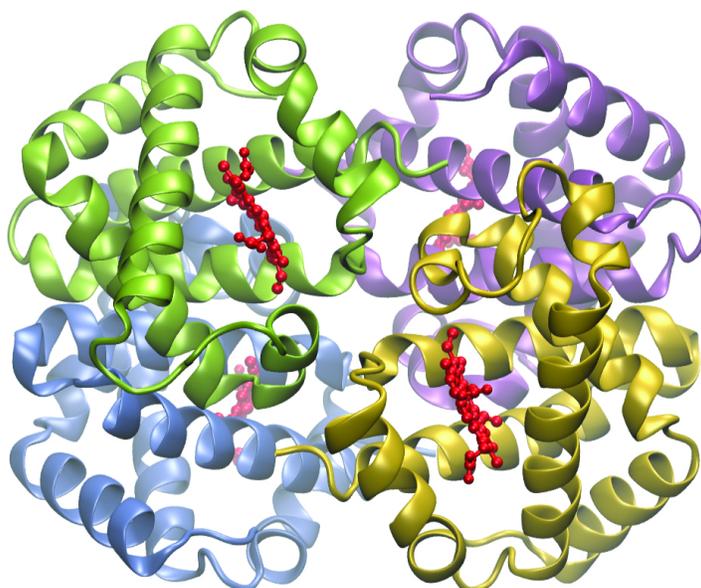
Figure 6.3.18: Hemoglobin contains four protein subunits, each of which has an iron center attached to a heme ligand (shown in red), which is coordinated to a globin protein. Each subunit is shown in a different color.

Complexing agents often are used for water softening because they tie up such ions as Ca^{2+}, Mg^{2+}, and Fe^{2+}, which make water hard. Many metal ions are also undesirable in food products because these ions can catalyze reactions that change the color of food. Coordination complexes are useful as preservatives. For example, the ligand EDTA, $(HO_2CCH_2)_2NCH_2CH_2N(CH_2CO_2H)_2$, coordinates to metal ions through six donor atoms and prevents the metals from reacting (Figure 6.3.19). This ligand also is used to sequester metal ions in paper production, textiles, and detergents, and has pharmaceutical uses.
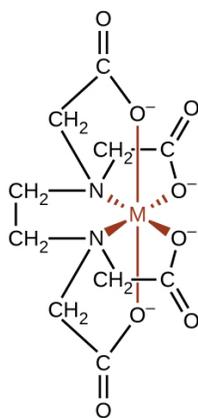
Figure 6.3.19: The ligand EDTA binds tightly to a variety of metal ions by forming hexadentate complexes.

Complexing agents that tie up metal ions are also used as drugs. British Anti-Lewisite (BAL), $HSCH_2CH(SH)CH_2OH$, is a drug developed during World War I as an antidote for the arsenic-based war gas Lewisite. BAL is now used to treat poisoning by heavy metals, such as arsenic, mercury, thallium, and chromium. The drug is a ligand and functions by making a water-soluble chelate of the metal; the kidneys eliminate this metal chelate (Figure 6.3.20). Another polydentate ligand, enterobactin, which is isolated from certain bacteria, is used to form complexes of iron and thereby to control the severe iron buildup found in patients suffering from blood diseases such as Cooley's anemia, who require frequent transfusions. As the transfused blood breaks down, the usual metabolic processes that remove iron are overloaded, and excess iron can build up to fatal levels. Enterobactin forms a water-soluble complex with excess iron, and the body can safely eliminate this complex.
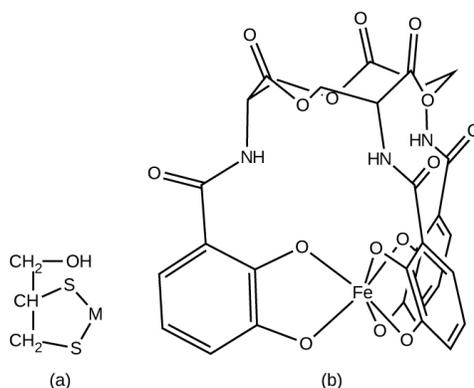
Figure 6.3.20: Coordination complexes are used as drugs. (a) British Anti-Lewisite is used to treat heavy metal poisoning by coordinating metals (M), and enterobactin (b) allows excess iron in the blood to be removed.

> ✔ **Example 6.3.3: Chelation Therapy**
>
> Ligands like BAL and enterobactin are important in medical treatments for heavy metal poisoning. However, chelation therapies can disrupt the normal concentration of ions in the body, leading to serious side effects, so researchers are searching for new chelation drugs. One drug that has been developed is dimercaptosuccinic acid (DMSA), shown in Figure 6.3.21. Identify which atoms in this molecule could act as donor atoms.
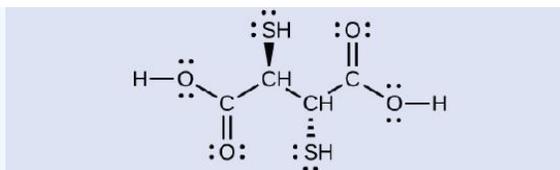
Figure 6.3.21: Dimercaptosuccinic acid is used to treat heavy metal poisoning.

Solution

All of the oxygen and sulfur atoms have lone pairs of electrons that can be used to coordinate to a metal center, so there are six possible donor atoms. Geometrically, only two of these atoms can be coordinated to a metal at once. The most common binding mode involves the coordination of one sulfur atom and one oxygen atom, forming a five-member ring with the metal.

> **? Exercise 6.3.1**
>
> Some alternative medicine practitioners recommend chelation treatments for ailments that are not clearly related to heavy metals, such as cancer and autism, although the practice is discouraged by many scientific organizations.[1] Identify at least two biologically important metals that could be disrupted by chelation therapy.
>
> **Answer**
>
> Ca, Fe, Zn, and Cu

Ligands are also used in the electroplating industry. When metal ions are reduced to produce thin metal coatings, metals can clump together to form clusters and nanoparticles. When metal coordination complexes are used, the ligands keep the metal atoms isolated from each other. It has been found that many metals plate out as a smoother, more uniform, better-looking, and more adherent surface when plated from a bath containing the metal as a complex ion. Thus, complexes such as $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ are used extensively in the electroplating industry.

In 1965, scientists at Michigan State University discovered that there was a platinum complex that inhibited cell division in certain microorganisms. Later work showed that the complex was *cis*-diamminedichloroplatinum(II), $[Pt(NH_3)_2(Cl)_2]$, and that the *trans* isomer was not effective. The inhibition of cell division indicated that this square planar compound could be an anticancer agent. In 1978, the US Food and Drug Administration approved this compound, known as cisplatin, for use in the treatment of certain forms of cancer. Since that time, many similar platinum compounds have been developed for the treatment of cancer. In all cases, these are the *cis* isomers and never the *trans* isomers. The diammine $(NH_3)_2$ portion is retained with other groups, replacing the dichloro $[(Cl)_2]$ portion. The newer drugs include carboplatin, oxaliplatin, and satraplatin.

Footnotes

- 1National Council against Health Fraud, *NCAHF Policy Statement on Chelation Therapy*, (Peabody, MA, 2002).

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6.4: Bonding, Spectroscopic and Magnetic Properties of Coordination Compounds

> **◀▶ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Outline the basic premise of crystal field theory (CFT)
> - Identify molecular geometries associated with various d-orbital splitting patterns
> - Predict electron configurations of split d orbitals for selected transition metal atoms or ions
> - Explain spectral and magnetic properties in terms of CFT concepts

The behavior of coordination compounds cannot be adequately explained by the same theories used for main group element chemistry. The observed geometries of coordination complexes are not consistent with hybridized orbitals on the central metal overlapping with ligand orbitals, as would be predicted by valence bond theory. The observed colors indicate that the d orbitals often occur at different energy levels rather than all being degenerate, that is, of equal energy, as are the three p orbitals. To explain the stabilities, structures, colors, and magnetic properties of transition metal complexes, a different bonding model has been developed. Just as valence bond theory explains many aspects of bonding in main group chemistry, crystal field theory is useful in understanding and predicting the behavior of transition metal complexes.

Crystal Field Theory

To explain the observed behavior of transition metal complexes (such as how colors arise), a model involving electrostatic interactions between the electrons from the ligands and the electrons in the unhybridized d orbitals of the central metal atom has been developed. This electrostatic model is **crystal field theory** (CFT). It allows us to understand, interpret, and predict the colors, magnetic behavior, and some structures of coordination compounds of transition metals.

CFT focuses on the nonbonding electrons on the central metal ion in coordination complexes not on the metal-ligand bonds. Like valence bond theory, CFT tells only part of the story of the behavior of complexes. However, it tells the part that valence bond theory does not. In its pure form, CFT ignores any covalent bonding between ligands and metal ions. Both the ligand and the metal are treated as infinitesimally small point charges.

All electrons are negative, so the electrons donated from the ligands will repel the electrons of the central metal. Let us consider the behavior of the electrons in the unhybridized d orbitals in an octahedral complex. The five d orbitals consist of lobe-shaped regions and are arranged in space, as shown in Figure 6.4.1. In an octahedral complex, the six ligands coordinate along the axes.
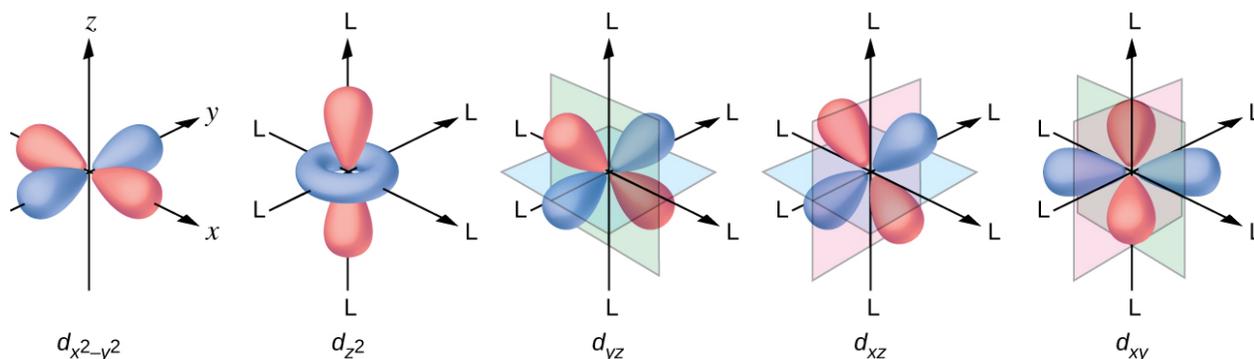
Figure 6.4.1: The directional characteristics of the five d orbitals are shown here. The shaded portions indicate the phase of the orbitals. The ligands (L) coordinate along the axes. For clarity, the ligands have been omitted from the orbital so that the axis labels could be shown.

In an uncomplexed metal ion in the gas phase, the electrons are distributed among the five d orbitals in accord with Hund's rule because the orbitals all have the same energy. However, when ligands coordinate to a metal ion, the energies of the d orbitals are no longer the same.

In octahedral complexes, the lobes in two of the five d orbitals, the d_{z^2} and $d_{x^2-y^2}$ orbitals, point toward the ligands (Figure 6.4.1). These two orbitals are called the e_g **orbitals** (the symbol actually refers to the symmetry of the orbitals, but we will use it as a convenient name for these two orbitals in an octahedral complex). The other three orbitals, the d_{xy}, d_{xz}, and d_{yz} orbitals, have

lobes that point between the ligands and are called the $\boldsymbol{t_{2g}}$ **orbitals** (again, the symbol really refers to the symmetry of the orbitals). As six ligands approach the metal ion along the axes of the octahedron, their point charges repel the electrons in the d orbitals of the metal ion. However, the repulsions between the electrons in the e_g orbitals (the d_{z^2} and $d_{x^2-y^2}$ orbitals) and the ligands are greater than the repulsions between the electrons in the t_{2g} orbitals (the d_{zy}, d_{xz}, and d_{yz} orbitals) and the ligands. This is because the lobes of the eg orbitals point directly at the ligands, whereas the lobes of the t_{2g} orbitals point between them. Thus, electrons in the eg orbitals of the metal ion in an octahedral complex have higher potential energies than those of electrons in the t_{2g} orbitals. The difference in energy may be represented as shown in Figure 6.4.2.
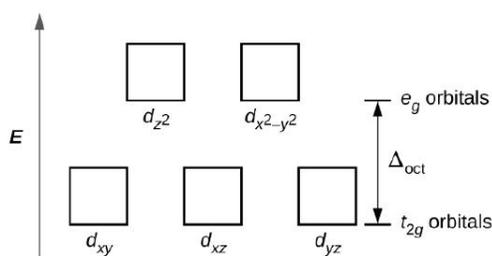
Figure 6.4.2: In octahedral complexes, the e_g orbitals are destabilized (higher in energy) compared to the t_{2g} orbitals because the ligands interact more strongly with the d orbitals at which they are pointed directly.

The difference in energy between the e_g and the t_{2g} orbitals is called the **crystal field splitting** and is symbolized by Δ_{oct}, where oct stands for octahedral.

The magnitude of Δ_{oct} depends on many factors, including the nature of the six ligands located around the central metal ion, the charge on the metal, and whether the metal is using 3d, 4d, or 5d orbitals. Different ligands produce different crystal field splittings. The increasing crystal field splitting produced by ligands is expressed in the **spectrochemical series**, a short version of which is given here:

$$I^- < Br^- < Cl^- < F^- < H_2O < NH_3 < en < NO_2^- < CN^-$$

a few ligands of the spectrochemical series, in order of increasing field strength of the ligand

In this series, ligands on the left cause small crystal field splittings and are **weak-field ligands**, whereas those on the right cause larger splittings and are **strong-field ligands**. Thus, the Δ_{oct} value for an octahedral complex with iodide ligands (I$^-$) is much smaller than the Δ_{oct} value for the same metal with cyanide ligands (CN$^-$).

Electrons in the d orbitals follow the aufbau ("filling up") principle, which says that the orbitals will be filled to give the lowest total energy, just as in main group chemistry. When two electrons occupy the same orbital, the like charges repel each other. The energy needed to pair up two electrons in a single orbital is called the **pairing energy** (P). Electrons will always singly occupy each orbital in a degenerate set before pairing. P is similar in magnitude to Δ_{oct}. When electrons fill the d orbitals, the relative magnitudes of Δ_{oct} and P determine which orbitals will be occupied.

In [Fe(CN)$_6$]$^{4-}$, the strong field of six cyanide ligands produces a large Δ_{oct}. Under these conditions, the electrons require less energy to pair than they require to be excited to the e_g orbitals (Δ_{oct} > P). The six 3d electrons of the Fe^{2+} ion pair in the three t_{2g} orbitals (Figure 6.4.3). Complexes in which the electrons are paired because of the large crystal field splitting are called **low-spin complexes** because the number of unpaired electrons (spins) is minimized.
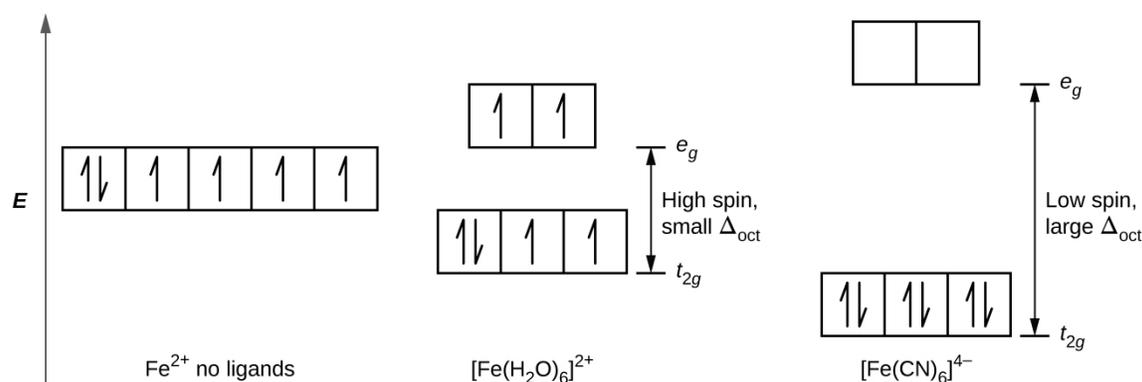
Figure 6.4.3: Iron(II) complexes have six electrons in the 5d orbitals. In the absence of a crystal field, the orbitals are degenerate. For coordination complexes with strong-field ligands such as [Fe(CN)$_6$]$^{4-}$, Δ_{oct} is greater than P, and the electrons pair in the lower energy t_{2g} orbitals before occupying the eg orbitals. With weak-field ligands such as H$_2$O, the ligand field splitting is less than the pairing energy, Δ_{oct} less than P, so the electrons occupy all d orbitals singly before any pairing occurs.

In [Fe(H$_2$O)$_6$]$^{2+}$, on the other hand, the weak field of the water molecules produces only a small crystal field splitting ($\Delta_{oct} < P$). Because it requires less energy for the electrons to occupy the e_g orbitals than to pair together, there will be an electron in each of the five 3d orbitals before pairing occurs. For the six d electrons on the iron(II) center in [Fe(H$_2$O)$_6$]$^{2+}$, there will be one pair of electrons and four unpaired electrons (Figure 6.4.3). Complexes such as the [Fe(H$_2$O)$_6$]$^{2+}$ ion, in which the electrons are unpaired because the crystal field splitting is not large enough to cause them to pair, are called high-spin complexes because the number of unpaired electrons (spins) is maximized.

A similar line of reasoning shows why the [Fe(CN)$_6$]$^{3-}$ ion is a low-spin complex with only one unpaired electron, whereas both the [Fe(H$_2$O)$_6$]$^{3+}$ and [FeF$_6$]$^{3-}$ ions are high-spin complexes with five unpaired electrons.

✔ Example 6.4.1: High- and Low-Spin Complexes

Predict the number of unpaired electrons.

a. K$_3$[CrI$_6$]
b. [Cu(en)$_2$(H$_2$O)$_2$]Cl$_2$
c. Na$_3$[Co(NO$_2$)$_6$]

Solution

The complexes are octahedral.

a. Cr^{3+} has a d^3 configuration. These electrons will all be unpaired.
b. Cu^{2+} is d^9, so there will be one unpaired electron.
c. Co^{3+} has d^6 valence electrons, so the crystal field splitting will determine how many are paired. Nitrite is a strong-field ligand, so the complex will be low spin. Six electrons will go in the t_{2g} orbitals, leaving 0 unpaired.

? Exercise 6.4.1

The size of the crystal field splitting only influences the arrangement of electrons when there is a choice between pairing electrons and filling the higher-energy orbitals. For which d-electron configurations will there be a difference between high- and low-spin configurations in octahedral complexes?

Answer

d^4, d^5, d^6, and d^7

✔ Example 6.4.2: CFT for Other Geometries

CFT is applicable to molecules in geometries other than octahedral. In octahedral complexes, remember that the lobes of the e_g set point directly at the ligands. For tetrahedral complexes, the d orbitals remain in place, but now we have only four ligands located between the axes (Figure 6.4.4). None of the orbitals points directly at the tetrahedral ligands. However, the e_g set

(along the Cartesian axes) overlaps with the ligands less than does the t_{2g} set. By analogy with the octahedral case, predict the energy diagram for the d orbitals in a tetrahedral crystal field. To avoid confusion, the octahedral e_g set becomes a tetrahedral e set, and the octahedral t_{2g} set becomes a t_2 set.
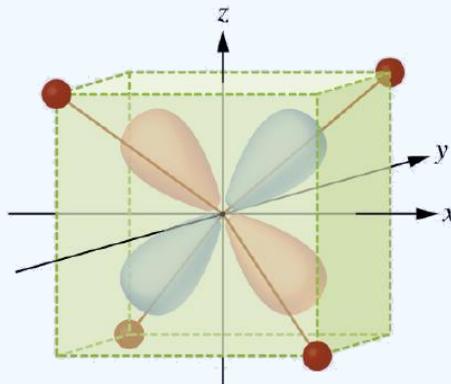
Figure 6.4.4: This diagram shows the orientation of the tetrahedral ligands with respect to the axis system for the orbitals.

Solution

Since CFT is based on electrostatic repulsion, the orbitals closer to the ligands will be destabilized and raised in energy relative to the other set of orbitals. The splitting is less than for octahedral complexes because the overlap is less, so Δ_{tet} is usually small $\left(\Delta_{\text{tet}} = \frac{4}{9}\Delta_{oct}\right)$
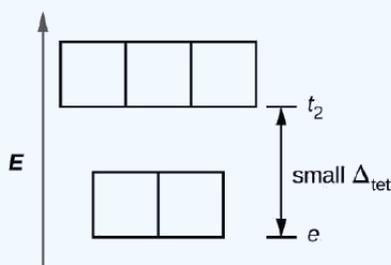
> ? **Exercise** 6.4.2
>
> Explain how many unpaired electrons a tetrahedral d^4 ion will have.
>
> **Answer**
>
>   4; because Δ_{tet} is small, all tetrahedral complexes are high spin and the electrons go into the t_2 orbitals before pairing

The other common geometry is square planar. It is possible to consider a square planar geometry as an octahedral structure with a pair of *trans* ligands removed. The removed ligands are assumed to be on the z-axis. This changes the distribution of the d orbitals, as orbitals on or near the z-axis become more stable, and those on or near the x- or y-axes become less stable. This results in the octahedral t_{2g} and the e_g sets splitting and gives a more complicated pattern, as depicted below:

E

$d_{x^2-y^2}$

d_{xy}

d_{z^2}

d_{xz} d_{yz}
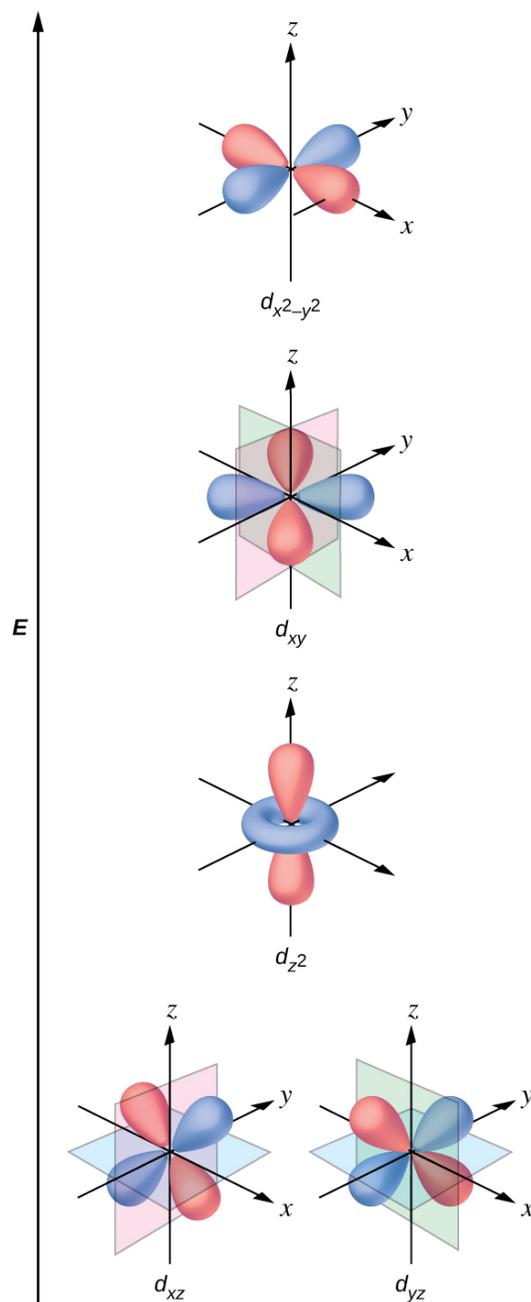
Magnetic Moments of Molecules and Ions

Experimental evidence of magnetic measurements supports the theory of high- and low-spin complexes. Remember that molecules such as O_2 that contain unpaired electrons are paramagnetic. Paramagnetic substances are attracted to magnetic fields. Many transition metal complexes have unpaired electrons and hence are paramagnetic. Molecules such as N_2 and ions such as Na^+ and $[Fe(CN)_6]^{4-}$ that contain no unpaired electrons are diamagnetic. Diamagnetic substances have a slight tendency to be repelled by magnetic fields.

When an electron in an atom or ion is unpaired, the magnetic moment due to its spin makes the entire atom or ion paramagnetic. The size of the magnetic moment of a system containing unpaired electrons is related directly to the number of such electrons: the greater the number of unpaired electrons, the larger the magnetic moment. Therefore, the observed magnetic moment is used to determine the number of unpaired electrons present. The measured magnetic moment of low-spin d^6 $[Fe(CN)_6]^{4-}$ confirms that iron is diamagnetic, whereas high-spin d^6 $[Fe(H_2O)_6]^{2+}$ has four unpaired electrons with a magnetic moment that confirms this arrangement.

Colors of Transition Metal Complexes

When atoms or molecules absorb light at the proper frequency, their electrons are excited to higher-energy orbitals. For many main group atoms and molecules, the absorbed photons are in the ultraviolet range of the electromagnetic spectrum, which cannot be detected by the human eye. For coordination compounds, the energy difference between the d orbitals often allows photons in the visible range to be absorbed.

The human eye perceives a mixture of all the colors, in the proportions present in sunlight, as white light. Complementary colors, those located across from each other on a color wheel, are also used in color vision. The eye perceives a mixture of two complementary colors, in the proper proportions, as white light. Likewise, when a color is missing from white light, the eye sees its complement. For example, when red photons are absorbed from white light, the eyes see the color green. When violet photons are removed from white light, the eyes see lemon yellow. The blue color of the $[Cu(NH_3)_4]^{2+}$ ion results because this ion absorbs orange and red light, leaving the complementary colors of blue and green (Figure $6.4.5$).

(a)   (b)

(c)
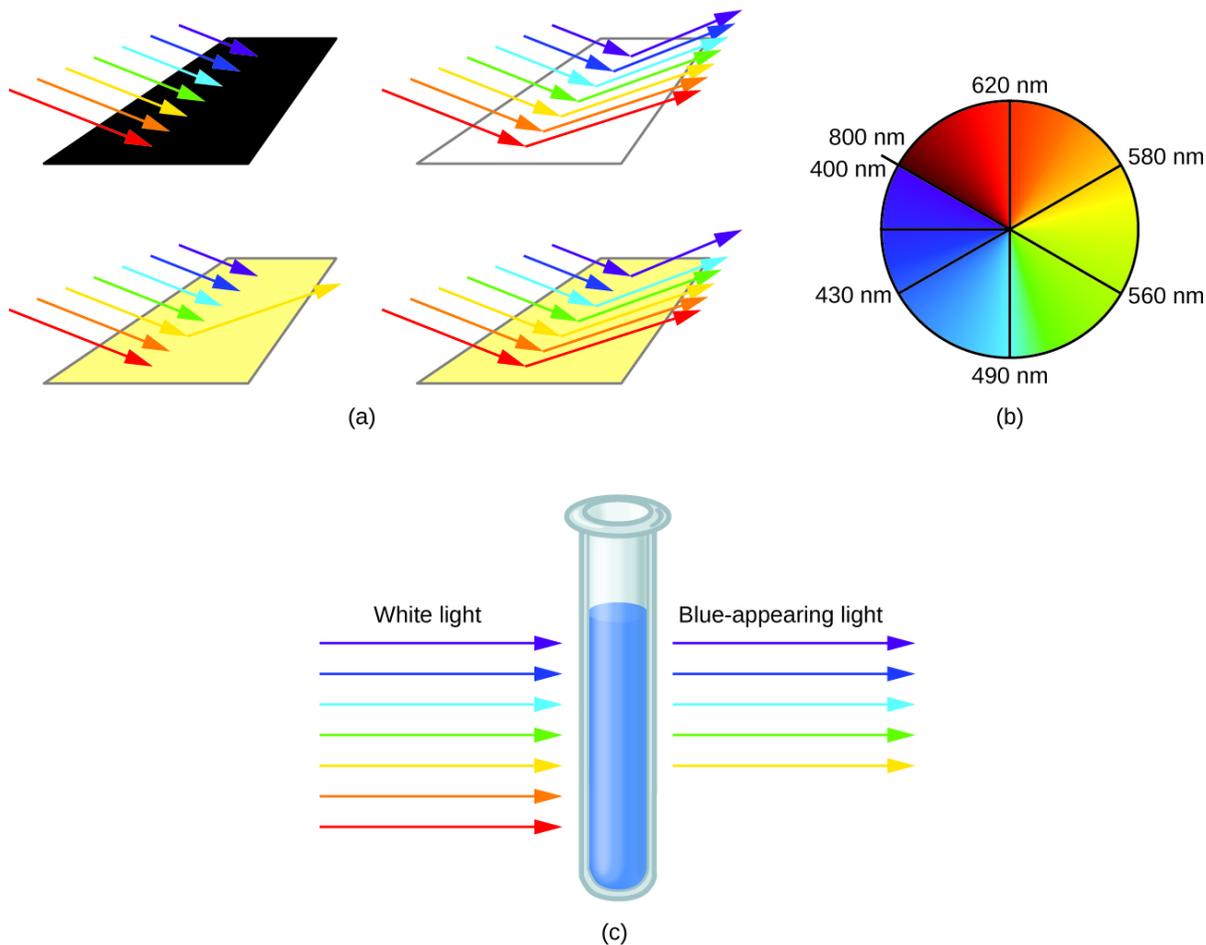
Figure $6.4.5$: (a) An object is black if it absorbs all colors of light. If it reflects all colors of light, it is white. An object has a color if it absorbs all colors except one, such as this yellow strip. The strip also appears yellow if it absorbs the complementary color from white light (in this case, indigo). (b) Complementary colors are located directly across from one another on the color wheel. (c) A solution of $[Cu(NH_3)_4]^{2+}$ ions absorbs red and orange light, so the transmitted light appears as the complementary color, blue.

✔ **Example $6.4.3$: Colors of Complexes**

The octahedral complex $[Ti(H_2O)_6]^{3+}$ has a single d electron. To excite this electron from the ground state t_{2g} orbital to the e_g orbital, this complex absorbs light from 450 to 600 nm. The maximum absorbance corresponds to Δ_{oct} and occurs at 499 nm. Calculate the value of Δ_{oct} in Joules and predict what color the solution will appear.

Solution

Using Planck's equation (refer to the section on electromagnetic energy), we calculate:

$$\nu = \frac{c}{\lambda} \text{ so } \frac{3.00 \times 10^8 m/s}{\frac{499nm \times 1m}{10^9 nm}} = 6.01 \times 10^{14} Hz$$

$$E = h\nu \text{ so } 6.63 \times 10^{-34} J \cdot s \times 6.01 \times 10^{14} Hz = 3.99 \times 10^{-19} \text{ Joules/ion}$$

Because the complex absorbs 600 nm (orange) through 450 (blue), the indigo, violet, and red wavelengths will be transmitted, and the complex will appear purple.

? Exercise 6.4.3

A complex that appears green, absorbs photons of what wavelengths?

Answer

red, 620–800 nm

Small changes in the relative energies of the orbitals that electrons are transitioning between can lead to drastic shifts in the color of light absorbed. Therefore, the colors of coordination compounds depend on many factors. As shown in Figure 6.4.6, different aqueous metal ions can have different colors. In addition, different oxidation states of one metal can produce different colors, as shown for the vanadium complexes in the link below.

Figure 6.4.6: The partially filled *d* orbitals of the stable ions $Cr^{3+}(aq)$, $Fe^{3+}(aq)$, and $Co^{2+}(aq)$ (left, center and right, respectively) give rise to various colors. (credit: Sahar Atwa)

The specific ligands coordinated to the metal center also influence the color of coordination complexes. For example, the iron(II) complex $[Fe(H_2O)_6]SO_4$ appears blue-green because the high-spin complex absorbs photons in the red wavelengths (Figure 6.4.7). In contrast, the low-spin iron(II) complex $K_4[Fe(CN)_6]$ appears pale yellow because it absorbs higher-energy violet photons.

(a)   (b)

Figure 6.4.7: Both (a) hexaaquairon(II) sulfate and (b) potassium hexacyanoferrate(II) contain d^6 iron(II) octahedral metal centers, but they absorb photons in different ranges of the visible spectrum.

⊤ Link to Learning

Watch this video of the reduction of vanadium complexes to observe the colorful effect of changing oxidation states.

In general, strong-field ligands cause a large split in the energies of *d* orbitals of the central metal atom (large Δ_{oct}). Transition metal coordination compounds with these ligands are yellow, orange, or red because they absorb higher-energy violet or blue light.

On the other hand, coordination compounds of transition metals with weak-field ligands are often blue-green, blue, or indigo because they absorb lower-energy yellow, orange, or red light.

A coordination compound of the Cu^+ ion has a d^{10} configuration, and all the e_g orbitals are filled. To excite an electron to a higher level, such as the $4p$ orbital, photons of very high energy are necessary. This energy corresponds to very short wavelengths in the ultraviolet region of the spectrum. No visible light is absorbed, so the eye sees no change, and the compound appears white or colorless. A solution containing $[Cu(CN)_2]^-$, for example, is colorless. On the other hand, octahedral Cu^{2+} complexes have a vacancy in the e_g orbitals, and electrons can be excited to this level. The wavelength (energy) of the light absorbed corresponds to the visible part of the spectrum, and Cu^{2+} complexes are almost always colored—blue, blue-green violet, or yellow (Figure 6.4.8). Although CFT successfully describes many properties of coordination complexes, molecular orbital explanations (beyond the introductory scope provided here) are required to understand fully the behavior of coordination complexes.
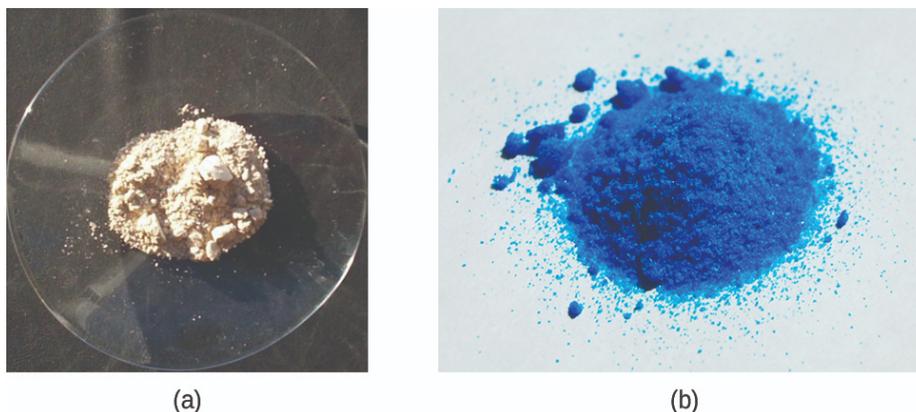
Figure 6.4.8: (a) Copper(I) complexes with d^{10} configurations such as CuI tend to be colorless, whereas (b) d^9 copper(II) complexes such as $Cu(NO_3)_2 \cdot 5H_2O$ are brightly colored.

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6.5: Key Terms

actinide series | (also, actinoid series) actinium and the elements in the second row or the *f*-block, atomic numbers 89–103

bidentate ligand | ligand that coordinates to one central metal through coordinate bonds from two different atoms

central metal | ion or atom to which one or more ligands is attached through coordinate covalent bonds

chelate | complex formed from a polydentate ligand attached to a central metal

chelating ligand | ligand that attaches to a central metal ion by bonds from two or more donor atoms

***cis* configuration** | configuration of a geometrical isomer in which two similar groups are on the same side of an imaginary reference line on the molecule

coordination compound | stable compound in which the central metal atom or ion acts as a Lewis acid and accepts one or more pairs of electrons

coordination compound | substance consisting of atoms, molecules, or ions attached to a central atom through Lewis acid-base interactions

coordination number | number of coordinate covalent bonds to the central metal atom in a complex or the number of closest contacts to an atom in a crystalline form

coordination sphere | central metal atom or ion plus the attached ligands of a complex

crystal field splitting (Δ_{oct}) | difference in energy between the t_{2g} and e_g sets or t and e sets of orbitals

crystal field theory | model that explains the energies of the orbitals in transition metals in terms of electrostatic interactions with the ligands but does not include metal ligand bonding

***d*-block element** | one of the elements in groups 3–11 with valence electrons in *d* orbitals

donor atom | atom in a ligand with a lone pair of electrons that forms a coordinate covalent bond to a central metal

e_g orbitals | set of two *d* orbitals that are oriented on the Cartesian axes for coordination complexes; in octahedral complexes, they are higher in energy than the t_{2g} orbitals

***f*-block element** | (also, inner transition element) one of the elements with atomic numbers 58–71 or 90–103 that have valence electrons in *f* orbitals; they are frequently shown offset below the periodic table

first transition series | transition elements in the fourth period of the periodic table (first row of the *d*-block), atomic numbers 21–29

fourth transition series | transition elements in the seventh period of the periodic table (fourth row of the *d*-block), atomic numbers 89 and 104–111

geometric isomers | isomers that differ in the way in which atoms are oriented in space relative to each other, leading to different physical and chemical properties

high-spin complex | complex in which the electrons maximize the total electron spin by singly populating all of the orbitals before pairing two electrons into the lower-energy orbitals

hydrometallurgy | process in which a metal is separated from a mixture by first converting it into soluble ions, extracting the ions, and then reducing the ions to precipitate the pure metal

ionization isomer | (or coordination isomer) isomer in which an anionic ligand is replaced by the counter ion in the inner coordination sphere

lanthanide series | (also, lanthanoid series) lanthanum and the elements in the first row or the *f*-block, atomic numbers 57–71

ligand | ion or neutral molecule attached to the central metal ion in a coordination compound

linkage isomer | coordination compound that possesses a ligand that can bind to the transition metal in two different ways (CN^- vs. NC^-)

low-spin complex | complex in which the electrons minimize the total electron spin by pairing in the lower-energy orbitals before populating the higher-energy orbitals

monodentate | ligand that attaches to a central metal through just one coordinate covalent bond

optical isomer | (also, enantiomer) molecule that is a nonsuperimposable mirror image with identical chemical and physical properties, except when it reacts with other optical isomers

pairing energy (P) | energy required to place two electrons with opposite spins into a single orbital

platinum metals | group of six transition metals consisting of ruthenium, osmium, rhodium, iridium, palladium, and platinum that tend to occur in the same minerals and demonstrate similar chemical properties

polydentate ligand | ligand that is attached to a central metal ion by bonds from two or more donor atoms, named with prefixes specifying how many donors are present (e.g., hexadentate = six coordinate bonds formed)

rare earth element | collection of 17 elements including the lanthanides, scandium, and yttrium that often occur together and have similar chemical properties, making separation difficult

second transition series | transition elements in the fifth period of the periodic table (second row of the *d*-block), atomic numbers 39–47

smelting | process of extracting a pure metal from a molten ore

spectrochemical series | ranking of ligands according to the magnitude of the crystal field splitting they induce

steel | material made from iron by removing impurities in the iron and adding substances that produce alloys with properties suitable for specific uses

strong-field ligand | ligand that causes larger crystal field splittings

superconductor | material that conducts electricity with no resistance

t_{2g} orbitals | set of three *d* orbitals aligned between the Cartesian axes for coordination complexes; in octahedral complexes, they are lowered in energy compared to the e_g orbitals according to CFT

third transition series | transition elements in the sixth period of the periodic table (third row of the *d*-block), atomic numbers 57 and 72–79

***trans* configuration** | configuration of a geometrical isomer in which two similar groups are on opposite sides of an imaginary reference line on the molecule

weak-field ligand | ligand that causes small crystal field splittings

6.6: Summary

The transition metals are elements with partially filled d orbitals, located in the d-block of the periodic table. The reactivity of the transition elements varies widely from very active metals such as scandium and iron to almost inert elements, such as the platinum metals. The type of chemistry used in the isolation of the elements from their ores depends upon the concentration of the element in its ore and the difficulty of reducing ions of the elements to the metals. Metals that are more active are more difficult to reduce.

Transition metals exhibit chemical behavior typical of metals. For example, they oxidize in air upon heating and react with elemental halogens to form halides. Those elements that lie above hydrogen in the activity series react with acids, producing salts and hydrogen gas. Oxides, hydroxides, and carbonates of transition metal compounds in low oxidation states are basic. Halides and other salts are generally stable in water, although oxygen must be excluded in some cases. Most transition metals form a variety of stable oxidation states, allowing them to demonstrate a wide range of chemical reactivity.

The transition elements and main group elements can form coordination compounds, or complexes, in which a central metal atom or ion is bonded to one or more ligands by coordinate covalent bonds. Ligands with more than one donor atom are called polydentate ligands and form chelates. The common geometries found in complexes are tetrahedral and square planar (both with a coordination number of four) and octahedral (with a coordination number of six). *Cis* and *trans* configurations are possible in some octahedral and square planar complexes. In addition to these geometrical isomers, optical isomers (molecules or ions that are mirror images but not superimposable) are possible in certain octahedral complexes. Coordination complexes have a wide variety of uses including oxygen transport in blood, water purification, and pharmaceutical use.

Crystal field theory treats interactions between the electrons on the metal and the ligands as a simple electrostatic effect. The presence of the ligands near the metal ion changes the energies of the metal d orbitals relative to their energies in the free ion. Both the color and the magnetic properties of a complex can be attributed to this crystal field splitting. The magnitude of the splitting (Δ_{oct}) depends on the nature of the ligands bonded to the metal. Strong-field ligands produce large splitting and favor low-spin complexes, in which the t_{2g} orbitals are completely filled before any electrons occupy the e_g orbitals. Weak-field ligands favor formation of high-spin complexes. The t_{2g} and the e_g orbitals are singly occupied before any are doubly occupied.

6.7: Exercises

1.

Write the electron configurations for each of the following elements:

  a. Sc
  b. Ti
  c. Cr
  d. Fe
  e. Ru

2.

Write the electron configurations for each of the following elements and its ions:

  a. Ti
  b. Ti^{2+}
  c. Ti^{3+}
  d. Ti^{4+}

3.

Write the electron configurations for each of the following elements and its 3+ ions:

  a. La
  b. Sm
  c. Lu

4.

Why are the lanthanoid elements not found in nature in their elemental forms?

5.

Which of the following elements is most likely to be used to prepare La by the reduction of La_2O_3: Al, C, or Fe? Why?

6.

Which of the following is the strongest oxidizing agent: or

7.

Which of the following elements is most likely to form an oxide with the formula MO_3: Zr, Nb, or Mo?

8.

The following reactions all occur in a blast furnace. Which of these are redox reactions?

  a. (f)

9.

Why is the formation of slag useful during the smelting of iron?

10.

Would you expect an aqueous manganese(VII) oxide solution to have a pH greater or less than 7.0? Justify your answer.

11.

Iron(II) can be oxidized to iron(III) by dichromate ion, which is reduced to chromium(III) in acid solution. A 2.5000-g sample of iron ore is dissolved and the iron converted into iron(II). Exactly 19.17 mL of 0.0100 M $Na_2Cr_2O_7$ is required in the titration. What percentage of the ore sample was iron?

12.

How many cubic feet of air at a pressure of 760 torr and 0 °C is required per ton of Fe_2O_3 to convert that Fe_2O_3 into iron in a blast furnace? For this exercise, assume air is 19% oxygen by volume.

13.

Find the potentials of the following electrochemical cell:

Cd | Cd^{2+}, $M = 0.10$ ‖ Ni^{2+}, $M = 0.50$ | Ni
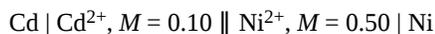
14.

A 2.5624-g sample of a pure solid alkali metal chloride is dissolved in water and treated with excess silver nitrate. The resulting precipitate, filtered and dried, weighs 3.03707 g. What was the percent by mass of chloride ion in the original compound? What is the identity of the salt?

15.

The standard reduction potential for the reaction is about 1.8 V. The reduction potential for the reaction is +0.1 V. Calculate the cell potentials to show whether the complex ions, $[Co(H_2O)_6]^{2+}$ and/or $[Co(NH_3)_6]^{2+}$, can be oxidized to the corresponding cobalt(III) complex by oxygen.

16.

Predict the products of each of the following reactions. (Note: In addition to using the information in this chapter, also use the knowledge you have accumulated at this stage of your study, including information on the prediction of reaction products.)

  a. (f)

17.

Predict the products of each of the following reactions. (Note: In addition to using the information in this chapter, also use the knowledge you have accumulated at this stage of your study, including information on the prediction of reaction products.)

  a. (f)

18.

Describe the electrolytic process for refining copper.

19.

Predict the products of the following reactions and balance the equations.

  a. (f) $FeCl_3$ is added to an aqueous solution of NaOH.

20.

What is the gas produced when iron(II) sulfide is treated with a nonoxidizing acid?

21.

Predict the products of each of the following reactions and then balance the chemical equations.

  a. (f) $FeCO_3$ is added to a solution of $HClO_4$.

    (g) Fe is heated in air.

22.

Balance the following equations by oxidation-reduction methods; note that *three* elements change oxidation state.

23.

Dilute sodium cyanide solution is slowly dripped into a slowly stirred silver nitrate solution. A white precipitate forms temporarily but dissolves as the addition of sodium cyanide continues. Use chemical equations to explain this observation. Silver cyanide is similar to silver chloride in its solubility.

24.

Predict which will be more stable, $[CrO_4]^{2-}$ or $[WO_4]^{2-}$, and explain.

25.

Give the oxidation state of the metal for each of the following oxides of the first transition series. (Hint: Oxides of formula M_3O_4 are examples of *mixed valence compounds* in which the metal ion is present in more than one oxidation state. It is possible to write these compound formulas in the equivalent format $MO \cdot M_2O_3$, to permit estimation of the metal's two oxidation states.)

  a. (i) Cu_2O

26.

Indicate the coordination number for the central metal atom in each of the following coordination compounds:

  a. (f) $[Fe(en)_2(CN)_2]^+$ (en = ethylenediamine, $C_2H_8N_2$)
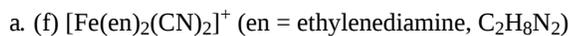
27.

Give the coordination numbers and write the formulas for each of the following, including all isomers where appropriate:

  a. (f) hexaamminecobalt(III) hexacyanochromate(III)

    (g) dibromobis(ethylenediamine) cobalt(III) nitrate

28.

Give the coordination number for each metal ion in the following compounds:

  a. $[Co(CO_3)_3]^{3-}$ (note that CO_3^{2-} is bidentate in this complex)
  b. $[Cu(NH_3)_4]^{2+}$
  c. $[Co(NH_3)_4Br_2]_2(SO_4)_3$
  d. $[Pt(NH_3)_4][PtCl_4]$
  e. $[Cr(en)_3](NO_3)_3$
  f. $[Pd(NH_3)_2Br_2]$ (square planar)
  g. $K_3[Cu(Cl)_5]$
  h. $[Zn(NH_3)_2Cl_2]$
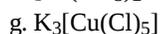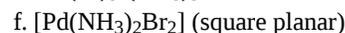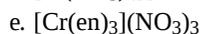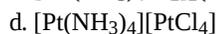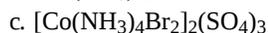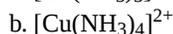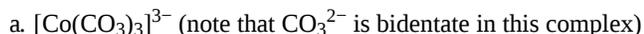
29.

Sketch the structures of the following complexes. Indicate any *cis*, *trans*, and optical isomers.

  a. (f) $[Co(C_2O_4)_2Cl_2]^{3-}$ (note that is the bidentate oxalate ion,
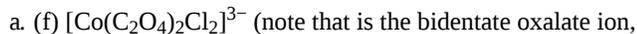
30.

Draw diagrams for any *cis, trans*, and optical isomers that could exist for the following (en is ethylenediamine):

  a. $[Co(en)_2(NO_2)Cl]^+$
  b. $[Co(en)_2Cl_2]^+$
  c. $[Pt(NH_3)_2Cl_4]$
  d. $[Cr(en)_3]^{3+}$
  e. $[Pt(NH_3)_2Cl_2]$
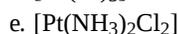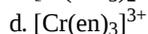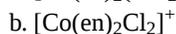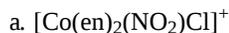
31.

Name each of the compounds or ions given in Exercise 19.28, including the oxidation state of the metal.

32.

Name each of the compounds or ions given in Exercise 19.30.

33.

Specify whether the following complexes have isomers.

  a. tetrahedral $[Ni(CO)_2(Cl)_2]$
  b. trigonal bipyramidal $[Mn(CO)_4NO]$
  c. $[Pt(en)_2Cl_2]Cl_2$
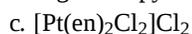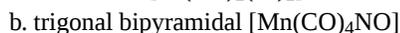
34.

Predict whether the carbonate ligand will coordinate to a metal center as a monodentate, bidentate, or tridentate ligand.

35.

Draw the geometric, linkage, and ionization isomers for $[CoCl_5CN][CN]$.

36.

Determine the number of unpaired electrons expected for $[Fe(NO_2)_6]^{3-}$ and for $[FeF_6]^{3-}$ in terms of crystal field theory.

37.

Draw the crystal field diagrams for $[Fe(NO_2)_6]^{4-}$ and $[FeF_6]^{3-}$. State whether each complex is high spin or low spin, paramagnetic or diamagnetic, and compare Δ_{oct} to P for each complex.

38.

Give the oxidation state of the metal, number of d electrons, and the number of unpaired electrons predicted for $[Co(NH_3)_6]Cl_3$.

39.

The solid anhydrous solid $CoCl_2$ is blue in color. Because it readily absorbs water from the air, it is used as a humidity indicator to monitor if equipment (such as a cell phone) has been exposed to excessive levels of moisture. Predict what product is formed by this reaction, and how many unpaired electrons this complex will have.

40.

Is it possible for a complex of a metal in the transition series to have six unpaired electrons? Explain.

41.

How many unpaired electrons are present in each of the following?

a. $[CoF_6]^{3-}$ (high spin)
b. $[Mn(CN)_6]^{3-}$ (low spin)
c. $[Mn(CN)_6]^{4-}$ (low spin)
d. $[MnCl_6]^{4-}$ (high spin)
e. $[RhCl_6]^{3-}$ (low spin)

42.

Explain how the diphosphate ion, $[O_3P-O-PO_3]^{4-}$, can function as a water softener that prevents the precipitation of Fe^{2+} as an insoluble iron salt.

43.

For complexes of the same metal ion with no change in oxidation number, the stability increases as the number of electrons in the t_{2g} orbitals increases. Which complex in each of the following pairs of complexes is more stable?

a. $[Fe(H_2O)_6]^{2+}$ or $[Fe(CN)_6]^{4-}$
b. $[Co(NH_3)_6]^{3+}$ or $[CoF_6]^{3-}$
c. $[Mn(CN)_6]^{4-}$ or $[MnCl_6]^{4-}$

44.

Trimethylphosphine, $P(CH_3)_3$, can act as a ligand by donating the lone pair of electrons on the phosphorus atom. If trimethylphosphine is added to a solution of nickel(II) chloride in acetone, a blue compound that has a molecular mass of approximately 270 g and contains 21.5% Ni, 26.0% Cl, and 52.5% $P(CH_3)_3$ can be isolated. This blue compound does not have any isomeric forms. What are the geometry and molecular formula of the blue compound?

45.

Would you expect the complex $[Co(en)_3]Cl_3$ to have any unpaired electrons? Any isomers?

46.

Would you expect the $Mg_3[Cr(CN)_6]_2$ to be diamagnetic or paramagnetic? Explain your reasoning.

47.

Would you expect salts of the gold(I) ion, Au^+, to be colored? Explain.

48.

$[CuCl_4]^{2-}$ is green. $[Cu(H_2O)_6]^{2+}$ is blue. Which absorbs higher-energy photons? Which is predicted to have a larger crystal field splitting?

CHAPTER OVERVIEW

7: Symmetry and Group Theory

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7.1: Symmetry Elements and Operations

Click here to see a lecture on this topic.

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 7.1.1). In this example, the symmetry operation is the rotation and the symmetry element is the axis of rotation.
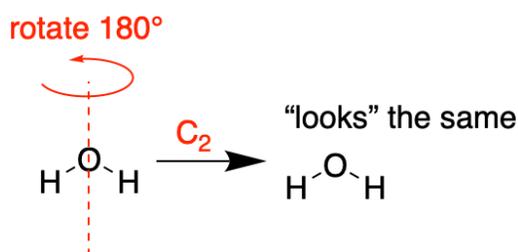
Figure 7.1.1: An example of a symmetry operation is a 180° rotation where the resulting position is indistinguishable from the original. A 180° rotation is called a C_2 operation; the axis of rotation is the symmetry element. (Kathryn Haas; CC-NC-BY-SA)

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 7.1.1.

Table 7.1.1: Table of elements and operations

Element	Operation	Symbol
Identity	identity	E
Proper axis	rotation by $(360/n)°$	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 $(360/n)°$, 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.

> **PRINCIPAL AXIS**: The principal 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 principal 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 principal 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 tetrahedrons, 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, an S_n operation is equivalent to C_n followed by σ_h.

References

1. Introduction to Molecular Symmetry by J. S Ogden
2. Inorganic Chemistry by Catherine Housecroft And Alan G. Sharpe.

7.2: Point Groups

Click here to see a lecture on this topic.

Introduction

A **Point Group** describes all the symmetry operations that can be performed on a molecule that result in a conformation indistinguishable from the original. Point groups are used in Group Theory, the mathematical analysis of groups, to determine properties such as a molecule's molecular orbitals.

Assigning Point Groups

While a point group contains all of the symmetry operations that can be performed on a given molecule, it is not necessary to identify all of these operations to determine the molecule's overall point group. Instead, a molecule's point group can be determined by following a set of steps which analyze the presence (or absence) of particular symmetry elements.

> 📌 **Steps for assigning a molecule's point group:**
>
> 1. Determine if the molecule is of high or low symmetry.
> 2. If not, find the highest order rotation axis, C_n.
> 3. Determine whether the molecule has any C_2 axes perpendicular to the principal C_n axis. If so, then there are n such C_2 axes, and the molecule is in the D set of point groups. If not, it is in either the C or S set of point groups.
> 4. Determine whether the molecule has a horizontal mirror plane (σ_h) perpendicular to the principal C_n axis. If so, the molecule is either in the C_{nh} or D_{nh} set of point groups.
> 5. Determine whether the molecule has a vertical mirror plane (σ_v) containing the principal C_n axis. If so, the molecule is either in the C_{nv} or D_{nd} set of point groups. If not, and if the molecule has n perpendicular C_2 axes, then it is part of the D_n set of point groups.
> 6. Determine whether there is an improper rotation axis, S_{2n}, collinear with the principal C_n axis. If so, the molecule is in the S_{2n} point group. If not, the molecule is in the C_n point group.
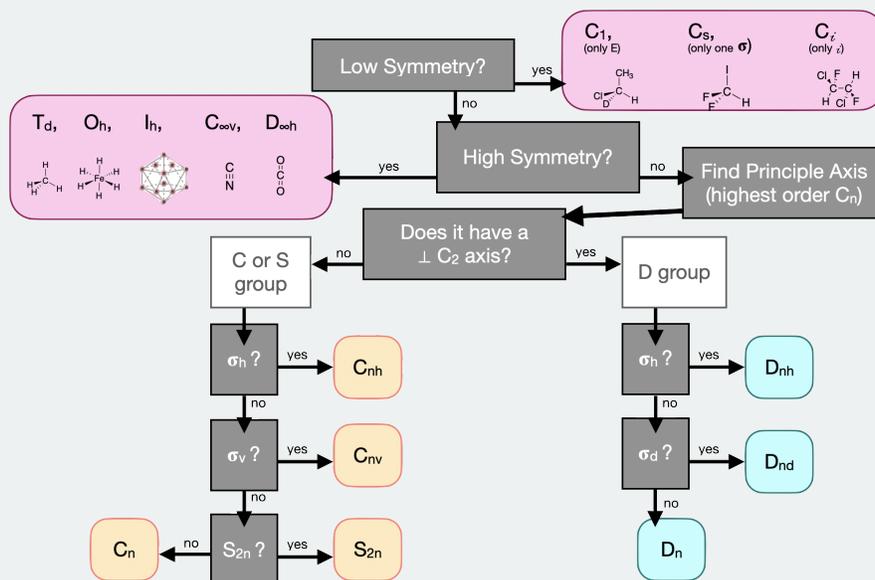
Figure 7.2.1: Decision tree for determining a molecule's point group (CC-BY-NC-SA; Kathryn Haas)

> ✔ **Example 7.2.1**
>
> Find the point group of benzene (C_6H_6).
>
> **Answer**

Solution

1. Benzene is neither high nor low symmetry

2. Highest order rotation axis: C_6

3. There are 6 C_2 axes perpendicular to the principal axis

4. There is a horizontal mirror plane (σ_h)

Benzene is in the D_{6h} point group.

See Also

Symmetry Gallery

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7.2.1: Groups of Low and High Symmetry

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Low Symmetry Point Groups

Low symmetry point groups include the C_1, C_s, and C_i groups

Group	Description	Example
C_1	only the identity operation (E)	CHFClBr
C_s	only the identity operation (E) and one mirror plane	C_2H_2ClBr
C_i	only the identity operation (E) and a center of inversion (i)	$C_2H_2Cl_2Br$

High Symmetry Point Groups

High symmetry point groups include the T_d, O_h, I_h, $C_{\infty v}$, and $D_{\infty h}$ groups. The table below describes their characteristic symmetry operations. The full set of symmetry operations included in the point group is described in the corresponding character table.

Group	Description	Example
$C_{\infty v}$	linear molecule with an infinite number of rotation axes and vertical mirror planes (σ_v)	HBr
$D_{\infty h}$	linear molecule with an infinite number of rotation axes, vertical mirror planes (σ_v), perpendicular C_2 axes, a horizontal mirror plane (σ_h), and an inversion center (i)	CO_2
T_d	typically have tetrahedral geometry, with 4 C_4 axes, 3 C_2 axes, 3 S_4 axes, and 6 dihedral mirror planes (σ_d)	CH_4
O_h	typically have octahedral geometry, with 3 C_4 axes, 4 C_3 axes, and an inversion center (i) as characteristic symmetry operations	SF_6
I_h	typically have an icosahedral structure, with 6 C_5 axes as characteristic symmetry operations	$B_{12}H_{12}^{2-}$

See Also

[Symmetry Gallery](#)

7.2.2: Other Groups

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D Groups

The D set of point groups is classified as D_{nh}, D_{nd}, or D_n, where n refers to the principal axis of rotation. Overall, the D groups are characterized by the presence of n C_2 axes perpendicular to the principal C_n axis. Further classification of a molecule in the D groups depends on the presence of horizontal or vertical/dihedral mirror planes.

Group	Description	Example
D_{nh}	n perpendicular C_2 axes, and a horizontal mirror plane (σ_h)	benzene, C_6H_6 is D_{6h}
D_{nd}	n perpendicular C_2 axes, and a vertical mirror plane (σ_v)	propadiene, C_3H_4 is D_{2d}
D_n	n perpendicular C_2 axes, no mirror planes	$[Co(en)_3]^{3+}$ is D_3

C Groups

The C set of point groups is classified as C_{nh}, C_{nv}, or C_n, where n refers to the principal axis of rotation. The C set of groups is characterized by the absence of n C_2 axes perpendicular to the principal C_n axis. Further classification of a molecule in the C groups depends on the presence of horizontal or vertical/dihedral mirror planes.

Group	Description	Example
C_{nh}	horizontal mirror plane (σ_h) perpendicular to the principal C_n axis	boric acid, H_3BO_3, is C_{3h}
C_{nv}	vertical mirror plane (σ_v) containing the principal C_n axis	ammonia, NH_3, is C_{3v}
C_n	no mirror planes	$P(C_6H_5)_3$ is C_3

S Groups

The S set of point groups is classified as S_{2n}, where n refers to the principal axis of rotation. The S set of groups is characterized by the absence of n C_2 axes perpendicular to the principal C_n axis, as well as the absence of horizontal and vertical/dihedral mirror planes. However, there is an improper rotation (or a rotation-reflection) axis collinear with the principal C_n axis.

Group	Description	Example
S_{2n}	improper rotation (or a rotation-reflection) axis collinear with the principal C_n axis	12-crown-4 is S_4

See Also

Symmetry Gallery

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7.3: Properties and Representations of Groups

Group Multiplication

Now we will investigate what happens when we apply two symmetry operations in sequence. As an example, consider the NH_3 molecule, which belongs to the C_{3v} point group. Consider what happens if we apply a C_3 rotation (120° counter-clockwise) followed by a σ_v reflection (reflection over the σ_v axis). We write this combined operation $\sigma_v C_3$ (when written, symmetry operations operate on the thing directly to their right, just as operators do in quantum mechanics – we therefore have to work backwards from right to left from the notation to get the correct order in which the operators are applied). As we shall soon see, the order in which the operations are applied is important.
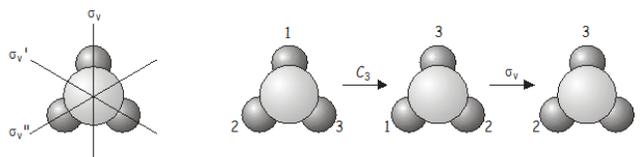
The combined operation $\sigma_v C_3$ is equivalent to σ_v'' (note the double prime on σ_v''!), which is also a symmetry operation of the C_{3v} point group. Now let's see what happens if we apply the operators in the reverse order, i.e., $C_3 \sigma_v$ is (σ_v followed by C_3).
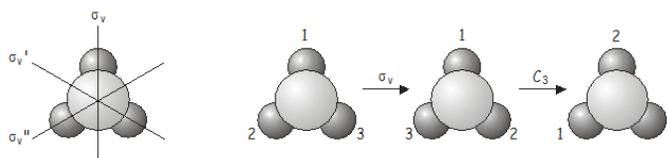
Again, the combined operation $C_3 \sigma_v$ is equivalent to another operation of the point group, this time σ_v' (note the single prime on σ_v'!).

There are two important points that are illustrated by this example:

1. The order in which two operations are applied is important. For two symmetry operations A and B, AB is not necessarily the same as BA, i.e. symmetry operations do not in general ***commute***. In some groups the symmetry elements do commute; such groups are said to be ***Abelian***.
2. If two operations from the same point group are applied in sequence, the result will be equivalent to another operation from the point group. Symmetry operations that are related to each other by other symmetry operations of the group are said to belong to the same ***class***. In NH_3, the three mirror planes σ_v, σ_v' and σ_v'' belong to the same class (related to each other through a C_3 rotation), as do the rotations C_3^+ and C_3^- (anticlockwise and clockwise rotations about the principal axis, related to each other by a vertical mirror plane).

Four Properties of Mathematical Groups

Now that we have explored some of the properties of symmetry operations and elements and their behavior within point groups, we are ready to introduce the formal mathematical definition of a group. The definitions below will be put into the context of *molecular* symmetry.

A mathematical group is defined as a set of elements (A_1, A_2, A_3...) together with a rule for forming combinations A_i, A_j... For our purposes, A_1, A_2, A_3, etc. are symmetry elements and A_i, A_j, etc. are symmetry operations described in a previous section. The elements of the group and the rule for combining them must satisfy the following four criteria.

1. The group must include the **identity E**, which commutes with other members of the group. In other terms, $\boldsymbol{EA_i = A_i}$ for all the elements of the group. Application of the identity operation before or after another operation, A_i, results in the same outcome as A_i alone.
2. The elements must satisfy the group property that the combination of any pair of elements is also an element of the group. For example, in the C_{3v} point group, a C_3 rotation followed by a σ_v gives another operation that is already part of the group: a σ_v ".
3. Each symmetry operation A_i must have an inverse A_i^{-1}, which is also an element of the group, such that

$$A_i A_i^{-1} = A_i^{-1} A_i = E$$

The inverse g_i^{-1} effectively 'undoes' the effect of the symmetry operation g_i. For example, in the C_{3v} point group, the inverse of C_3^+ is C_3^-.

4. The rule of combination must be associative

$$(A_i A_j)(A_k) = A_i(A_j A_k)$$

Or $A(BC) = (AB)C$. In other words, the order of operations should not matter.

Group theory is an important area in mathematics, and luckily for chemists the mathematicians have already done most of the work for us. Along with the formal definition of a group comes a comprehensive mathematical framework that allows us to carry out a rigorous treatment of symmetry in molecular systems and learn about its consequences.

Many problems involving operators or operations (such as those found in quantum mechanics or group theory) may be reformulated in terms of matrices. Any of you who have come across transformation matrices before will know that symmetry operations such as rotations and reflections may be represented by matrices. It turns out that the set of matrices representing the symmetry operations in a group obey all the conditions laid out above in the mathematical definition of a group, and using matrix representations of symmetry operations simplifies carrying out calculations in group theory. Before we learn how to use matrices in group theory, it will probably be helpful to review some basic definitions and properties of matrices.

*This page was adapted from here (click).

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7.3.1: Matrices

The symmetry of molecules is essential for understanding the structures and properties of organic and inorganic compounds. The properties of chemical compounds are often easily explained by consideration of symmetry. For example, the symmetry of a molecule determines whether the molecule has a permanent dipole moment or not. The theories that describe optical activity, infrared and ultraviolet spectroscopy, and crystal structure involve the application of symmetry considerations. Matrix algebra is the most important mathematical tool in the description of symmetry.

The properties of symmetry groups are organized in character tables (discussed later in this chapter). Character tables are constructed based on matrices. This page is a brief description of matrices and matrix multiplication.

What is a matrix?

An $m \times n$ matrix $\mathbf{A}$ is a rectangular array of numbers with m rows and n columns. The numbers m and n are the dimensions of $\mathbf{A}$. The numbers in the matrix are called its entries. The entry in row i and column j is called a_{ij}.
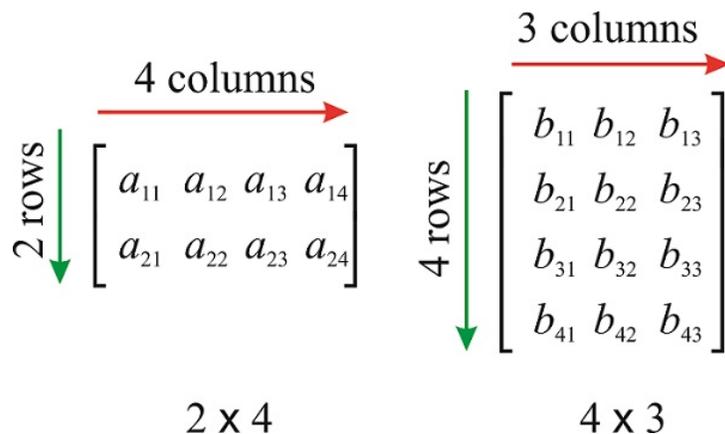
Figure 7.3.1.1: Matrices of different dimensions

Some types of matrices have special names:

- A square matrix:

$$\begin{pmatrix} 3 & -2 & 4 \\ 5 & 3i & 3 \\ -i & 1/2 & 9 \end{pmatrix}$$

  with $m = n$
- A rectangular matrix:

$$\begin{pmatrix} 3 & -2 & 4 \\ 5 & 3i & 3 \end{pmatrix}$$

  with $m \neq n$
- A column vector:

$$\begin{pmatrix} 3 \\ 5 \\ -i \end{pmatrix}$$

  with $n = 1$
- A row vector:

$$\begin{pmatrix} 3 & -2 & 4 \end{pmatrix}$$

  with $m = 1$
- The identity matrix:

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

with $a_{ij} = \delta_{i,j}$, where $\delta_{i,j}$ is a function defined as $\delta_{i,j} = 1$ if $i = j$ and $\delta_{i,j} = 0$ if $i \neq j$.

- A diagonal matrix:

$$\begin{pmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{pmatrix}$$

with $a_{ij} = c_i \delta_{i,j}$.

- An upper triangular matrix:

$$\begin{pmatrix} a & b & c \\ 0 & d & e \\ 0 & 0 & f \end{pmatrix}$$

All the entries below the main diagonal are zero.

- A lower triangular matrix:

$$\begin{pmatrix} a & 0 & 0 \\ b & c & 0 \\ d & e & f \end{pmatrix}$$

All the entries above the main diagonal are zero.

- A triangular matrix is one that is either lower triangular or upper triangular.

The Trace of a Matrix

The trace of an $n \times n$ square matrix $\mathbf{A}$ is the sum of the diagonal elements, and formally defined as $Tr(\mathbf{A}) = \sum_{i=1}^{n} a_{ii}$.

For example,

$$\mathbf{A} = \begin{pmatrix} 3 & -2 & 4 \\ 5 & 3i & 3 \\ -i & 1/2 & 9 \end{pmatrix} ; Tr(\mathbf{A}) = 12 + 3i$$

Singular and Nonsingular Matrices

A square matrix with nonzero determinant is called *nonsingular*. A matrix whose determinant is zero is called *singular*. (Note that you cannot calculate the determinant of a non-square matrix).

For a 2x2 matrix,

$$\mathbf{B} = \begin{pmatrix} a & b \\ c & d \end{pmatrix} ; det(\mathbf{B}) = ad - cb$$

For a 3x3 matrix,

$$\mathbf{C} = \begin{pmatrix} a & b & c \\ d & e & f \\ g & h & i \end{pmatrix}$$

$$det(\mathbf{C}) = a \begin{pmatrix} e & f \\ h & i \end{pmatrix} - b \begin{pmatrix} d & f \\ g & i \end{pmatrix} + c \begin{pmatrix} d & e \\ g & h \end{pmatrix}$$

$$det(\mathbf{C}) = aei - ahf - bdi + bgf + cdh - cge$$

The Matrix Transpose

The matrix transpose, most commonly written $\mathbf{A}^T$, is the matrix obtained by exchanging $\mathbf{A}$'s rows and columns. It is obtained by replacing all elements a_{ij} with a_{ji}. For example:

$$\mathbf{A} = \begin{pmatrix} 3 & -2 & 4 \\ 5 & 3i & 3 \end{pmatrix} \rightarrow \mathbf{A}^T = \begin{pmatrix} 3 & 5 \\ -2 & 3i \\ 4 & 3 \end{pmatrix}$$

Matrix Multiplication

To multiply two matrices, the number of vertical columns in the first matrix must be the same as the number of rows in the second matrix. If $\mathbf{A}$ has dimensions $m \times n$ and $\mathbf{B}$ has dimensions $n \times p$, then the product $\mathbf{A}\mathbf{B}$ is defined, and has dimensions $m \times p$.

$$c_{ij} = \sum a_{ij} \times b_{ij}$$

The entry $a_{ij} \times b_{ij}$ is obtained by multiplying row i of $\mathbf{A}$ by column j of $\mathbf{B}$, which is done by multiplying corresponding entries together and then adding the results:

Figure 7.3.1.1: Matrix multiplication

✔ **Example 7.3.1.1**

Calculate the product

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix}$$

Solution

We need to multiply a 3×3 matrix by a 3×2 matrix, so we expect a 3×2 matrix as a result.

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \\ e & f \end{pmatrix}$$

To calculate a, which is entry (1,1), we use row 1 of the matrix on the left and column 1 of the matrix on the right:

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \\ e & f \end{pmatrix} \rightarrow a = 1 \times 1 + (-2) \times 5 + 4 \times (-1) = -13$$

To calculate b, which is entry (1,2), we use row 1 of the matrix on the left and column 2 of the matrix on the right:

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \\ e & f \end{pmatrix} \rightarrow b = 1 \times 0 + (-2) \times 3 + 4 \times 0 = -6$$

To calculate c, which is entry (2,1), we use row 2 of the matrix on the left and column 1 of the matrix on the right:

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \\ e & f \end{pmatrix} \rightarrow c = 5 \times 1 + 0 \times 5 + 3 \times (-1) = 2$$

To calculate d, which is entry (2,2), we use row 2 of the matrix on the left and column 2 of the matrix on the right:

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \\ e & f \end{pmatrix} \rightarrow d = 5 \times 0 + 0 \times 3 + 3 \times 0 = 0$$

To calculate e, which is entry (3,1), we use row 3 of the matrix on the left and column 1 of the matrix on the right:

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \\ e & f \end{pmatrix} \rightarrow e = 0 \times 1 + 1/2 \times 5 + 9 \times (-1) = -13/2$$

To calculate f, which is entry (3,2), we use row 3 of the matrix on the left and column 2 of the matrix on the right:

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} a & b \\ c & d \\ e & f \end{pmatrix} \rightarrow f = 0 \times 0 + 1/2 \times 3 + 9 \times 0 = 3/2$$

The result is:

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \\ 0 & 1/2 & 9 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 5 & 3 \\ -1 & 0 \end{pmatrix} = \begin{pmatrix} -13 & -6 \\ 2 & 0 \\ -13/2 & 3/2 \end{pmatrix}$$

✔ Example 7.3.1.2

Calculate

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \end{pmatrix} \begin{pmatrix} 1 \\ 5 \\ -1 \end{pmatrix}$$

Solution

We are asked to multiply a 2×3 matrix by a 3×1 matrix (a column vector). The result will be a 2×1 matrix (a vector).

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \end{pmatrix} \begin{pmatrix} 1 \\ 5 \\ -1 \end{pmatrix} = \begin{pmatrix} a \\ b \end{pmatrix}$$

$$a = 1 \times 1 + (-2) \times 5 + 4 \times (-1) = -13$$

$$b = 5 \times 1 + 0 \times 5 + 3 \times (-1) = 2$$

The solution is:

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \end{pmatrix} \begin{pmatrix} 1 \\ 5 \\ -1 \end{pmatrix} = \begin{pmatrix} -13 \\ 2 \end{pmatrix}$$

Need help? The link below contains solved examples: Multiplying matrices of different shapes (three examples): http://tinyurl.com/kn8ysqq

External links:

- Multiplying matrices, example 1: http://patrickjmt.com/matrices-multiplying-a-matrix-by-another-matrix/
- Multiplying matrices, example 2: http://patrickjmt.com/multiplying-matrices-example-2/
- Multiplying matrices, example 3: http://patrickjmt.com/multiplying-matrices-example-3/

The Commutator

Matrix multiplication is not, in general, commutative. For example, we can perform

$$\begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \end{pmatrix} \begin{pmatrix} 1 \\ 5 \\ -1 \end{pmatrix} = \begin{pmatrix} -13 \\ 2 \end{pmatrix}$$

but cannot perform

$$\begin{pmatrix} 1 \\ 5 \\ -1 \end{pmatrix} \begin{pmatrix} 1 & -2 & 4 \\ 5 & 0 & 3 \end{pmatrix}$$

Even with square matrices, that can be multiplied both ways, multiplication is not commutative. In this case, it is useful to define the **commutator**, defined as:

$$[\mathbf{A}, \mathbf{B}] = \mathbf{A}\mathbf{B} - \mathbf{B}\mathbf{A}$$

✔ **Example 7.3.1.3**

Given $\mathbf{A} = \begin{pmatrix} 3 & 1 \\ 2 & 0 \end{pmatrix}$ and $\mathbf{B} = \begin{pmatrix} 1 & 0 \\ -1 & 2 \end{pmatrix}$

Calculate the commutator $[\mathbf{A}, \mathbf{B}]$

Solution

$$[\mathbf{A}, \mathbf{B}] = \mathbf{A}\mathbf{B} - \mathbf{B}\mathbf{A}$$

$$\mathbf{A}\mathbf{B} = \begin{pmatrix} 3 & 1 \\ 2 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ -1 & 2 \end{pmatrix} = \begin{pmatrix} 3 \times 1 + 1 \times (-1) & 3 \times 0 + 1 \times 2 \\ 2 \times 1 + 0 \times (-1) & 2 \times 0 + 0 \times 2 \end{pmatrix} = \begin{pmatrix} 2 & 2 \\ 2 & 0 \end{pmatrix}$$

$$\mathbf{B}\mathbf{A} = \begin{pmatrix} 1 & 0 \\ -1 & 2 \end{pmatrix} \begin{pmatrix} 3 & 1 \\ 2 & 0 \end{pmatrix} = \begin{pmatrix} 1 \times 3 + 0 \times 2 & 1 \times 1 + 0 \times 0 \\ -1 \times 3 + 2 \times 2 & -1 \times 1 + 2 \times 0 \end{pmatrix} = \begin{pmatrix} 3 & 1 \\ 1 & -1 \end{pmatrix}$$

$$[\mathbf{A}, \mathbf{B}] = \mathbf{A}\mathbf{B} - \mathbf{B}\mathbf{A} = \begin{pmatrix} 2 & 2 \\ 2 & 0 \end{pmatrix} - \begin{pmatrix} 3 & 1 \\ 1 & -1 \end{pmatrix} = \begin{pmatrix} -1 & 1 \\ 1 & 1 \end{pmatrix}$$

$$[\mathbf{A}, \mathbf{B}] = \begin{pmatrix} -1 & 1 \\ 1 & 1 \end{pmatrix}$$

Multiplication of a vector by a scalar

The multiplication of a vector $\vec{v_1}$ by a scalar n produces another vector of the same dimensions that lies in the same direction as $\vec{v_1}$;

$$n \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} nx \\ ny \end{pmatrix}$$

The scalar can stretch or compress the length of the vector, but cannot rotate it (figure [fig:vector_by_scalar]).
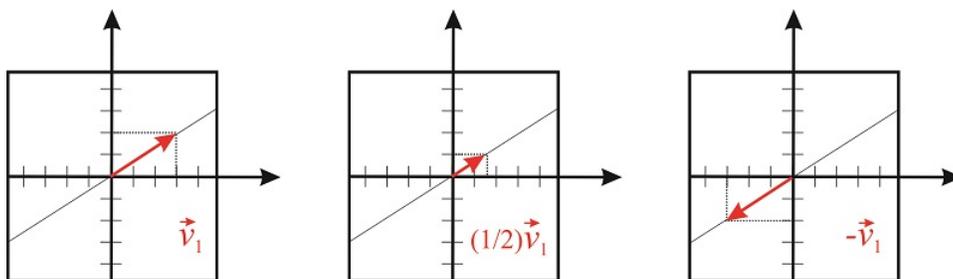
Figure 7.3.1.2: Multiplication of a vector by a scalar

Multiplication of a square matrix by a vector

The multiplication of a vector $\vec{v_1}$ by a square matrix produces another vector of the same dimensions of $\vec{v_1}$. For example, we can multiply a 2×2 matrix and a 2-dimensional vector:

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} ax+by \\ cx+dy \end{pmatrix}$$

For example, consider the matrix

$$\mathbf{A} = \begin{pmatrix} -2 & 0 \\ 0 & 1 \end{pmatrix}$$

The product

$$\begin{pmatrix} -2 & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

is

$$\begin{pmatrix} -2x \\ y \end{pmatrix}$$

We see that 2×2 matrices act as operators that transform one 2-dimensional vector into another 2-dimensional vector. This particular matrix keeps the value of y constant and multiplies the value of x by -2 (Figure 7.3.1.3).
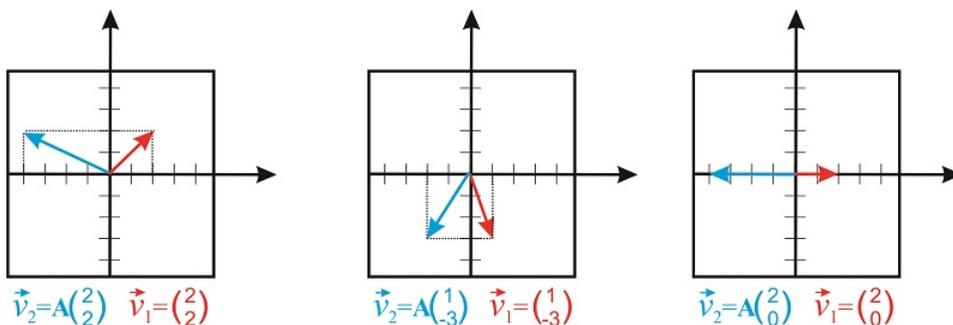
Figure 7.3.1.3: Multiplication of a vector by a square matrix

Notice that matrices are useful ways of representing operators that change the orientation and size of a vector. An important class of operators that are of particular interest to chemists are the so-called symmetry operators.

Attribution

This page was adapted from Matrices (click here), contributed by Marcia Levitus, Associate Professor (Biodesign Institute) at Arizona State University.

Curated or created by Kathryn Haas

7.3.2: Representations of Point Groups

Symmetry Operations: Matrix Representations

A **symmetry operation**, such as a rotation around a symmetry axis or a reflection through a plane, is an operation that, when performed on an object, results in a new orientation of the object that is indistinguishable from the original. For example, if we rotate a square in the plane by $\pi/2$ or π, the new orientation of the square is superimposable on the original one (Figure 7.3.2.1).

If rotation by an angle θ of a molecule (or object) about some axis results in an orientation of the molecule (or object) that is superimposable on the original, the axis is called a rotation axis. The molecule (or object) is said to have an n-fold rotational axis, where n is $2\pi/\theta$. The axis is denoted as C_n. The square of Figure 7.3.2.1 has a C_4 axis perpendicular to the plane because a $90°$ rotation leaves the figure indistinguishable from the initial orientation. This axis is also a C_2 axis because a $180°$ degree rotation leaves the square indistinguishable from the original square. In addition, the figure has several other C_2 axis that lie on the same plane as the square:
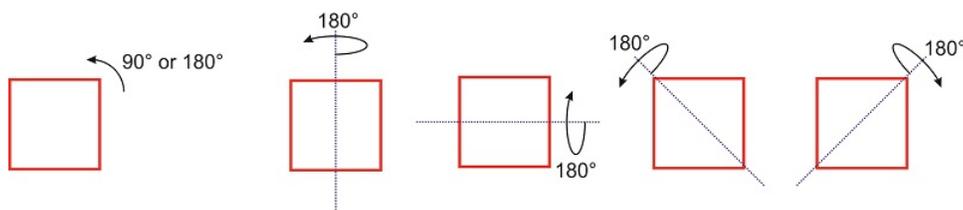
Figure 7.3.2.1: Symmetry operations performed on a square

A symmetry operation moves all the points of the object from one initial position to a final position, and that means that symmetry operators are 3×3 square matrices (or 2×2 in two dimensions). Each symmetry operation can be expressed as a **transformation matrix** where the vector (x', y', z') represents the new coordinates of the point (x, y, z) after the symmetry operation.

$$[\text{New Coordinates}(x', y', z')] = [\text{Transformation Matrix}] \times [\text{Old Coordinates}(x, y, z)]$$

We will use the example of water, which is in the C_{2v} point group, to illustrate how transformation matrices can be used to represent the symmetry of a group.

Figure 7.3.2.2 shows the three symmetry elements of the molecule of water (H_2O). This molecule has only one rotation axis, which is 2-fold, and therefore we call it a "$\boldsymbol{C_2}$ axis." It also has two mirror planes, one that contains the two hydrogen atoms ($\boldsymbol{\sigma_{yz}}$), and another one perpendicular to it ($\boldsymbol{\sigma_{xz}}$). Both planes contain the C_2 axis.
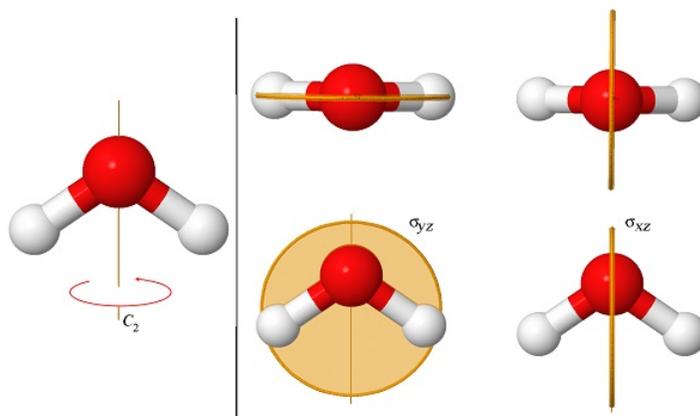
Figure 7.3.2.2: The symmetry elements of the molecule of water

Transformation Matrix of $\boldsymbol{C_2}$ rotation

A 2-fold rotation around the $z-$axis changes the location of a point (x, y, z) to $(-x, -y, z)$ (see Figure 7.3.2.3). By convention, rotations are always taken in the counterclockwise direction.
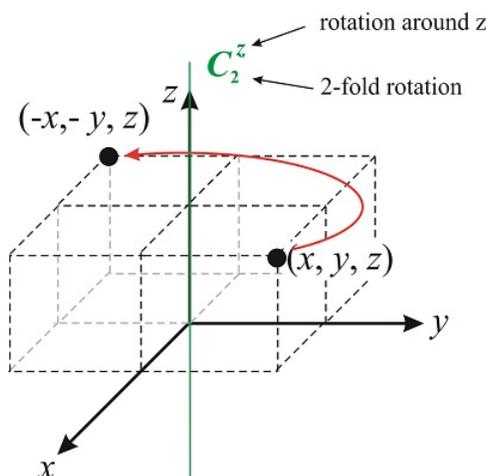
Figure 7.3.2.3: A 2-fold rotation around the z-axis

What is the matrix that represents the C_2 rotation? The matrix transforms the vector (x, y, z) into $(-x, -y, z)$, so

$$C_2(x, y, z) = (-x, -y, z)$$

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ -y \\ z \end{pmatrix}$$

We know the matrix is a 3×3 square matrix because it needs to multiply a 3-dimensional vector. In addition, we write the vector as a vertical column to satisfy the requirements of matrix multiplication.

$$\begin{pmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$a_{11}x + a_{12}y + a_{13}z = -x$$

$$a_{21}x + a_{22}y + a_{23}z = -y$$

$$a_{31}x + a_{32}y + a_{33}z = z$$

and we conclude that $a_{11} = -1$, $a_{12} = a_{13} = 0$, $a_{22} = -1$, $a_{21} = a_{23} = 0$ and $a_{33} = 1$, $a_{31} = a_{32} = 0$. The transformation matrix of the C_2 operation of the C_{2v} point group is:

$$C_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{7.3.2.1}$$

Transformation Matrix of σ_{xz} reflection

Rotations are not the only symmetry operations we can perform on a molecule. Figure 7.3.2.4 illustrates the reflection of a point through the xz plane. This operation transforms the vector (x, y, z) into the vector $(x, -y, z)$. Symmetry operators involving reflections through a plane are usually denoted with the letter σ, so the operator that reflects a point through the xz plane is $\hat{\sigma}_{xz}$:

$$\sigma_{xz}(x, y, z) = (x, -y, z)$$
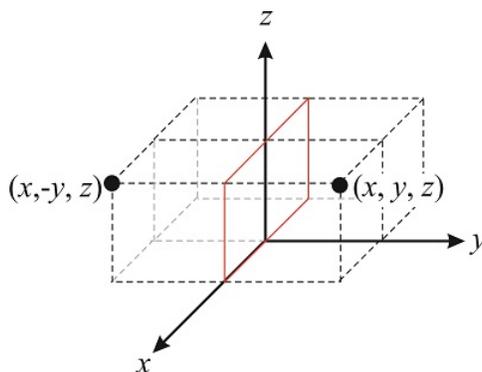
Figure 7.3.2.3: A reflection through the xz plane

Following the same logic we used for the rotation matrix, we can write the σ_{xz} transformation matrix as:

$$\sigma_{x,z} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{7.3.2.2}$$

This is true because

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ -y \\ z \end{pmatrix}$$

> **? Exercise 7.3.2.1**
>
> Find the transformation matrix of the identity (E) and the $\sigma_{y,z}$ operations under the C_{2v} point group.
>
> **Answer**
>
> The transformation matrix for E is $\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$.
>
> The transformation matrix for $\sigma_{v(yz)^{\prime\prime}}$ is $\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$.

Characters

For a square matrix, the ***character*** is the trace of the matrix. For the C_2 operation, with the transformation matrix

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

the trace is $(-1)+(-1)+1=-1$.

The set of characters for a point group is called a **reducible representation (Γ)**. The reducible representation for the C_{2v} point group is:

C_{2v}	E	C_2	σ_v	σ_v'
Γ	3	-1	1	1

? Exercise 7.3.2.1

Prove that the characters in the reducible representation for C_{2v} are correct:

C_{2v}	E	C_2	σ_v	σ_v'
Γ	3	−1	1	1

Answer

For the E operation, with the transformation matrix $\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$, the trace is $1+1+1 = \ 3$.

For the C_2^z operation, with the transformation matrix $\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$, the trace is $(-1)+(-1)+1 = \ -1$.

For the $\sigma_{v(xz)'}$ operation, with the transformation matrix $\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$, the trace is $1+(-1)+1 = \ 1$.

For the $\sigma_{v(yz)''}$ operation, with the transformation matrix $\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$, the trace is $-1+1+1 = \ 1$.

This gives the reducible representation

C_{2v}	E	C_2	σ_v	σ_v'
Γ	3	−1	1	1

Reducible and Irreducible Representations

Let us now go back and look in more detail at the transformation matrices of the C_{2v} point group that we derived above. If we look at the matrices carefully we see that they all take the same block diagonal form (a square matrix is said to be **block diagonal** if all the elements are zero except for a set of submatrices lying along the diagonal).

$$E = \begin{pmatrix} [1] & 0 & 0 \\ 0 & [1] & 0 \\ 0 & 0 & [1] \end{pmatrix}, \ C_2 = \begin{pmatrix} [-1] & 0 & 0 \\ 0 & [-1] & 0 \\ 0 & 0 & [1] \end{pmatrix}, \ \sigma_{v(xz)}' = \begin{pmatrix} [1] & 0 & 0 \\ 0 & [-1] & 0 \\ 0 & 0 & [1] \end{pmatrix}, \ \sigma_{v(yz)''} = \begin{pmatrix} [-1] & 0 & 0 \\ 0 & [1] & 0 \\ 0 & 0 & [1] \end{pmatrix}$$

All the non-zero elements become 1x1 matrices that each represent individual x, y, z coordinates. In other words, the element a_{11} represents x, a_{22} represents y, and a_{33} represents z. The matrix elements for x from each transformation matrix combine to form an irreducible representation of the C_{2v} point group. Likewise, the matrix elements for y combine to form a second irreducible representation, and the same is true for z elements. These irreducible representations are shown below:

C_{2v}	E	C_2	σ_v	σ_v'	Coordinate Used
	1	−1	1	−1	x
	1	−1	−1	1	y
	1	1	1	1	z
Γ	3	−1	1	1	

The irreducible representations add to form the reducible representation, Γ. This Γ, which is the set of 3x3 matrices, can be reduced to the set of 1x1 matrices of the irreducible representations. The irreducible representations cannot be reduced further, hence their name.

Sources & Attribution

- Parts of this page was adapted from Matrices (click here) (Symmetry Operators), contributed by Marcia Levitus, Associate Professor (Biodesign Institute) at Arizona State University.
- Parts of this page were adapted from Reductions of Representations, contributed by

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- Curated or created by Kathryn Haas

7.3.3: Character Tables

Introduction to Character Tables, using C_{2v} as example

A character table is the complete set of irreducible representations of a symmetry group. In the previous section, we derived three of the four irreducible representations for the C_{2v} point group. These three irreducible representations are labeled A_1, B_1, and B_2. The fourth irreducible representation, A_2, can be derived using the properties (or "rules") for irreducible representations listed below.

📌 **Properties of Characters of Irreducible Representations in Point Groups**

1. There is always a totally symmetric representation in which all the characters are 1.
   e.g. In C_{2v}, A_1 is totally symmetric.
2. The order of the group (h) is the total number of symmetry operations in the group.
   e.g. In C_{2v}, $h = 4$
3. Similar operations are listed as classes (R) and appear as columns in the table.
   e.g. In C_{2v}, there are four classes of operations, E, C_2, $\sigma_{v(xz)}$, and $\sigma'_{v(yz)}$
4. The number of irreducible representations (rows) must equal the number of classes (columns). This results in all character tables being square.
   e.g. In C_{2v}, there are four classes and four irreducible representations.
5. The sum of squares of all characters under E is equal to the order of the group: $h = \sum[\chi_i]^2$
   e.g. In C_{2v}, $h = 1^2 + 1^2 + 1^2 + 1^2 = 4$
6. For any irreducible representation (i), the sum of squares of its characters multiplied by the number of operations in the class is the order of the group: $h = \sum[\chi_i(R)]^2$
   e.g. For A_2 in C_{2v}, $h = (1 \times 1)^2 + (1 \times 1)^2 + (-1 \times 1)^2 + (-1 \times 1)^2 = 4$
7. Irreducible representations are orthogonal. For any two representations (i and j): $\sum[\chi_i * (R)\chi_j(R)] = 0$
   e.g. For B_1 and B_2 of C_{2v}, $[1 \times 1] + [-1 \times -1] + [1 \times -1] + [-1 \times 1] = 0$

The complete character table for C_{2v} is given below.

C_{2v}	E	C_2	σ_v	σ'_v	$h = 4$	
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

The various sections of the table are as follows:

    i. The first element in the table gives the name of the point group, usually in Schoenflies (C_{2v}) notation.
    ii. Along the first row are the symmetry operations of the group, E, C_2, σ_v and σ_v ", followed by the order of the group, h.
    iii. In the first column are the irreducible representations of the group, represented by Mulliken Labels. In C_{2v} the irreducible representations are A_1, A_2, B_1 and B_2. The Mulliken labels indicate the symmetry of each representation (explained further below).
    iv. The characters (χ) of the irreducible representations under each symmetry operation are given in the bulk of the table.
    v. The final column(s) of the table lists a number of functions that transform as the various irreducible representations of the group. These are the Cartesian axes (x, y, z), the Cartesian products ($z^2, x^2 + y^2, xy, xz, yz$), and the rotations ($R_x, R_y, R_z$) (explained further below).

Another example: C_{3v}

Th C_{3v} point group has three classes of operations: E, C_3, and $\sigma_{v(xz)}$. The derivation of transformation matrices for E and $\sigma_{v(xz)}$ is similar to the case for C_{2v}. However, the C_{3v} operation does not give simple 1 or -1 characters. If we carry out a rotation about z by an angle θ, our x and y axes are transformed onto new axes x' and y'. The new axes can each be written as a linear combination of our original x and y axes. The derivation of the rotation matrices will not be covered in this text, but is described elsewhere:

$$\begin{aligned} x' &= x\cos\theta + y\sin\theta \\ y' &= -x\sin\theta + y\cos\theta \end{aligned}$$

For a C_3 rotation counterclockwise through 120° (or $\frac{2\pi}{3}$):

$$\begin{aligned} x' &= x\cos(2\pi/3) + y\sin(2\pi/3) &= -\tfrac{1}{2}x - \tfrac{\sqrt{3}}{2}y \\ y' &= -x\sin(2\pi/3) + y\cos(2\pi/3) &= \tfrac{\sqrt{3}}{2}x - \tfrac{1}{2}y \end{aligned}$$

The transformation matrices for symmetry operations of C_{3v} are as follows:

$$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad C_3 = \begin{pmatrix} [-\tfrac{1}{2} & -\tfrac{\sqrt{3}}{2}] & 0 \\ [\tfrac{\sqrt{3}}{2} & -\tfrac{1}{2}] & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \sigma'_{v(xz)} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The C_3 transformation matrix contains off-diagonal entries, and therefore it cannot be block diagonalized as 1x1 matrices. However, the first two lines can be diagonalized as a 2x2 and the last line as a 1x1 matrix (Figure $7.3.3.1$):

2x2 matrices

$$E = \begin{bmatrix} [1 & 0] & 0 \\ [0 & 1] & 0 \\ 0 & 0 & [1] \end{bmatrix} \quad C_3 = \begin{bmatrix} [-\tfrac{1}{2} & -\tfrac{\sqrt{3}}{2}] & 0 \\ [\tfrac{\sqrt{3}}{2} & -\tfrac{1}{2}] & 0 \\ 0 & 0 & [1] \end{bmatrix} \quad \sigma'_{v(xz)} = \begin{bmatrix} [1 & 0] & 0 \\ [0 & -1] & 0 \\ 0 & 0 & [1] \end{bmatrix}$$

Figure $7.3.3.1$: The C_3 transformation matrix contains off-diagonal entries, and therefore it cannot be block diagonalized as 1x1 matrices. However, the first two lines can be diagonalized as a 2x2 and the last line as a 1x1 matrix. (CC-BY-NC-SA; Kathryn Haas)

The character from a 2x2 matrix is the sum of the trace of that matrix. So, for the C_3 operation, the 2x2 matrix gives the character -1 (from $-\tfrac{1}{2} + -\tfrac{1}{2}$).

The character table for C_{3v} is shown below.

C_{3v}	E	$2C_3$	$3\sigma_v$	$h = 6$
A_1	1	1	1	z, z^2, x^2+y^2
A_2	1	1	-1	R_z
E	2	-1	0	$(x,y), (xy, x^2+y^2\,), (xz, yz), (R_x, R_y)$

Additional features of character tables

> 📌 Additional Features of Character Tables
>
> 1. Symmetry operations of the same class are grouped into the same column (class) in the character table and not listed separately.
>   e.g. In the C_{3v} point group, there are four operations: E, C_3, C_3^2, and σ_v. The C_3 and C_3^2 operations are listed together in the character table as $2C_3$.
> 2. IF there are multiple C_2 axes (in a D group), the C_2 axes that are perpendicular to the principle axis are labeled with primes (e.g. C_2' and C_2''); when there are multiple types of perpendicular C_2 axes, one prime (C_2') means that it passes through more atoms, while a double prime (C_2'') means it goes between atoms.
> 3. Mirror planes that are perpendicular to the principle axis are "horizontal" mirror planes and are designated with an h subscript (σ_h). Mirror planes that are in-plane with the principle axis are "vertical" mirror planes, σ_v. When there are two types of vertical mirror planes, those that run through more atoms are σ_v while those that run between atoms are "dihedral", σ_d.
> 4. Matching the symmetry operations listed in the character table to the symmetry operations of a molecule can confirm its point group.

5. Irreducible representations are each assigned a Mulliken label, listed in the left-hand column, that indicates the symmetry of that representation as follows:

Mulliken Labels	meaning
A	singly degenerate (1x1), symmetric to principle axis
B	singly degenerate (1x1), antisymmetric to principle axis
E	doubly degenerate (2x2)
T	triply degenerate (3x3)
Subscripts and superscripts	**meaning**
1	symmetric to σ_v or perpendicular to C_2
2	anti-symmetric to σ_v or perpendicular to C_2
g	symmetric to inversion center
u	anti-symmetric to inversion center
$'$	symmetric to σ_h
$''$	anti-symmetric to σ_h

6. The right-hand columns of the character table list a number of functions that transform as the various irreducible representations of the group. These are the Cartesian axes (x, y, z), the Cartesian products ($z^2, x^2 + y^2, xy, xz, yz$), and the rotations (R_x, R_y, R_z). These expressions indicate the properties of orbitals within the symmetry group. The s-orbital, which is totally symmetric, corresponds to the irreducible representation that possesses symmetry of x^2, y^2 and z^2 combined. The p-orbitals each possess the symmetry of the corresponding axis (e.g. p_x corresponds to the x axis). Each of the d-orbitals possess the symmetry of the corresponding binary product (e.g. d_{xy} corresponds to the binary product, xy, in the character table).

The functions listed in the final column of the table are important in many chemical applications of group theory, particularly in spectroscopy. For example, by looking at the transformation properties of x, y and z (sometimes given in character tables as T_x, T_y, T_z) we can discover the symmetry of translations along the x, y, and z axes. Similarly, R_x, R_y and R_z represent rotations about the three Cartesian axes. The transformation properties of x, y, and z can be used to determine whether or not a molecule is IR-active or whether or not it can absorb a photon of x-, y-, or z-polarized light and undergo a spectroscopic transition. The Cartesian products play a similar role in determining selection rules for Raman transitions, which involve two photons.

A visual summary of the sections and their significance is given in Figure $7.3.3.2$ Character tables for common point groups are given in the References section of LibreTexts Bookshelves.

Point Group
(Shoenflies notation)

Symmetry operations (**R**)
organized into *classes*

Order of the group

C_{2v}	E	C_2	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	zx
B_2	1	-1	-1	1	y, R_x	yz

Characters (χ)

Mulliken labels *(i,j..)* ..tell us "at a glance" about the symmetry of a representation

Labels
A = 1x1, symmetric to principle axis
B = 1x1, anti-symmetric to principle axis
E = 2x2
T = 3x3
Subscripts and superscripts
1 = symmetric to σ_v or $\perp C_2$
2 = anti-symmetric to σ_v or $\perp C_2$
g = symmetric to inversion center
u = anti-symmetric to inversion center
' = symmetric to σ_h
" = anti-symmetric to σ_h

Quadratic functions (translations):
Symmetry of d-orbitals.
Raman active modes.

Linear functions (transformations):
x, y, z axes and rotations around axes (R_x, R_y, R_z).
Symmetry of the p-orbitals.
IR active modes.

Figure 7.3.3.2: Visual summary of the sections of a character table and their meaning. (CC-BY-NC-SA; Kathryn Haas)

Contributors and Attributions

- Curated or created by Kathryn Haas

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  adapted from Character Tables (click here)

SECTION OVERVIEW

7.4: Examples and Applications of Symmetry

The purpose of learning group theory is that molecular symmetry can be applied to understand the properties of molecules. This chapter introduces two applications of symmetry: chirality and molecular vibrations (in the context of analyzing IR and Raman spectra). An additional application of symmetry, to understand molecular bonding, deserves its own chapter and will be explored in Chapter 5.

7.4.1: Chirality

7.4.2: Molecular Vibrations

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7.4.1: Chirality

Introduction

Around the year 1847, the French scientist Louis Pasteur provided an explanation for the optical activity of tartaric acid salts. When he carried out a particular reaction, Pasteur observed that two types of crystals precipitated. Patiently and carefully using tweezers, Pasteur was able to separate the two types of crystals. Pasteur noticed that the types rotated plane-polarized light by the same amount but in different directions. These two compounds are called enantiomers.
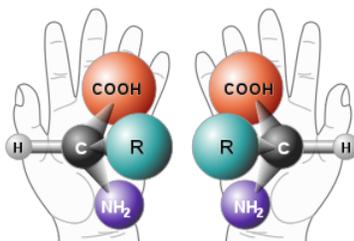
Figure 7.4.1.1: Two enantiomers of an amino acid (with side chain R).

What is chirality?

A molecule is **chiral** (or **dissymetric**) if it is non-superimposable on its mirror image. The two mirror images of a chiral molecule are called enantiomers. Enantiomers have the same physical properties (e.g., melting point, etc.). They differ in their ability to rotate plane polarized light and in their reactivity with other chiral molecules. Due to their ability to rotate plane polarized light, they are referred to as being *optically active*.

Using Symmetry to Determine Chirality

There are some general rules of thumb that help determine whether a molecule is chiral or achiral. The point group of the molecule, and the symmetry operations within that point group, can give clues as to whether the molecule is chiral.

> ⚷ Symmetry operations of chiral molecules
>
> A chiral molecule cannot possess a plane of symmetry (σ), a center of inversion (i), or an improper rotation (S_n). Due to the fact that all groups that lack both σ and i also lack S_n, **a molecule that belongs to any group that lacks S_n is chiral**.

An example of an inorganic coordination complex is tris(ethylenediamine)cobalt(III) (Figure 7.4.1.1). Figure 7.4.1.1 shows the two enantiomers of tris(ethylenediamine)cobalt(III): the Δ and Λ isomers.
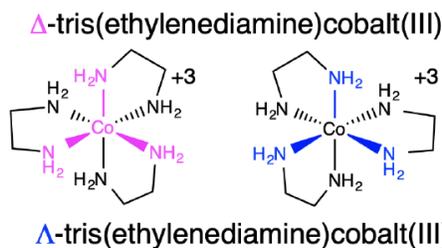
Figure 7.4.1.2: Two chiral enantiomers of tris(ethylenediamine)coalt(III).

You can visualize the Λ and Δ isomers by imagining that the ligands around the metal centers are blades of a fan. To push the air toward you, you would need to rotate the Δ isomer clockwise, and the Λ isomer counter-clockwise.

> ❓ Exercise 7.4.1.1
>
> Which point groups are possible for chiral molecules?
>
> **Answer**
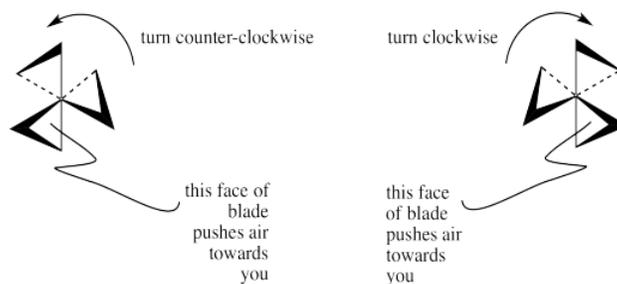
Figure 7.4.1.3: Another way of thinking about the chirality of the two chiral enantiomers of tris(ethylenediamine)coalt(III) shown in Figure 7.4.1.2. This figure was taken from Structure and Reactivity in Organic, Biological, and Inorganic Chemistry.

As a result of the previous discussion, there are a few classes of point groups that lack an improper axis. Those classes are C_1, C_n, and D_n.

7.4.2: Molecular Vibrations

Symmetry and group theory can be applied to understand molecular vibrations. This is particularly useful in the context of predicting the number of peaks expected in the infrared (IR) and Raman spectra of a given compound.

We will use water as a case study to illustrate how group theory is used to predict the number of peaks in IR and Raman spectra.

How many IR and Raman peaks would we expect for H_2O?

To answer this question with group theory, a pre-requisite is that you **assign the molecule's point group and assign an axis system** to the entire molecule. By convention, the z axis is collinear with the principle axis, the x axis is in-plane with the molecule or the most number of atoms. It is a good idea to stick with this convention (see Figure $7.4.2.1$).

What is the point group for H_2O? (click to see answer)

H_2O has the following operations: E, C_2, σ_v, σ_v'. The point group is C_{2v}.
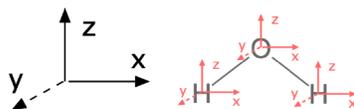
Figure $7.4.2.1$: The first step to finding normal modes is to assign a consistent axis system to the entire molecule and to each atom. (CC-BY-SA; Kathryn Haas)

Now that we know the molecule's point group, we can use group theory to determine the symmetry of all motions in the molecule, or the symmetry of each of its degrees of freedom. Then we will subtract rotational and translational degrees of freedom to find the vibrational degrees of freedom. The number of degrees of freedom depends on the number of atoms (N) in a molecule. Each atom in the molecule can move in three dimensions (x, y, z), and so the number of degrees of freedom is three dimensions times N number of atoms, or $3N$. The total degrees of freedom include a number of vibrations, three translations (in x, y, and z), and either two or three rotations. Linear molecules have two rotational degrees of freedom, while non-linear molecules have three. The vibrational modes are represented by the following expressions:

$$\text{Linear Molecule Degrees of Freedom} \quad = \quad 3N - 5$$
$$\text{Non-Linear Molecule Degrees of Freedom} \quad = \quad 3N - 6$$

Our goal is to find the symmetry of all degrees of freedom, and then determine which are vibrations that are IR- and Raman-active.

STEP 1: Find the reducible representation for all normal modes Γ_{modes}.

The first major step is to **find a reducible representation (Γ)** for the movement of all atoms in the molecule (including rotational, translational, and vibrational degrees of freedom). We'll refer to this as Γ_{modes}. To find normal modes using group theory, **assign an axis system** to each individual atom to represent the three dimensions in which each atom can move. Each axis on each atom should be consistent with the conventional axis system you previously assigned to the entire molecule (see Figure $7.4.2.1$).

Γ_{modes} is the sum of the characters (trace) of the transformation matrix for the entire molecule (in the case of water, there are 9 degrees of freedom and this is now a 9x9 matrix). Let's walk through this step-by-step. The transformation matrix of E and C_2 are shown below:

$$E = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_{oxygen} \\ y_{oxygen} \\ z_{oxygen} \\ x_{hydrogen-a} \\ y_{hydrogen-a} \\ z_{hydrogen-a} \\ x_{hydrogen-b} \\ y_{hydrogen-b} \\ z_{hydrogen-b} \end{pmatrix} = \begin{pmatrix} x'_{oxygen} \\ y'_{oxygen} \\ z'_{oxygen} \\ x'_{hydrogen-a} \\ y'_{hydrogen-a} \\ z'_{hydrogen-a} \\ x'_{hydrogen-b} \\ y'_{hydrogen-b} \\ z'_{hydrogen-b} \end{pmatrix}, \chi = 9$$

$$C_2 = \begin{pmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} x_{oxygen} \\ y_{oxygen} \\ z_{oxygen} \\ x_{hydrogen-a} \\ y_{hydrogen-a} \\ z_{hydrogen-a} \\ x_{hydrogen-b} \\ y_{hydrogen-b} \\ z_{hydrogen-b} \end{pmatrix} = \begin{pmatrix} x'_{oxygen} \\ y'_{oxygen} \\ z'_{oxygen} \\ x'_{hydrogen-a} \\ y'_{hydrogen-a} \\ z'_{hydrogen-a} \\ x'_{hydrogen-b} \\ y'_{hydrogen-b} \\ z'_{hydrogen-b} \end{pmatrix}, \chi = 1$$

It is unnecessary to find the transformation matrix for each operation since it is only the TRACE that gives us the character, and any off-diagonal entries do not contribute to Γ_{modes}. The values that contribute to the trace can be found simply by performing each operation in the point group and assigning a value to each individual atom to represent how it is changed by that operation. If the atom moves away from itself, that atom gets a character of zero (this is because any non-zero characters of the transformation matrix are off of the diagonal). If the atom remains in place, each of its three dimensions is assigned a value of $\cos\theta$. For the example of H_2O under the C_{2v} point group, the axes that remain unchanged ($\theta = 0°$) are assigned a value of $\cos(0°) = 1$, while those that are moved into the negative of themselves (rotated or reflected to $\theta = 180°$) are assigned $\cos(180°) = -1$. The character for Γ is the sum of the values for each transformation.

Let's walk through the steps to assign characters of Γ_{modes} for H_2O to illustrate how this works:

For the operation $\boldsymbol{E}$, performed on H_2O, all three atoms remain in place. The three axes x, y, z on each atom remain unchanged. Thus, each of the three axes on each of three atom (nine axes) is assigned the value $\cos(0°) = 1$, resulting in a sum of $\boldsymbol{\chi = 9}$ for the Γ_{modes}.

For the operation $\boldsymbol{C_2}$, the two hydrogen atoms are moved away from their original position, and so the hydrogens are assigned a value of zero. The oxygen remains in place; the z-axis on oxygen is unchanged ($\cos(0°) = 1$), while the x and y axes are inverted ($\cos(180°)$). The sum of these characters gives $\boldsymbol{\chi = -1}$ in the Γ_{modes}.

Now you try! Find the characters of $\sigma_{v(xz)}$ and $\sigma_{v(yz)}$ under the C_{2v} point group. Compare what you find to the Γ_{modes} for all normal modes given below.

$$\begin{array}{c|cccc} C_{2v} & E & C_2 & \sigma_v & \sigma'_v \\ \hline \Gamma_{modes} & 9 & -1 & 3 & 1 \end{array} \tag{7.4.2.1}$$

STEP 2: Break Γ_{modes} into its component irreducible representations.

Now that we've found the Γ_{modes} (7.4.2.1), we need to break it down into the individual irreducible representations ($i, j, k. . .$) for the point group. We can do this systematically using the following formula:

$$\# \text{ of } i = \frac{1}{h} \sum (\# \text{ of operations in class}) \times (\chi_\Gamma) \times (\chi_i) \tag{7.4.2.2}$$

In other words, the number of irreducible representations of type i is equal to the sum of the number of operations in the class $\times$ the character of the Γ_{modes} $\times$ the character of i, and that sum is divided by the order of the group (h).

Using equation 7.4.2.2, we find that for all normal modes of H_2O:

$$\Gamma_{modes} = 3A_1 + 1A_2 + 3B_1 + 2B_2 \tag{7.4.2.3}$$

.

Notice there are 9 irreducible representations in Equation 7.4.2.3 These irreducible representations represent the symmetries of all 9 motions of the molecule: vibrations, rotations, and translations.

? **Exercise 7.4.2.1: Derive the irreducible representation in equation 7.4.2.3.**

Derive the nine irreducible representations of Γ_{modes} for H_2O, expression 7.4.2.3

Hint

To find the number of each kind of irreducible representation that combine to form the Γ_{modes}, we need the characters of Γ_{modes} that we found above (7.4.2.1), the C_{2v} character table (below), and equation 7.4.2.2

C_{2v}	$1E$	$1C_2$	$1\sigma_v$	$1\sigma_v'$	$h = 4$	
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

In the C_{2v} point group, each class has only one operation, so the number of operations in each class (from equation 7.4.2.2) is 1 for each class. This has been explicitly added to the character table above for emphasis.

Answer

The number of $A_1 = \frac{1}{4}[(1 \times 9 \times 1) + (1 \times (-1) \times 1) + (1 \times 3 \times 1) + (1 \times 1 \times 1)] = 3A_1$

The number of $A_2 = \frac{1}{4}[(1 \times 9 \times 1) + (1 \times (-1) \times 1) + ((-1) \times 3 \times 1) + ((-1) \times 1 \times 1)] = 1A_2$

The number of $B_1 = \frac{1}{4}[(1 \times 9 \times 1) + ((-1) \times (-1) \times 1) + (1 \times 3 \times 1) + ((-1) \times 1 \times 1)] = 3B_1$

The number of $B_2 = \frac{1}{4}[(1 \times 9 \times 1) + ((-1) \times (-1) \times 1) + ((-1) \times 3 \times 1) + (1 \times 1 \times 1)] = 2B_2$

STEP 3: Subtract rotations and translations to find vibrational modes.

Because we are interested in molecular vibrations, we need to subtract the rotations and translations from the total degrees of freedom.

$$\text{Vibrations} = \Gamma_{modes} - \text{Rotations} - \text{Translations}$$

In the example of H_2O, the total degrees of freedom are given above in equation 7.4.2.3, and therefore the vibrational degrees of freedom can be found by:

$$H_2O \text{ vibrations} = (3A_1 + 1A_2 + 3B_1 + 2B_2) - \text{Rotations} - \text{Translations} \tag{7.4.2.4}$$

But which of the irreducible representations are ones that represent rotations and translations? The symmetry of rotational and translational degree modes can be found by inspecting the right-hand columns of any character table. Rotational modes correspond to irreducible representations that include R_x, R_y, and R_z in the table, while each of the three translational modes has the same symmetry as the x, y and z axes. For a non-linear molecule, subtract three rotational irreducible representations and three translational irreducible representations from the total Γ_{modes}.

In the specific case of water, we refer to the C_{2v} character table:

C_{2v}	E	C_2	σ_v	σ_v'	$h = 4$	
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

In C_{2v}, translations correspond to B_1, B_2, and A_1 (respectively for $x, y z$), and rotations correspond to B_2, B_1, and A_1 (respectively for R_x, R_y, R_z). Subtracting these six irreducible representations from Γ_{modes} will leave us with the irreducible representations for vibrations.

$$
\begin{aligned}
H_2O \text{ vibrations} \quad &= \quad \Gamma_{modes} - \text{Rotations} - \text{Translations} \\
&= \quad (3A_1 + 1A_2 + 3B_1 + 2B_2) - (A_1 + B_1 + B_2) - (A_2 + B_1 + B_2) \\
&= \quad 2A_1 + 1B_1
\end{aligned}
$$

The three vibrational modes for H_2O are $2A_1 + 1B_1$. Note that we have the correct number of vibrational modes based on the expectation of $3N - 6$ vibrations for a non-linear molecule.

STEP 4: Determine which of the vibrational modes are IR-active and Raman-active.

The next step is to determine which of the vibrational modes is IR-active and Raman-active. To do this, we apply the IR and Raman Selection Rules below:

> 📌 **IR and Raman Selection Rules**
>
> #### Infrared selection rules:
>
> If a vibration results in the change in the molecular dipole moment, it is IR-active. In the character table, we can recognize the vibrational modes that are IR-active by those with symmetry of the x, y, and z axes.
>
> In C_{2v}, any vibrations with A_1, B_1 or B_2 symmetry would be IR-active.
>
> #### Raman selection rules:
>
> If a vibration results in a change in the molecular polarizability, it will be Raman-active. In the character table, we can recognize the vibrational modes that are Raman-active by those with symmetry of any of the binary products (xy, xz, yz, x^2, y^2, and z^2) or a linear combination of binary products (e.g. $x^2 - y^2$).
>
> In C_{2v}, any vibrations with A_1, A_2, B_1 or B_2 symmetry would be Raman-active.

In our H_2O example, we found that of the three vibrational modes, two have A_1 and one has B_1 symmetry. Both A_1 and B_1 are IR-active, and both are also Raman-active. ***There are two possible IR peaks and three possible Raman peaks expected for water.****

*It is important to note that this prediction tells only what is possible, but not what we might actually see in the IR and Raman spectra. For example, if the two IR peaks overlap, we might actually notice only one peak in the spectrum. Or, if one or more peaks is off-scale, we wouldn't see it in actual data. Group theory tells us what is *possible and allows us to make predictions or interpretations of spectra.*

Summary of Analysis for Water

Each molecular motion for water, or any molecule, can be assigned a symmetry under the molecule's point group. For water, we found that there are a total of 9 molecular motions; $3A_1 + A_2 + 3B_1 + 2B_2$. Six of these motions are not the translations and rotations. The remaining motions are vibrations; two with A_1 symmetry and one with B_1 symmetry.

We can tell what these vibrations would look like based on their symmetries. The two A_1 vibrations must be completely symmetric, while the B_1 vibration is antisymmetric with respect to the principal C_2 axis.
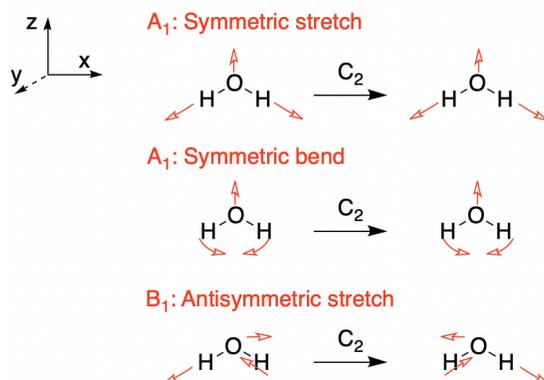
Figure 7.4.2.2: Illustration of the vibrational motions of water. The antisymmetric stretch has B_1 symmetry, while the symmetric stretch and symmetric bend both have A_1 symmetry. (Click here to see animation) (CC-BY-NC-SA; Kathryn Haas)

Table 7.4.2.1: Summary of the Symmetry of Molecular Motions for Water

All Motions (step 2 above)	Translations (x,y,z)	Rotations (R_x, R_y, R_z)	**Remaining Vibrations**	Description of Vibration
$3A_1$	$1A_1$		$\mathbf{2A_1}$	One is a symmetric stretch. The other is a symmetric bend. Both are *IR-active* and *Raman-active*
A_2		$1A_2$		
$3B_1$	$1B_1$	$1B_1$	$\mathbf{1B_1}$	Antisymmetric stretch that is *IR-active* and *Raman-active*.
$2B_2$	$1B_2$	$1B_2$		

? Exercise 7.4.2.2

Find the symmetries of all motions of the square planar complex, tetrachloroplatinate (II). Determine which are rotations, translations, and vibrations. Determine which vibrations are IR and Raman active.

Answer

The point group of $[\mathrm{PtCl_4}]^{2-}$ is D_{4h} (refer to its character table). There are five atoms and 15 vectors (x, y, z for each atom × 5 atoms).

STEP 1: The first major step is to **find a reducible representation (Γ)** for the movement of all atoms in the molecule.

C_{2v}	E	$2C_4$	C_2	$2C_2'$	$2C_2$ "	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_{modes}	15	1	-1	-3	-1	-3	-1	5	3	1

$$(7.4.2.5)$$

.

STEP 2: Break Γ_{modes} into its component irreducible representations.

Following the process described earlier, we come to $A_{1g} + A_{2g} + B_{1g} + B_{2g} + E_g + 2A_{2u} + B_{2u} + 3E_u$. This accounts for all modes of movement, including rotations and translations.

STEP 3: Subtract rotations and translations to find vibrational modes.

The translations are $A_{2u} + E_u$ and the rotations are $A_{2g} + E_g$.
The remaining normal modes are: $A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$

STEP 4: Determine which of the vibrational modes are IR-active and Raman-active:

$A_{2u} + E_u$ are IR-active. Since A_{2u} is singly degenerate and E_u is doubly degenerate, we expect three possible IR bands. $A_{1g} + B_{1g} + B_{2g}$ are Raman-Active. Each of these is singly degenerate, so we expect three possible Raman bands.

Summary

It is possible to distinguish between the two isomers of square planar $ML_2(CO)_2$ using either IR or Raman vibrational spectroscopy. The *cis*- $ML_2(CO)_2$ can produce two CO stretches in an IR or Raman spectrum, while the *trans*- $ML_2(CO)_2$ isomer can produce only one band in either type of vibrational spectrum. If a sample of $ML_2(CO)_2$ produced two CO stretching bands, we could rule out the possibility of a pure sample of *trans*-$ML_2(CO)_2$.

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7.5: Exercises

1. Identify the symmetry elements for the following compounds:

a) BCl_3 b) SiF_4 c) *cis*-1,2-dibromocyclobutane d) *trans*-1,2-dibromocyclobutane e) PH_3 f) $AsCl_5$ g) $XeCl_4$ h) HCl

2. Identify the point group for the molecules compounds above

3. Identify the point group for the following molecules

a) $AuCl_4^-$ b) SO_2 c) SO_3 d) CO e) H_2O_2 f) N_3^- g) *cis*-$[Pt(NH_3)_4Cl_2]^{2+}$ h) *trans*-$[Pt(NH_3)_4Cl_2]^{2+}$

i) *cis*-1,2-dichloroethene j) *trans*-1,2-dichloroethene

4. Using group theory, find the symmetries of all motions of CO_2. Determine which are rotations, translations, and vibrations. Determine which vibrations are IR and Raman active.

5. Using group theory, find the symmetries of all motions of NO_3^-. Determine which are rotations, translations, and vibrations. Determine which vibrations are IR and Raman active.

8: Liquids and Solids

The great distances between atoms and molecules in a gaseous phase, and the corresponding absence of any significant interactions between them, allows for simple descriptions of many physical properties that are the same for all gases, regardless of their chemical identities. As described in the final module of the chapter on gases, this situation changes at high pressures and low temperatures—conditions that permit the atoms and molecules to interact to a much greater extent. In the liquid and solid states, these interactions are of considerable strength and play an important role in determining a number of physical properties that *do* depend on the chemical identity of the substance. In this chapter, the nature of these interactions and their effects on various physical properties of liquid and solid phases will be examined.

8.1: Introduction

Leprosy has been a devastating disease throughout much of human history. Aside from the symptoms and complications of the illness, its social stigma led sufferers to be cast out of communities and isolated in colonies; in some regions this practice lasted well into the twentieth century. At that time, the best potential treatment for leprosy was oil from the chaulmoogra tree, but the oil was extremely thick, causing blisters and making usage painful and ineffective. Healthcare professionals seeking a better application contacted Alice Ball, a young chemist at the University of Hawaii, who had focused her masters thesis on a similar plant. Ball initiated a sequence of procedures (repeated acidification and purification to change the characteristics of the oil and isolate the active substances (esters, discussed later in this text). The "Ball Method" as it later came to be called, became the standard treatment for leprosy for decades.
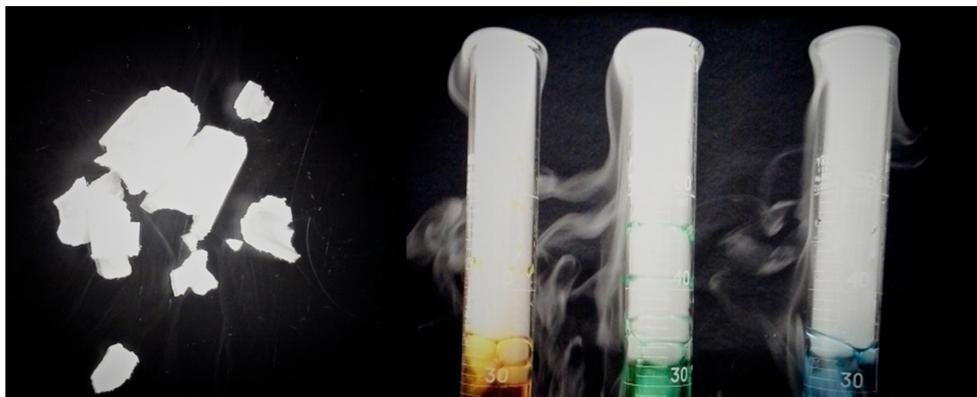
Figure 8.1.1: Solid carbon dioxide ("dry ice", left) sublimes vigorously when placed in a liquid (right), cooling the liquid and generating a dense mist of water above the cylinder. (credit: modification of work by Paul Flowers)

In the liquid and solid states, atomic and molecular interactions are of considerable strength and play an important role in determining a number of physical properties of the substance. For example, the thickness, or viscosity, of the chaulmoogra oil was due to its intermolecular forces. In this chapter, the nature of these interactions and their effects on various physical properties of liquid and solid phases will be examined.

8.2: Intermolecular Forces

> **◑ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Describe the types of intermolecular forces possible between atoms or molecules in condensed phases (dispersion forces, dipole-dipole attractions, and hydrogen bonding)
> - Identify the types of intermolecular forces experienced by specific molecules based on their structures
> - Explain the relation between the intermolecular forces present within a substance and the temperatures associated with changes in its physical state

As was the case for gaseous substances, the kinetic molecular theory may be used to explain the behavior of solids and liquids. In the following description, the term *particle* will be used to refer to an atom, molecule, or ion. Note that we will use the popular phrase "intermolecular attraction" to refer to attractive forces between the particles of a substance, regardless of whether these particles are molecules, atoms, or ions.

Consider these two aspects of the molecular-level environments in solid, liquid, and gaseous matter:

- Particles in a solid are tightly packed together and often arranged in a regular pattern; in a liquid, they are close together with no regular arrangement; in a gas, they are far apart with no regular arrangement.
- Particles in a solid vibrate about fixed positions and do not generally move in relation to one another; in a liquid, they move past each other but remain in essentially constant contact; in a gas, they move independently of one another except when they collide.

The differences in the properties of a solid, liquid, or gas reflect the strengths of the attractive forces between the atoms, molecules, or ions that make up each phase. The phase in which a substance exists depends on the relative extents of its **intermolecular forces** (IMFs) and the kinetic energies (KE) of its molecules. IMFs are the various forces of attraction that may exist between the atoms and molecules of a substance due to electrostatic phenomena, as will be detailed in this module. These forces serve to hold particles close together, whereas the particles' KE provides the energy required to overcome the attractive forces and thus increase the distance between particles. Figure 8.2.1 illustrates how changes in physical state may be induced by changing the temperature, hence, the average KE, of a given substance.
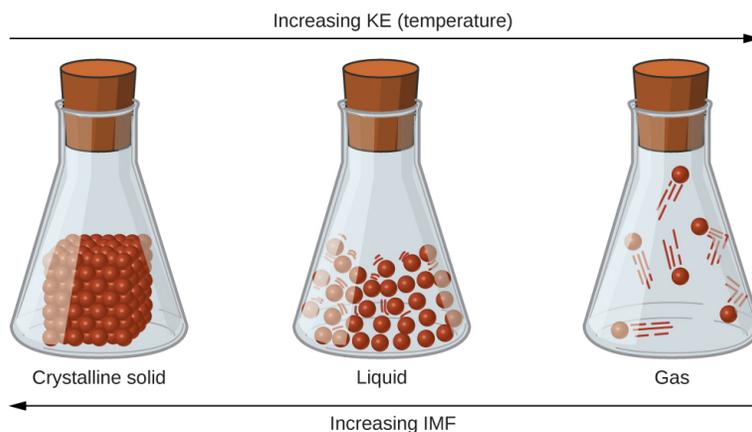
Figure 8.2.1: Transitions between solid, liquid, and gaseous states of a substance occur when conditions of temperature or pressure favor the associated changes in intermolecular forces. (Note: The space between particles in the gas phase is much greater than shown.)

As an example of the processes depicted in this figure, consider a sample of water. When gaseous water is cooled sufficiently, the attractions between H_2O molecules will be capable of holding them together when they come into contact with each other; the gas condenses, forming liquid H_2O. For example, liquid water forms on the outside of a cold glass as the water vapor in the air is cooled by the cold glass, as seen in Figure 8.2.2.

(a)   (b)

Figure 8.2.2: Condensation forms when water vapor in the air is cooled enough to form liquid water, such as (a) on the outside of a cold beverage glass or (b) in the form of fog. (credit a: modification of work by Jenny Downing; credit b: modification of work by Cory Zanker)

We can also liquefy many gases by compressing them, if the temperature is not too high. The increased pressure brings the molecules of a gas closer together, such that the attractions between the molecules become strong relative to their KE. Consequently, they form liquids. Butane, C_4H_{10}, is the fuel used in disposable lighters and is a gas at standard temperature and pressure. Inside the lighter's fuel compartment, the butane is compressed to a pressure that results in its condensation to the liquid state, as shown in Figure 8.2.3.

Figure 8.2.3: Gaseous butane is compressed within the storage compartment of a disposable lighter, resulting in its condensation to the liquid state. (credit: modification of work by "Sam-Cat"/Flickr)

Finally, if the temperature of a liquid becomes sufficiently low, or the pressure on the liquid becomes sufficiently high, the molecules of the liquid no longer have enough KE to overcome the IMF between them, and a solid forms. A more thorough discussion of these and other changes of state, or phase transitions, is provided in a later module of this chapter.

📌 Link to Learning

Access this interactive simulation on states of matter, phase transitions, and intermolecular forces. This simulation is useful for visualizing concepts introduced throughout this chapter.

Forces between Molecules

Under appropriate conditions, the attractions between all gas molecules will cause them to form liquids or solids. This is due to intermolecular forces, not *intra*molecular forces. *Intra*molecular forces are those *within* the molecule that keep the molecule together, for example, the bonds between the atoms. *Inter*molecular forces are the attractions *between* molecules, which determine many of the physical properties of a substance. Figure 8.2.4 illustrates these different molecular forces. The strengths of these attractive forces vary widely, though usually the IMFs between small molecules are weak compared to the intramolecular forces that bond atoms together within a molecule. For example, to overcome the IMFs in one mole of liquid HCl and convert it into gaseous HCl requires only about 17 kilojoules. However, to break the covalent bonds between the hydrogen and chlorine atoms in one mole of HCl requires about 25 times more energy—430 kilojoules.
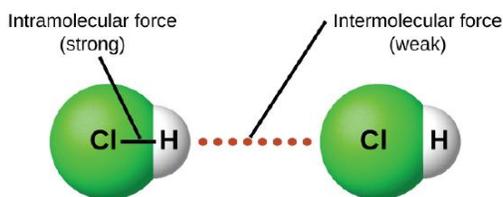
Figure 8.2.4: *Intra*molecular forces keep a molecule intact. *Inter*molecular forces hold multiple molecules together and determine many of a substance's properties.

All of the attractive forces between neutral atoms and molecules are known as van der Waals forces, although they are usually referred to more informally as intermolecular attraction. We will consider the various types of IMFs in the next three sections of this module.

Dispersion Forces

One of the three van der Waals forces is present in all condensed phases, regardless of the nature of the atoms or molecules composing the substance. This attractive force is called the London dispersion force in honor of German-born American physicist Fritz London who, in 1928, first explained it. This force is often referred to as simply the **dispersion force**. Because the electrons of an atom or molecule are in constant motion (or, alternatively, the electron's location is subject to quantum-mechanical variability), at any moment in time, an atom or molecule can develop a temporary, **instantaneous dipole** if its electrons are distributed asymmetrically. The presence of this dipole can, in turn, distort the electrons of a neighboring atom or molecule, producing an **induced dipole**. These two rapidly fluctuating, temporary dipoles thus result in a relatively weak electrostatic attraction between the species—a so-called dispersion force like that illustrated in Figure 8.2.5.
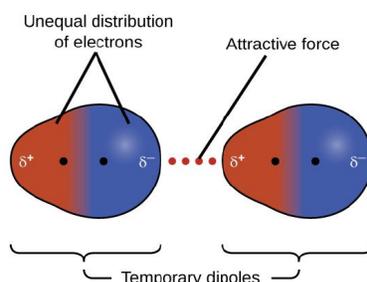
Figure 8.2.5: Dispersion forces result from the formation of temporary dipoles, as illustrated here for two nonpolar diatomic molecules.

Dispersion forces that develop between atoms in different molecules can attract the two molecules to each other. The forces are relatively weak, however, and become significant only when the molecules are very close. Larger and heavier atoms and molecules exhibit stronger dispersion forces than do smaller and lighter atoms and molecules. F_2 and Cl_2 are gases at room temperature (reflecting weaker attractive forces); Br_2 is a liquid, and I_2 is a solid (reflecting stronger attractive forces). Trends in observed melting and boiling points for the halogens clearly demonstrate this effect, as seen in Table 8.2.1.

Table 8.2.1: Melting and Boiling Points of the Halogens

Halogen	Molar Mass	Atomic Radius	Melting Point	Boiling Point
fluorine, F_2	38 g/mol	72 pm	53 K	85 K
chlorine, Cl_2	71 g/mol	99 pm	172 K	238 K
bromine, Br_2	160 g/mol	114 pm	266 K	332 K
iodine, I_2	254 g/mol	133 pm	387 K	457 K
astatine, At_2	420 g/mol	150 pm	575 K	610 K

The increase in melting and boiling points with increasing atomic/molecular size may be rationalized by considering how the strength of dispersion forces is affected by the electronic structure of the atoms or molecules in the substance. In a larger atom, the valence electrons are, on average, farther from the nuclei than in a smaller atom. Thus, they are less tightly held and can more easily form the temporary dipoles that produce the attraction. The measure of how easy or difficult it is for another electrostatic

charge (for example, a nearby ion or polar molecule) to distort a molecule's charge distribution (its electron cloud) is known as polarizability. A molecule that has a charge cloud that is easily distorted is said to be very polarizable and will have large dispersion forces; one with a charge cloud that is difficult to distort is not very polarizable and will have small dispersion forces.

✔ **Example 8.2.1: London Forces and Their Effects**

Order the following compounds of a group 14 element and hydrogen from lowest to highest boiling point: CH_4, SiH_4, GeH_4, and SnH_4. Explain your reasoning.

Solution

Applying the skills acquired in the chapter on chemical bonding and molecular geometry, all of these compounds are predicted to be nonpolar, so they may experience only dispersion forces: the smaller the molecule, the less polarizable and the weaker the dispersion forces; the larger the molecule, the larger the dispersion forces. The molar masses of CH_4, SiH_4, GeH_4, and SnH_4 are approximately 16 g/mol, 32 g/mol, 77 g/mol, and 123 g/mol, respectively. Therefore, CH_4 is expected to have the lowest boiling point and SnH_4 the highest boiling point. The ordering from lowest to highest boiling point is expected to be $CH_4 <$ $SiH_4 < GeH_4 < SnH_4$.

A graph of the actual boiling points of these compounds versus the period of the group 14 element shows this prediction to be correct:

Carbon Family
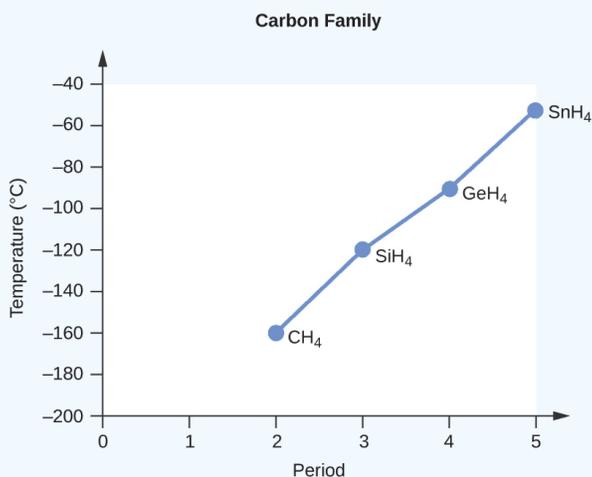
? **Exercise 8.2.1**

Order the following hydrocarbons from lowest to highest boiling point: C_2H_6, C_3H_8, and C_4H_{10}.

Answer

$C_2H_6 < C_3H_8 < C_4H_{10}$. All of these compounds are nonpolar and only have London dispersion forces: the larger the molecule, the larger the dispersion forces and the higher the boiling point. The ordering from lowest to highest boiling point is therefore $C_2H_6 < C_3H_8 < C_4H_{10}$.

The shapes of molecules also affect the magnitudes of the dispersion forces between them. For example, boiling points for the isomers *n*-pentane, isopentane, and neopentane (shown in Figure 8.2.6) are 36 °C, 27 °C, and 9.5 °C, respectively. Even though these compounds are composed of molecules with the same chemical formula, C_5H_{12}, the difference in boiling points suggests that dispersion forces in the liquid phase are different, being greatest for *n*-pentane and least for neopentane. The elongated shape of *n*-pentane provides a greater surface area available for contact between molecules, resulting in correspondingly stronger dispersion forces. The more compact shape of isopentane offers a smaller surface area available for intermolecular contact and, therefore, weaker dispersion forces. Neopentane molecules are the most compact of the three, offering the least available surface area for intermolecular contact and, hence, the weakest dispersion forces. This behavior is analogous to the connections that may be formed between strips of VELCRO brand fasteners: the greater the area of the strip's contact, the stronger the connection.
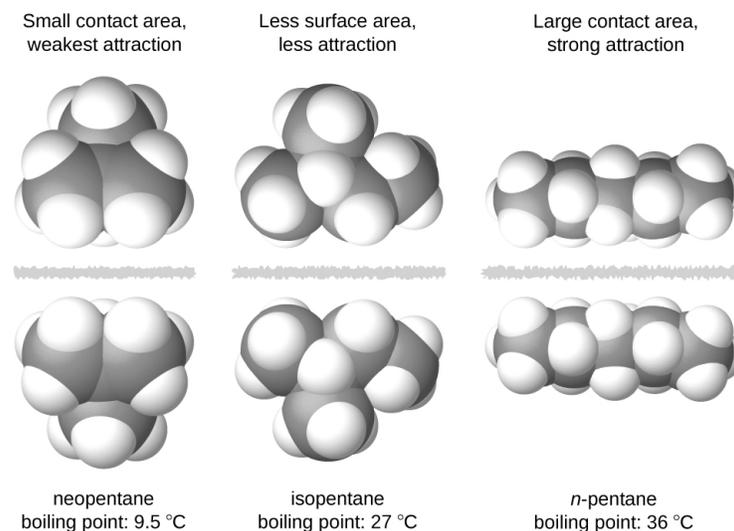
Figure 8.2.6: The strength of the dispersion forces increases with the contact area between molecules, as demonstrated by the boiling points of these pentane isomers.

📌 Chemistry in Everyday Life: Geckos and Intermolecular Forces

Geckos have an amazing ability to adhere to most surfaces. They can quickly run up smooth walls and across ceilings that have no toe-holds, and they do this without having suction cups or a sticky substance on their toes. And while a gecko can lift its feet easily as it walks along a surface, if you attempt to pick it up, it sticks to the surface. How are geckos (as well as spiders and some other insects) able to do this? Although this phenomenon has been investigated for hundreds of years, scientists only recently uncovered the details of the process that allows geckos' feet to behave this way.

Geckos' toes are covered with hundreds of thousands of tiny hairs known as *setae*, with each seta, in turn, branching into hundreds of tiny, flat, triangular tips called *spatulae*. The huge numbers of spatulae on its setae provide a gecko, shown in Figure 8.2.7, with a large total surface area for sticking to a surface. In 2000, Kellar Autumn, who leads a multi-institutional gecko research team, found that geckos adhered equally well to both polar silicon dioxide and nonpolar gallium arsenide. This proved that geckos stick to surfaces because of dispersion forces—weak intermolecular attractions arising from temporary, synchronized charge distributions between adjacent molecules. Although dispersion forces are very weak, the total attraction over millions of spatulae is large enough to support many times the gecko's weight.

In 2014, two scientists developed a model to explain how geckos can rapidly transition from "sticky" to "non-sticky." Alex Greaney and Congcong Hu at Oregon State University described how geckos can achieve this by changing the angle between their spatulae and the surface. Geckos' feet, which are normally nonsticky, become sticky when a small shear force is applied. By curling and uncurling their toes, geckos can alternate between sticking and unsticking from a surface, and thus easily move across it. Later research led by Alyssa Stark at University of Akron showed that geckos can maintain their hold on hydrophobic surfaces (similar to the leaves in their habitats) equally well whether the surfaces were wet or dry. Stark's experiment used a ribbon to gently pull the geckos until they slipped, so that the researchers could determine the geckos' ability to hold various surfaces under wet and dry conditions. Further investigations may eventually lead to the development of better adhesives and other applications.
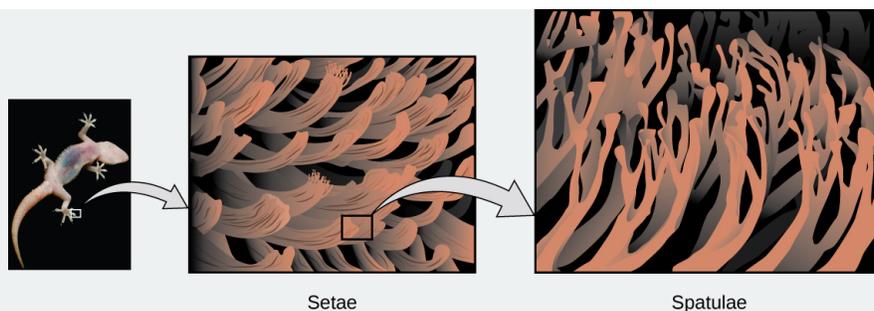
Figure 8.2.7: Geckos' toes contain large numbers of tiny hairs (setae), which branch into many triangular tips (spatulae). Geckos adhere to surfaces because of van der Waals attractions between the surface and a gecko's millions of spatulae. By changing how the spatulae contact the surface, geckos can turn their stickiness "on" and "off." (credit photo: modification of work by "JC*+A!"/Flickr)

📌 Link to Learning

Watch this video to learn more about Kellar Autumn's research that determined that van der Waals forces are responsible for a gecko's ability to cling and climb.

Dipole-Dipole Attractions

Recall from the chapter on chemical bonding and molecular geometry that *polar* molecules have a partial positive charge on one side and a partial negative charge on the other side of the molecule—a separation of charge called a *dipole*. Consider a polar molecule such as hydrogen chloride, HCl. In the HCl molecule, the more electronegative Cl atom bears the partial negative charge, whereas the less electronegative H atom bears the partial positive charge. An attractive force between HCl molecules results from the attraction between the positive end of one HCl molecule and the negative end of another. This attractive force is called a dipole-dipole attraction—the electrostatic force between the partially positive end of one polar molecule and the partially negative end of another, as illustrated in Figure 8.2.8.
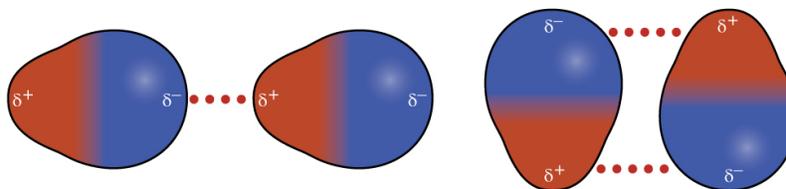
Figure 8.2.8: This image shows two arrangements of polar molecules, such as HCl, that allow an attraction between the partial negative end of one molecule and the partial positive end of another.

The effect of a dipole-dipole attraction is apparent when we compare the properties of HCl molecules to nonpolar F_2 molecules. Both HCl and F_2 consist of the same number of atoms and have approximately the same molecular mass. At a temperature of 150 K, molecules of both substances would have the same average KE. However, the dipole-dipole attractions between HCl molecules are sufficient to cause them to "stick together" to form a liquid, whereas the relatively weaker dispersion forces between nonpolar F_2 molecules are not, and so this substance is gaseous at this temperature. The higher normal boiling point of HCl (188 K) compared to F_2 (85 K) is a reflection of the greater strength of dipole-dipole attractions between HCl molecules, compared to the attractions between nonpolar F_2 molecules. We will often use values such as boiling or freezing points, or enthalpies of vaporization or fusion, as indicators of the relative strengths of IMFs of attraction present within different substances.

✔ Example 8.2.2: Dipole-Dipole Forces and Their Effects

Predict which will have the higher boiling point: N_2 or CO. Explain your reasoning.

Solution

CO and N_2 are both diatomic molecules with masses of about 28 amu, so they experience similar London dispersion forces. Because CO is a polar molecule, it experiences dipole-dipole attractions. Because N_2 is nonpolar, its molecules cannot exhibit dipole-dipole attractions. The dipole-dipole attractions between CO molecules are comparably stronger than the dispersion forces between nonpolar N_2 molecules, so CO is expected to have the higher boiling point.

> **? Exercise 8.2.2**
>
> Predict which will have the higher boiling point: ICl or Br$_2$. Explain your reasoning.
>
> **Answer**
>
> ICl. ICl and Br$_2$ have similar masses (~160 amu) and therefore experience similar London dispersion forces. ICl is polar and thus also exhibits dipole-dipole attractions; Br$_2$ is nonpolar and does not. The relatively stronger dipole-dipole attractions require more energy to overcome, so ICl will have the higher boiling point.

Hydrogen Bonding

Nitrosyl fluoride (ONF, molecular mass 49 amu) is a gas at room temperature. Water (H$_2$O, molecular mass 18 amu) is a liquid, even though it has a lower molecular mass. We clearly cannot attribute this difference between the two compounds to dispersion forces. Both molecules have about the same shape and ONF is the heavier and larger molecule. It is, therefore, expected to experience more significant dispersion forces. Additionally, we cannot attribute this difference in boiling points to differences in the dipole moments of the molecules. Both molecules are polar and exhibit comparable dipole moments. The large difference between the boiling points is due to a particularly strong dipole-dipole attraction that may occur when a molecule contains a hydrogen atom bonded to a fluorine, oxygen, or nitrogen atom (the three most electronegative elements). The very large difference in electronegativity between the H atom (2.1) and the atom to which it is bonded (4.0 for an F atom, 3.5 for an O atom, or 3.0 for a N atom), combined with the very small size of a H atom and the relatively small sizes of F, O, or N atoms, leads to *highly concentrated partial charges* with these atoms. Molecules with F-H, O-H, or N-H moieties are very strongly attracted to similar moieties in nearby molecules, a particularly strong type of dipole-dipole attraction called hydrogen bonding. Examples of hydrogen bonds include HF⋯HF, H$_2$O⋯HOH, and H$_3$N⋯HNH$_2$, in which the hydrogen bonds are denoted by dots. Figure 8.2.9 illustrates hydrogen bonding between water molecules.
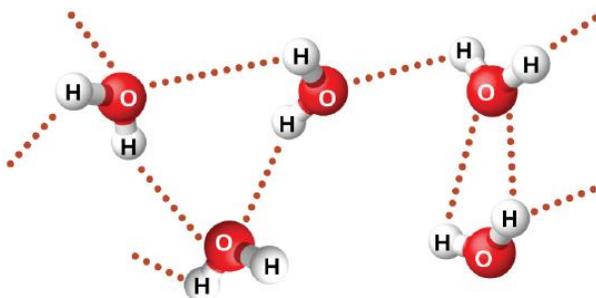
Figure 8.2.9: Water molecules participate in multiple hydrogen-bonding interactions with nearby water molecules.

Despite use of the word "bond," keep in mind that hydrogen bonds are *intermolecular* attractive forces, not *intramolecular* attractive forces (covalent bonds). Hydrogen bonds are much weaker than covalent bonds, only about 5 to 10% as strong, but are generally much stronger than other dipole-dipole attractions and dispersion forces.

Hydrogen bonds have a pronounced effect on the properties of condensed phases (liquids and solids). For example, consider the trends in boiling points for the binary hydrides of group 15 (NH$_3$, PH$_3$, AsH$_3$, and SbH$_3$), group 16 hydrides (H$_2$O, H$_2$S, H$_2$Se, and H$_2$Te), and group 17 hydrides (HF, HCl, HBr, and HI). The boiling points of the heaviest three hydrides for each group are plotted in Figure 8.2.10. As we progress down any of these groups, the polarities of the molecules decrease slightly, whereas the sizes of the molecules increase substantially. The effect of increasingly stronger dispersion forces dominates that of increasingly weaker dipole-dipole attractions, and the boiling points are observed to increase steadily.
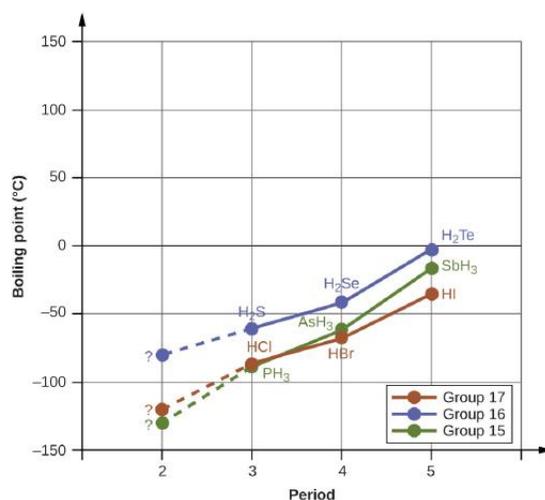
Figure 8.2.10: For the group 15, 16, and 17 hydrides, the boiling points for each class of compounds increase with increasing molecular mass for elements in periods 3, 4, and 5.

If we use this trend to predict the boiling points for the lightest hydride for each group, we would expect NH_3 to boil at about −120 °C, H_2O to boil at about −80 °C, and HF to boil at about −110 °C. However, when we measure the boiling points for these compounds, we find that they are dramatically higher than the trends would predict, as shown in Figure 8.2.11. The stark contrast between our naïve predictions and reality provides compelling evidence for the strength of hydrogen bonding.
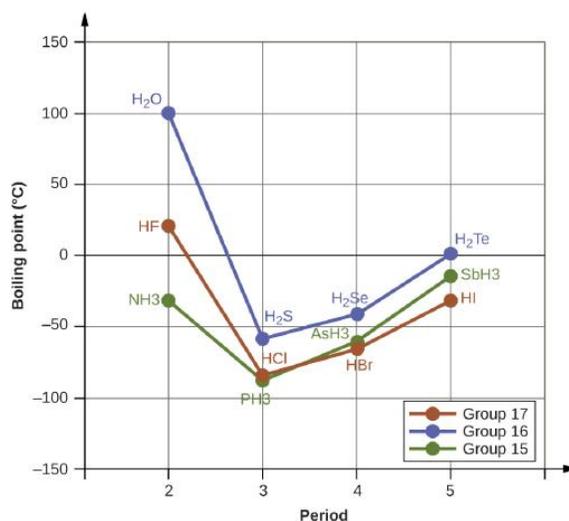
Figure 8.2.11: In comparison to periods 3−5, the binary hydrides of period 2 elements in groups 17, 16 and 15 (F, O and N, respectively) exhibit anomalously high boiling points due to hydrogen bonding.

✔ Example 8.2.3: Effect of Hydrogen Bonding on Boiling Points

Consider the compounds dimethylether (CH_3OCH_3), ethanol (CH_3CH_2OH), and propane ($CH_3CH_2CH_3$). Their boiling points, not necessarily in order, are −42.1 °C, −24.8 °C, and 78.4 °C. Match each compound with its boiling point. Explain your reasoning.

Solution

The VSEPR-predicted shapes of CH_3OCH_3, CH_3CH_2OH, and $CH_3CH_2CH_3$ are similar, as are their molar masses (46 g/mol, 46 g/mol, and 44 g/mol, respectively), so they will exhibit similar dispersion forces. Since $CH_3CH_2CH_3$ is nonpolar, it may exhibit *only* dispersion forces. Because CH_3OCH_3 is polar, it will also experience dipole-dipole attractions. Finally, CH_3CH_2OH has an −OH group, and so it will experience the uniquely strong dipole-dipole attraction known as hydrogen bonding. So the ordering in terms of strength of IMFs, and thus boiling points, is $CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CH_2OH$. The boiling point of propane is −42.1 °C, the boiling point of dimethylether is −24.8 °C, and the boiling point of ethanol is 78.5 °C.

? Exercise 8.2.3

Ethane (CH_3CH_3) has a melting point of −183 °C and a boiling point of −89 °C. Predict the melting and boiling points for methylamine (CH_3NH_2). Explain your reasoning.

Answer

The melting point and boiling point for methylamine are predicted to be significantly greater than those of ethane. CH_3CH_3 and CH_3NH_2 are similar in size and mass, but methylamine possesses an −NH group and therefore may exhibit hydrogen bonding. This greatly increases its IMFs, and therefore its melting and boiling points. It is difficult to predict values, but the known values are a melting point of −93 °C and a boiling point of −6 °C.

⚲ How Sciences Interconnect: Hydrogen Bonding and DNA

Deoxyribonucleic acid (DNA) is found in every living organism and contains the genetic information that determines the organism's characteristics, provides the blueprint for making the proteins necessary for life, and serves as a template to pass this information on to the organism's offspring. A DNA molecule consists of two (anti-)parallel chains of repeating nucleotides, which form its well-known double helical structure, as shown in Figure 8.2.12.
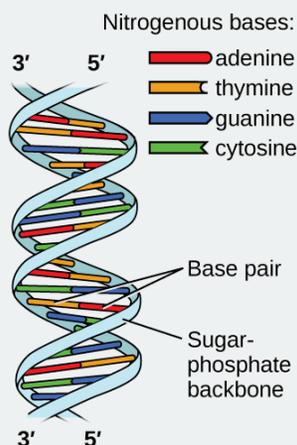
Figure 8.2.12: Two separate DNA molecules form a double-stranded helix in which the molecules are held together via hydrogen bonding. (credit: modification of work by Jerome Walker, Dennis Myts)

Each nucleotide contains a (deoxyribose) sugar bound to a phosphate group on one side, and one of four nitrogenous bases on the other. Two of the bases, cytosine (C) and thymine (T), are single-ringed structures known as pyrimidines. The other two, adenine (A) and guanine (G), are double-ringed structures called purines. These bases form complementary base pairs consisting of one purine and one pyrimidine, with adenine pairing with thymine, and cytosine with guanine. Each base pair is held together by hydrogen bonding. A and T share two hydrogen bonds, C and G share three, and both pairings have a similar shape and structure Figure 8.2.13.
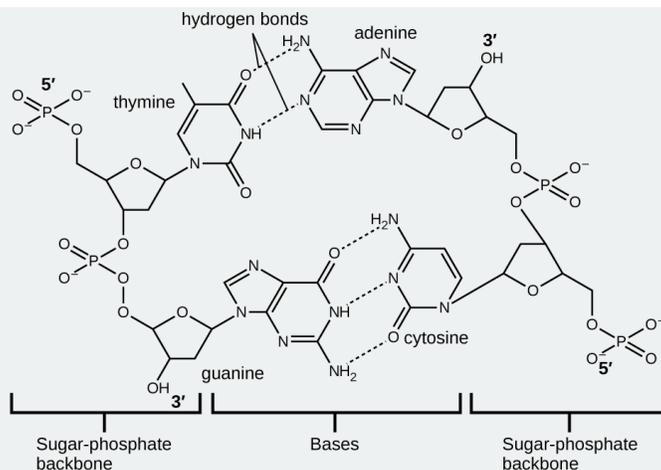
Figure 8.2.13: The geometries of the base molecules result in maximum hydrogen bonding between adenine and thymine (AT) and between guanine and cytosine (GC), so-called "complementary base pairs."

The cumulative effect of millions of hydrogen bonds effectively holds the two strands of DNA together. Importantly, the two strands of DNA can relatively easily "unzip" down the middle since hydrogen bonds are relatively weak compared to the covalent bonds that hold the atoms of the individual DNA molecules together. This allows both strands to function as a template for replication.

8.3: Properties of Liquids

> **◑ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Distinguish between adhesive and cohesive forces
> - Define viscosity, surface tension, and capillary rise
> - Describe the roles of intermolecular attractive forces in each of these properties/phenomena

When you pour a glass of water, or fill a car with gasoline, you observe that water and gasoline flow freely. But when you pour syrup on pancakes or add oil to a car engine, you note that syrup and motor oil do not flow as readily. The **viscosity** of a liquid is a measure of its resistance to flow. Water, gasoline, and other liquids that flow freely have a low viscosity. Honey, syrup, motor oil, and other liquids that do not flow freely, like those shown in Figure 8.3.1, have higher viscosities. We can measure viscosity by measuring the rate at which a metal ball falls through a liquid (the ball falls more slowly through a more viscous liquid) or by measuring the rate at which a liquid flows through a narrow tube (more viscous liquids flow more slowly).

(a)   (b)
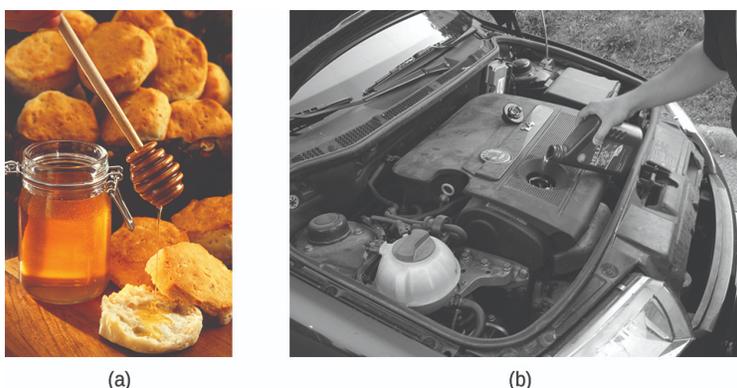
Figure 8.3.1: (a) Honey and (b) motor oil are examples of liquids with high viscosities; they flow slowly. (credit a: modification of work by Scott Bauer; credit b: modification of work by David Nagy)

The IMFs between the molecules of a liquid, the size and shape of the molecules, and the temperature determine how easily a liquid flows. As Table 8.3.1 shows, the more structurally complex are the molecules in a liquid and the stronger the IMFs between them, the more difficult it is for them to move past each other and the greater is the viscosity of the liquid. As the temperature increases, the molecules move more rapidly and their kinetic energies are better able to overcome the forces that hold them together; thus, the viscosity of the liquid decreases.

Table 8.3.1: Viscosities of Common Substances at 25 °C

Substance	Formula	Viscosity (mPa·s)
water	H_2O	0.890
mercury	Hg	1.526
ethanol	C_2H_5OH	1.074
octane	C_8H_{18}	0.508
ethylene glycol	$CH_2(OH)CH_2(OH)$	16.1
honey	variable	~2,000–10,000
motor oil	variable	~50–500

The various IMFs between identical molecules of a substance are examples of cohesive forces. The molecules within a liquid are surrounded by other molecules and are attracted equally in all directions by the cohesive forces within the liquid. However, the molecules on the surface of a liquid are attracted only by about one-half as many molecules. Because of the unbalanced molecular attractions on the surface molecules, liquids contract to form a shape that minimizes the number of molecules on the surface—that

is, the shape with the minimum surface area. A small drop of liquid tends to assume a spherical shape, as shown in Figure 8.3.2, because in a sphere, the ratio of surface area to volume is at a minimum. Larger drops are more greatly affected by gravity, air resistance, surface interactions, and so on, and as a result, are less spherical.
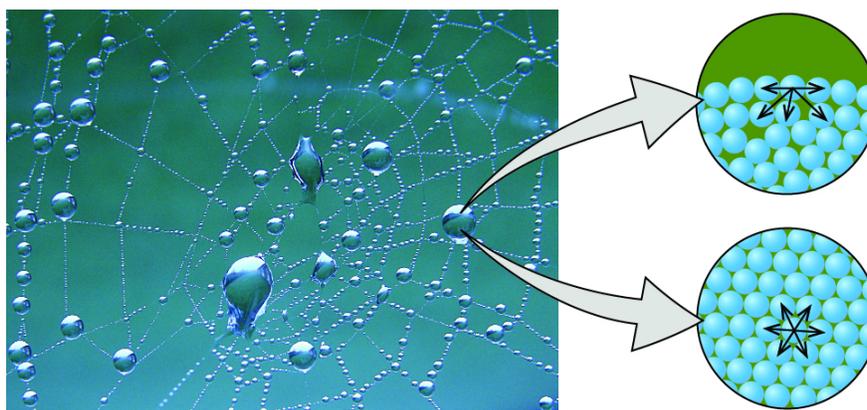
Figure 8.3.2: Attractive forces result in a spherical water drop that minimizes surface area; cohesive forces hold the sphere together; adhesive forces keep the drop attached to the web. (credit photo: modification of work by "OliBac"/Flickr)

Surface tension is defined as the energy required to increase the surface area of a liquid, or the force required to increase the length of a liquid surface by a given amount. This property results from the cohesive forces between molecules at the surface of a liquid, and it causes the surface of a liquid to behave like a stretched rubber membrane. Surface tensions of several liquids are presented in Table 8.3.2. Among common liquids, water exhibits a distinctly high surface tension due to strong hydrogen bonding between its molecules. As a result of this high surface tension, the surface of water represents a relatively "tough skin" that can withstand considerable force without breaking. A steel needle carefully placed on water will float. Some insects, like the one shown in Figure 8.3.3, even though they are denser than water, move on its surface because they are supported by the surface tension.

Table 8.3.2: Surface Tensions of Common Substances at 25 °C

Substance	Formula	Surface Tension (mN/m)
water	H_2O	71.99
mercury	Hg	458.48
ethanol	C_2H_5OH	21.97
octane	C_8H_{18}	21.14
ethylene glycol	$CH_2(OH)CH_2(OH)$	47.99

Surface tension is affected by a variety of variables, including the introduction of additional substances on the surface. In the late 1800s, Agnes Pockels, who was initially blocked from pursuing a scientific career but studied on her own, began investigating the impact and characteristics of soapy and greasy films in water. Using homemade materials, she developed an instrument known as a trough for measuring surface contaminants and their effects. With the support of renowned scientist Lord Rayleigh, her 1891 paper showed that surface contamination significantly reduces surface tension, and also that changing the characteristics of the surface (compressing or expanding it) also affects surface tension. Decades later, Irving Langmuir and Katharine Blodgett built on Pockels' work in their own trough and important advances in surface chemistry. Langmuir pioneered methods for producing single-molecule layers of film; Blodgett applied these to the development of non-reflective glass (critical for film-making and other applications), and also studied methods related to cleaning surfaces, which are important in semiconductor fabrication.
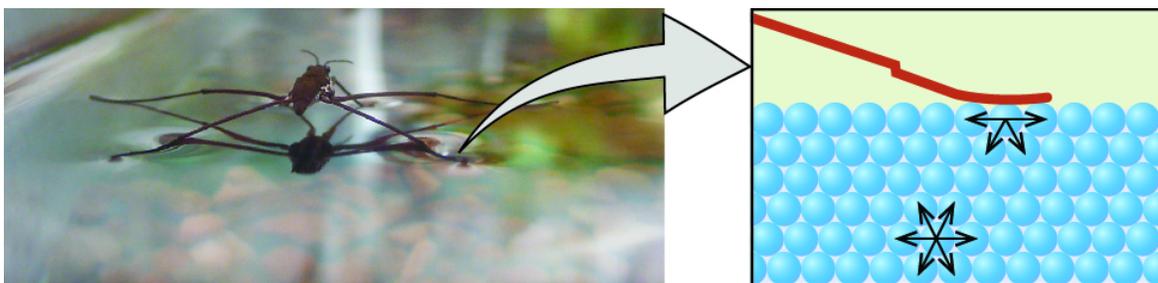
Figure 8.3.3: Surface tension (right) prevents this insect, a "water strider," from sinking into the water.

The IMFs of attraction between two *different* molecules are called **adhesive forces**. Consider what happens when water comes into contact with some surface. If the adhesive forces between water molecules and the molecules of the surface are weak compared to the cohesive forces between the water molecules, the water does not "wet" the surface. For example, water does not wet waxed surfaces or many plastics such as polyethylene. Water forms drops on these surfaces because the cohesive forces within the drops are greater than the adhesive forces between the water and the plastic. Water spreads out on glass because the adhesive force between water and glass is greater than the cohesive forces within the water. When water is confined in a glass tube, its meniscus (surface) has a concave shape because the water wets the glass and creeps up the side of the tube. On the other hand, the cohesive forces between mercury atoms are much greater than the adhesive forces between mercury and glass. Mercury therefore does not wet glass, and it forms a convex meniscus when confined in a tube because the cohesive forces within the mercury tend to draw it into a drop (Figure 8.3.4).
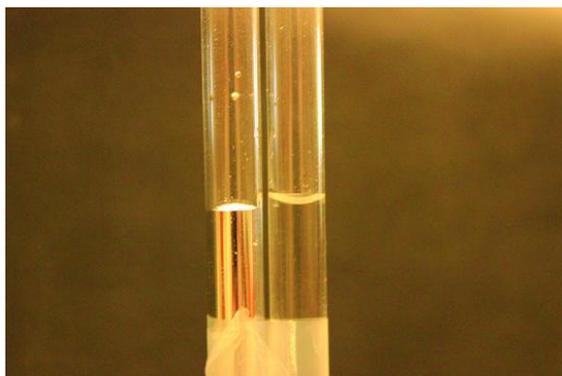
Figure 8.3.4: Differences in the relative strengths of cohesive and adhesive forces result in different meniscus shapes for mercury (left) and water (right) in glass tubes. (credit: Mark Ott)

If you place one end of a paper towel in spilled wine, as shown in Figure 8.3.5, the liquid wicks up the paper towel. A similar process occurs in a cloth towel when you use it to dry off after a shower. These are examples of **capillary action**—when a liquid flows within a porous material due to the attraction of the liquid molecules to the surface of the material and to other liquid molecules. The adhesive forces between the liquid and the porous material, combined with the cohesive forces within the liquid, may be strong enough to move the liquid upward against gravity.
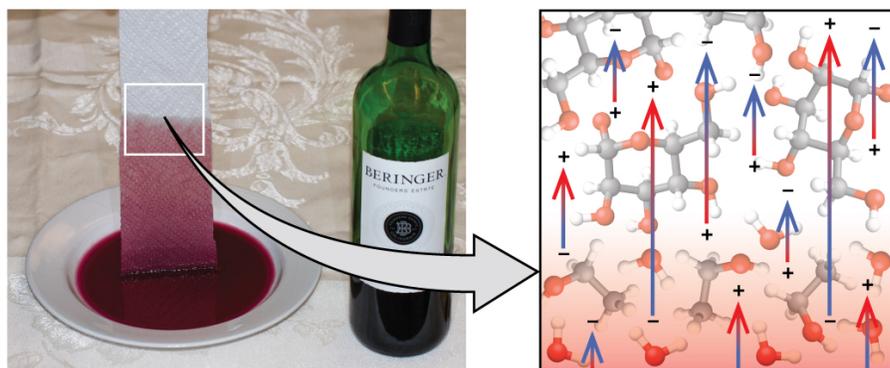
Figure 8.3.5: Wine wicks up a paper towel (left) because of the strong attractions of water (and ethanol) molecules to the −OH groups on the towel's cellulose fibers and the strong attractions of water molecules to other water (and ethanol) molecules (right). (credit photo: modification of work by Mark Blaser)

Towels soak up liquids like water because the fibers of a towel are made of molecules that are attracted to water molecules. Most cloth towels are made of cotton, and paper towels are generally made from paper pulp. Both consist of long molecules of cellulose that contain many −OH groups. Water molecules are attracted to these −OH groups and form hydrogen bonds with them, which draws the H_2O molecules up the cellulose molecules. The water molecules are also attracted to each other, so large amounts of water are drawn up the cellulose fibers.

Capillary action can also occur when one end of a small diameter tube is immersed in a liquid, as illustrated in Figure 8.3.6. If the liquid molecules are strongly attracted to the tube molecules, the liquid creeps up the inside of the tube until the weight of the liquid and the adhesive forces are in balance. The smaller the diameter of the tube is, the higher the liquid climbs. It is partly by capillary action occurring in plant cells called xylem that water and dissolved nutrients are brought from the soil up through the roots and into a plant. Capillary action is the basis for thin layer chromatography, a laboratory technique commonly used to separate small quantities of mixtures. You depend on a constant supply of tears to keep your eyes lubricated and on capillary action to pump tear fluid away.
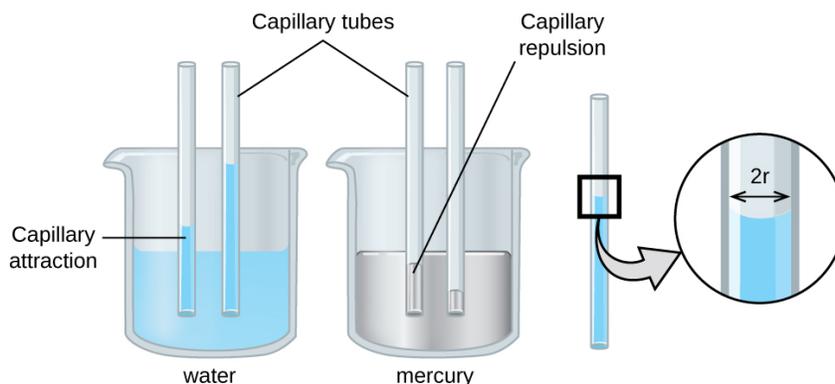
Figure 8.3.6: Depending upon the relative strengths of adhesive and cohesive forces, a liquid may rise (such as water) or fall (such as mercury) in a glass capillary tube. The extent of the rise (or fall) is directly proportional to the surface tension of the liquid and inversely proportional to the density of the liquid and the radius of the tube.

The height to which a liquid will rise in a capillary tube is determined by several factors as shown in the following equation:

$$h = \frac{2T \cos \theta}{r \rho g} \tag{8.3.1}$$

In this equation, h is the height of the liquid inside the capillary tube relative to the surface of the liquid outside the tube, T is the surface tension of the liquid, θ is the contact angle between the liquid and the tube, r is the radius of the tube, ρ is the density of the liquid, and g is the acceleration due to gravity, 9.8 m/s^2. When the tube is made of a material to which the liquid molecules are

strongly attracted, they will spread out completely on the surface, which corresponds to a contact angle of 0°. This is the situation for water rising in a glass tube.

> ✔ Example 8.3.1: Capillary Rise
>
> At 25 °C, how high will water rise in a glass capillary tube with an inner diameter of 0.25 mm?
>
> For water, T = 71.99 mN/m and ρ = 1.0 g/cm^3.
>
> **Solution**
> The liquid will rise to a height h given by Equation 8.3.1:
>
> $$h = \frac{2T \cos\theta}{r\rho g}$$
>
> The Newton is defined as a kg m/s^2, and so the provided surface tension is equivalent to 0.07199 kg/s^2. The provided density must be converted into units that will cancel appropriately: ρ = 1000 kg/m^3. The diameter of the tube in meters is 0.00025 m, so the radius is 0.000125 m. For a glass tube immersed in water, the contact angle is θ = 0°, so cos θ = 1. Finally, acceleration due to gravity on the earth is g = 9.8 m/s^2. Substituting these values into the equation, and cancelling units, we have:
>
> $$h = \frac{2\left(0.07199 kg/s^2\right)}{(0.000125 m)\left(1000 kg/m^3\right)\left(9.8 m/s^2\right)} = 0.12 m = 12 cm$$

> ? Exercise 8.3.1
>
> Water rises in a glass capillary tube to a height of 8.4 cm. What is the diameter of the capillary tube?
>
> **Answer**
> diameter = 0.36 mm

> 📌 Chemistry in Everyday Life: Biomedical Applications of Capillary Action
>
> Many medical tests require drawing a small amount of blood, for example to determine the amount of glucose in someone with diabetes or the hematocrit level in an athlete. This procedure can be easily done because of capillary action, the ability of a liquid to flow up a small tube against gravity, as shown in Figure 8.3.7. When your finger is pricked, a drop of blood forms and holds together due to surface tension—the unbalanced intermolecular attractions at the surface of the drop. Then, when the open end of a narrow-diameter glass tube touches the drop of blood, the adhesive forces between the molecules in the blood and those at the glass surface draw the blood up the tube. How far the blood goes up the tube depends on the diameter of the tube (and the type of fluid). A small tube has a relatively large surface area for a given volume of blood, which results in larger (relative) attractive forces, allowing the blood to be drawn farther up the tube. The liquid itself is held together by its own cohesive forces. When the weight of the liquid in the tube generates a downward force equal to the upward force associated with capillary action, the liquid stops rising.
>
>
>
> Figure 8.3.7: Blood is collected for medical analysis by capillary action, which draws blood into a small diameter glass tube. (credit: modification of work by Centers for Disease Control and Prevention)

8.4: Phase Transitions

> ⚪ **Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Define phase transitions and phase transition temperatures
> - Explain the relation between phase transition temperatures and intermolecular attractive forces
> - Describe the processes represented by typical heating and cooling curves, and compute heat flows and enthalpy changes accompanying these processes

We witness and utilize changes of physical state, or phase transitions, in a great number of ways. As one example of global significance, consider the evaporation, condensation, freezing, and melting of water. These changes of state are essential aspects of our earth's water cycle as well as many other natural phenomena and technological processes of central importance to our lives. In this module, the essential aspects of phase transitions are explored.

Vaporization and Condensation

When a liquid vaporizes in a closed container, gas molecules cannot escape. As these gas phase molecules move randomly about, they will occasionally collide with the surface of the condensed phase, and in some cases, these collisions will result in the molecules re-entering the condensed phase. The change from the gas phase to the liquid is called **condensation**. When the rate of condensation becomes equal to the rate of **vaporization**, neither the amount of the liquid nor the amount of the vapor in the container changes. The vapor in the container is then said to be *in equilibrium* with the liquid. Keep in mind that this is not a static situation, as molecules are continually exchanged between the condensed and gaseous phases. Such is an example of a **dynamic equilibrium**, the status of a system in which reciprocal processes (for example, vaporization and condensation) occur at equal rates. The pressure exerted by the vapor in equilibrium with a liquid in a closed container at a given temperature is called the liquid's **vapor pressure** (or equilibrium vapor pressure). The area of the surface of the liquid in contact with a vapor and the size of the vessel have no effect on the vapor pressure, although they do affect the time required for the equilibrium to be reached. We can measure the vapor pressure of a liquid by placing a sample in a closed container, like that illustrated in Figure 8.4.1, and using a manometer to measure the increase in pressure that is due to the vapor in equilibrium with the condensed phase.
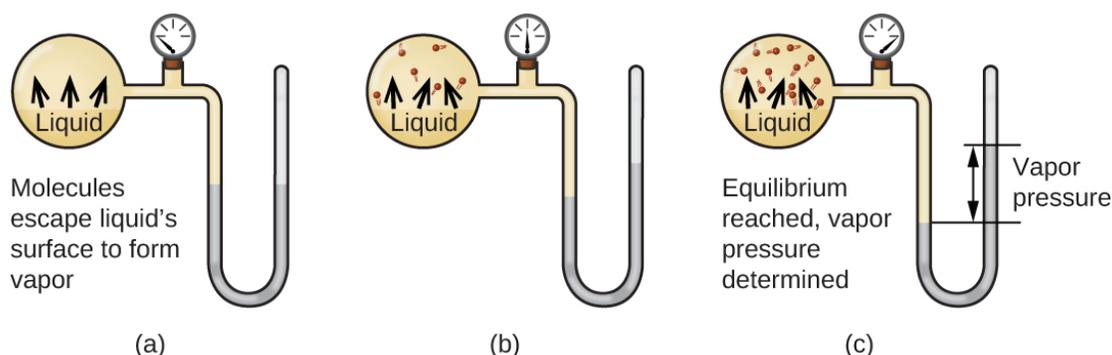
Figure 8.4.1: In a closed container, dynamic equilibrium is reached when (a) the rate of molecules escaping from the liquid to become the gas (b) increases and eventually (c) equals the rate of gas molecules entering the liquid. When this equilibrium is reached, the vapor pressure of the gas is constant, although the vaporization and condensation processes continue.

The chemical identities of the molecules in a liquid determine the types (and strengths) of intermolecular attractions possible; consequently, different substances will exhibit different equilibrium vapor pressures. Relatively strong intermolecular attractive forces will serve to impede vaporization as well as favoring "recapture" of gas-phase molecules when they collide with the liquid surface, resulting in a relatively low vapor pressure. Weak intermolecular attractions present less of a barrier to vaporization, and a reduced likelihood of gas recapture, yielding relatively high vapor pressures. The following example illustrates this dependence of vapor pressure on intermolecular attractive forces.

✔ **Example 8.4.1: Explaining Vapor Pressure in Terms of IMFs**

Given the shown structural formulas for these four compounds, explain their relative vapor pressures in terms of types and extents of IMFs:

$$\underset{\text{ethanol}}{H_3C\text{—}CH_2\overset{OH}{|}} \qquad \underset{\text{ethylene glycol}}{H_2C\text{—}CH_2 \overset{HO}{|}\overset{OH}{|}} \qquad \underset{\text{diethyl ether}}{CH_3\text{—}CH_2\text{—}O\text{—}CH_2\text{—}CH_3} \quad \text{and} \quad \underset{\text{water}}{H\text{—}O\text{—}H}$$
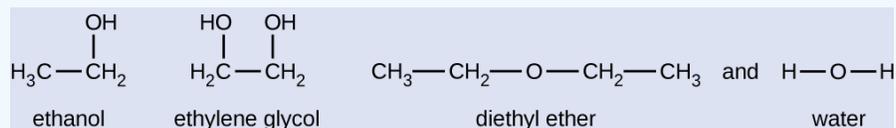
Solution

Diethyl ether has a very small dipole and most of its intermolecular attractions are London forces. Although this molecule is the largest of the four under consideration, its IMFs are the weakest and, as a result, its molecules most readily escape from the liquid. It also has the highest vapor pressure. Due to its smaller size, ethanol exhibits weaker dispersion forces than diethyl ether. However, ethanol is capable of hydrogen bonding and, therefore, exhibits stronger overall IMFs, which means that fewer molecules escape from the liquid at any given temperature, and so ethanol has a lower vapor pressure than diethyl ether. Water is much smaller than either of the previous substances and exhibits weaker dispersion forces, but its extensive hydrogen bonding provides stronger intermolecular attractions, fewer molecules escaping the liquid, and a lower vapor pressure than for either diethyl ether or ethanol. Ethylene glycol has two −OH groups, so, like water, it exhibits extensive hydrogen bonding. It is much larger than water and thus experiences larger London forces. Its overall IMFs are the largest of these four substances, which means its vaporization rate will be the slowest and, consequently, its vapor pressure the lowest.

? **Exercise 8.4.1**

At 20 °C, the vapor pressures of several alcohols are given in this table. Explain these vapor pressures in terms of types and extents of IMFs for these alcohols:

Compound	methanol CH_3OH	ethanol C_2H_5OH	propanol C_3H_7OH	butanol C_4H_9OH
Vapor Pressure at 20 °C	11.9 kPa	5.95 kPa	2.67 kPa	0.56 kPa

Answer

All these compounds exhibit hydrogen bonding; these strong IMFs are difficult for the molecules to overcome, so the vapor pressures are relatively low. As the size of molecule increases from methanol to butanol, dispersion forces increase, which means that the vapor pressures decrease as observed:

$$P_{\text{methanol}} > P_{\text{ethanol}} > P_{\text{propanol}} > P_{\text{butanol}}.$$

As temperature increases, the vapor pressure of a liquid also increases due to the increased average KE of its molecules. Recall that at any given temperature, the molecules of a substance experience a range of kinetic energies, with a certain fraction of molecules having a sufficient energy to overcome IMF and escape the liquid (vaporize). At a higher temperature, a greater fraction of molecules have enough energy to escape from the liquid, as shown in Figure 8.4.2. The escape of more molecules per unit of time and the greater average speed of the molecules that escape both contribute to the higher vapor pressure.
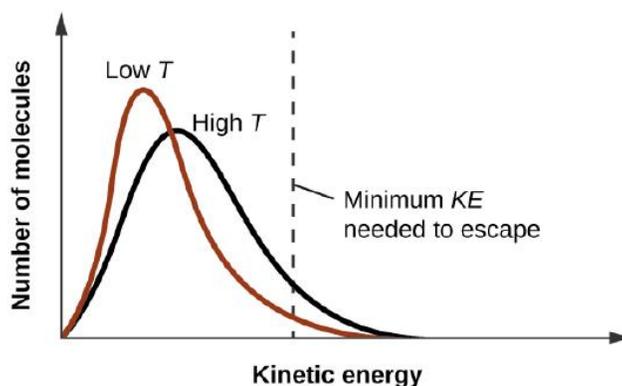
Figure 8.4.2: Temperature affects the distribution of kinetic energies for the molecules in a liquid. At the higher temperature, more molecules have the necessary kinetic energy, KE, to escape from the liquid into the gas phase.

Boiling Points

When the vapor pressure increases enough to equal the external atmospheric pressure, the liquid reaches its **boiling point**. The boiling point of a liquid is the temperature at which its equilibrium vapor pressure is equal to the pressure exerted on the liquid by its gaseous surroundings. For liquids in open containers, this pressure is that due to the earth's atmosphere. The **normal boiling point** of a liquid is defined as its boiling point when surrounding pressure is equal to 1 atm (101.3 kPa). Figure 8.4.3 shows the variation in vapor pressure with temperature for several different substances. Considering the definition of boiling point, these curves may be seen as depicting the dependence of a liquid's boiling point on surrounding pressure.
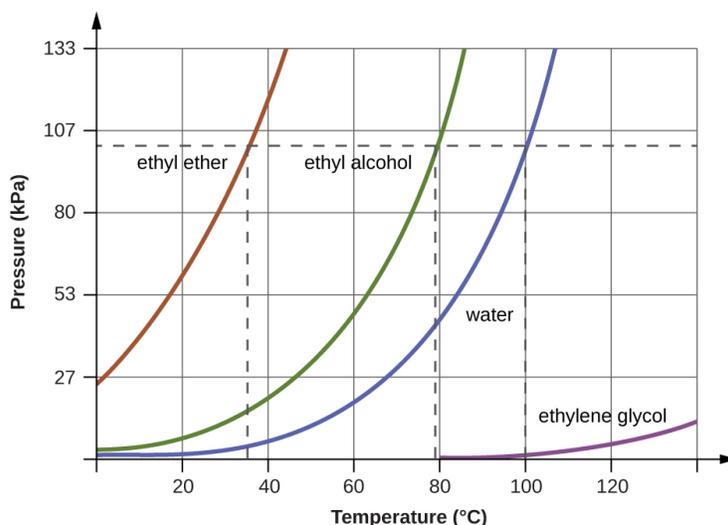
Figure 8.4.3: The boiling points of liquids are the temperatures at which their equilibrium vapor pressures equal the pressure of the surrounding atmosphere. Normal boiling points are those corresponding to a pressure of 1 atm (101.3 kPa.)

✔ Example 8.4.2: A Boiling Point at Reduced Pressure

A typical atmospheric pressure in Leadville, Colorado (elevation 10,200 feet) is 68 kPa. Use the graph in Figure 8.4.3 to determine the boiling point of water at this elevation.

Solution

The graph of the vapor pressure of water versus temperature in Figure 8.4.3 indicates that the vapor pressure of water is 68 kPa at about 90 °C. Thus, at about 90 °C, the vapor pressure of water will equal the atmospheric pressure in Leadville, and water will boil.

? Exercise 8.4.2

The boiling point of ethyl ether was measured to be 10 °C at a base camp on the slopes of Mount Everest. Use Figure 8.4.3 to determine the approximate atmospheric pressure at the camp.

Answer

Approximately 40 kPa (0.4 atm)

The quantitative relation between a substance's vapor pressure and its temperature is described by the Clausius-Clapeyron equation:

$$P = Ae^{-\Delta H_{vap}/RT}$$

where ΔH_{vap} is the enthalpy of vaporization for the liquid, R is the gas constant, and A is a constant whose value depends on the chemical identity of the substance. Temperature T must be in Kelvin in this equation. This equation is often rearranged into logarithmic form to yield the linear equation:

$$\ln P = -\frac{\Delta H_{vap}}{RT} + \ln A$$

This linear equation may be expressed in a two-point format that is convenient for use in various computations, as demonstrated in the example exercises that follow. If at temperature T_1, the vapor pressure is P_1, and at temperature T_2, the vapor pressure is P_2, the corresponding linear equations are:

$$\ln P_1 = -\frac{\Delta H_{vap}}{RT_1} + \ln A$$

and

$$\ln P_2 = -\frac{\Delta H_{vap}}{RT_2} + \ln A$$

Since the constant, A, is the same, these two equations may be rearranged to isolate ln A and then set them equal to one another:

$$\ln P_1 + \frac{\Delta H_{vap}}{RT_1} = \ln P_2 + \frac{\Delta H_{vap}}{RT_2}$$

which can be combined into:

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

✔ Example 8.4.3: Estimating Enthalpy of Vaporization

Isooctane (2,2,4-trimethylpentane) has an octane rating of 100. It is used as one of the standards for the octane-rating system for gasoline. At 34.0 °C, the vapor pressure of isooctane is 10.0 kPa, and at 98.8 °C, its vapor pressure is 100.0 kPa. Use this information to estimate the enthalpy of vaporization for isooctane.

Solution

The enthalpy of vaporization, ΔH_{vap}, can be determined by using the Clausius-Clapeyron equation:

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Since we have two vapor pressure-temperature values (T_1 = 34.0 °C = 307.2 K, P_1 = 10.0 kPa and T_2 = 98.8 °C = 372.0 K, P_2 = 100 kPa), we can substitute them into this equation and solve for ΔH_{vap}. Rearranging the Clausius-Clapeyron equation and solving for ΔH_{vap} yields:

$$\Delta H_{\text{vap}} = \frac{R \cdot \ln\left(\frac{P_2}{P_1}\right)}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} = \frac{(8.3145\,J/mol \cdot K) \cdot \ln\left(\frac{100kPa}{10.0kPa}\right)}{\left(\frac{1}{307.2K} - \frac{1}{372.0K}\right)} = 33,800\,J/mol = 33.8kJ/mol$$

Note that the pressure can be in any units, so long as they agree for both P values, but the temperature must be in kelvin for the Clausius-Clapeyron equation to be valid.

? Exercise 8.4.3

At 20.0 °C, the vapor pressure of ethanol is 5.95 kPa, and at 63.5 °C, its vapor pressure is 53.3 kPa. Use this information to estimate the enthalpy of vaporization for ethanol.

Answer

41,360 J/mol or 41.4 kJ/mol

✔ Example 8.4.4: Estimating Temperature (or Vapor Pressure)

For benzene (C_6H_6), the normal boiling point is 80.1 °C and the enthalpy of vaporization is 30.8 kJ/mol. What is the boiling point of benzene in Denver, where atmospheric pressure = 83.4 kPa?

Solution

If the temperature and vapor pressure are known at one point, along with the enthalpy of vaporization, ΔH_{vap}, then the temperature that corresponds to a different vapor pressure (or the vapor pressure that corresponds to a different temperature) can be determined by using the Clausius-Clapeyron equation:

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{\text{vap}}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Since the normal boiling point is the temperature at which the vapor pressure equals atmospheric pressure at sea level, we know one vapor pressure-temperature value (T_1 = 80.1 °C = 353.3 K, P_1 = 101.3 kPa, ΔH_{vap} = 30.8 kJ/mol) and want to find the temperature (T_2) that corresponds to vapor pressure P_2 = 83.4 kPa. We can substitute these values into the Clausius-Clapeyron equation and then solve for T_2. Rearranging the Clausius-Clapeyron equation and solving for T_2 yields:

$$T_2 = \left(\frac{-R \cdot \ln\left(\frac{P_2}{P_1}\right)}{\Delta H_{\text{vap}}} + \frac{1}{T_1}\right)^{-1} = \left(\frac{-(8.3145\,J/mol \cdot K) \cdot \ln\left(\frac{83.4kPa}{101.3kPa}\right)}{30,800\,J/mol} + \frac{1}{353.3K}\right)^{-1} = 346.9$$

? Exercise 8.4.4

For acetone ($CH_3)_2CO$, the normal boiling point is 56.5 °C and the enthalpy of vaporization is 31.3 kJ/mol. What is the vapor pressure of acetone at 25.0 °C?

Answer

30.1 kPa

Enthalpy of Vaporization

Vaporization is an endothermic process. The cooling effect can be evident when you leave a swimming pool or a shower. When the water on your skin evaporates, it removes heat from your skin and causes you to feel cold. The energy change associated with the vaporization process is the enthalpy of vaporization, ΔH_{vap}. For example, the vaporization of water at standard temperature is represented by:

$$H_2O(l) \longrightarrow H_2O(g) \qquad \Delta H_{vap} = 44.01kJ/mol$$

As described in the chapter on thermochemistry, the reverse of an endothermic process is exothermic. And so, the condensation of a gas releases heat:

$$H_2O(g) \longrightarrow H_2O(l) \qquad \Delta H_{con} = -\Delta H_{vap} = -44.01 kJ/mol$$

✔ Example 8.4.5: Using Enthalpy of Vaporization

One way our body is cooled is by evaporation of the water in sweat (Figure 8.4.4). In very hot climates, we can lose as much as 1.5 L of sweat per day. Although sweat is not pure water, we can get an approximate value of the amount of heat removed by evaporation by assuming that it is. How much heat is required to evaporate 1.5 L of water (1.5 kg) at T = 37 °C (normal body temperature); ΔH_{vap} = 43.46 kJ/mol at 37 °C.

Figure 8.4.4: Evaporation of sweat helps cool the body. (credit: "Kullez"/Flickr)

Solution

We start with the known volume of sweat (approximated as just water) and use the given information to convert to the amount of heat needed:

$$1.5 \text{ L} \times \frac{1000 \text{ g}}{1 \text{ L}} \times \frac{1 \text{ mol}}{18 \text{ g}} \times \frac{43.46 \text{ kJ}}{1 \text{ mol}} = 3.6 \times 10^3 \text{ kJ}$$

Thus, 3600 kJ of heat are removed by the evaporation of 1.5 L of water.

? Exercise 8.4.1

How much heat is required to evaporate 100.0 g of liquid ammonia, NH_3, at its boiling point if its enthalpy of vaporization is 4.8 kJ/mol?

Answer

28 kJ

Melting and Freezing

When we heat a crystalline solid, we increase the average energy of its atoms, molecules, or ions and the solid gets hotter. At some point, the added energy becomes large enough to partially overcome the forces holding the molecules or ions of the solid in their fixed positions, and the solid begins the process of transitioning to the liquid state, or melting. At this point, the temperature of the solid stops rising, despite the continual input of heat, and it remains constant until all of the solid is melted. Only after all of the solid has melted will continued heating increase the temperature of the liquid (Figure 8.4.5).

(a)   (b)   (c)   (d)

Figure 8.4.5: (a) This beaker of ice has a temperature of −12.0 °C. (b) After 10 minutes the ice has absorbed enough heat from the air to warm to 0 °C. A small amount has melted. (c) Thirty minutes later, the ice has absorbed more heat, but its temperature is still 0 °C. The ice melts without changing its temperature. (d) Only after all the ice has melted does the heat absorbed cause the temperature to increase to 22.2 °C. (credit: modification of work by Mark Ott)

If we stop heating during melting and place the mixture of solid and liquid in a perfectly insulated container so no heat can enter or escape, the solid and liquid phases remain in equilibrium. This is almost the situation with a mixture of ice and water in a very good thermos bottle; almost no heat gets in or out, and the mixture of solid ice and liquid water remains for hours. In a mixture of solid and liquid at equilibrium, the reciprocal processes of melting and **freezing** occur at equal rates, and the quantities of solid and liquid therefore remain constant. The temperature at which the solid and liquid phases of a given substance are in equilibrium is called the **melting point** of the solid or the freezing point of the liquid. Use of one term or the other is normally dictated by the direction of the phase transition being considered, for example, solid to liquid (melting) or liquid to solid (freezing).

The enthalpy of fusion and the melting point of a crystalline solid depend on the strength of the attractive forces between the units present in the crystal. Molecules with weak attractive forces form crystals with low melting points. Crystals consisting of particles with stronger attractive forces melt at higher temperatures.

The amount of heat required to change one mole of a substance from the solid state to the liquid state is the enthalpy of fusion, ΔH_{fus} of the substance. The enthalpy of fusion of ice is 6.0 kJ/mol at 0 °C. Fusion (melting) is an endothermic process:

$$H_2O(s) \longrightarrow H_2O(l) \quad \Delta H_{\text{fus}} = 6.01 kJ/mol$$

The reciprocal process, freezing, is an exothermic process whose enthalpy change is −6.0 kJ/mol at 0 °C:

$$H_2O(l) \longrightarrow H_2O(s) \quad \Delta H_{\text{frz}} = -\Delta H_{\text{fus}} = -6.01 kJ/mol$$
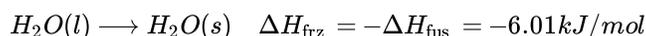
Sublimation and Deposition

Some solids can transition directly into the gaseous state, bypassing the liquid state, via a process known as **sublimation**. At room temperature and standard pressure, a piece of dry ice (solid CO_2) sublimes, appearing to gradually disappear without ever forming any liquid. Snow and ice sublime at temperatures below the melting point of water, a slow process that may be accelerated by winds and the reduced atmospheric pressures at high altitudes. When solid iodine is warmed, the solid sublimes and a vivid purple vapor forms (Figure 8.4.6). The reverse of sublimation is called **deposition**, a process in which gaseous substances condense directly into the solid state, bypassing the liquid state. The formation of frost is an example of deposition.
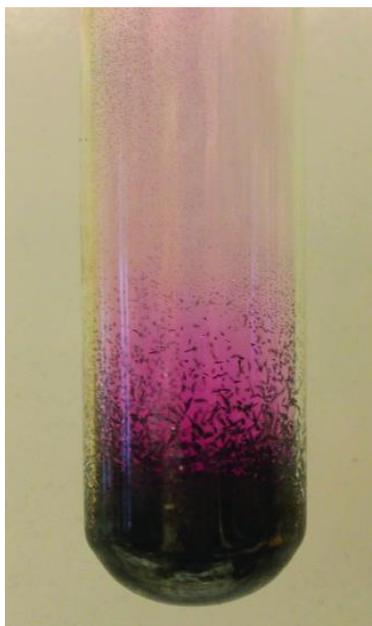
Figure 8.4.6: Sublimation of solid iodine in the bottom of the tube produces a purple gas that subsequently deposits as solid iodine on the colder part of the tube above. (credit: modification of work by Mark Ott)

Like vaporization, the process of sublimation requires an input of energy to overcome intermolecular attractions. The enthalpy of sublimation, ΔH_{sub}, is the energy required to convert one mole of a substance from the solid to the gaseous state. For example, the sublimation of carbon dioxide is represented by:

$$CO_2(s) \longrightarrow CO_2(g) \qquad \Delta H_{sub} = 26.1 kJ/mol$$

Likewise, the enthalpy change for the reverse process of deposition is equal in magnitude but opposite in sign to that for sublimation:

$$CO_2(g) \longrightarrow CO_2(s) \qquad \Delta H_{dep} = -\Delta H_{sub} = -26.1 kJ/mol$$

Consider the extent to which intermolecular attractions must be overcome to achieve a given phase transition. Converting a solid into a liquid requires that these attractions be only partially overcome; transition to the gaseous state requires that they be completely overcome. As a result, the enthalpy of fusion for a substance is less than its enthalpy of vaporization. This same logic can be used to derive an approximate relation between the enthalpies of all phase changes for a given substance. Though not an entirely accurate description, sublimation may be conveniently modeled as a sequential two-step process of melting followed by vaporization in order to apply Hess's Law. Viewed in this manner, the enthalpy of sublimation for a substance may be estimated as the sum of its enthalpies of fusion and vaporization, as illustrated in Figure 8.4.7. For example:

$$
\begin{aligned}
\text{solid} &\longrightarrow \text{liquid} & \Delta H_{fus} \\
\text{liquid} &\longrightarrow \text{gas} & \Delta H_{vap} \\
\hline
\text{solid} &\longrightarrow \text{gas} & \Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}
\end{aligned}
$$
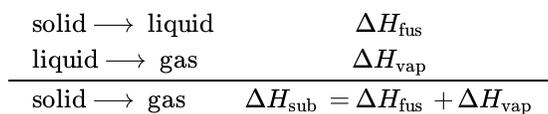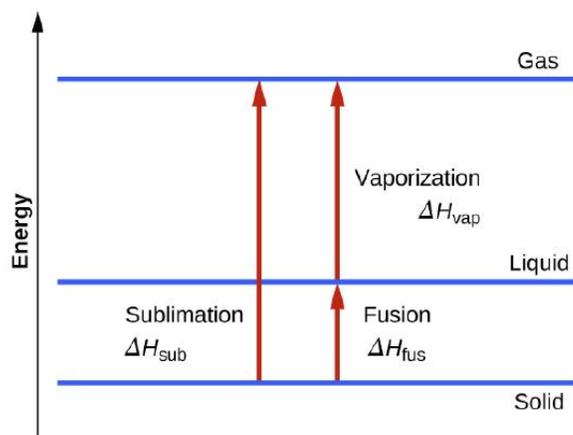
Figure 8.4.7: For a given substance, the sum of its enthalpy of fusion and enthalpy of vaporization is approximately equal to its enthalpy of sublimation.

Heating and Cooling Curves

In the chapter on thermochemistry, the relation between the amount of heat absorbed or released by a substance, q, and its accompanying temperature change, ΔT, was introduced:

$$q = mc\Delta T$$

where m is the mass of the substance and c is its specific heat. The relation applies to matter being heated or cooled, but not undergoing a change in state. When a substance being heated or cooled reaches a temperature corresponding to one of its phase transitions, further gain or loss of heat is a result of diminishing or enhancing intermolecular attractions, instead of increasing or decreasing molecular kinetic energies. While a substance is undergoing a change in state, its temperature remains constant. Figure 8.4.8 shows a typical heating curve.

Consider the example of heating a pot of water to boiling. A stove burner will supply heat at a roughly constant rate; initially, this heat serves to increase the water's temperature. When the water reaches its boiling point, the temperature remains constant despite the continued input of heat from the stove burner. This same temperature is maintained by the water as long as it is boiling. If the burner setting is increased to provide heat at a greater rate, the water temperature does not rise, but instead the boiling becomes more vigorous (rapid). This behavior is observed for other phase transitions as well: For example, temperature remains constant while the change of state is in progress.
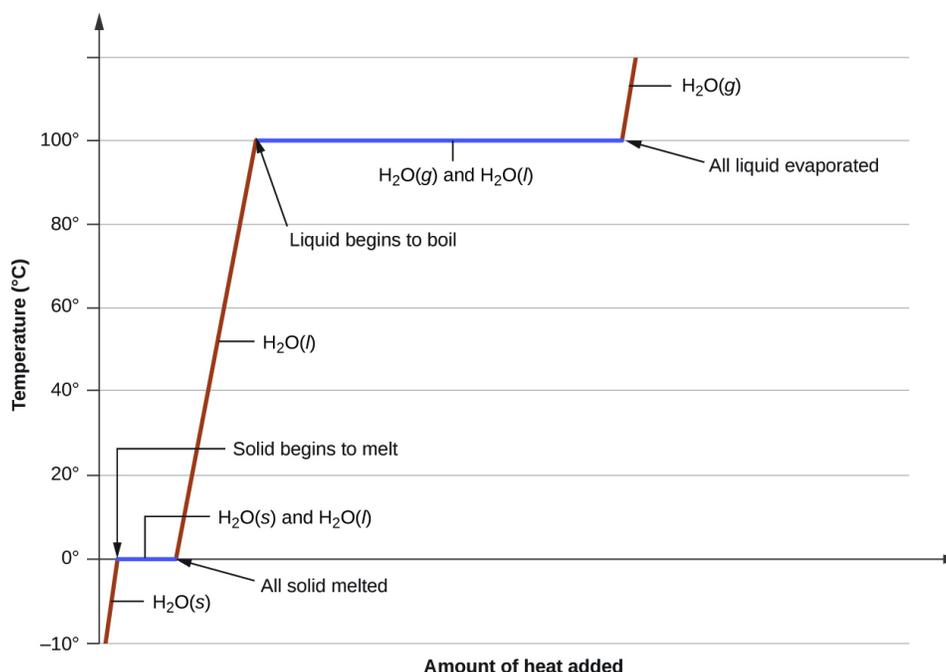
Figure 8.4.8: A typical heating curve for a substance depicts changes in temperature that result as the substance absorbs increasing amounts of heat. Plateaus in the curve (regions of constant temperature) are exhibited when the substance undergoes phase transitions.

✔ **Example 8.4.6: Total Heat Needed to Change Temperature and Phase for a Substance**

How much heat is required to convert 135 g of ice at −15 °C into water vapor at 120 °C?

Solution

The transition described involves the following steps:

1. Heat ice from −15 °C to 0 °C
2. Melt ice
3. Heat water from 0 °C to 100 °C
4. Boil water
5. Heat steam from 100 °C to 120 °C

The heat needed to change the temperature of a given substance (with no change in phase) is: $q = mc\Delta T$. The heat needed to induce a given change in phase is given by $q = n\Delta H$.

Using these equations with the appropriate values for specific heat of ice, water, and steam, and enthalpies of fusion and vaporization, we have:

$$q_{\text{total}} = (m \cdot c \cdot \Delta T)_{\text{ice}} + n \cdot \Delta H_{\text{fus}} + (m \cdot c \cdot \Delta T)_{\text{water}} + n \cdot \Delta H_{\text{vap}} + (m \cdot c \cdot \Delta T)_{\text{steam}}$$

$$= (135g \cdot 2.09 J/g \cdot {}^\circ C \cdot 15 {}^\circ C) + \left(135 \cdot \frac{1 mol}{18.02 g} \cdot 6.01 kJ/mol\right)$$

$$+ (135g \cdot 4.18 J/g \cdot {}^\circ C \cdot 100 {}^\circ C) + \left(135 g \cdot \frac{1 mol}{18.02 g} \cdot 40.67 kJ/mol\right)$$

$$+ (135g \cdot 1.86 J/g \cdot {}^\circ C \cdot 20 {}^\circ C)$$

$$= 4230 J + 45.0 kJ + 56,500 J + 305 kJ + 5022 J$$

Converting the quantities in J to kJ permits them to be summed, yielding the total heat required:

$$q_{\text{total}} = 4.23 kJ + 45.0 kJ + 56.5 kJ + 305 kJ + 5.02 kJ = 416 kJ$$

> NOTE: The value of ΔH_{vap} at the boiling point of water (40.67 kJ/mol) is used here instead of the value at standard temperature (44.01 kJ/mol).

? Exercise 8.4.6

What is the total amount of heat released when 94.0 g water at 80.0 °C cools to form ice at −30.0 °C?

Answer

68.7 kJ

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8.5: Phase Diagrams

 ◆ Learning Objectives

 By the end of this section, you will be able to:

 - Explain the construction and use of a typical phase diagram
 - Use phase diagrams to identify stable phases at given temperatures and pressures, and to describe phase transitions resulting from changes in these properties
 - Describe the supercritical fluid phase of matter

In the previous module, the variation of a liquid's equilibrium vapor pressure with temperature was described. Considering the definition of boiling point, plots of vapor pressure versus temperature represent how the boiling point of the liquid varies with pressure. Also described was the use of heating and cooling curves to determine a substance's melting (or freezing) point. Making such measurements over a wide range of pressures yields data that may be presented graphically as a phase diagram. A **phase diagram** combines plots of pressure versus temperature for the liquid-gas, solid-liquid, and solid-gas phase-transition equilibria of a substance. These diagrams indicate the physical states that exist under specific conditions of pressure and temperature, and also provide the pressure dependence of the phase-transition temperatures (melting points, sublimation points, boiling points). A typical phase diagram for a pure substance is shown in Figure 8.5.1.
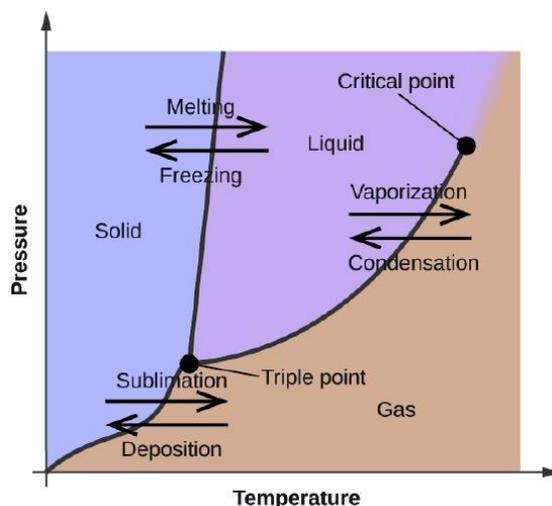
Figure 8.5.1: The physical state of a substance and its phase-transition temperatures are represented graphically in a phase diagram.

To illustrate the utility of these plots, consider the phase diagram for water shown in Figure 8.5.2.
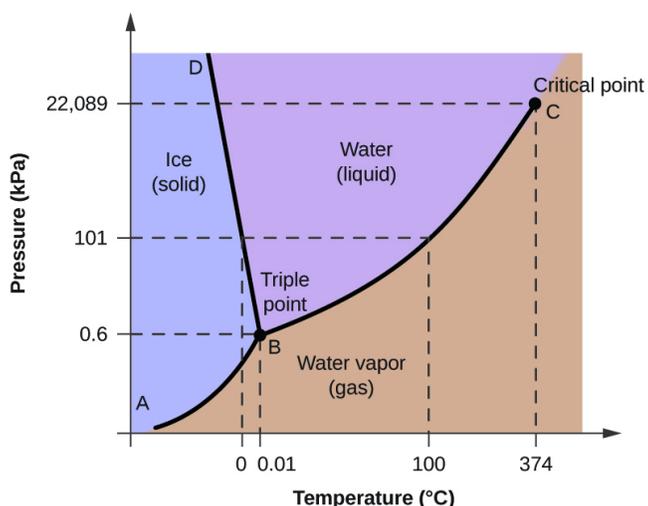
Figure 8.5.2: The pressure and temperature axes on this phase diagram of water are not drawn to constant scale in order to illustrate several important properties.

We can use the phase diagram to identify the physical state of a sample of water under specified conditions of pressure and temperature. For example, a pressure of 50 kPa and a temperature of −10 °C correspond to the region of the diagram labeled "ice." Under these conditions, water exists only as a solid (ice). A pressure of 50 kPa and a temperature of 50 °C correspond to the "water" region—here, water exists only as a liquid. At 25 kPa and 200 °C, water exists only in the gaseous state. Note that on the H_2O phase diagram, the pressure and temperature axes are not drawn to a constant scale in order to permit the illustration of several important features as described here.

The curve BC in Figure 8.5.2 is the plot of vapor pressure versus temperature as described in the previous module of this chapter. This "liquid-vapor" curve separates the liquid and gaseous regions of the phase diagram and provides the boiling point for water at any pressure. For example, at 1 atm, the boiling point is 100 °C. Notice that the liquid-vapor curve terminates at a temperature of 374 °C and a pressure of 218 atm, indicating that water cannot exist as a liquid above this temperature, regardless of the pressure. The physical properties of water under these conditions are intermediate between those of its liquid and gaseous phases. This unique state of matter is called a supercritical fluid, a topic that will be described in the next section of this module.

The solid-vapor curve, labeled AB in Figure 8.5.2, indicates the temperatures and pressures at which ice and water vapor are in equilibrium. These temperature-pressure data pairs correspond to the sublimation, or deposition, points for water. If we could zoom in on the solid-gas line in Figure 8.5.2, we would see that ice has a vapor pressure of about 0.20 kPa at −10 °C. Thus, if we place a frozen sample in a vacuum with a pressure less than 0.20 kPa, ice will sublime. This is the basis for the "freeze-drying" process often used to preserve foods, such as the ice cream shown in Figure 8.5.3.

Figure 8.5.3: Freeze-dried foods, like this ice cream, are dehydrated by sublimation at pressures below the triple point for water. (credit: "lwao"/Flickr)

The solid-liquid curve labeled BD shows the temperatures and pressures at which ice and liquid water are in equilibrium, representing the melting/freezing points for water. Note that this curve exhibits a slight negative slope (greatly exaggerated for

clarity), indicating that the melting point for water decreases slightly as pressure increases. Water is an unusual substance in this regard, as most substances exhibit an increase in melting point with increasing pressure. This behavior is partly responsible for the movement of glaciers, like the one shown in Figure 8.5.4. The bottom of a glacier experiences an immense pressure due to its weight that can melt some of the ice, forming a layer of liquid water on which the glacier may more easily slide.

Figure 8.5.4: The immense pressures beneath glaciers result in partial melting to produce a layer of water that provides lubrication to assist glacial movement. This satellite photograph shows the advancing edge of the Perito Moreno glacier in Argentina. (credit: NASA)

The point of intersection of all three curves is labeled B in Figure 8.5.2. At the pressure and temperature represented by this point, three phases of water coexist in equilibrium. This temperature-pressure data pair is called the triple point. At pressures lower than the triple point, water cannot exist as a liquid, regardless of the temperature.

✔ Example 8.5.1: Determining the State of Water

Using the phase diagram for water given in Figure 8.5.2, determine the state of water at the following temperatures and pressures:

a. −10 °C and 50 kPa
b. 25 °C and 90 kPa
c. 50 °C and 40 kPa
d. 80 °C and 5 kPa
e. −10 °C and 0.3 kPa
f. 50 °C and 0.3 kPa

Solution

Using the phase diagram for water, we can determine that the state of water at each temperature and pressure given are as follows: (a) solid; (b) liquid; (c) liquid; (d) gas; (e) solid; (f) gas.

? Exercise 8.5.1

What phase changes can water undergo as the temperature changes if the pressure is held at 0.3 kPa? If the pressure is held at 50 kPa?

Answer

At 0.3 kPa: at −58 °C. At 50 kPa: at 0 °C, l $\longrightarrow$ g at 78 °C

Consider the phase diagram for carbon dioxide shown in Figure 8.5.5 as another example. The solid-liquid curve exhibits a positive slope, indicating that the melting point for CO_2 increases with pressure as it does for most substances (water being a notable exception as described previously). Notice that the triple point is well above 1 atm, indicating that carbon dioxide cannot exist as a liquid under ambient pressure conditions. Instead, cooling gaseous carbon dioxide at 1 atm results in its deposition into the solid state. Likewise, solid carbon dioxide does not melt at 1 atm pressure but instead sublimes to yield gaseous CO_2. Finally, notice that the critical point for carbon dioxide is observed at a relatively modest temperature and pressure in comparison to water.
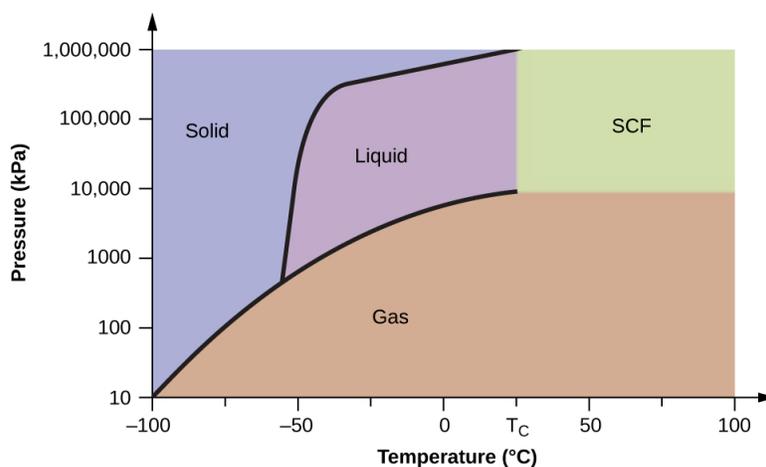
Figure 8.5.5: A phase diagram for carbon dioxide is shown. The pressure axis is plotted on a logarithmic scale to accommodate the large range of values.

✔ Example 8.5.2: Determining the State of Carbon Dioxide

Using the phase diagram for carbon dioxide shown in Figure 8.5.5, determine the state of CO_2 at the following temperatures and pressures:

a. −30 °C and 2000 kPa
b. −90 °C and 1000 kPa
c. −60 °C and 100 kPa
d. −40 °C and 1500 kPa
e. 0 °C and 100 kPa
f. 20 °C and 100 kPa

Solution

Using the phase diagram for carbon dioxide provided, we can determine that the state of CO_2 at each temperature and pressure given are as follows: (a) liquid; (b) solid; (c) gas; (d) liquid; (e) gas; (f) gas.

? Exercise 8.5.2

Identify the phase changes that carbon dioxide will undergo as its temperature is increased from −100 °C while holding its pressure constant at 1500 kPa. At 50 kPa. At what approximate temperatures do these phase changes occur?

Answer

at 1500 kPa: at −55 °C, at −10 °C;

at 50 kPa: at −60 °C

Supercritical Fluids

If we place a sample of water in a sealed container at 25 °C, remove the air, and let the vaporization-condensation equilibrium establish itself, we are left with a mixture of liquid water and water vapor at a pressure of 0.03 atm. A distinct boundary between the more dense liquid and the less dense gas is clearly observed. As we increase the temperature, the pressure of the water vapor increases, as described by the liquid-gas curve in the phase diagram for water (Figure 8.5.2), and a two-phase equilibrium of liquid and gaseous phases remains. At a temperature of 374 °C, the vapor pressure has risen to 218 atm, and any further increase in temperature results in the disappearance of the boundary between liquid and vapor phases. All of the water in the container is now present in a single phase whose physical properties are intermediate between those of the gaseous and liquid states. This phase of matter is called a **supercritical fluid**, and the temperature and pressure above which this phase exists is the **critical point** (Figure 8.5.6). Above its critical temperature, a gas cannot be liquefied no matter how much pressure is applied. The pressure required to

liquefy a gas at its critical temperature is called the critical pressure. The critical temperatures and critical pressures of some common substances are given in the following table.

Substance	Critical Temperature (°C)	Critical Pressure (kPa)
hydrogen	−240.0	1300
nitrogen	−147.2	3400
oxygen	−118.9	5000
carbon dioxide	31.1	7400
ammonia	132.4	11,300
sulfur dioxide	157.2	7800
water	374.0	22,000
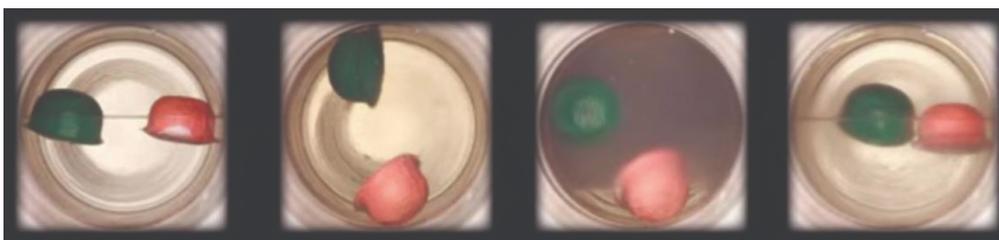
Figure 8.5.6: (a) A sealed container of liquid carbon dioxide slightly below its critical point is heated, resulting in (b) the formation of the supercritical fluid phase. Cooling the supercritical fluid lowers its temperature and pressure below the critical point, resulting in the reestablishment of separate liquid and gaseous phases (c and d). Colored floats illustrate differences in density between the liquid, gaseous, and supercritical fluid states. (credit: modification of work by "mrmrobin"/YouTube)

📌 Link to Learning

Observe the liquid-to-supercritical fluid transition for carbon dioxide.

Like a gas, a supercritical fluid will expand and fill a container, but its density is much greater than typical gas densities, typically being close to those for liquids. Similar to liquids, these fluids are capable of dissolving nonvolatile solutes. They exhibit essentially no surface tension and very low viscosities, however, so they can more effectively penetrate very small openings in a solid mixture and remove soluble components. These properties make supercritical fluids extremely useful solvents for a wide range of applications. For example, supercritical carbon dioxide has become a very popular solvent in the food industry, being used to decaffeinate coffee, remove fats from potato chips, and extract flavor and fragrance compounds from citrus oils. It is nontoxic, relatively inexpensive, and not considered to be a pollutant. After use, the CO_2 can be easily recovered by reducing the pressure and collecting the resulting gas.

✔ Example 8.5.3: The Critical Temperature of Carbon Dioxide

If we shake a carbon dioxide fire extinguisher on a cool day (18 °C), we can hear liquid CO_2 sloshing around inside the cylinder. However, the same cylinder appears to contain no liquid on a hot summer day (35 °C). Explain these observations.

Solution

On the cool day, the temperature of the CO_2 is below the critical temperature of CO_2, 304 K or 31 °C, so liquid CO_2 is present in the cylinder. On the hot day, the temperature of the CO_2 is greater than its critical temperature of 31 °C. Above this temperature no amount of pressure can liquefy CO_2 so no liquid CO_2 exists in the fire extinguisher.

> **? Exercise 8.5.3**
>
> Ammonia can be liquefied by compression at room temperature; oxygen cannot be liquefied under these conditions. Why do the two gases exhibit different behavior?
>
> **Answer**
>
> The critical temperature of ammonia is 405.5 K, which is higher than room temperature. The critical temperature of oxygen is below room temperature; thus oxygen cannot be liquefied at room temperature.

📌 Chemistry in Everyday Life: Decaffeinating Coffee Using Supercritical CO₂

Coffee is the world's second most widely traded commodity, following only petroleum. Across the globe, people love coffee's aroma and taste. Many of us also depend on one component of coffee—caffeine—to help us get going in the morning or stay alert in the afternoon. But late in the day, coffee's stimulant effect can keep you from sleeping, so you may choose to drink decaffeinated coffee in the evening.

Since the early 1900s, many methods have been used to decaffeinate coffee. All have advantages and disadvantages, and all depend on the physical and chemical properties of caffeine. Because caffeine is a somewhat polar molecule, it dissolves well in water, a polar liquid. However, since many of the other 400-plus compounds that contribute to coffee's taste and aroma also dissolve in H_2O, hot water decaffeination processes can also remove some of these compounds, adversely affecting the smell and taste of the decaffeinated coffee. Dichloromethane (CH_2Cl_2) and ethyl acetate ($CH_3CO_2C_2H_5$) have similar polarity to caffeine, and are therefore very effective solvents for caffeine extraction, but both also remove some flavor and aroma components, and their use requires long extraction and cleanup times. Because both of these solvents are toxic, health concerns have been raised regarding the effect of residual solvent remaining in the decaffeinated coffee.

Supercritical fluid extraction using carbon dioxide is now being widely used as a more effective and environmentally friendly decaffeination method (Figure 8.5.7). At temperatures above 304.2 K and pressures above 7376 kPa, CO_2 is a supercritical fluid, with properties of both gas and liquid. Like a gas, it penetrates deep into the coffee beans; like a liquid, it effectively dissolves certain substances. Supercritical carbon dioxide extraction of steamed coffee beans removes 97−99% of the caffeine, leaving coffee's flavor and aroma compounds intact. Because CO_2 is a gas under standard conditions, its removal from the extracted coffee beans is easily accomplished, as is the recovery of the caffeine from the extract. The caffeine recovered from coffee beans via this process is a valuable product that can be used subsequently as an additive to other foods or drugs.
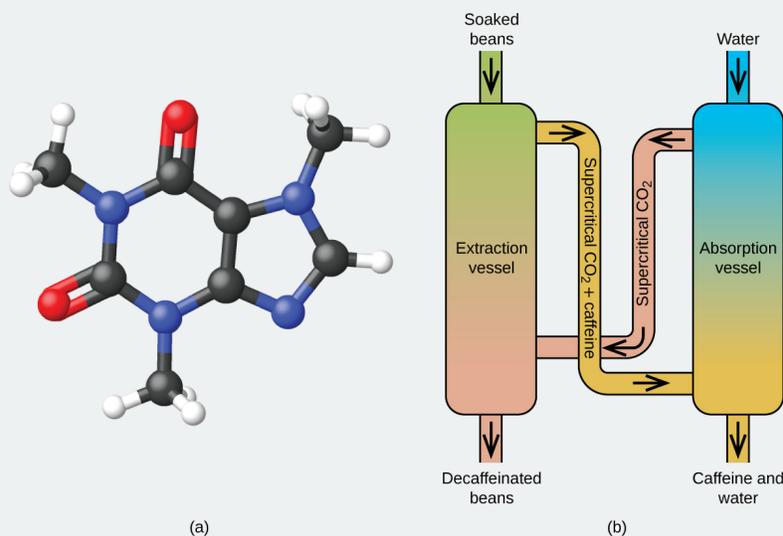
Figure 8.5.7: (a) Caffeine molecules have both polar and nonpolar regions, making it soluble in solvents of varying polarities. (b) The schematic shows a typical decaffeination process involving supercritical carbon dioxide.

8.6: The Solid State of Matter

> **◐ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - 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 8.6.1).
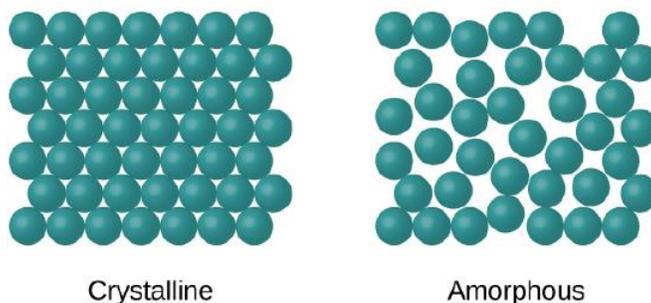
Figure 8.6.1: The entities of a solid phase may be arranged in a regular, repeating pattern (crystalline solids) or randomly (amorphous).

Metals and ionic compounds typically form ordered, crystalline solids. Substances that consist of large molecules, or a mixture of molecules whose movements are more restricted, often form amorphous solids. For examples, candle waxes are amorphous solids composed of large hydrocarbon molecules. Some substances, such as silicon dioxide (shown in Figure 8.6.2), 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.
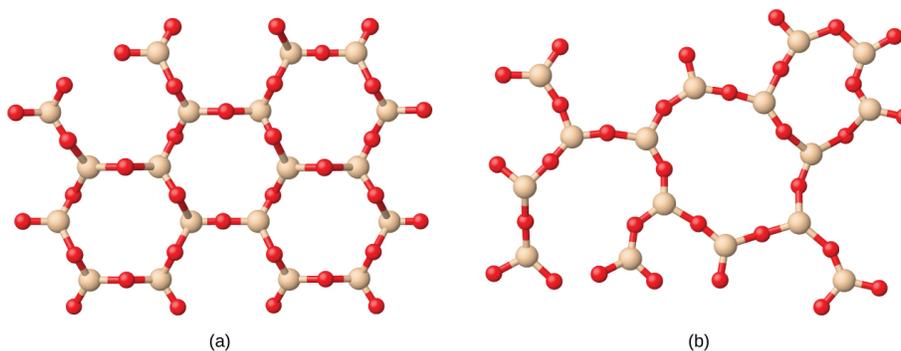
Figure 8.6.2: (a) Silicon dioxide, SiO_2, is abundant in nature as one of several crystalline forms of the mineral quartz. (b) Rapid cooling of molten SiO_2 yields an amorphous solid known as "fused silica".

Crystalline solids are generally classified according to 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 8.6.3). 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.
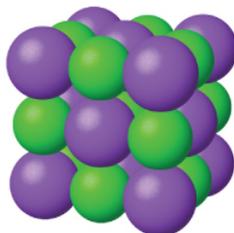
Figure 8.6.3: Sodium chloride is an ionic solid.

Metallic Solids

Metallic solids such as crystals of copper, aluminum, and iron are formed by metal atoms Figure 8.6.4. 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.
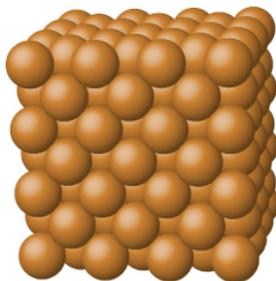
Figure 8.6.4: Copper is a metallic solid.

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 8.6.5. 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.
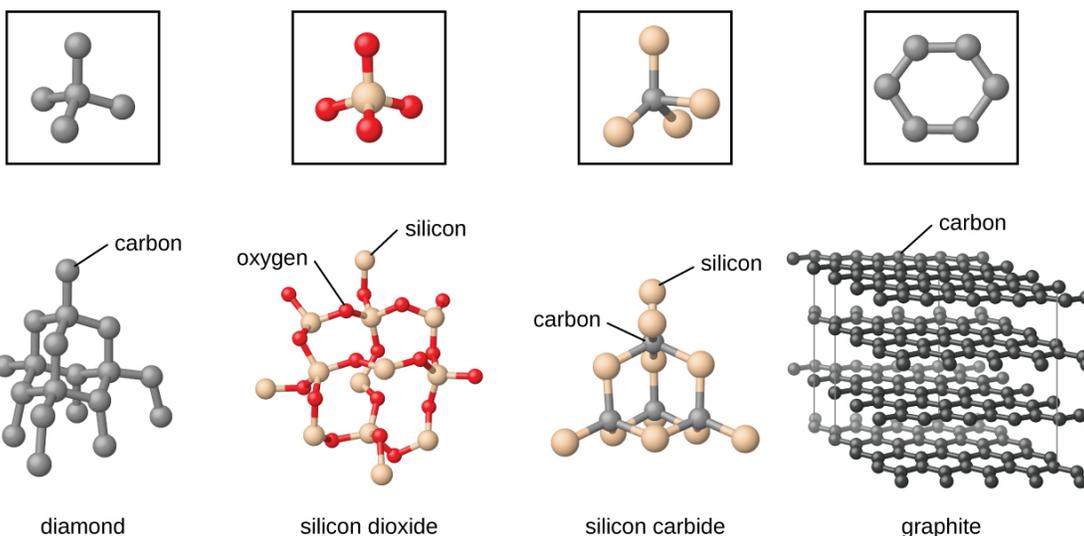
Figure 8.6.5: A covalent crystal contains a three-dimensional network of covalent bonds, as illustrated by the structures of diamond, silicon dioxide, silicon carbide, and graphite. Graphite is an exceptional example, composed of planar sheets of covalent crystals that are held together in layers by noncovalent forces. Unlike typical covalent solids, graphite is very soft and electrically conductive.

Molecular Solids

Molecular solids, such as ice, sucrose (table sugar), and iodine, as shown in Figure 8.6.6: , 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).
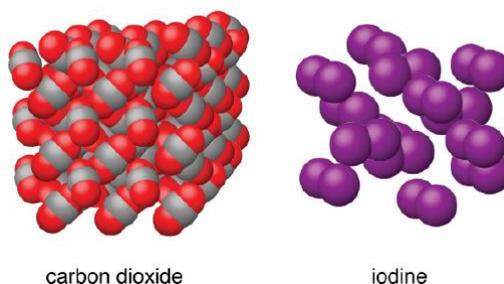
Figure 8.6.6: Carbon dioxide (CO_2) consists of small, nonpolar molecules and forms a molecular solid with a melting point of −78 °C. Iodine (I_2) consists of larger, nonpolar molecules and forms a molecular solid that melts at 114 °C.

Properties of Solids

A crystalline solid, like those listed in Table 8.6.1, 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 8.6.1: Types of Crystalline Solids and Their Properties

Type of Solid	Type of Particles	Type of Attractions	Properties	Examples

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, $C_{12}H_{22}O_{11}$

📌 How Sciences Interconnect: 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 8.6.7. 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.

1.4 × 10⁻¹⁰ m
Distance between center of atoms

diamond   graphite   Graphite surface
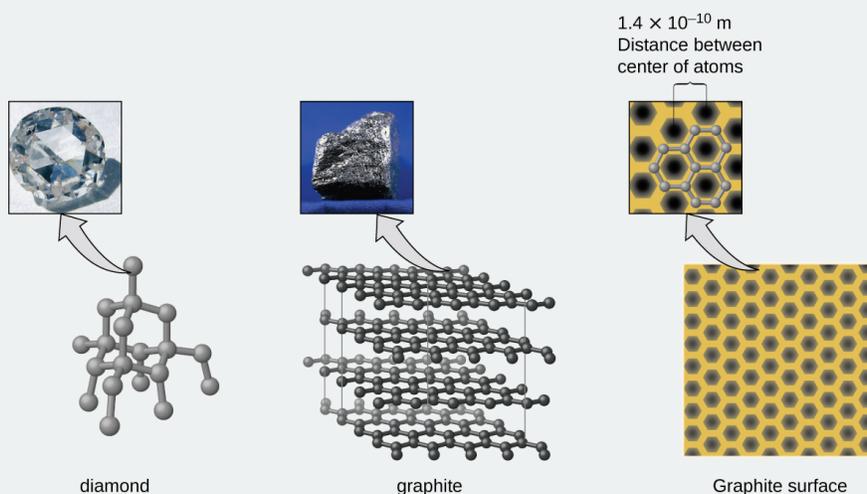
Figure 8.6.7: Diamond is extremely hard because of the strong bonding between carbon atoms in all directions. Graphite (in pencil lead) rubs off onto paper due to the weak attractions between the carbon layers. An image of a graphite surface shows the distance between the centers of adjacent carbon atoms. (credit left photo: modification of work by Steve Jurvetson; credit middle photo: modification of work by United States Geological Survey)

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 8.6.8: , 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.

Graphene sheet

Buckyball   **Nanotube**   **Stacked sheets**

Figure 8.6.8: Graphene sheets can be formed into buckyballs, nanotubes, and stacked layers.
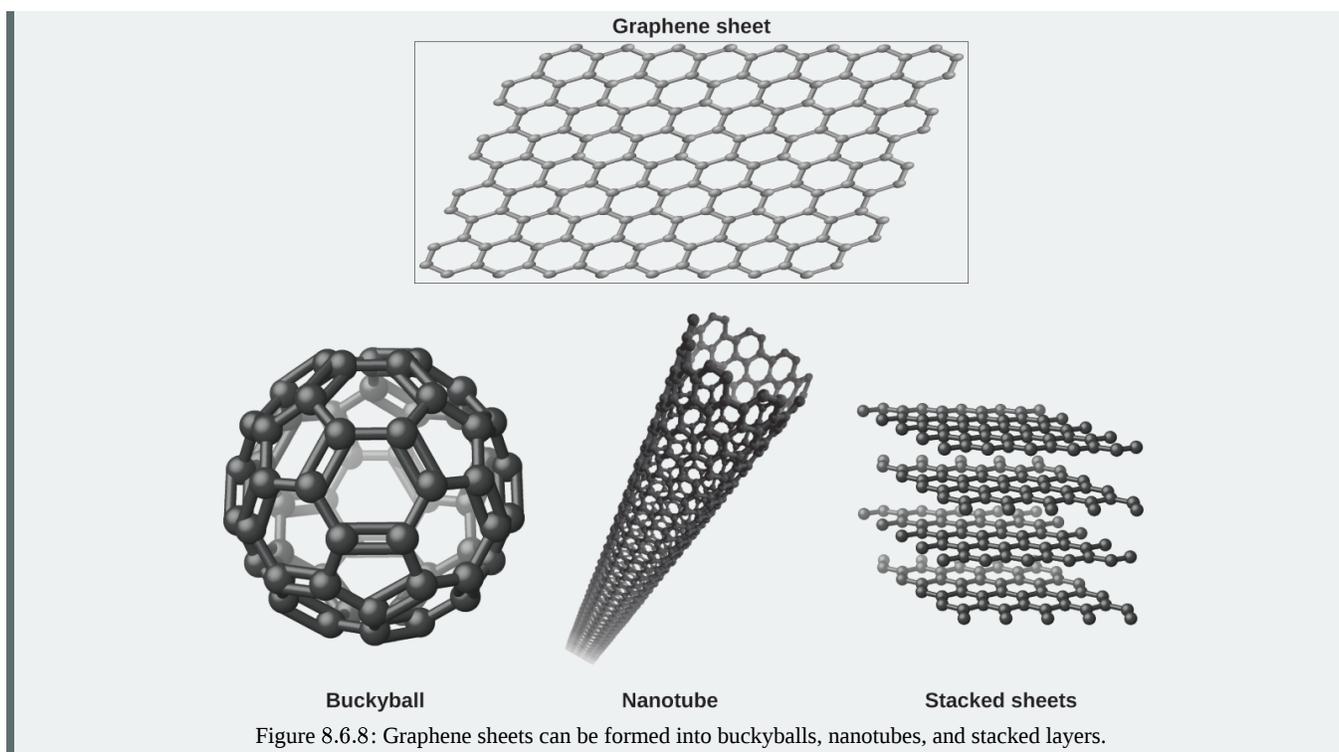
Crystal Defects

In a crystalline solid, the atoms, ions, or molecules are arranged in a definite repeating pattern, but occasional defects may occur in the pattern. Several types of defects are known, as illustrated in Figure 8.6.9. **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.
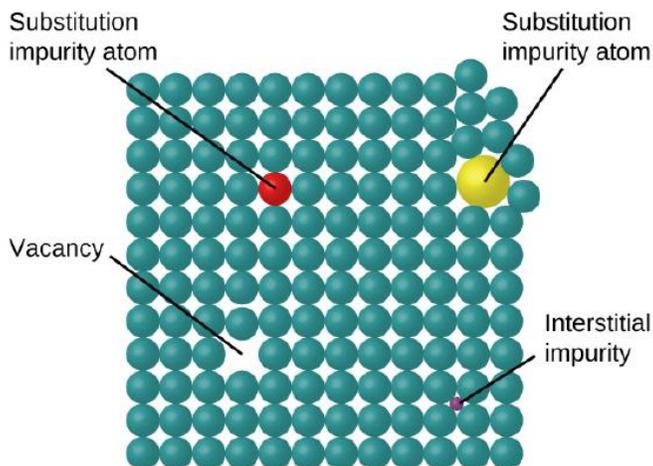
Figure 8.6.9: Types of crystal defects include vacancies, interstitial atoms, and substitutions impurities.

8.7: Lattice Structures in Crystalline Solids

> ◑ Learning Objectives
>
> By the end of this section, you will be able to:
>
> - 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 8.7.1.
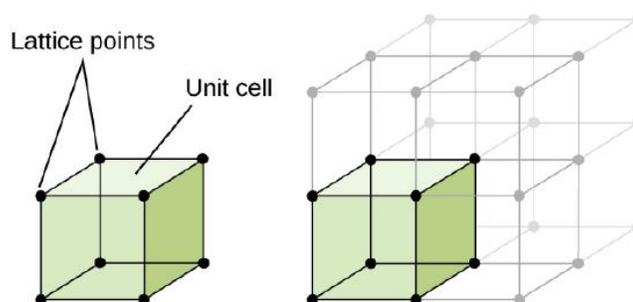
Figure 8.7.1: A unit cell shows the locations of lattice points repeating in all directions.

Let us begin our investigation of crystal lattice structure and unit cells with the most straightforward structure and the most basic unit cell. To visualize this, imagine taking a large number of identical spheres, such as tennis balls, and arranging them uniformly in a container. The simplest way to do this would be to make layers in which the spheres in one layer are directly above those in the layer below, as illustrated in Figure 8.7.2. This arrangement is called **simple cubic structure**, and the unit cell is called the **simple cubic unit cell** or primitive cubic unit cell.
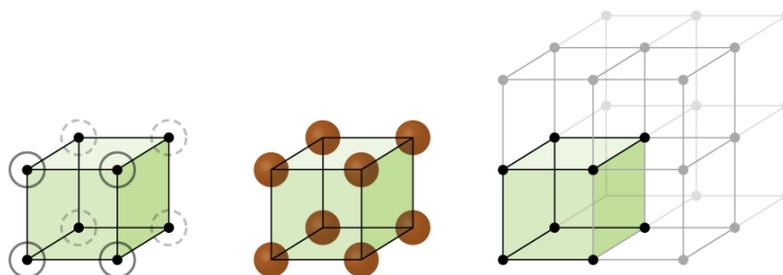
Figure 8.7.2: When metal atoms are arranged with spheres in one layer directly above or below spheres in another layer, the lattice structure is called simple cubic. Note that the spheres are in contact.

In a simple cubic structure, the spheres are not packed as closely as they could be, and they only "fill" about 52% of the volume of the container. This is a relatively inefficient arrangement, and only one metal (polonium, Po) crystallizes in a simple cubic structure. As shown in Figure 8.7.3, 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.
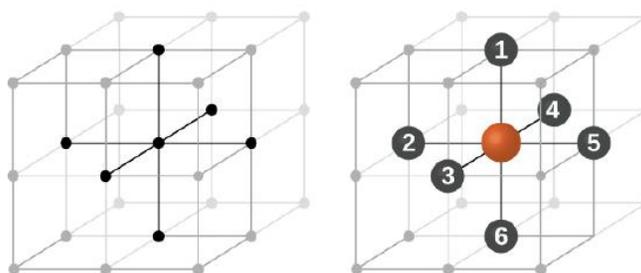
Figure 8.7.3: An atom in a simple cubic lattice structure contacts six other atoms, so it has a coordination number of six.

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 8.7.4. 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.

Lattice points

Lattice points

Simple cubic lattice cell
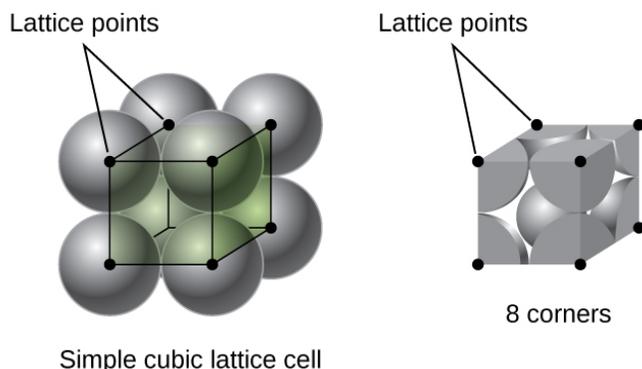
8 corners

Figure 8.7.4: A simple cubic lattice unit cell contains one-eighth of an atom at each of its eight corners, so it contains one atom total.

> ✔ Example 8.7.1: Calculation of 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:
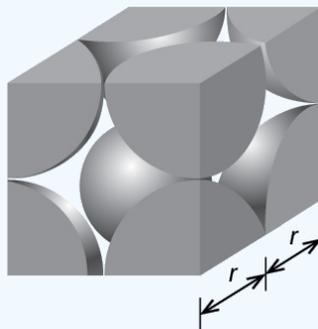
a. Two adjacent Po atoms contact each other, so the edge length of this cell is equal to two Po atomic radii: $l = 2r$. Therefore, the radius of Po is:

$$r = \frac{l}{2} = \frac{336pm}{2} = 168pm.$$

b. Density is given by density $= \frac{mass}{volume}$. 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

$$1 \text{ Po unit cell } \times \frac{1 \text{ Po atom}}{1 \text{ Po unit cell}} \times \frac{1molPo}{6.022 \times 10^{23} \text{ Po atoms}} \times \frac{208.998g}{1molPo} = 3.47 \times 10^{-22}g$$

The volume of a Po unit cell can be found by:

$$V = l^3 = \left(336 \times 10^{-10}cm\right)^3 = 3.79 \times 10^{-23}cm^3$$

(Note that the edge length was converted from pm to cm to get the usual volume units for density.) Therefore, the density is

$$\text{Po } = \frac{3.471 \times 10^{-22}g}{3.79 \times 10^{-23}cm^3} = 9.16g/cm^3$$

? Exercise 8.7.1

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 was simple cubic, its density would be given by:

$$1Ni \text{ atom } \times \frac{1molNi}{6.022 \times 10^{23}Ni \text{ atoms}} \times \frac{58.693g}{1molNi} = 9.746 \times 10^{-23}g$$

$$V = l^3 = \left(3.524 \times 10^{-8}cm\right)^3 = 4.376 \times 10^{-23}cm^3$$

Then the density of Ni would be

$$= \frac{9.746 \times 10^{-23}g}{4.376 \times 10^{-23}cm^3} = 2.23 g/cm^3$$

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 8.7.5. (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.)

Lattice point locations

Cubic unit cells

Simple cubic   Body-centered cubic   Face-centered cubic
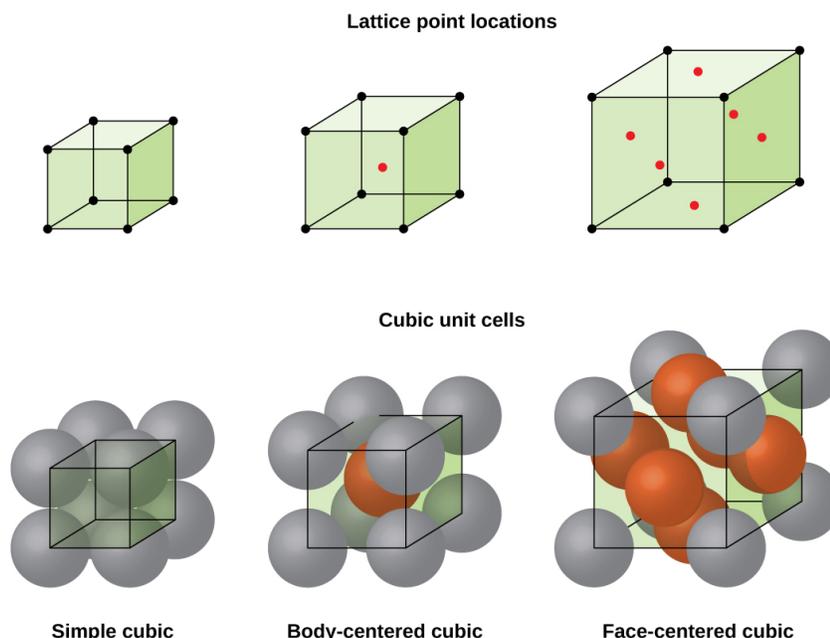
Figure 8.7.5: Cubic unit cells of metals show (in the upper figures) the locations of lattice points and (in the lower figures) metal atoms located in the unit cell.

Some metals crystallize in an arrangement that has a cubic unit cell with atoms at all of the corners and an atom in the center, as shown in Figure 8.7.6. 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 atom from the 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.
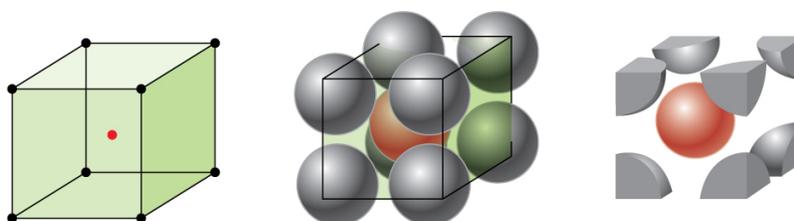
Body-centered cubic structure

Figure 8.7.6: In a body-centered cubic structure, atoms in a specific layer do not touch each other. Each atom touches four atoms in the layer above it and four atoms in the layer below it.

Atoms in BCC arrangements are much more efficiently packed than in a simple cubic structure, occupying about 68% of the total volume. Isomorphous metals with a BCC structure include K, Ba, Cr, Mo, W, and Fe at room temperature. (Elements or compounds that crystallize with the same structure are said to be **isomorphous**.)

Many other metals, such as aluminum, copper, and lead, crystallize in an arrangement that has a cubic unit cell with atoms at all of the corners and at the centers of each face, as illustrated in Figure 8.7.7. 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 atom from the corners ($8 \times \frac{1}{8} = 1$ atom from the corners) and one-half of an atom on each of the six faces atoms from the faces ($6 \times \frac{1}{2} = 3$ atom 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.
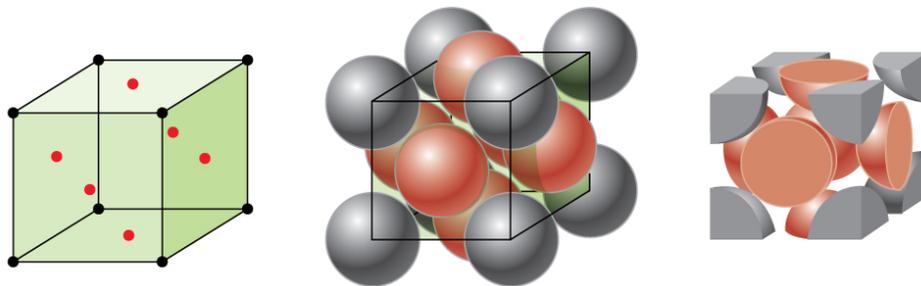
Face-centered cubic structure

Figure 8.7.7: A face-centered cubic solid has atoms at the corners and, as the name implies, at the centers of the faces of its unit cells.

Atoms in an FCC arrangement are packed as closely together as possible, with atoms occupying 74% of the volume. This structure is also called **cubic closest packing** (CCP). In CCP, there are three repeating layers of hexagonally arranged atoms. Each atom contacts six atoms in its own layer, three in the layer above, and three in the layer below. In this arrangement, each atom touches 12 near neighbors, and therefore has a coordination number of 12. The fact that FCC and CCP arrangements are equivalent may not be immediately obvious, but why they are actually the same structure is illustrated in Figure 8.7.8.

| Side view | Top view | Rotated view |
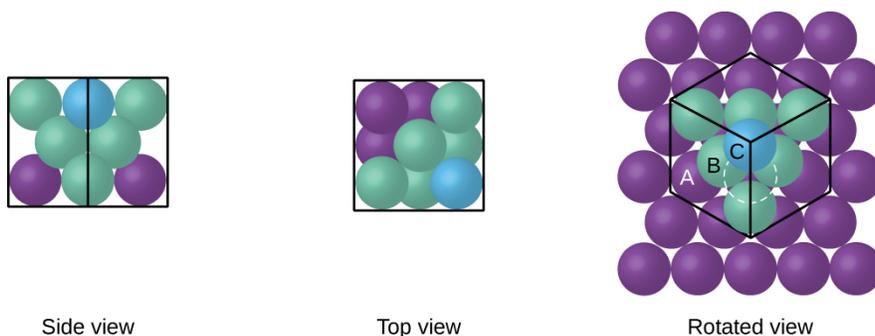
Cubic closest packed structure

Figure 8.7.8: 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.

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 8.7.9. 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.
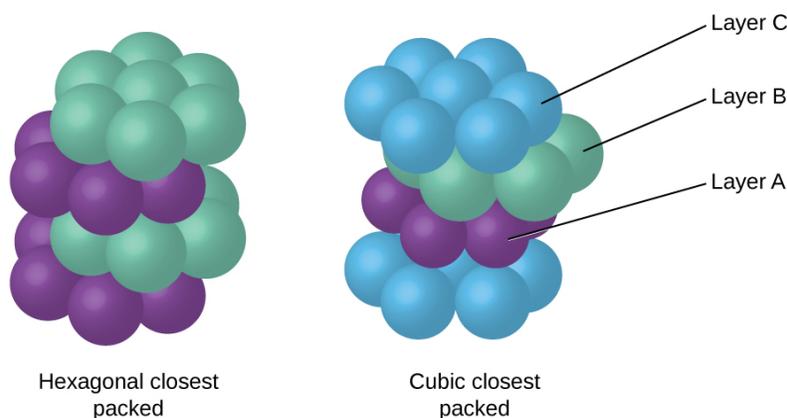
Figure 8.7.9: In both types of closest packing, atoms are packed as compactly as possible. Hexagonal closest packing consists of two alternating layers (ABABAB…). Cubic closest packing consists of three alternating layers (ABCABCABC…).

✔ Example 8.7.2: Calculation of 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
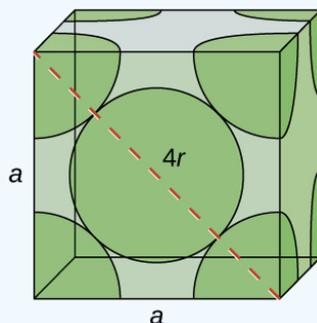
(a) In an FCC structure, Ca atoms contact each other across the diagonal of the face, so the length of the diagonal is equal to four Ca atomic radii (d = 4r). Two adjacent edges and the diagonal of the face form a right triangle, with the length of each side equal to 558.8 pm and the length of the hypotenuse equal to four Ca atomic radii:

$$a^2 + a^2 = d^2 \longrightarrow (558.8pm)^2 + (558.5pm)^2 = (4r)^2$$

Solving this gives

$$r = \sqrt{\frac{(558.8pm)^2 + (558.5pm)^2}{16}} = 197.6pm \text{ for a Ca radius.}$$

(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 from the corners) and one-half of an atom on each of the six faces ($6 \times \frac{1}{2} = 3$ atom), for a total of four atoms in the unit cell.

The mass of the unit cell can be found by:

$$1Ca \text{ unit cell} \times \frac{4Ca \text{ atoms}}{1Ca \text{ unit cell}} \times \frac{1 molCa}{6.022 \times 10^{23} Ca \text{ atoms}} \times \frac{40.078 g}{1 molCa} = 2.662 \times 10^{-22} g$$

The volume of a Ca unit cell can be found by:

$$V = a^3 = \left(558.8 \times 10^{-10} cm\right)^3 = 1.745 \times 10^{-22} cm^3$$

(Note that the edge length was converted from pm to cm to get the usual volume units for density.)

Then, the density of Ca is

$$\frac{2.662 \times 10^{-22} g}{1.745 \times 10^{-22} cm^3} = 1.53 g/cm^3$$

? Exercise 8.7.2

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
    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 8.7.10. The axes are defined as being the lengths between points in the space lattice. Consequently, unit cell axes join points with identical environments.
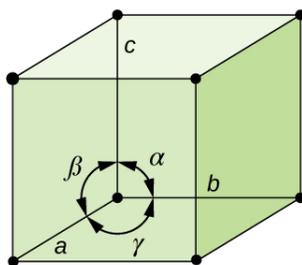
Figure 8.7.10: A unit cell is defined by the lengths of its three axes (a, b, and c) and the angles (α, β, and γ) between the axes.

There are seven different lattice systems, some of which have more than one type of lattice, for a total of fourteen different unit cells, which have the shapes shown in Figure 8.7.11.

System/Axes/Angles	Unit Cells			
Cubic $a = b = c$ $\alpha = \beta = \gamma = 90°$	Simple	Face-centered	Body-centered	
Tetragonal $a = b \neq c$ $\alpha = \beta = \gamma = 90°$	Simple	Body-centered		
Orthorhombic $a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$	Simple	Body-centered	Base-centered	Face-centered
Monoclinic $a \neq b \neq c$ $\alpha = \gamma = 90°; \beta \neq 90°$	Simple	Base-centered		
Triclinic $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90°$				
Hexagonal $a = b \neq c$ $\alpha = \beta = 90°; \gamma = 120°$				
Rhombohedral $a = b = c$ $\alpha = \beta = \gamma \neq 90°$				
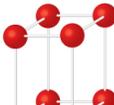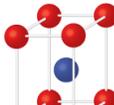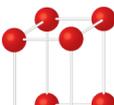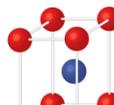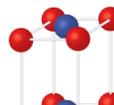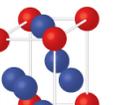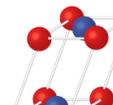
Figure 8.7.11: There are seven different lattice systems and 14 different unit cells.

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 8.7.12 illustrates both of these types of holes.
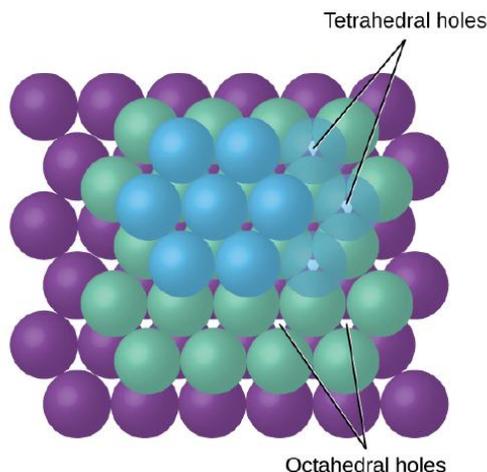
Figure 8.7.12: Cations may occupy two types of holes between anions: octahedral holes or tetrahedral holes.

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 8.7.13. 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.

Tetrahedral hole	Octahedral hole	Cubic hole
Cation radius is about 22.5 to 41.4% of the anion radius	Cation radius is about 41.4 to 73.2% of the anion radius	Cation radius is about 73.2 to 100% of the anion radius
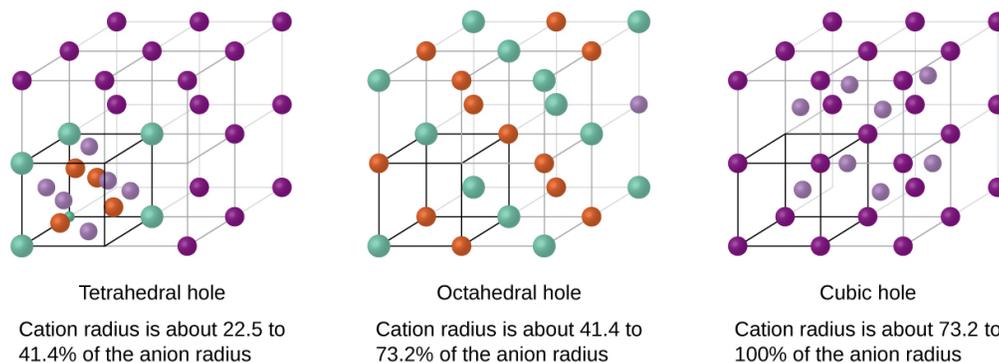
Figure 8.7.13: A cation's size and the shape of the hole occupied by the compound are directly related.

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 8.7.3: 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 8.7.3
>
> Lithium selenide can be described as a closest-packed array of selenide ions with lithium ions in all of the tetrahedral holes. What it the formula of lithium selenide?
>
> **Answer**
>
> Li_2Se

The ratio of octahedral holes to anions in either an HCP or CCP structure is 1:1. Thus, compounds with cations in octahedral holes in a closest-packed array of anions can have a maximum cation:anion ratio of 1:1. In NiO, MnS, NaCl, and KH, for example, all of the octahedral holes are filled. Ratios of less than 1:1 are observed when some of the octahedral holes remain empty.

> **✔** Example 8.7.4: Stoichiometry of Ionic Compounds
>
> Sapphire is aluminum oxide. 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 $Al_{\frac{2}{3}}O$. The simplest whole number ratio is 2:3, so the formula is Al_2O_3.

> **?** Exercise 8.7.4
>
> 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**
>
> TiO_2

In a simple cubic array of anions, there is one cubic hole that can be occupied by a cation for each anion in the array. In CsCl, and in other compounds with the same structure, all of the cubic holes are occupied. Half of the cubic holes are occupied in SrH_2, UO_2, $SrCl_2$, and CaF_2.

Different types of ionic compounds often crystallize in the same structure when the relative sizes of their ions and their stoichiometries (the two principal features that determine structure) are similar.

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, (illustrated in Figure 8.7.14) is an example of this, with Cs^+ and Cl^- having radii of 174 pm and 181 pm, respectively. We can think of this as chloride ions forming a simple cubic unit cell, with a cesium ion in the center; or as cesium ions forming a unit cell with a chloride ion in the center; or as simple cubic unit cells formed by Cs^+ ions overlapping unit cells formed by Cl^- ions. Cesium ions and chloride ions touch along the body diagonals of the unit cells. One cesium ion and one chloride ion are present per unit cell, giving the l:l stoichiometry required by the formula for cesium chloride. Note that there is no lattice point in the center of the cell, and CsCl is not a BCC structure because a cesium ion is not identical to a chloride ion.
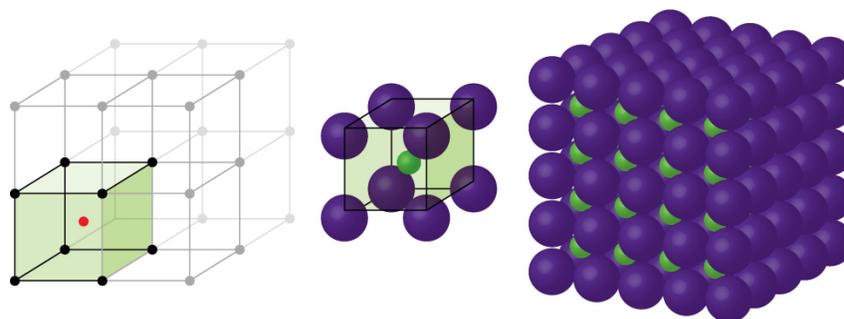
Simple cubic structure

Figure 8.7.14: 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.

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 8.7.15. 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.
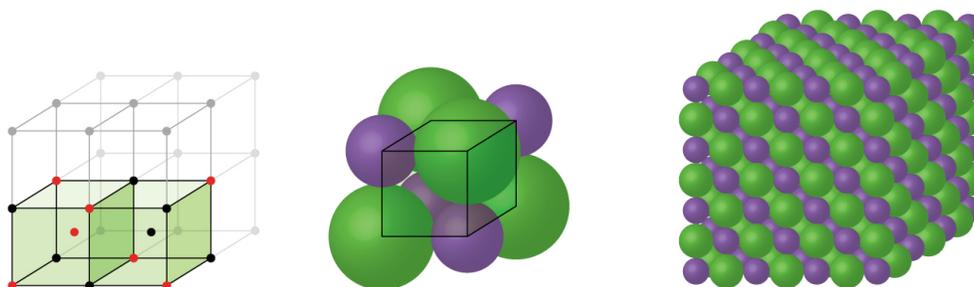
Face-centered simple cubic structure

Figure 8.7.15: 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.

The cubic form of zinc sulfide, zinc blende, also crystallizes in an FCC unit cell, as illustrated in Figure 8.7.16. 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.
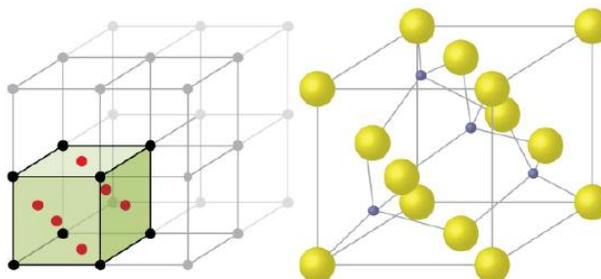
ZnS face-centered unit cell

Figure 8.7.16: 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.

A calcium fluoride unit cell, like that shown in Figure 8.7.17, 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 8.7.17 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.
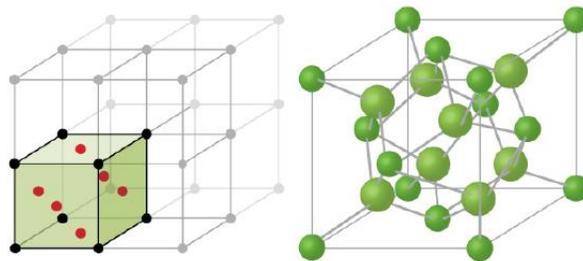
CaF$_2$ face-centered unit cell

Figure 8.7.17: 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.

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 8.7.5: 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, as in Figure 8.7.15, 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 \nonumber \]
>
> which yields:
>
> $$(0.514 nm)^2 + (0.514 nm)^2 = (4r)^2 = 16r^2$$
>
> Solving this gives:
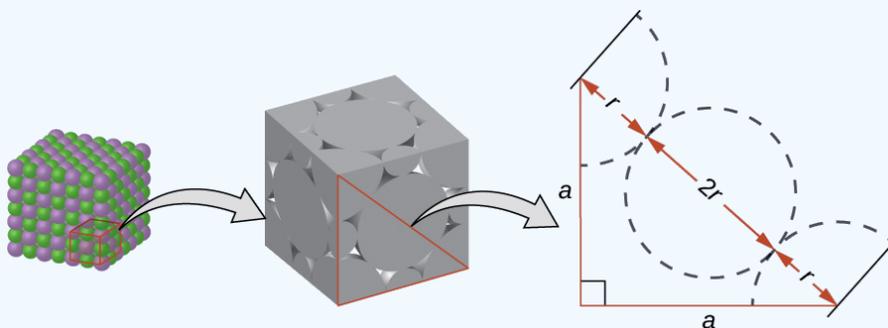
$$r = \sqrt{\frac{(0.514nm)^2 + (0.514nm)^2}{16}} = 0.182nm(1.82\text{Å}) \text{ for a } Cl^- \text{ radius.}$$

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 (see Figure 8.7.18).
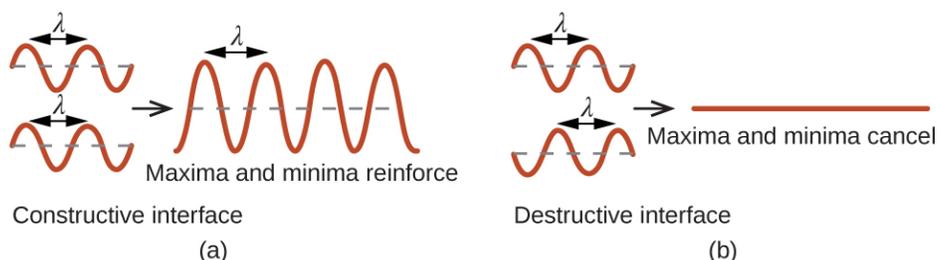
Figure 8.7.18: Light waves occupying the same space experience interference, combining to yield waves of greater (a) or lesser (b) intensity, depending upon the separation of their maxima and minima.

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:

$$n\lambda = 2d\sin\theta \qquad (8.7.1)$$

This relation is known as the **Bragg equation** in honor of W. H. Bragg, the English physicist who first explained this phenomenon. Figure 8.7.19 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.

Constructive interference

Destructive interference
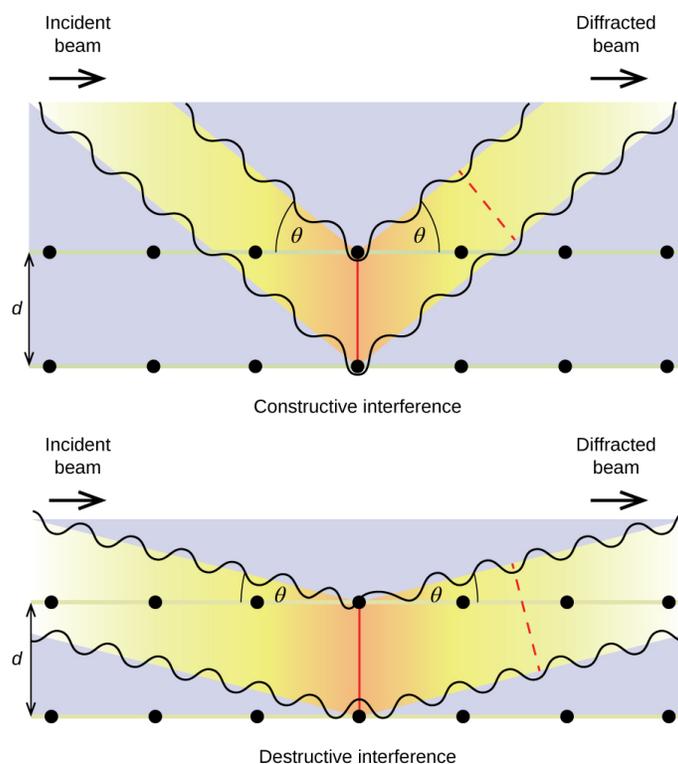
Figure 8.7.19: The diffraction of X-rays scattered by the atoms within a crystal permits the determination of the distance between the atoms. The top image depicts constructive interference between two scattered waves and a resultant diffracted wave of high intensity. The bottom image depicts destructive interference and a low intensity diffracted wave.

📌 Link to Learning

Visit this site for more details on the Bragg equation and a simulator that allows you to explore the effect of each variable on the intensity of the diffracted wave.

An X-ray diffractometer, such as the one illustrated in Figure 8.7.20, 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.

(a)   (b)
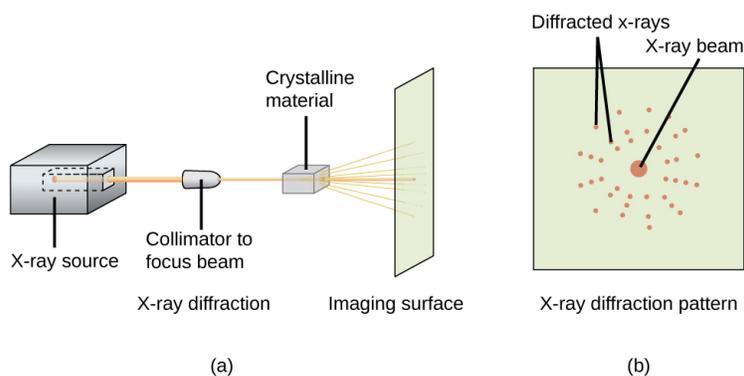
Figure 8.7.20: (a) In a diffractometer, a beam of X-rays strikes a crystalline material, producing (b) an X-ray diffraction pattern that can be analyzed to determine the crystal structure.

✔ Example 8.7.6: 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 $\theta = 25.25°$. Determine the spacing between the diffracting planes in copper.

Solution

The distance between the planes is found by solving the Bragg equation (Equation $8.7.1$), $n\lambda = 2d\sin\theta$, for d.

This gives:

$$d = \frac{n\lambda}{2\sin\theta} = \frac{1(0.1315nm)}{2\sin(25.25°)} = 0.154nm$$

? Exercise 8.7.6

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

10.8°

📌 Portrait of a Chemist: 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 (Figure $8.7.21$) 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 8.7.21: This illustration shows an X-ray diffraction image similar to the one Franklin found in her research. (credit: National Institutes of Health)

8.8: Key Terms

adhesive force | force of attraction between molecules of different chemical identities

amorphous solid | (also, noncrystalline solid) solid in which the particles lack an ordered internal structure

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

boiling point | temperature at which the vapor pressure of a liquid equals the pressure of the gas above it

Bragg equation | equation that relates the angles at which X-rays are diffracted by the atoms within a crystal

capillary action | flow of liquid within a porous material due to the attraction of the liquid molecules to the surface of the material and to other liquid molecules

Clausius-Clapeyron equation | mathematical relationship between the temperature, vapor pressure, and enthalpy of vaporization for a substance

cohesive force | force of attraction between identical molecules

condensation | change from a gaseous to a liquid state

coordination number | number of atoms closest to any given atom in a crystal or to the central metal atom in a complex

covalent network solid | solid whose particles are held together by covalent bonds

critical point | temperature and pressure above which a gas cannot be condensed into a liquid

crystalline solid | solid in which the particles are arranged in a definite repeating pattern

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)

deposition | change from a gaseous state directly to a solid state

diffraction | redirection of electromagnetic radiation that occurs when it encounters a physical barrier of appropriate dimensions

dipole-dipole attraction | intermolecular attraction between two permanent dipoles

dispersion force | (also, London dispersion force) attraction between two rapidly fluctuating, temporary dipoles; significant only when particles are very close together

dynamic equilibrium | state of a system in which reciprocal processes are occurring at equal rates

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

freezing | change from a liquid state to a solid state

freezing point | temperature at which the solid and liquid phases of a substance are in equilibrium; see also *melting point*

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

hydrogen bonding | occurs when exceptionally strong dipoles attract; bonding that exists when hydrogen is bonded to one of the three most electronegative elements: F, O, or N

induced dipole | temporary dipole formed when the electrons of an atom or molecule are distorted by the instantaneous dipole of a neighboring atom or molecule

instantaneous dipole | temporary dipole that occurs for a brief moment in time when the electrons of an atom or molecule are distributed asymmetrically

intermolecular force | noncovalent attractive force between atoms, molecules, and/or ions

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

isomorphous | possessing the same crystalline structure

melting | change from a solid state to a liquid state

melting point | temperature at which the solid and liquid phases of a substance are in equilibrium; see also *freezing point*

metallic solid | solid composed of metal atoms

molecular solid | solid composed of neutral molecules held together by intermolecular forces of attraction

normal boiling point | temperature at which a liquid's vapor pressure equals 1 atm (760 torr)

octahedral hole | open space in a crystal at the center of six particles located at the corners of an octahedron

phase diagram | pressure-temperature graph summarizing conditions under which the phases of a substance can exist

polarizability | measure of the ability of a charge to distort a molecule's charge distribution (electron cloud)

simple cubic structure | crystalline structure with a cubic unit cell with lattice points only at the corners

simple cubic unit cell | (also, primitive cubic unit cell) unit cell in the simple cubic structure

space lattice | all points within a crystal that have identical environments

sublimation | change from solid state directly to gaseous state

supercritical fluid | substance at a temperature and pressure higher than its critical point; exhibits properties intermediate between those of gaseous and liquid states

surface tension | energy required to increase the area, or length, of a liquid surface by a given amount

tetrahedral hole | tetrahedral space formed by four atoms or ions in a crystal

triple point | temperature and pressure at which three phases of a substance are in equilibrium

unit cell | smallest portion of a space lattice that is repeated in three dimensions to form the entire lattice

vacancy | defect that occurs when a position that should contain an atom or ion is vacant

van der Waals force | attractive or repulsive force between molecules, including dipole-dipole, dipole-induced dipole, and London dispersion forces; does not include forces due to covalent or ionic bonding, or the attraction between ions and molecules

vapor pressure | (also, equilibrium vapor pressure) pressure exerted by a vapor in equilibrium with a solid or a liquid at a given temperature

vaporization | change from liquid state to gaseous state

viscosity | measure of a liquid's resistance to flow

X-ray crystallography | experimental technique for determining distances between atoms in a crystal by measuring the angles at which X-rays are diffracted when passing through the crystal

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8.9: Key Equations

8.10: Summary

The physical properties of condensed matter (liquids and solids) can be explained in terms of the kinetic molecular theory. In a liquid, intermolecular attractive forces hold the molecules in contact, although they still have sufficient KE to move past each other.

Intermolecular attractive forces, collectively referred to as van der Waals forces, are responsible for the behavior of liquids and solids and are electrostatic in nature. Dipole-dipole attractions result from the electrostatic attraction of the partial negative end of one polar molecule for the partial positive end of another. The temporary dipole that results from the motion of the electrons in an atom can induce a dipole in an adjacent atom and give rise to the London dispersion force. London forces increase with increasing molecular size. Hydrogen bonds are a special type of dipole-dipole attraction that results when hydrogen is bonded to one of the three most electronegative elements: F, O, or N.

The intermolecular forces between molecules in the liquid state vary depending upon their chemical identities and result in corresponding variations in various physical properties. Cohesive forces between like molecules are responsible for a liquid's viscosity (resistance to flow) and surface tension (elasticity of a liquid surface). Adhesive forces between the molecules of a liquid and different molecules composing a surface in contact with the liquid are responsible for phenomena such as surface wetting and capillary rise.

Phase transitions are processes that convert matter from one physical state into another. There are six phase transitions between the three phases of matter. Melting, vaporization, and sublimation are all endothermic processes, requiring an input of heat to overcome intermolecular attractions. The reciprocal transitions of freezing, condensation, and deposition are all exothermic processes, involving heat as intermolecular attractive forces are established or strengthened. The temperatures at which phase transitions occur are determined by the relative strengths of intermolecular attractions and are, therefore, dependent on the chemical identity of the substance.

The temperature and pressure conditions at which a substance exists in solid, liquid, and gaseous states are summarized in a phase diagram for that substance. Phase diagrams are combined plots of pressure-temperature equilibrium curves representing the relationships between phase transition temperatures and pressures. The point of intersection of any three curves in a phase diagram represents a substance's triple point—the temperature and pressure at which three different phases are in equilibrium. At pressures below a solid-liquid-gas triple point, a substance cannot exist in the liquid state, regardless of its temperature. The terminus of the liquid-gas curve represents the substance's critical point, the pressure and temperature above which a liquid phase cannot exist.

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.

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.

8.11: Exercises

1.

In terms of their bulk properties, how do liquids and solids differ? How are they similar?

2.

In terms of the kinetic molecular theory, in what ways are liquids similar to solids? In what ways are liquids different from solids?

3.

In terms of the kinetic molecular theory, in what ways are liquids similar to gases? In what ways are liquids different from gases?

4.

Explain why liquids assume the shape of any container into which they are poured, whereas solids are rigid and retain their shape.

5.

What is the evidence that all neutral atoms and molecules exert attractive forces on each other?

6.

Open the PhET States of Matter Simulation to answer the following questions:

   a. Select the Solid, Liquid, Gas tab. Explore by selecting different substances, heating and cooling the systems, and changing the state. What similarities do you notice between the four substances for each phase (solid, liquid, gas)? What differences do you notice?
   b. For each substance, select each of the states and record the given temperatures. How do the given temperatures for each state correlate with the strengths of their intermolecular attractions? Explain.
   c. Select the Interaction Potential tab, and use the default neon atoms. Move the Ne atom on the right and observe how the potential energy changes. Select the Total Force button, and move the Ne atom as before. When is the total force on each atom attractive and large enough to matter? Then select the Component Forces button, and move the Ne atom. When do the attractive (van der Waals) and repulsive (electron overlap) forces balance? How does this relate to the potential energy versus the distance between atoms graph? Explain.

7.

Define the following and give an example of each:

   a. dispersion force
   b. dipole-dipole attraction
   c. hydrogen bond

8.

The types of intermolecular forces in a substance are identical whether it is a solid, a liquid, or a gas. Why then does a substance change phase from a gas to a liquid or to a solid?

9.

Why do the boiling points of the noble gases increase in the order He < Ne < Ar < Kr < Xe?

10.

Neon and HF have approximately the same molecular masses.

   a. Explain why the boiling points of Neon and HF differ.
   b. Compare the change in the boiling points of Ne, Ar, Kr, and Xe with the change of the boiling points of HF, HCl, HBr, and HI, and explain the difference between the changes with increasing atomic or molecular mass.

11.

Arrange each of the following sets of compounds in order of increasing boiling point temperature:

   a. HCl, H_2O, SiH_4
   b. F_2, Cl_2, Br_2
   c. CH_4, C_2H_6, C_3H_8

 d. O_2, NO, N_2

12.

The molecular mass of butanol, C_4H_9OH, is 74.14; that of ethylene glycol, $CH_2(OH)CH_2OH$, is 62.08, yet their boiling points are 117.2 °C and 174 °C, respectively. Explain the reason for the difference.

13.

On the basis of intermolecular attractions, explain the differences in the boiling points of *n*–butane (−1 °C) and chloroethane (12 °C), which have similar molar masses.

14.

On the basis of dipole moments and/or hydrogen bonding, explain in a qualitative way the differences in the boiling points of acetone (56.2 °C) and 1-propanol (97.4 °C), which have similar molar masses.

15.

The melting point of $H_2O(s)$ is 0 °C. Would you expect the melting point of $H_2S(s)$ to be −85 °C, 0 °C, or 185 °C? Explain your answer.

16.

Silane (SiH_4), phosphine (PH_3), and hydrogen sulfide (H_2S) melt at −185 °C, −133 °C, and −85 °C, respectively. What does this suggest about the polar character and intermolecular attractions of the three compounds?

17.

Explain why a hydrogen bond between two water molecules is weaker than a hydrogen bond between two hydrogen fluoride molecules.

18.

Under certain conditions, molecules of acetic acid, CH_3COOH, form "dimers," pairs of acetic acid molecules held together by strong intermolecular attractions:
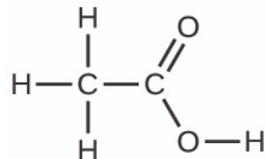
Draw a dimer of acetic acid, showing how two CH_3COOH molecules are held together, and stating the type of IMF that is responsible.

19.

Proteins are chains of amino acids that can form in a variety of arrangements, one of which is a helix. What kind of IMF is responsible for holding the protein strand in this shape? On the protein image, show the locations of the IMFs that hold the protein together:
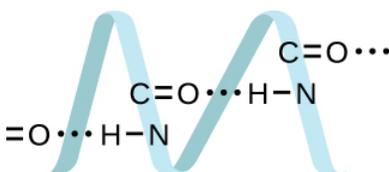
20.

The density of liquid NH_3 is 0.64 g/mL; the density of gaseous NH_3 at STP is 0.0007 g/mL. Explain the difference between the densities of these two phases.

21.

Identify the intermolecular forces present in the following solids:

 a. CH_3CH_2OH
 b. $CH_3CH_2CH_3$

  c. CH_3CH_2Cl

22.

The test tubes shown here contain equal amounts of the specified motor oils. Identical metal spheres were dropped at the same time into each of the tubes, and a brief moment later, the spheres had fallen to the heights indicated in the illustration.

Rank the motor oils in order of increasing viscosity, and explain your reasoning:
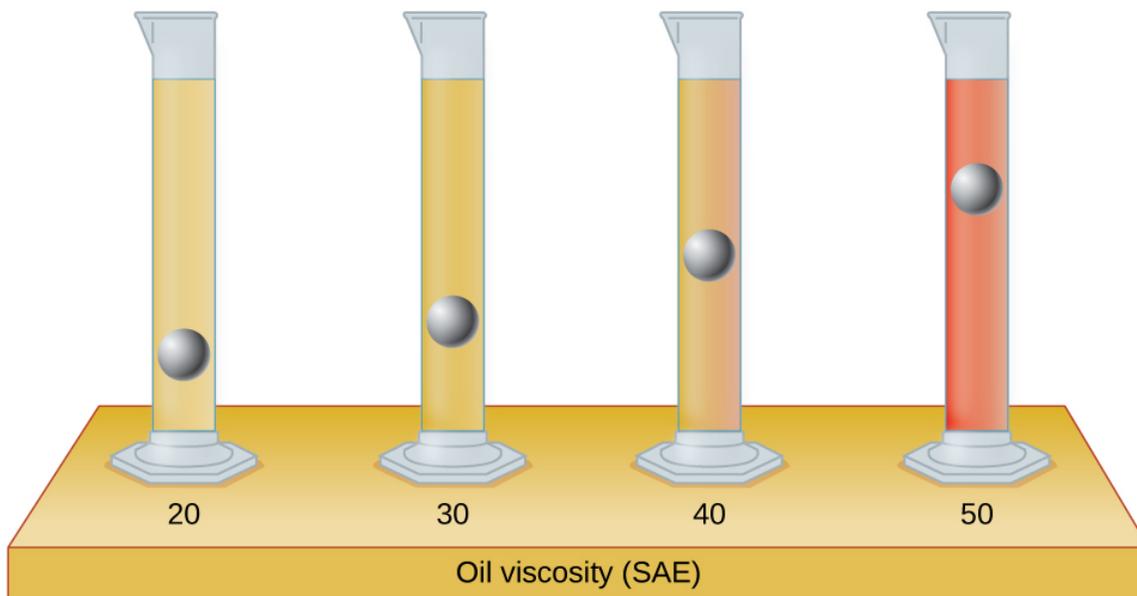
23.

Although steel is denser than water, a steel needle or paper clip placed carefully lengthwise on the surface of still water can be made to float. Explain at a molecular level how this is possible.

Figure 10.67 (credit: Cory Zanker)

24.

The surface tension and viscosity values for diethyl ether, acetone, ethanol, and ethylene glycol are shown here.

Compound	Molecule	Surface Tension (mN/m)	Viscosity (mPa s)
diethyl ether $C_2H_5OC_2H_5$		17	0.22
acetone CH_3COCH_3		23	0.31
ethanol C_2H_5OH		22	1.07
ethylene glycol $CH_2(OH)CH_2(OH)$		48	16.1
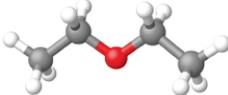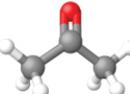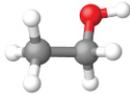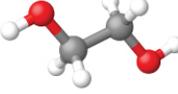
  a. Explain their differences in viscosity in terms of the size and shape of their molecules and their IMFs.
  b. Explain their differences in surface tension in terms of the size and shape of their molecules and their IMFs:

25.

You may have heard someone use the figure of speech "slower than molasses in winter" to describe a process that occurs slowly. Explain why this is an apt idiom, using concepts of molecular size and shape, molecular interactions, and the effect of changing temperature.

26.

It is often recommended that you let your car engine run idle to warm up before driving, especially on cold winter days. While the benefit of prolonged idling is dubious, it is certainly true that a warm engine is more fuel efficient than a cold one. Explain the reason for this.

27.

The surface tension and viscosity of water at several different temperatures are given in this table.

Water	Surface Tension (mN/m)	Viscosity (mPa s)
0 °C	75.6	1.79
20 °C	72.8	1.00
60 °C	66.2	0.47
100 °C	58.9	0.28

  a. As temperature increases, what happens to the surface tension of water? Explain why this occurs, in terms of molecular interactions and the effect of changing temperature.
  b. As temperature increases, what happens to the viscosity of water? Explain why this occurs, in terms of molecular interactions and the effect of changing temperature.

28.

At 25 °C, how high will water rise in a glass capillary tube with an inner diameter of 0.63 mm? Refer to Example 10.4 for the required information.

29.

Water rises in a glass capillary tube to a height of 17 cm. What is the diameter of the capillary tube?

30.

Heat is added to boiling water. Explain why the temperature of the boiling water does not change. What does change?

31.

Heat is added to ice at 0 °C. Explain why the temperature of the ice does not change. What does change?

32.

What feature characterizes the dynamic equilibrium between a liquid and its vapor in a closed container?

33.

Identify two common observations indicating some liquids have sufficient vapor pressures to noticeably evaporate?

34.

Identify two common observations indicating some solids, such as dry ice and mothballs, have vapor pressures sufficient to sublime?

35.

What is the relationship between the intermolecular forces in a liquid and its vapor pressure?

36.

What is the relationship between the intermolecular forces in a solid and its melting temperature?

37.

Why does spilled gasoline evaporate more rapidly on a hot day than on a cold day?

38.

Carbon tetrachloride, CCl_4, was once used as a dry cleaning solvent, but is no longer used because it is carcinogenic. At 57.8 °C, the vapor pressure of CCl_4 is 54.0 kPa, and its enthalpy of vaporization is 33.05 kJ/mol. Use this information to estimate the normal boiling point for CCl_4.

39.

When is the boiling point of a liquid equal to its normal boiling point?

40.

How does the boiling of a liquid differ from its evaporation?

41.

Use the information in Figure 10.24 to estimate the boiling point of water in Denver when the atmospheric pressure is 83.3 kPa.

42.

A syringe at a temperature of 20 °C is filled with liquid ether in such a way that there is no space for any vapor. If the temperature is kept constant and the plunger is withdrawn to create a volume that can be occupied by vapor, what would be the approximate pressure of the vapor produced?

43.

Explain the following observations:

  a. It takes longer to cook an egg in Ft. Davis, Texas (altitude, 5000 feet above sea level) than it does in Boston (at sea level).
  b. Perspiring is a mechanism for cooling the body.

44.

The enthalpy of vaporization of water is larger than its enthalpy of fusion. Explain why.

45.

Explain why the molar enthalpies of vaporization of the following substances increase in the order $CH_4 < C_2H_6 < C_3H_8$, even though the type of IMF (dispersion) is the same.

46.

Explain why the enthalpies of vaporization of the following substances increase in the order $CH_4 < NH_3 < H_2O$, even though all three substances have approximately the same molar mass.

47.

The enthalpy of vaporization of $CO_2(l)$ is 9.8 kJ/mol. Would you expect the enthalpy of vaporization of $CS_2(l)$ to be 28 kJ/mol, 9.8 kJ/mol, or −8.4 kJ/mol? Discuss the plausibility of each of these answers.

48.

The hydrogen fluoride molecule, HF, is more polar than a water molecule, H_2O (for example, has a greater dipole moment), yet the molar enthalpy of vaporization for liquid hydrogen fluoride is lesser than that for water. Explain.

49.

Ethyl chloride (boiling point, 13 °C) is used as a local anesthetic. When the liquid is sprayed on the skin, it cools the skin enough to freeze and numb it. Explain the cooling effect of liquid ethyl chloride.

50.

Which contains the compounds listed correctly in order of increasing boiling points?

 a. $N_2 < CS_2 < H_2O < KCl$
 b. $H_2O < N_2 < CS_2 < KCl$
 c. $N_2 < KCl < CS_2 < H_2O$
 d. $CS_2 < N_2 < KCl < H_2O$
 e. $KCl < H_2O < CS_2 < N_2$

51.

How much heat is required to convert 422 g of liquid H_2O at 23.5 °C into steam at 150 °C?

52.

Evaporation of sweat requires energy and thus take excess heat away from the body. Some of the water that you drink may eventually be converted into sweat and evaporate. If you drink a 20-ounce bottle of water that had been in the refrigerator at 3.8 °C, how much heat is needed to convert all of that water into sweat and then to vapor? (Note: Your body temperature is 36.6 °C. For the purpose of solving this problem, assume that the thermal properties of sweat are the same as for water.)

53.

Titanium tetrachloride, $TiCl_4$, has a melting point of −23.2 °C and has a ΔH_{fusion} = 9.37 kJ/mol.

 a. How much energy is required to melt 263.1 g $TiCl_4$?
 b. For $TiCl_4$, which will likely have the larger magnitude: ΔH_{fusion} or $\Delta H_{vaporization}$? Explain your reasoning.

54.

From the phase diagram for water (Figure 10.31), determine the state of water at:

 a. (f) 60 °C and 50 kPa

55.

What phase changes will take place when water is subjected to varying pressure at a constant temperature of 0.005 °C? At 40 °C? At −40 °C?

56.

Pressure cookers allow food to cook faster because the higher pressure inside the pressure cooker increases the boiling temperature of water. A particular pressure cooker has a safety valve that is set to vent steam if the pressure exceeds 3.4 atm. What is the approximate maximum temperature that can be reached inside this pressure cooker? Explain your reasoning.

57.

From the phase diagram for carbon dioxide in Figure 10.34, determine the state of CO_2 at:

 a. (f) −80 °C and 10 kPa

58.

Determine the phase changes that carbon dioxide undergoes as pressure is increased at a constant temperature of (a) −50 °C and (b) 50 °C. If the temperature is held at −40 °C? At 20 °C? (See the phase diagram in Figure 10.34.)

59.

Consider a cylinder containing a mixture of liquid carbon dioxide in equilibrium with gaseous carbon dioxide at an initial pressure of 65 atm and a temperature of 20 °C. Sketch a plot depicting the change in the cylinder pressure with time as gaseous carbon dioxide is released at constant temperature.

60.

Dry ice, $CO_2(s)$, does not melt at atmospheric pressure. It sublimes at a temperature of −78 °C. What is the lowest pressure at which $CO_2(s)$ will melt to give $CO_2(l)$? At approximately what temperature will this occur? (See Figure 10.34 for the phase diagram.)

61.

If a severe storm results in the loss of electricity, it may be necessary to use a clothesline to dry laundry. In many parts of the country in the dead of winter, the clothes will quickly freeze when they are hung on the line. If it does not snow, will they dry anyway? Explain your answer.

62.

Is it possible to liquefy nitrogen at room temperature (about 25 °C)? Is it possible to liquefy sulfur dioxide at room temperature? Explain your answers.

63.

Elemental carbon has one gas phase, one liquid phase, and two different solid phases, as shown in the phase diagram:
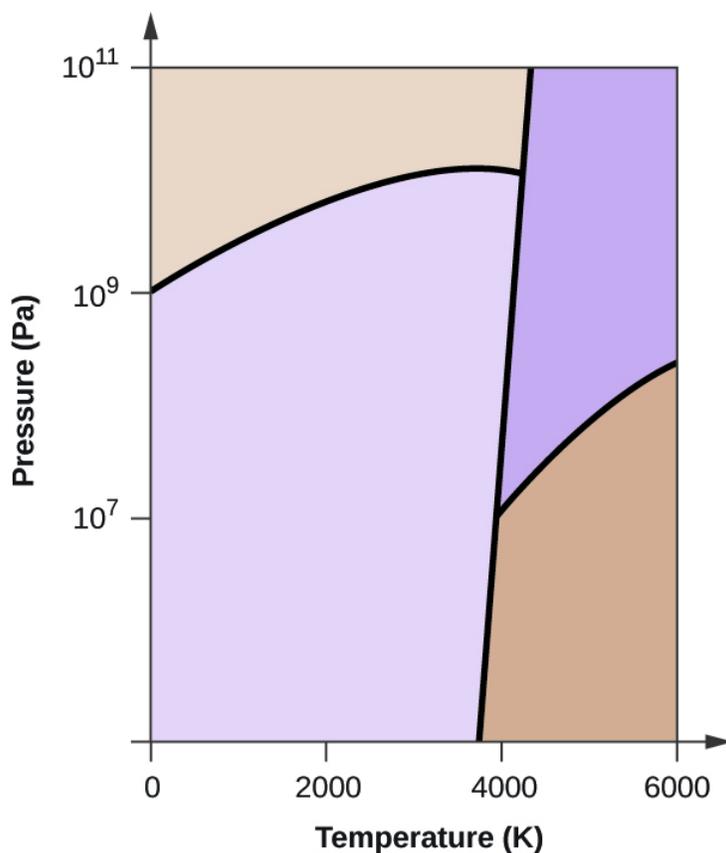
a. (f) If the temperature of a sample of carbon increases from 3000 K to 5000 K at a constant pressure of 10^6 Pa, which phase transition occurs, if any?

64.

What types of liquids typically form amorphous solids?

65.

At very low temperatures oxygen, O_2, freezes and forms a crystalline solid. Which best describes these crystals?

a. ionic
b. covalent network
c. metallic
d. amorphous
e. molecular crystals

66.

As it cools, olive oil slowly solidifies and forms a solid over a range of temperatures. Which best describes the solid?

a. ionic
b. covalent network
c. metallic
d. amorphous
e. molecular crystals

67.

Explain why ice, which is a crystalline solid, has a melting temperature of 0 °C, whereas butter, which is an amorphous solid, softens over a range of temperatures.

68.

Identify the type of crystalline solid (metallic, network covalent, ionic, or molecular) formed by each of the following substances:

a. (i) C_2H_5OH

69.

Identify the type of crystalline solid (metallic, network covalent, ionic, or molecular) formed by each of the following substances:

a. (i) K_3PO_4

70.

Classify each substance in the table as either a metallic, ionic, molecular, or covalent network solid:

Substance	Appearance	Melting Point	Electrical Conductivity	Solubility in Water
X	lustrous, malleable	1500 °C	high	insoluble
Y	soft, yellow	113 °C	none	insoluble
Z	hard, white	800 °C	only if melted/dissolved	soluble

71.

Classify each substance in the table as either a metallic, ionic, molecular, or covalent network solid:

Substance	Appearance	Melting Point	Electrical Conductivity	Solubility in Water
X	brittle, white	800 °C	only if melted/dissolved	soluble
Y	shiny, malleable	1100 °C	high	insoluble
Z	hard, colorless	3550 °C	none	insoluble

72.

Identify the following substances as ionic, metallic, covalent network, or molecular solids:

Substance A is malleable, ductile, conducts electricity well, and has a melting point of 1135 °C. Substance B is brittle, does not conduct electricity as a solid but does when molten, and has a melting point of 2072 °C. Substance C is very hard, does not conduct electricity, and has a melting point of 3440 °C. Substance D is soft, does not conduct electricity, and has a melting point of 185 °C.

73.

Substance A is shiny, conducts electricity well, and melts at 975 °C. Substance A is likely a(n):

a. ionic solid
b. metallic solid
c. molecular solid
d. covalent network solid

74.

Substance B is hard, does not conduct electricity, and melts at 1200 °C. Substance B is likely a(n):

a. ionic solid
b. metallic solid
c. molecular solid
d. covalent network solid

75.

Describe the crystal structure of iron, which crystallizes with two equivalent metal atoms in a cubic unit cell.

76.

Describe the crystal structure of Pt, which crystallizes with four equivalent metal atoms in a cubic unit cell.

77.

What is the coordination number of a chromium atom in the body-centered cubic structure of chromium?

78.

What is the coordination number of an aluminum atom in the face-centered cubic structure of aluminum?

79.

Cobalt metal crystallizes in a hexagonal closest packed structure. What is the coordination number of a cobalt atom?

80.

Nickel metal crystallizes in a cubic closest packed structure. What is the coordination number of a nickel atom?

81.

Tungsten crystallizes in a body-centered cubic unit cell with an edge length of 3.165 Å.

a. What is the atomic radius of tungsten in this structure?
b. Calculate the density of tungsten.

82.

Platinum (atomic radius = 1.38 Å) crystallizes in a cubic closely packed structure. Calculate the edge length of the face-centered cubic unit cell and the density of platinum.

83.

Barium crystallizes in a body-centered cubic unit cell with an edge length of 5.025 Å

a. What is the atomic radius of barium in this structure?
b. Calculate the density of barium.

84.

Aluminum (atomic radius = 1.43 Å) crystallizes in a cubic closely packed structure. Calculate the edge length of the face-centered cubic unit cell and the density of aluminum.

85.

The density of aluminum is 2.7 g/cm^3; that of silicon is 2.3 g/cm^3. Explain why Si has the lower density even though it has heavier atoms.

86.

The free space in a metal may be found by subtracting the volume of the atoms in a unit cell from the volume of the cell. Calculate the percentage of free space in each of the three cubic lattices if all atoms in each are of equal size and touch their nearest

neighbors. Which of these structures represents the most efficient packing? That is, which packs with the least amount of unused space?

87.

Cadmium sulfide, sometimes used as a yellow pigment by artists, crystallizes with cadmium, occupying one-half of the tetrahedral holes in a closest packed array of sulfide ions. What is the formula of cadmium sulfide? Explain your answer.

88.

A compound of cadmium, tin, and phosphorus is used in the fabrication of some semiconductors. It crystallizes with cadmium occupying one-fourth of the tetrahedral holes and tin occupying one-fourth of the tetrahedral holes in a closest packed array of phosphide ions. What is the formula of the compound? Explain your answer.

89.

What is the formula of the magnetic oxide of cobalt, used in recording tapes, that crystallizes with cobalt atoms occupying one-eighth of the tetrahedral holes and one-half of the octahedral holes in a closely packed array of oxide ions?

90.

A compound containing zinc, aluminum, and sulfur crystallizes with a closest-packed array of sulfide ions. Zinc ions are found in one-eighth of the tetrahedral holes and aluminum ions in one-half of the octahedral holes. What is the empirical formula of the compound?

91.

A compound of thallium and iodine crystallizes in a simple cubic array of iodide ions with thallium ions in all of the cubic holes. What is the formula of this iodide? Explain your answer.

92.

Which of the following elements reacts with sulfur to form a solid in which the sulfur atoms form a closest-packed array with all of the octahedral holes occupied: Li, Na, Be, Ca, or Al?

93.

What is the percent by mass of titanium in rutile, a mineral that contains titanium and oxygen, if structure can be described as a closest packed array of oxide ions with titanium ions in one-half of the octahedral holes? What is the oxidation number of titanium?

94.

Explain why the chemically similar alkali metal chlorides NaCl and CsCl have different structures, whereas the chemically different NaCl and MnS have the same structure.

95.

As minerals were formed from the molten magma, different ions occupied the same cites in the crystals. Lithium often occurs along with magnesium in minerals despite the difference in the charge on their ions. Suggest an explanation.

96.

Rubidium iodide crystallizes with a cubic unit cell that contains iodide ions at the corners and a rubidium ion in the center. What is the formula of the compound?

97.

One of the various manganese oxides crystallizes with a cubic unit cell that contains manganese ions at the corners and in the center. Oxide ions are located at the center of each edge of the unit cell. What is the formula of the compound?

98.

NaH crystallizes with the same crystal structure as NaCl. The edge length of the cubic unit cell of NaH is 4.880 Å.

  a. Calculate the ionic radius of H^-. (The ionic radius of Li^+ is 0.0.95 Å.)
  b. Calculate the density of NaH.

99.

Thallium(I) iodide crystallizes with the same structure as CsCl. The edge length of the unit cell of TlI is 4.20 Å. Calculate the ionic radius of Tl^+. (The ionic radius of I^- is 2.16 Å.)

100.

A cubic unit cell contains manganese ions at the corners and fluoride ions at the center of each edge.

a. What is the empirical formula of this compound? Explain your answer.
b. What is the coordination number of the Mn^{3+} ion?
c. Calculate the edge length of the unit cell if the radius of a Mn^{3+} ion is 0.65 A.
d. Calculate the density of the compound.

101.

What is the spacing between crystal planes that diffract X-rays with a wavelength of 1.541 nm at an angle θ of 15.55° (first order reflection)?

102.

A diffractometer using X-rays with a wavelength of 0.2287 nm produced first order diffraction peak for a crystal angle θ = 16.21°. Determine the spacing between the diffracting planes in this crystal.

103.

A metal with spacing between planes equal to 0.4164 nm diffracts X-rays with a wavelength of 0.2879 nm. What is the diffraction angle for the first order diffraction peak?

104.

Gold crystallizes in a face-centered cubic unit cell. The second-order reflection (n = 2) of X-rays for the planes that make up the tops and bottoms of the unit cells is at θ = 22.20°. The wavelength of the X-rays is 1.54 Å. What is the density of metallic gold?

105.

When an electron in an excited molybdenum atom falls from the L to the K shell, an X-ray is emitted. These X-rays are diffracted at an angle of 7.75° by planes with a separation of 2.64 Å. What is the difference in energy between the K shell and the L shell in molybdenum assuming a first order diffraction?

9: Acid-Base and Donor-Acceptor Chemistry

> *In a very real sense, we can make an acid anything we wish. The differences between the various acid-base concepts are not concerned with which is 'right', but which is most convenient to use in a particular situation.*
>
> *James E. Huheey, Ellen A. Keiter, and Richard L. Keiter*

The concept of acids and bases is often associated with the movement of hydrogen ions from one molecule or ion to another. However, a host of acid base concepts have been developed to help chemists organize and make sense of a wide range of reactions (Table 6.1).

Table 6.1. Summary of major acid-base models.

Definition	Theoretical paradigm and notable features.	Acid	Base	Illustrative sample reactions
Arrhenius (1894)	Interested in what the substance does to the state of an aqueous solution. Readily accommodates the pH concept as a measure of the state of a solution	Increases $[H_3O^+]$	Increases [OH-]	$HCl \rightarrow H^+ + Cl^-$ $\underset{acid}{} $ $NaOH \rightarrow Na^+ + OH^-$ $\underset{base}{}$
Brønsted-Lowry (1923)	Envisions acid-base reactivity in terms of the transfer of a H^+ from one substance to another. Allows for conjugate acids and bases and solvent autoionization.	Donates H^+	Accepts H^+	$\underset{acid}{HCl} + \underset{base}{H_2O} \rightarrow \underset{conj.\,acid}{H_3O^+} + c$ $\underset{acid}{HOAc} + \underset{base}{NH_3} \rightarrow \underset{conj.\,acid}{NH_4^+} +$ $\underset{amphoteric}{2\,H_2O} \rightarrow \underset{conj.\,acid}{H_3O^+} + \underset{conj.\,ba}{OH^-}$ $\underset{base}{NH_3} + H_2O \rightarrow NH_4^+ + O$
Lewis (1923)	Envisions acid-base reactivity in terms of electron pair donation. Encompasses the Arrhenius, Brønsted-Lowry, Lux-Flood, and Solvent System definitions and readily integrates with molecular orbital descriptions of chemical reactivity in Frontier orbital theory.	Accepts an electron pair	Donates an electron pair	$: \underset{base}{NH_3} + \underset{acid}{BF_3} \rightarrow \underset{adduct}{H_3N}$
Nucleophile-Electrophile	Applies the Lewis concept to organic reactivity. Nucleophiles are Lewis bases which tend to react to form a bond with Lewis acid sites called electrophilic centers.	(The electrophile) Tends to react by receiving an electron pair from a nucleophile, forming a bond in the process	(The nucleophile) Donates an electron pair to form a bond to an electrophile	$\underset{base}{Br^-} + \underset{acid}{CH_3-Cl} \rightarrow Br-C$

Definition	Theoretical paradigm and notable features.	Acid	Base	Illustrative sample reactions
Frontier Orbital (1960s)	Envisions Lewis Acid-base/Electrophile-nucleophile reactions in terms of the donation and acceptance of electrons between the reactant's frontier orbitals. Specifically, the reaction is envisioned in terms of donation of the base's HOMO electrons into the acid's HOMO level.	Possesses a LUMO capable of forming an occupied bonding MO on mixing with a base's HOMO.	Possesses an electron-bearing HOMO capable of forming a filled bonding MO on mixing with an acid's LUMO.	base acid adduct
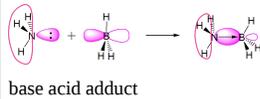
Some concepts involve defining acids and bases in particular ways that allow for the understanding of particular types of chemical systems. For example, the familiar Arhennius and Brønsted acids and base concepts used in general chemistry help chemists make sense of the behavior of compounds which can transfer H^+ ions among themselves, often in aqueous solution. However, some acid-base definitions seek to encompass an extremely wide range of chemical reactions. For instance, the Lewis acid-base definition encompasses the Arrhenius and Brønsted theories, while some Lewis acid-base interactions may be described by the Frontier Orbital approach in terms of interacting molecular orbitals on the acid and base.

References

Huheey, J. E.; Keiter, E. A.; Keiter, R. L., *Inorganic Chemistry: Principles of Structure and Reactivity. 4th ed.*; HarperCollins: New York, NY, 1993, pg. 318.

Contributors and Attributions

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> **◖◗ Learning Objectives**
>
> - Understand when to apply different acid and base theories
> - Identify conjugate acids and bases, and rules for strong & weak acids/bases, in both Brønsted and Lewis acid-base systems
> - Describe and rationalize acid/base chemistry of "non-traditional" Brønsted acids.
> - Predict favorable and stable compounds using hard-soft acid-base (HSAB) theory.

9.1: Arrhenius Model

The Arrhenius acid-base concept defines acids and bases in terms of how they affect the amount of hydronium ions, H_3O^+, (and by extension hydroxide ions, OH^-) in aqueous solutions. Simply, in the Arrhenius definition an acid is a substance that increases the concentration of hydronium ions when it is dissolved in water. This typically occurs when the acid dissociates by loss of a proton to water according to the general equation:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \tag{9.1.1}$$
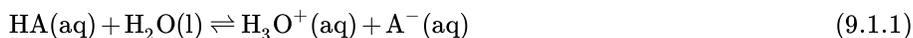
where A is the deprotonated form of the acid. For example, what hydrochloric and acetic acid, CH_3CO_2H, have in common is that both increase the amount of hydronium ion when they are dissociated in solution.

$$HCl(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + Cl^-(aq)$$

$$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$
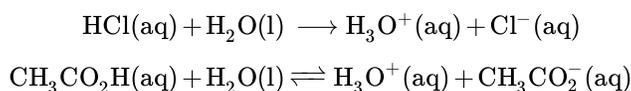
In terms of the Arrhenius definition, the major difference between hydrochloric and acetic acid is that hydrochloric acid dissociates completely in solution to yield stoichiometric amounts of H_3O^+, while acetic acid only partially dissociates. Acids like HCl that completely dissociate in water are classified as strong in the Arrhenius definition, while those like acetic acid that do not are classified as weak.

Although all weak acids incompletely dissociate, the extent of dissociation can vary widely. The relative strengths of weak Arrhenius acids is conveniently expressed in terms of the equilibrium constant for their acid dissociation reaction, K_a.

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

The pK_a values for selected weak acids are given in Table 9.1.1.

Table 9.1.1: Values of K_a, pK_a, K_b, and pK_b for selected monoprotic acids.

Acid	HA	K_a	pK_a	A^-	K_b	pK_b
sulfuric acid (2nd ionization)	HSO_4^-	1.0×10^{-2}	1.99	SO_4^{2-}	9.8×10^{-13}	12.01
hydrofluoric acid	HF	6.3×10^{-4}	3.20	F^-	1.6×10^{-11}	10.80
nitrous acid	HNO_2	5.6×10^{-4}	3.25	NO_2^-	1.8×10^{-11}	10.75
formic acid	HCO_2H	1.78×10^{-4}	3.750	HCO_2^-	5.6×10^{-11}	10.25
benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	4.20	$C_6H_5CO_2^-$	1.6×10^{-10}	9.80
acetic acid	CH_3CO_2H	1.7×10^{-5}	4.76	$CH_3CO_2^-$	5.8×10^{-10}	9.24
pyridinium ion	$C_5H_5NH^+$	5.9×10^{-6}	5.23	C_5H_5N	1.7×10^{-9}	8.77
hypochlorous acid	$HOCl$	4.0×10^{-8}	7.40	OCl^-	2.5×10^{-7}	6.60
hydrocyanic acid	HCN	6.2×10^{-10}	9.21	CN^-	1.6×10^{-5}	4.79
ammonium ion	NH_4^+	5.6×10^{-10}	9.25	NH_3	1.8×10^{-5}	4.75
water	H_2O	1.0×10^{-14}	14.00	OH^-	**1.00**	0.00
acetylene	C_2H_2	1×10^{-26}	26.0	HC_2^-	1×10^{12}	−12.0
ammonia	NH_3	1×10^{-35}	35.0	NH_2^-	1×10^{21}	−21.0

*The number in parentheses indicates the ionization step referred to for a polyprotic acid.

As can be seen from the table the K_a values for weak acids are less than one (otherwise they would not be weak) and vary over many orders of magnitude. Consequently it is customary to tabulate acid ionization constants as pK_a values:

$$pK_a = -\log K_a$$

Because pK$_a$ values essentially place the K$_a$ values on a negative base ten logarithmic scale, the stronger the weak acid, the lower its pK$_a$. Weak acids with larger K$_a$ values will have lower pK$_a$ values than weaker acids with smaller K$_a$. Moreover, each unit increase or decrease in the pK$_a$ corresponds to a tenfold increase or decrease in the corresponding K$_a$.

While Arrhenius acids increase the concentration of H_3O^+ in aqueous solution, Arrhenius bases decrease H_3O^+. Strong bases do this stoichiometrically. Most are hydroxide salts of alkali metals or quaternary ammonium salts that dissociate completely when dissolved in water:

$$\mathrm{MOH(aq) \longrightarrow M^+(aq) + OH^-(aq)}$$
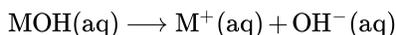
This added hydroxide decreases the concentration of H_3O^+ by shifting the water autoionization equilibrium towards water.

$$\mathrm{2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)}$$
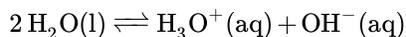
In contrast, most weak bases react with water to produce an equilibrium concentration of hydroxide ion according to the base dissociation reaction

$$\mathrm{B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)}$$
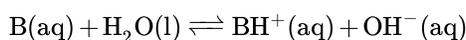
in which B is the weak base. The ionization constant for this reaction, called the **base ionization constant** or K_b, is typically used as a measure of a weak base's strength.

Because both hydroxide and hydronium ion are products of water autoionization, the concentrations of hydronium ion and hydroxide ion in aqueous solution will vary reciprocally with one another. This means that Arrhenius acids can be recognized as substances that decrease the hydroxide concentration and Arrhenius bases as substances that increase it.

Since the Arrhenius acid-base concept is concerned about the state of the water autoionization reaction, Arrhenius acids and bases may also be recognized by their effect on the solution pH. Arrhenius acids decrease the pH and Arrhenius bases will increase it.

> 📌 NOTE
>
> To qualify as an Arrhenius acid, upon the introduction to water, the chemical must cause, either directly or otherwise:
>
> - an increase in the aqueous hydronium concentration,
> - a decrease in the aqueous hydroxide concentration, or
> - a decrease in the solution pH.
>
> Conversely, to qualify as an Arrhenius base, upon the introduction to water, the chemical must cause, either directly or otherwise:
>
> - a decrease in the aqueous hydronium concentration,
> - an increase in the aqueous hydroxide concentration, or
> - an increase in the solution pH.

Because the Arrhenius acid-base model defines acids and bases in terms of their impact on the state of an aqueous solution the Arrhenius concept is unable to describe reactions in nonaqueous solvents, gases, molten liquids, and the solid state. Consequently other models should be used to describe reactions involving the transfer of H^+ and other fragments in nonaqueous media.

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9.2: Brønsted-Lowry Model

The Brønsted-Lowry Acid Base Concept

The Brønsted-Lowry acid base concept overcomes the Arrhenius system's inability to describe reactions that take place outside of aqueous solution by moving the focus away from the solution and onto the acid and base themselves. It does this by redefining acid-base reactivity as involving the transfer of a hydrogen ion, H^+, between an acid and a base. Specifically, a Brønsted acid is a substance that loses a H^+ ion by donating it to a base. This means that a Brønsted base is defined as a substance which accepts H^+ from an acid when it reacts.
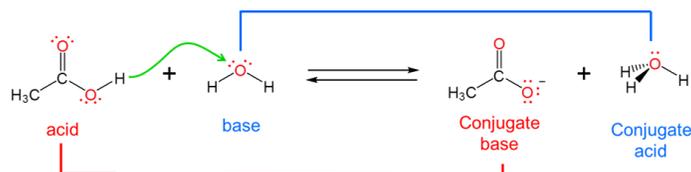
Because the Brønsted-Lowry concept is concerned with H^+ ion transfer rather than the creation of a particular chemical species it is able to handle a diverse array of acid-base concepts. In fact, from the viewpoint of the Brønsted-Lowry concept, Arrhenius acids and bases are just a special case involving hydrogen ion donation and acceptance involving water. Arrhenius acids donate H$^+$ ion to water, which acts as a Brønsted base to give H$_3$O$^+$

$$HA(aq) + H_2O \rightleftharpoons H_3O^+(aq) + A^-(aq)$$
$$\quad\quad acid \quad\quad base$$

$$(9.2.1)$$
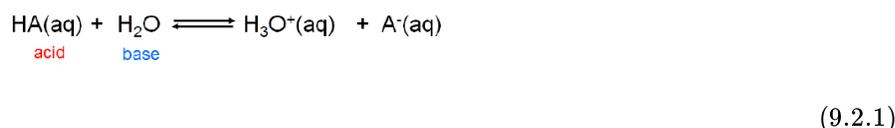
Similarly, Arrhenius bases act as Brønsted bases in accepting a hydrogen ion from the Brønsted acid water:

$$B(aq) + H_2O(aq) \rightleftharpoons BH^+(aq) + OH^-(aq)$$
$$\quad base \quad\quad acid$$

$$(9.2.2)$$
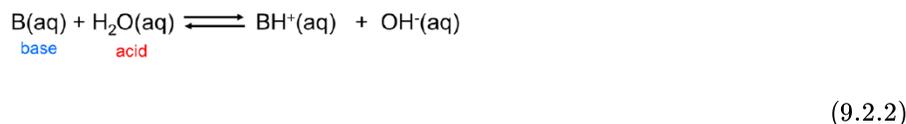
In this way it can be seen that Arrhenius acids and bases are defined in terms of their causing hydrogen ions to be donated to and abstracted from water, respectively, while Brønsted acids and bases are defined in terms of their ability to donate and accept hydrogen ions to and from anything.

Because the Brønsted-Lowry concept can handle any sort of hydrogen ion transfer it readily accommodates many reactions that Arrhenius theory cannot, including those that take place outside of water, such as the reaction between gaseous hydrochloric acid and ammonia:

$$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$$
$$\quad\, base \quad\quad acid$$

$$(9.2.3)$$

The classification of acids as strong or weak usually refers to their ability to donate or abstract hydrogen ions to or from water to give H_3O^+ and OH^-, respectively, - *i.e.* their Arrhenius acidity and basicity. However, acids and bases may be classified as strong and weak under the Brønsted-Lowry definition based on whether they completely transfer or accept hydrogen ions; it is just that in this case it is important to specify the conditions under which a given acid or base acts strong or weak. For example, acetic acid acts as a weak base in water but is a strong base in triethylamine, since in the latter case it completely transfers a hydrogen ion to triethylamine to give triethylammonium acetate. Alternatively, the acidity or basicity of a compound may be specified using a thermodynamic scale like the Hammett acidity.

Conjugate Acids and Bases

By redefining acids and bases in terms of hydrogen ion donation and acceptance the Brønsted-Lowry system makes it easy to recognize that when an acid loses its hydrogen ion it becomes a substance that is capable of receiving it back again, namely a base.

Consider, for example, the base dissociation of ammonia in water. When ammonia acts as a Brønsted base and receives a hydrogen ion from water ammonium ion and hydroxide are formed:

$$NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

base   acid   Conjugate acid   Conjugate base
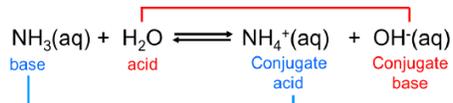
(9.2.4)

The ammonium ion is itself a weak acid that can undergo dissociation:

$$NH_4^+(aq) + H_2O(aq) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

acid   base   Conjugate base   Conjugate acid
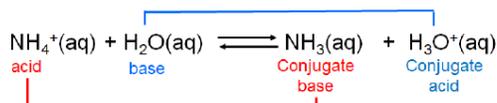
(9.2.5)

In this case ammonia and ammonium ion are acid-base conjugates. In general acids and bases that differ by a *single ionizable hydrogen ion* are said to be conjugates of one another.

The strengths of conjugates vary reciprocally with one another so that the stronger the acid the weaker the base and vice versa. For example, in water, acetic acid acts as a weak Brønsted acid:
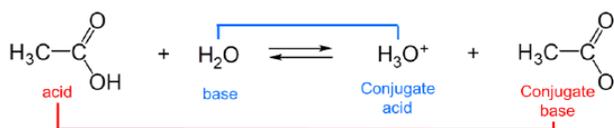
(9.2.6)

and acetic acid's conjugate base, acetate, acts as a weak Brønsted base.
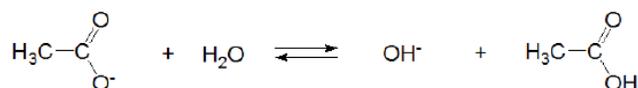
(9.2.7)

However, in liquid ammonia acetic acid acts as a strong Brønsted acid:

(9.2.8)

while its conjugate base, acetate, is neutral.
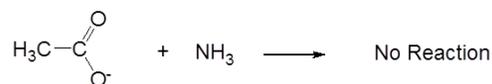
(9.2.9)

The reciprocal relationship between the strengths of acids and their conjugate bases has several consequences:

1. Under conditions when an acid or base acts as a weak acid or base its conjugate acts as weak as well. Conversely, when an acid or base acts as a strong acid or base its conjugate acts as a neutral species.
2. When a Brønsted acid and base react with one another the equilibrium favors formation of the weakest acid-base pair. That is why the acid-base reaction between acetic acid and ammonia in liquid ammonia proceeded to give the weak acid ammonium ion and neutral acetate. This consequence is particularly important for understanding the behavior of acids and bases in nonaqueous solvents, as illustrated by the following example.

> ✔ Example 9.2.1
>
> Can a solution of lithium diisopropylamide in heptane be used to form lithium cyclopentadienide? The pK_a of cyclopentadiene and diisopropylamine are ~15 and 40, respectively, and the proposed reaction is as follows:
>
>
>
> **Solution:**
>
> > Since cyclopentadiene is a stronger acid than diisopropylamine (the stronger the acid the lower the pK_a) the equilibrium will favor protonation of the diisopropylamine by cyclopentadiene. Consequently addition of a heptane solution lithium diisopropylamide to monomeric cyclopentadiene should give lithium cyclopentadienide.
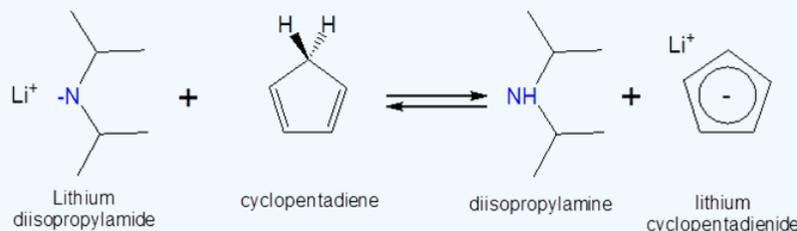
Molecular Structure and Brønsted Acidity and Basicity

Because the acidity of a given substance depends on the interplay between the relatively large values of its proton affinity and the energy associated with solvation of an acid's conjugate base it can be sometimes difficult to estimate the strength of an acid in a given solvent in the absence of detailed computations. Nevertheless a variety of simple ideas may be used to roughly estimate the relative strengths of acids. These should never be substituted for a detailed consideration of solvation but can serve as useful aids when thinking about trends and designing new Brønsted acids and bases.

Some simple factors that it can be helpful to consider when thinking about the strength of a given acid or base are:

Bond strength effects

The weaker the bond to the ionizable hydrogen, the stronger the acid. Strongly bonded hydrogen ions are difficult to remove, weakly bonded ones much less so.

Inductive effects

Inductive effects involve the donation or withdrawal of electrons from an atom by a group connected to it through bonds. Electron donating groups increase the electron density while electron withdrawing groups decrease it. Atoms or groups that withdraw electron density away from a center increase its acidity while those which donate electrons to the center decrease its acidity. The reasons for this follow from the heterolytic bond cleavage of acid ionization:

$$E - H \rightarrow E:^- + H^+ \tag{9.2.10}$$

- When a bond to hydrogen is more polarized away from the H (more like $^{-\delta}E - H^{\delta+}$) it is easier to cleave off the hydrogen ion from that E-H bond. This may be seen from how the pK$_a$ values of acetic acid and its mono-, di-, and tri-chlorinated derivatives decreases with the extent of chlorination of the methyl group.
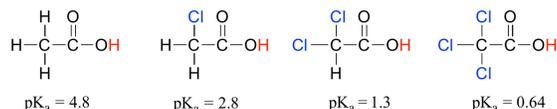
- Polarized E-H bonds also make for stronger Brønsted acids because the resulting $E:^-$ conjugate base is more stable.

This leads to the third major factor that should be considered when thinking about acid strength.

Electronegativity effects

The more stable the acid's conjugate base, the stronger the Brønsted acid. All reactions are in theory reversible and so when considering the propensity of an acid to donate hydrogen ions it can be helpful to look at the reverse of hydrogen ion donation,

namely protonation of the acid's conjugate base. If deprotonation of the acid gives a very stable conjugate base then deprotonation of the acid will be more favorable.

Two factors determine the stability of an acid's conjugate base.

- Conjugate bases in which a small amount of charge is on a large atom, spread over a large number atoms, and on electronegative atoms tend to be more stable. Conjugate bases in which a small amount of charge are spread over a large number of electronegative atoms are especially stable. That is why magic acid, a mixture of HF and SbF_5, is so acidic; the single negative charge on its conjugate base is spread over six F atoms and on Sb in SbF_6^-.

- Groups which tend to inductively polarize E-H bonds also tend to stabilize the conjugate base formed when that bond ionizes. In general, the more electronegative an atom, the better able it is to bear a negative charge. All other things being equal weaker bases have negative charges on more electronegative atoms; stronger bases have negative charges on less electronegative atoms. This is apparent from how inductive effects lead to an increase in the acidity of E-H bonds as the electronegativity of the element to which the acidic hydrogen is bound increases from left to right across a row of the periodic table. This horizontal periodic trend in acidity and basicity is apparent from the homologous series below in Figure 9.2.1.
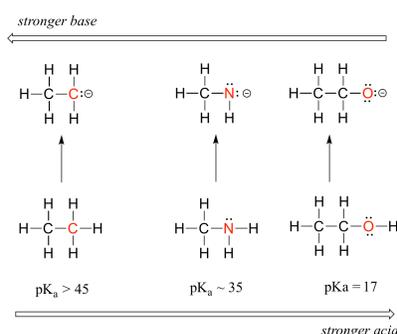
Figure 9.2.1: Horizontal periodic trend in acidity and basicity.

Notice how the inductive polarization of the E-H bond which results in greater acidity contributes to the greater stability of the conjugate base. For the case above look at where the negative charge ends up in each conjugate base. In the conjugate base of ethane, the negative charge is borne by a carbon atom, while on the conjugate base of methylamine and ethanol the negative charge is located on a nitrogen and an oxygen, respectively. Remember that electronegativity also increases as we move from left to right along a row of the periodic table, meaning that oxygen is the most electronegative of the three atoms, and carbon the least.

Thus, the methoxide anion is the most stable (lowest energy, least basic) of the three conjugate bases, and the ethyl carbanion anion is the least stable (highest energy, most basic). Conversely, ethanol is the strongest acid, and ethane the weakest acid.

Size effects

There are two classes of size effects to be considered:

a. The larger the atom to which a H is bound in an E-H bond, the weaker the bond and the stronger the acid.
b. Increased charge delocalization with increasing size. Electrostatic charges, whether positive or negative, are more stable when they are 'spread out' over a larger area. The greater the volume over which charge is spread in the acid's conjugate base, the more stable that base and the stronger the acid.

The impact of size effects are readily seen in the increase in acidity of the hydrogen halides, as illustrated by the vertical periodic trend in acidity and basicity below in Figure 9.2.2.
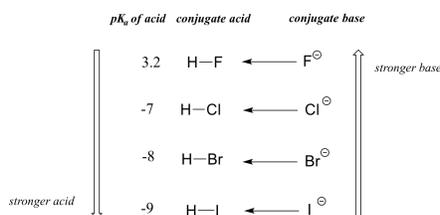
Figure 9.2.2: Vertical periodic trend in acidity and basicity.

On going vertically down the halogen group from F to I the H-X bond strength decreases in the acid, making it easier to ionize, while the charge becomes more diffuse in the resultant X⁻ ion, making the conjugate base more stable.

*negative charge spread out
over larger volume*

I⁻   F⁻
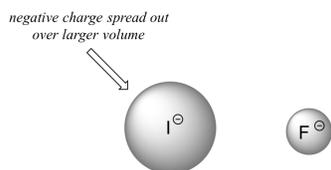
The increase in the acidity of the hydrogen halides down a group suggests that size effects are more important than inductive effects. In the case of the hydrogen halides because fluorine is the most electronegative halogen element, we might expect fluoride to also be the least basic halogen ion. But in fact, it is the *least* stable, and the most basic! It turns out that when moving vertically in the periodic table, the *size* of the atom trumps its electronegativity with regard to basicity. The atomic radius of iodine is approximately twice that of fluorine, so in an iodide ion, the negative charge is spread out over a significantly larger volume.

Now that we know how to quantify the strength of an acid or base, our next job is to gain an understanding of the fundamental reasons behind why one compound is more acidic or more basic than another. This is a big step: we are, for the first time, taking our knowledge of organic structure and applying it to a question of organic reactivity. Many of the ideas that we'll see for the first here will continue to apply throughout the book as we tackle many other organic reaction types.

Periodic trends

First, we will focus on individual atoms, and think about trends associated with the position of an element on the periodic table. We'll use as our first models the simple organic compounds ethane, methylamine, and ethanol, but the concepts apply equally to more complex biomolecules with the same functionalities, for example the side chains of the amino acids alanine (alkane), lysine (amine), and serine (alcohol).

Horizontal periodic trend in acidity and basicity:
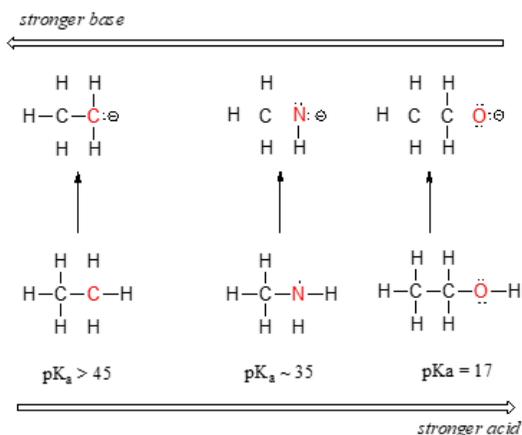
We can see a clear trend in acidity as we move from left to right along the second row of the periodic table from carbon to nitrogen to oxygen. The key to understanding this trend is to consider the hypothetical conjugate base in each case: the more stable (weaker) the conjugate base, the stronger the acid. Look at where the negative charge ends up in each conjugate base. In the conjugate base of ethane, the negative charge is borne by a carbon atom, while on the conjugate base of methylamine and ethanol the negative charge is located on a nitrogen and an oxygen, respectively. Remember from section 2.4A that electronegativity also increases as we move from left to right along a row of the periodic table, meaning that oxygen is the most electronegative of the three atoms, and carbon the least.

> 📌 Note
>
> The more electronegative an atom, the better able it is to bear a negative charge. Weaker bases have negative charges on more electronegative atoms; stronger bases have negative charges on less electronegative atoms.

Thus, the methoxide anion is the most stable (lowest energy, least basic) of the three conjugate bases, and the ethyl carbanion anion is the least stable (highest energy, most basic). Conversely, ethanol is the strongest acid, and ethane the weakest acid.

When moving vertically within a given column of the periodic table, we again observe a clear periodic trend in acidity. This is best illustrated with the haloacids and halides: basicity, like electronegativity, increases as we move up the column.

Vertical periodic trend in acidity and basicity:

Conversely, acidity in the haloacids increases as we move down the column.

In order to make sense of this trend, we will once again consider the stability of the conjugate bases. Because fluorine is the most electronegative halogen element, we might expect fluoride to also be the least basic halogen ion. But in fact, it is the least stable, and the most basic! It turns out that when moving vertically in the periodic table, the size of the atom trumps its electronegativity with regard to basicity. The atomic radius of iodine is approximately twice that of fluorine, so in an iodide ion, the negative charge is spread out over a significantly larger volume:

This illustrates a fundamental concept in organic chemistry:

Electrostatic charges, whether positive or negative, are more stable when they are 'spread out' over a larger area.

We will see this idea expressed again and again throughout our study of organic reactivity, in many different contexts. For now, we are applying the concept only to the influence of atomic radius on base strength. Because fluoride is the least stable (most basic) of the halide conjugate bases, HF is the least acidic of the haloacids, only slightly stronger than a carboxylic acid. HI, with a pK_a of about -9, is almost as strong as sulfuric acid.

More importantly to the study of biological organic chemistry, this trend tells us that thiols are more acidic than alcohols. The pK_a of the thiol group on the cysteine side chain, for example, is approximately 8.3, while the pK_a for the alcohol group on the serine side chain is on the order of 17.

Remember the concept of 'driving force' that was introduced in section 6.2? Recall that the driving force for a reaction is usually based on two factors: relative charge stability, and relative total bond energy. Let's see how this applies to a simple acid-base reaction between hydrochloric acid and fluoride ion:

$$HCl + F^- \rightarrow HF + Cl^- \tag{9.2.11}$$

We know that HCl (pK_a -7) is a stronger acid than HF (pK_a 3.2), so the equilibrium for the reaction lies on the product side: the reaction is exergonic, and a 'driving force' pushes reactant to product.

What explains this driving force? Consider first the charge factor: as we just learned, chloride ion (on the product side) is more stable than fluoride ion (on the reactant side). This partially accounts for the driving force going from reactant to product in this reaction: we are going from less stable ion to a more stable ion.

What about total bond energy, the other factor in driving force? If you consult a table of bond energies, you will see that the H-F bond on the product side is more energetic (stronger) than the H-Cl bond on the reactant side: 570 kJ/mol vs 432 kJ/mol, respectively). This also contributes to the driving force: we are moving from a weaker (less stable) bond to a stronger (more stable) bond.

Resonance effects

In the previous section we focused our attention on periodic trends - the differences in acidity and basicity between groups where the exchangeable proton was bound to different elements. Now, it is time to think about how the structure of different organic groups contributes to their relative acidity or basicity, even when we are talking about the same element acting as the proton

donor/acceptor. The first model pair we will consider is ethanol and acetic acid, but the conclusions we reach will be equally valid for all alcohol and carboxylic acid groups.

Despite the fact that they are both oxygen acids, the pKa values of ethanol and acetic acid are strikingly different. What makes a carboxylic acid so much more acidic than an alcohol? As before, we begin by considering the stability of the conjugate bases, remembering that a more stable (weaker) conjugate base corresponds to a stronger acid.
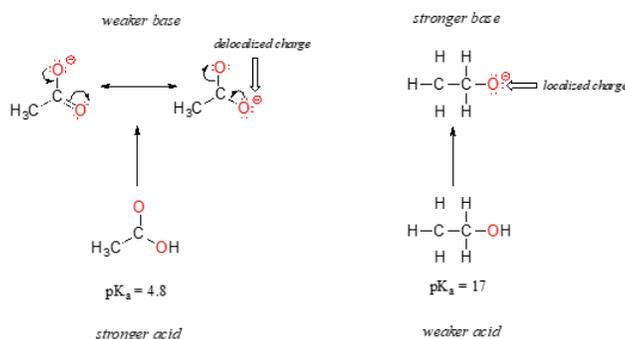
In both species, the negative charge on the conjugate base is located on oxygen, so periodic trends cannot be invoked. For acetic acid, however, there is a key difference: two resonance contributors can be drawn for the conjugate base, and the negative charge can be delocalized (shared) over two oxygen atoms. In the ethoxide ion, by contrast, the negative charge is localized, or 'locked' on the single oxygen – it has nowhere else to go. This makes the ethoxide ion much less stable.

Recall the important general statement that we made a little earlier: 'Electrostatic charges, whether positive or negative, are more stable when they are 'spread out' than when they are confined to one location.' Now, we are seeing this concept in another context, where a charge is being 'spread out' (in other words, delocalized) by resonance, rather than simply by the size of the atom involved.

The delocalization of charge by resonance has a very powerful effect on the reactivity of organic molecules, enough to account for the difference of over 12 pK_a units between ethanol and acetic acid (and remember, pK_a is a log expression, so we are talking about a factor of 10^{12} between the K_a values for the two molecules!)

The resonance effect also nicely explains why a nitrogen atom is basic when it is in an amine, but not basic when it is part of an amide group. Recall that in an amide, there is significant double-bond character to the carbon-nitrogen bond, due to a minor but still important resonance contributor in which the nitrogen lone pair is part of a π bond.
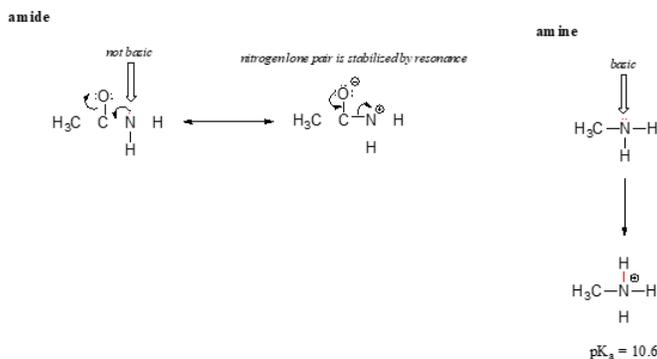
Whereas the lone pair of an amine nitrogen is 'stuck' in one place, the lone pair on an amide nitrogen is delocalized by resonance. Notice that in this case, we are extending our central statement to say that electron density – in the form of a lone pair – is stabilized by resonance delocalization, even though there is not a negative charge involved. Here's another way to think about it: the lone pair on an amide nitrogen is not available for bonding with a proton – these two electrons are too 'comfortable' being part of the delocalized π-bonding system. The lone pair on an amine nitrogen, by contrast, is not so comfortable - it is not part of a delocalized π system, and is available to form a bond with any acidic proton that might be nearby.

If an amide group is protonated, it will be at the oxygen rather than the nitrogen.

? Exercise 7.4.1

a. Draw the Lewis structure of nitric acid, HNO_3.
b. Nitric acid is a strong acid - it has a pK_a of -1.4. Make a structural argument to account for its strength. Your answer should involve the structure of the conjugate base of nitric acid.

? Exercise 7.4.2

Rank the compounds below from most acidic to least acidic, and explain your reasoning.
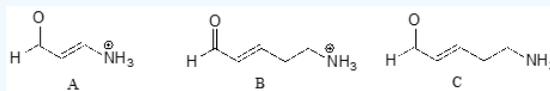
? Exercise 7.4.3

Often it requires some careful thought to predict the most acidic proton on a molecule. Ascorbic acid, also known as Vitamin C, has a pK_a of 4.1 - the fact that this is in the range of carboxylic acids suggest to us that the negative charge on the conjugate base can be delocalized by resonance to two oxygen atoms. Which if the four OH protons on the molecule is most acidic? Draw the structure of ascorbate, the conjugate base of ascorbic acid, then draw a second resonance contributor showing how the negative charge is delocalized to a second oxygen atom.

Hint

Try deprotonating each OH group in turn, then use your resonance drawing skills to figure out whether or not delocalization of charge can occur.

ascorbic acid
(Vitamin C)
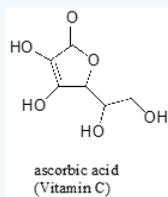
Inductive effects

Compare the pK_a values of acetic acid and its mono-, di-, and tri-chlorinated derivatives:
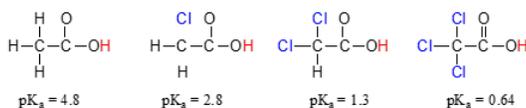
The presence of the chlorine atoms clearly increases the acidity of the carboxylic acid group, but the argument here does not have to do with resonance delocalization, because no additional resonance contributors can be drawn for the chlorinated molecules. Rather, the explanation for this phenomenon involves something called the inductive effect. A chlorine atom is more electronegative than a hydrogen, and thus is able to 'induce', or 'pull' electron density towards itself, away from the carboxylate group. In effect, the chlorine atoms are helping to further spread out the electron density of the conjugate base, which as we know has a stabilizing effect. In this context, the chlorine substituent can be referred to as an electron-withdrawing group. Notice that the pK_a-lowering effect of each chlorine atom, while significant, is not as dramatic as the delocalizing resonance effect illustrated by

the difference in pK_a values between an alcohol and a carboxylic acid. In general, resonance effects are more powerful than inductive effects.

Because the inductive effect depends on electronegativity, fluorine substituents have a more pronounced pK_a-lowered effect than chlorine substituents.

trichloroacetic acid
pK$_a$ = 0.64

trifluoroacetic acid
pK$_a$ = -0.25
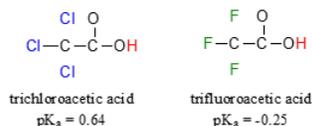
In addition, the inductive takes place through covalent bonds, and its influence decreases markedly with distance – thus a chlorine two carbons away from a carboxylic acid group has a decreased effect compared to a chlorine just one carbon away.

stronger acid
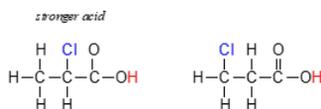
? Exercise 7.4.4

Rank the compounds below from most acidic to least acidic, and explain your reasoning.

A   B   C
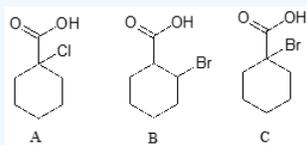
? Exercise 9.2.1

The structure of the amino acids serine and cysteine are shown below. Which do expect will have the more acidic side chain?
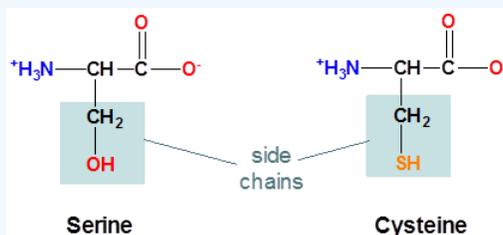
Serine   Cysteine

Answer

Cysteine, since the cysteine side chain possesses an ionizable S-H bond while serine's side chain possesses an ionizable O-H bond. Since S is larger than O cysteine's S-H bond will be weaker than serine's O-H bond the and cysteine side chain's thiolate conjugate base more stable than the serine side chian's alkoxide conjugate base. In fact, the side chain pK_a of cysteine is 8.3 while serine is considered to be nonionizable under physiological conditions.

Binary Hydrides

The compounds formed between the elements and hydrogen are called binary hydrides. All such compounds can in principle act as Brønsted acids in reactions with a suitably strong base. However, as the electronegativity decreases down a group and increases from left to right across the periodic table the acidity of binary hydrides increases. In fact, on the left side of the periodic table the hydrides of extremely electropositive alkali and alkaline earth metals are not acidic but basic. They are perhaps best considered to be ionic salts of the hydride ion (H^-). Consequently substances such as NaH and CaH_2 tend to act as Brønsted bases in their reactions.

$$NaH(s) + H_2O(l) \rightarrow Na^+(aq) + OH^-(aq) + H_2(g) \tag{9.2.12}$$

$$CaH_2(s) + 2\,H_2O(l) \rightarrow Ca^{2+}(aq) + 2\,OH^-(aq) + 2\,H_2(g) \tag{9.2.13}$$
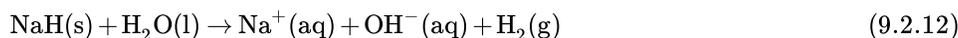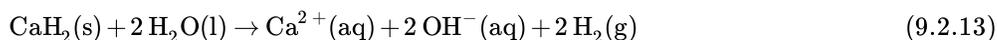
On the right side of the periodic table the binary hydrides of the nonmetals exhibit appreciable acidity.

$$HBr(aq) + H_2O(l) \rightarrow H^+(aq) + Br^-(aq) \tag{9.2.14}$$
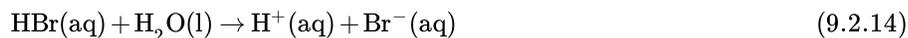
For this reason the binary nonmetal hydrides are termed acidic hydrides. Nevertheless not all are equally acidic. The dilute aqueous acid ionization constants for these hydrides are given in Figure $9.2.3$. As can be seen from the constants in Figure $9.2.2$ the ability of the hydrides to transfer a hydrogen to water increases across a period and down a group.

CH$_4$	NH$_3$	H$_2$O	HF
10^{-46}	10^{-35}	10^{-16}	10^{-3}
	PH$_3$	H$_2$S	HCl
	10^{-27}	10^{-7}	10^7
		H$_2$Te	HBr
		10^{-3}	10^9
			HI
			10^{10}

Figure 9.2.3: The acid ionization constants of nonmetal hydrides increase across a period and down a group.

These trends are largely due to changes in the electronegativity and size of the nonmetal atom:

1. Going across a period the acid strength increases as there is an increase in electronegativity and the molecule gets more polar, with the hydrogen getting a larger partial positive charge. This makes it easier to heterolytically cleave the E-H bond to produce a stable anion.

$$E - H \rightarrow E:^- + H^+ \tag{9.2.15}$$

2. Going down a group the acid strength increases because the bond strength decreases as a function of increasing size of the nonmetal, and this has a larger effect than the electronegativity. In fact HF is a weak acid because it is so small that the hydrogen-fluorine bond is so strong that it is hard to break. Remember, the weaker the bond, the strong the acid strength. This is further illustrated in Table $9.2.1$ where the weakest bond has produces the strongest acid.

Table 9.2.1 Acid strength as function of bond energy

Relative Acid Strength	HF	<<	HCl	<	HBr	<	HI
H–X Bond Energy (kJ/mol)	570		432		366		298
K_a	10^{-3}		10^7		10^9		10^{10}

\[\

Oxyacids

Oxyacids (also known as oxoacids) are compounds of the general formula $H_n EO_m$, where E is a nonmetal or early transition metal and the acidic hydrogens are attached directly to oxygen (not E). This class of compounds includes such well-known acids as nitric acid, HNO_3, and phosphoric acid, H_3PO_4.

The acidity of oxyacids follows three trends:

Electronegativity of the central atom

In a homologous series the acidity increases with the electronegativity of the central atom. Elements in the same group frequently form oxyacids of the same general formula. For example, chlorine, bromine, and iodine all form oxyacids of formula HOE: hypochlorous, hypobromous and hypoiodous acids. In the case of these homologous oxyacids the acidity is largely determined by the electronegativity of the central element. Central atoms which are better able to inductively pull electron density towards

themselves make the oxygen-hydrogen bond that is to be ionized more polar and stabilize the conjugate base, OE⁻. Thus the acid strength in such homologous series increases with the electronegativity of the central atom. This may be seen from the data for the hypohalous acids in Table 9.2.2, in which the acid strength increases with the electronegativity of the halogen so that the order of acidity is:

$$HClO > HBrO > HIO$$

Table 9.2.2: Relationship of central atoms electronegativity to acid ionization constant in the hypohalous acids.

HOE	Electronegativity of E	K_a
HOCl	3.0	4.0×10^{-8}
HOBr	2.8	2.8×10^{-9}
HOI	2.5	3.2×10^{-11}

Note this the influence of central atom electronegativity on the strength of oxyacids is exactly the opposite to that observed for the binary hydrides in Table $PageIndex5$, for which acidity increased down a group giving the order of acidity:

$$HI > HBr > HCl \gg HF \tag{9.2.16}$$

The reason for this is that in the hydrogen halides the bond to be broken (H-E bond) decreased in strength down the group while in oxyacids the bond to be broken is always an O-H bond and so varies much less in strength with the electronegativity of central atom.

Central element's oxidation state

For oxoacids of a given central atom the acidity increases with the central element's oxidation state or, in other words, the number of oxygens bound to the central atom. Here we are looking at the trend for acids in which there are variable numbers of oxygen bound to a given central atom. An examples is the perchloric ($HClO_4$), chloric ($HClO_3$), chlorous ($HClO_2$), and hypochlorous ($HClO$) acid series. In such series the greater the number of oxygens the stronger the acid. This can be explained in several ways. From the viewpoint of the acid itself the key factor is again the inductive effect, in this case involving the ability of the oxygens attached to the central atom to pull on electron density across the OH bond. This is seen from the charge density diagram for the chlorine oxoacids shown in Figure 9.2.4, in which the partial positive charge on the acidic hydrogen increases with the number of oxygens present.

HOCl (pK_a = 7.40)　　HOClO (pK_a = 1.96)

HOClO₂ (pK_a = −2.0)　　HOClO₃ (pK_a = −7.3 to −8)

electron rich ▬▬▬▬▬ electron poor
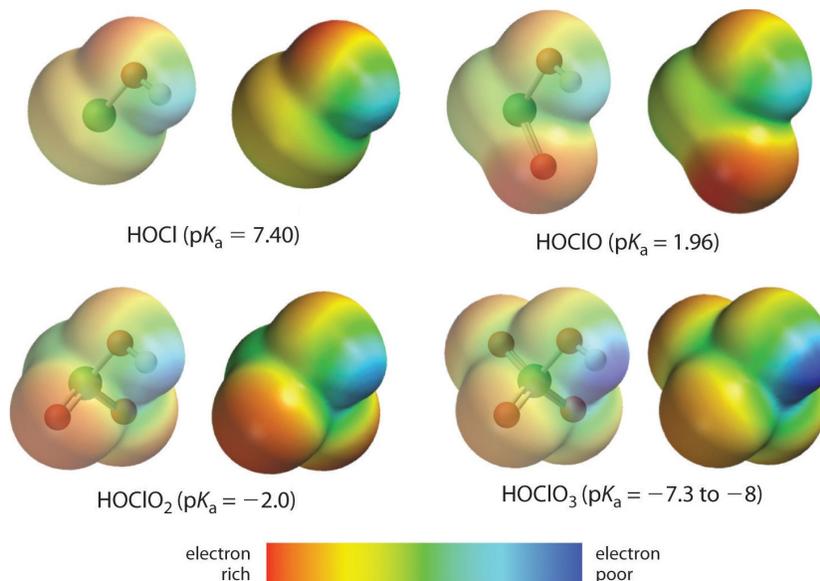
Figure 9.2.4: Increasing number of oxygens increases K_a as evidenced by the decreased electron density on the acidic hydrogen (which is most blue in HClO₄). Note, $K_a = 10^{-pK_a}$, and so the larger pK_a, the smaller K_a. (CC BY-SA-NC; anonymous)

The increase in oxoacid acidity with the number of oxygens bound to the central atom may also be seen by considering the stability of the conjugate oxyanion. That the stability of the conjugate base increases with the number of oxygens may be seen from the

charge distribution diagrams and Lewis bonding models for the chlorine oxyanions shown in figure 9.2.5. As the negative charge is spread over more oxygen atoms it becomes increasingly diffuse.
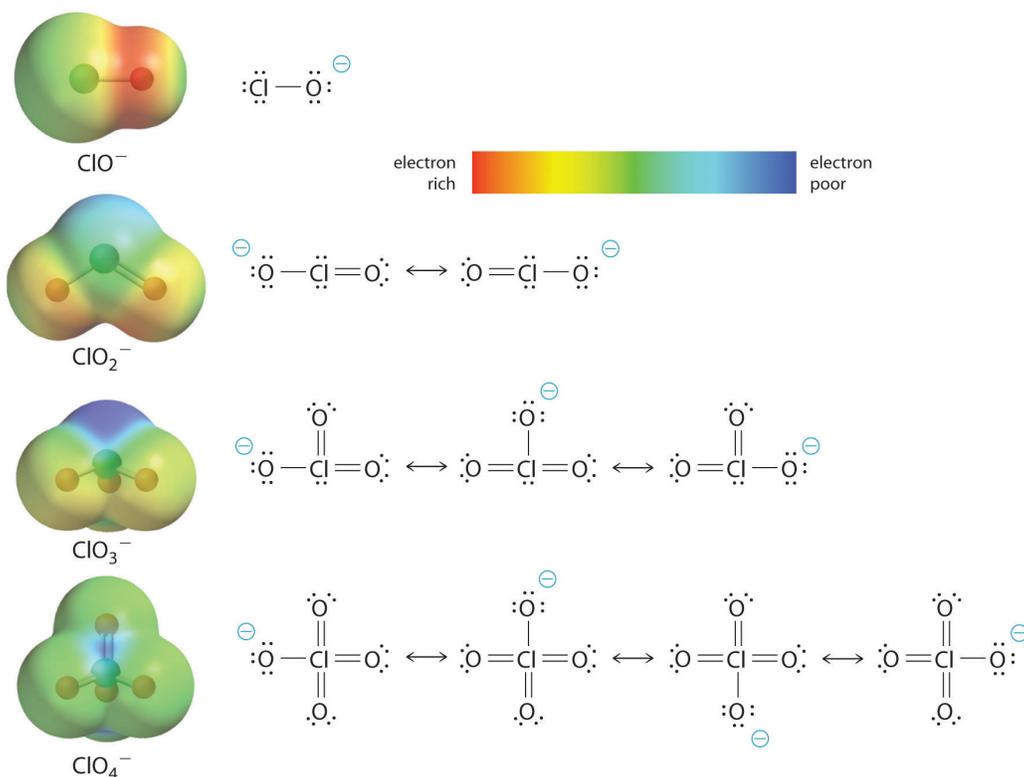
Figure 9.2.5: Increased diffusion of charge in chlorine oxyanions with increasing number of oxygens. The larger the ion the more dispersed the charge and thus the less the charge density, making the perchlorate the most stable anion in the series. Even the simplistic treatment of bonding depicted in the resonance structures correctly show an increased dispersion of the charge density. (CC BY-SA-NC 3.0; anonymous)

❓ Exercise 9.2.1

Sulfur and selenium both forms oxoacids of formula H_2EO_4 where E is either S or Se. These are called sulfurous and selenous acid, respectively. Which oxoacid would you expect to be more acidic: selenous acid or sulfurous acid?

Answer

Sulfurous acid should be more acidic. Since sulfur is more electronegative than selenium sulfur will polarize OH bonds to a greater extent, making them more acidic. This prediction is borne out by a comparison of the pK_a values for the acids:

Acid	pK_{a1}	pK_{a2}
sulfurous acid, H_2SO_3	1.85	7.2
selenous acid, H_2SeO_3	2.62	8.32

Successive proton removal

For polyprotic oxoacids the acidity decreases as each successive proton is removed. Oxoacids with multiple O-H bonds are called **polyprotic** since they can donate more than one hydrogen ion. In this case hydrogen ions are removed in successive ionization reactions. Examples include phosphoric and carbonic acid:

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \qquad pK_{a1} = 2.2 \tag{9.2.17}$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \qquad pK_{a2} = 7.2 \tag{9.2.18}$$

$$HPO_4 \rightleftharpoons H^+ + PO_4^{3-} \qquad pK_{a3} = 12.4 \tag{9.2.19}$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad pK_{a1} = 3.6 \qquad\qquad (9.2.20)$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad pK_{a1} = 10.3 \qquad\qquad (9.2.21)$$
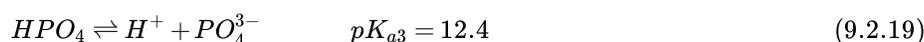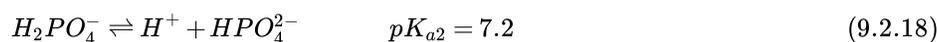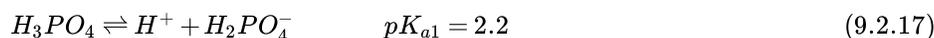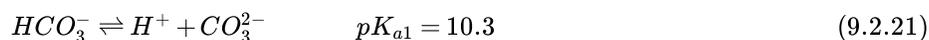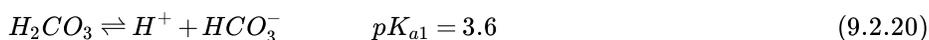
The dissociation constants for successive ionization constants decrease by about five orders of magnitude between successive hydrogen ions. This is reflected in Linus Pauling's rule for oxoacids and their oxyanions.

> ✎ **Pauling's Rules**
>
> 1. The pK_a or an oxyacid of general formula $\mathrm{E(OH)_q(O)_p}$ is given by
>
> $$pK_a = 8 - 5 \times p \qquad\qquad (9.2.22)$$
>
> 2. As an oxoaxid undergoes successive ionizations the pK_a increases by five each time.

The central theme of Pauling's Rules is that the more oxygen there are on the central atom, the more resonance structure that can be constructed of the conjugate base, which increases it stability and increases the acidity of the acid. However, as the acids successively ionize, they have fewer resonance structure. Pauling's Rules are phenomenological (i.e., not based on a theoretical basis). As with many empirical rules, they often work quite well, but they are approximations which may not work in all situations.

> ❓ **Exercise 9.2.2: How well do Pauling's rules for oxoacids work?**
>
> Calculate the theoretical pK_a values for phosphoric and carbonic acid and their dissociation produces and compare the results with the experimental pK_a values.
>
> **Answer**
>
> For phosphoric acid, Pauling's rules (Equation 9.2.22) predict the pK_a values quite well:
>
> - H_3PO_4: $p = 3$ and $q = 1$ and
>
> $$pK_{a1,predicted} = 8 - 5 \times 1 = 3$$
>
> This slightly greater than the observed value of 2.2.
> - $H_2PO_4^-$:
>
> $$pK_{a2,predicted} = pK_{a1,experimental} + 5 = 7.2$$
>
> This Spot on with experiment.
> - HPO_4^{2-}:
>
> $$pK_{a3,predicted} = pK_{a2,experimental} + 5 = 12.2$$
>
> . This is slightly less than the experimental value of 12.4.
>
> For carbonic acid Pauling's rules predict pK_{a1} reasonably well, but pK_{a2} less so:
>
> - H_2CO_3: $p = 2$, $q = 1$ and
>
> $$pK_{a1,predicted} = 8 - 5 \times 1 = 3$$
>
> This is slightly lower than the observed value of 3.6.
> - HCO_3^-:
>
> $$pK_{a2,predicted} = pK_{a1,experimental} + 5 = 8.6$$
>
> This is 1.7 units less than the experimental value of 10.3.
>
> In some cases discrepancies between experimental pK_a values and those predicted by Pauling's rules suggest that structural rearrangements may be taking place upon ionization or else that the reported pK_a values do not really represent the ionization in question because they do not fully account for all the equilibria taking place in solution. In the case of carbonic acid, however, the reason for the discrepancy between the predicted and experimental pK_{a2} values is not entirely clear.

Metal Ions as Acids

Aqueous solutions of simple salts of metal ions can also be acidic, even though a metal ion cannot donate a proton directly to water to produce H_3O^+. Instead, a metal ion can act as a Lewis acid and interact with water, a Lewis base, by coordinating to a lone pair of electrons on the oxygen atom to form a hydrated metal ion.

$$[Al(H_2O)_6]^{3+}(aq) \qquad H_2O(l) \qquad [Al(H_2O)_5OH]^{2+}(aq) \qquad H_3O^+(aq)$$
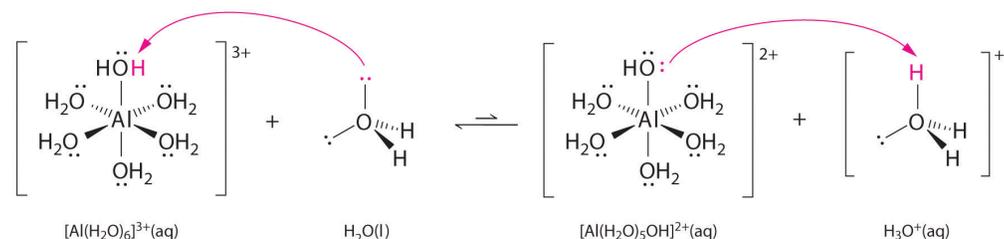
A water molecule coordinated to a metal ion is more acidic than a free water molecule for two reasons. First, repulsive electrostatic interactions between the positively charged metal ion and the partially positively charged hydrogen atoms of the coordinated water molecule make it easier for the coordinated water to lose a proton.

Second, the positive charge on the Al^{3+} ion attracts electron density from the oxygen atoms of the water molecules, which decreases the electron density in the O–H bonds, as shown in Figure $9.2.6b$. With less electron density between the O atoms and the H atoms, the O–H bonds are weaker than in a free H_2O molecule, making it easier to lose a H^+ ion. This is shown schematically in Figure $9.2.1$.

Figure $9.2.6$: Effect of a Metal Ion on the Acidity of Water (a) Reaction of the metal ion Al^{3+} with water to form the hydrated metal ion is an example of a Lewis acid–base reaction. (b) The positive charge on the aluminum ion attracts electron density from the oxygen atoms, which shifts electron density away from the O–H bonds. The decrease in electron density weakens the O–H bonds in the water molecules and makes it easier for them to lose a proton. (CC BY-NC-SA 3.0; anonymous)

Trends in Acidity

The acidity of a given metal ion largely depends on its charge to size ratio and electronegativity, although in some cases hardness and ligand field effects also play a role. The magnitude of this effect depends on the following factors, of which the first two are generally considered the most important.

The charge on the metal ion

A divalent ion (M^{2+}) has approximately twice as strong an effect on the electron density in a coordinated water molecule as a monovalent ion (M^+) of the same radius.

The radius of the metal ion

For metal ions with the same charge, the smaller the ion, the shorter the internuclear distance to the oxygen atom of the water molecule and the greater the effect of the metal on the electron density distribution in the water molecule.
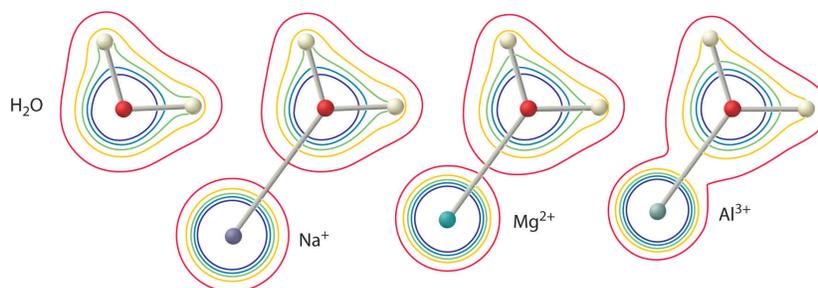
Figure 9.2.7: The Effect of the Charge and Radius of a Metal Ion on the Acidity of a Coordinated Water Molecule. The contours show the electron density on the O atoms and the H atoms in both a free water molecule (left) and water molecules coordinated to Na^+, Mg^{2+}, and Al^{3+} ions. These contour maps demonstrate that the smallest, most highly charged metal ion (Al^{3+}) causes the greatest decrease in electron density of the O–H bonds of the water molecule. Due to this effect, the acidity of hydrated metal ions increases as the charge on the metal ion increases and its radius decreases. (CC BY-NC-SA 3.0; anonymous)

The first two of these factors explain why most alkali metal cations exhibit little acidity while aqueous solutions of small, highly charged metal ions, such as Al^{3+} and Fe^{3+}, are acidic:

$$[Al(H_2O)_6]^{3+}_{(aq)} \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}_{(aq)} + H^+_{(aq)} \qquad (9.2.23)$$
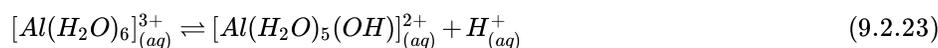
The $[Al(H_2O)_6]^{3+}$ ion has a pK_a of 5.0, making it almost as strong an acid as acetic acid. Because of the two factors described previously, the most important parameters for predicting the effect of a metal ion on the acidity of coordinated water molecules are the charge and ionic radius of the metal ion. Although the charge to size ratio is the simplest and most powerful predictor of metal ion acidity in water, three additional factors also can play a role:

Electronegativity

All other things being equal more electronegative elements are better able to withdraw electron density from a bound water ligand and consequently better at enhancing the ability of that water molecule to lose a hydrogen ion.

Hardness and Softness

Cation hardness or softness according to Pearson's Hard-Soft Acid Base Principle (HSAB). In general soft cations are more acidic than hard cations of the same charge and radius, as may be seen from the examples in Table 9.2.1. The greater than expected acidity of softer cations is thought to reflect the importance of covalent contributions to the metal-water bond.

Table 9.2.1: Comparison of the pK_a values at 25°C of hard and soft cations with approximately the same radius and charge. Based on Gutmann as reported by Burgess.

Cation	Classification	Radius (pm)	pK_a1
K^+	hard	1.33	14
Ag^+	soft	1.26	10
Mg^{2+}	hard	0.65	12.2
Cu^{2+}	soft	0.69	7.3
Ca^{2+}	hard	0.99	12.6
Cd^{2+}	soft	0.97	9.0
Sr^{2+}	hard	1.13	13.1
Hg^{2+}	soft	1.10	3.6

Solvent Autoionization

The Brønsted-Lowry concept allows for an understanding of hydrogen ion transfer chemistry in amphoteric protic solvents. Amphoteric protic solvents are those which can both accept and receive hydrogen ions. From the viewpoint of the Brønsted-Lowry concept the acid-base chemistry in these solvents is governed by autoionization equilibria analogous to water autoionization.

$$2H_2O(l) \rightleftharpoons H_3O^+ + OH^- \qquad K_w = 1.0 \times 10^{-14} \qquad (9.2.24)$$
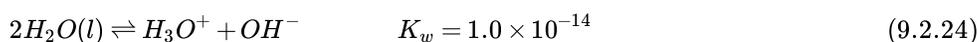
For example, sulfuric acid ionizes according to the equation:

$$2H_2SO_4(l) \rightleftharpoons H_3SO_4^+ + HSO_4^- \qquad K = 4 \times 10^{-4} \qquad (9.2.25)$$
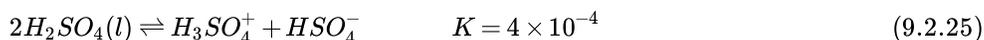
The magnitude of the solvent autoionization constant in a given amphoteric solvent determines the amount of protonated and deprotonated* solvent present. Since sulfuric acid's autoionization constant is much larger than that of water $K_w = 10^{-14}$ the concentration of $H_3SO_4^+$ and HSO_4^- present in pure sulfuric acid is ~0.02 M, much greater than the 10^{-7} M H^+ amd OH^- present in pure water.

In contrast, ammonia's autoionization constant is much less than that of water and only ~10^{-14} \{M NH_4^+\} and \{NH_2^-\} are present in pure ammonia.

$$2NH_3(l) \rightleftharpoons NH_4^+ + NH_2^- \qquad K = 10^{-27} \qquad (9.2.26)$$
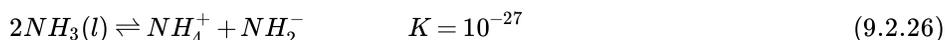
Solvent Leveling Effect

The solvent leveling effect limits the strongest acid or base that can exist in acidic, basic, and amphoteric solvents. The conjugate acid and base of the solvent are the strongest Brønsted acid and bases that can exist in that solvent. To see why this is the case for acids consider the reaction between a Brønsted acid (HA) and solvent (*S*):

$$HA + S \rightleftharpoons HS^+ + A^- \qquad (9.2.27)$$

This equilibrium will favor dissociation of whichever is a stronger acid - HA or HS$^+$. If the acid is stronger it will mostly dissociate to give HS$^+$, while if the solvent's conjugate acid is stronger the acid will be mostly un-ionized and remain as HA.

Any acid significantly stronger than HS$^+$ will act as a strong acid and effectively dissociate completely to give the solvent's conjugate acid HS$^+$. This also means that the relative acidity of acids stronger than HS$^+$ cannot be distinguished in solvent S. This is called the leveling effect since the solvent "levels" the behavior of acids much stronger acids than it to that of complete dissociation. For example, there is no way to distinguish the acidity of strong acids like HClO$_4$ and HCl in water since they both completely dissociate. However, it is possible to distinguish their relative acidities in solvents that are more weakly basic than the conjugate base of the strongest acid since then the acids will dissociate to different extents. Such solvents are called differentiating solvents. For example, acetonitrile (MeCN) acts as a differentiating solvent for HClO$_4$ and HCl. Both HClO$_4$ and HCl partially dissociate in MeCN, with the stronger acid HClO$_4$ dissociating to a greater extent than HCl.

The leveling effect can also occur in basic solutions. The strongest Brønsted base, B, that can exist in a solvent is determined by the relative acidity of the solvent and the base's conjugate acid, BH$^+$, determines whether the base will remain unprotonated and able to act as a base in that solvent. If the solvent is represented this time as HS then the relevant equilibrium is:

$$B + HS \rightleftharpoons BH^+ + S^- \qquad (9.2.28)$$

The position of this equilibrium depends on whether B or S$^-$ is the stronger base. If the solvent's conjugate base, S$^-$, is stronger then the base will remain unprotonated and available to act as a base. However, if B is a stronger base than S$^-$ it will deprotonate the solvent to give BH$^+$ and S$^-$. In this way the strongest base that can exist in a given solvent is the solvent's conjugate base. The relative strength of Brønsted bases can only be determined in solvents that are more weakly acidic than BH^+; otherwise the bases will all be leveled to S^-.

It is important to consider the levelling effect of protic solvents when performing syntheses that require the use of basic reagents. For instance, hydride and carbanion reagents (Lithium aluminum hydride, Grignard reagents, alklyllithium reagents, etc.) cannot be used as nucleophiles in protic solvents like water, alcohols, or enolizable aldehydes and ketones. Since carbanions are stronger bases than these solvent's conjugate bases they will instead act as Brønsted bases and deprotonate the solvent. For example if one adds n-butyllithium to water the result (along with much heat and possibly a fire) butane and a solution of lithium hydroxide will be obtained:

$$Li^+ + {}^-:CH_2CH_2CH_2CH_3 + H_2O(l) \rightarrow Li^+(aq) + OH^-(aq) + CH_3CH_2CH_2CH_3(g) \qquad (9.2.29)$$
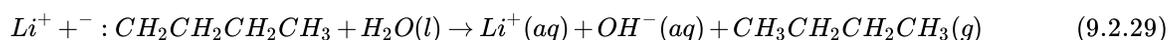
Since hydride and carbanion reagents cannot be used as nucleophiles in protic solvents like water or methanol they are commonly sold as solutions in solvents such as hexanes (for alklyllithium reagents) or tetrahydrofuran (for Grignard reagents and $LiAlH_4$).

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2. (a) Gutmann, V. *Allg. Prakt. Chem.* 1970, *21,* 116. (b) Gutmann, V. *Fortschr. Chem. Forsch.* 1972, *27*, 59.
3. Burgess, J. *Metal Ions in Solution* Ellis Horwood, 1978, pg. 268.

Contributors and Attributions

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who expanded this section from a combination of

https://chem.libretexts.org/Courses/University_of_Arkansas_Little_Rock/Chem_1403%3A_General_Chemistry_2/Text/16%3A_Acids_and_Bases/16.6%3A_Molecular_Structure%2C_Bonding%2C_and_Acid-Base_Behavior

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9.3: Lewis Concept and Frontier Orbitals

Lewis Acids and Bases

The Lewis acid base concept generalizes the Brønsted and solvent system acid base concepts by describing acid-base reactions in terms of the donation and acceptance of an electron pair. Under the Lewis definition Lewis acids are electron pair acceptors and Lewis bases are electron pair donors. In Lewis acid-base reactions a Lewis base donates an electron pair to the Lewis acid, which accepts it. The reaction between borane, BH_3, and NH_3 is the classic example:
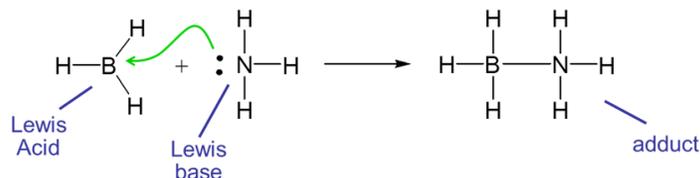
> **Definition: Lewis acid**
>
> A species that is an electron pair acceptor

> **Definition: Lewis base**
>
> A species that is an electron pair donor

In this case the Lewis acid-base reaction results in the formation of a bond between BH_3, and NH_3 . When the acid and base combine to form a larger unit that unit is said to be an adduct and the resulting bond is said to be a coordinate covalent or dative bond. Such coordinate covalent bonds are sometimes represented by an arrow that indicates the direction of electron donation from the base to the acid. For instance the reaction between BH_3, and NH_3 could also have been written as
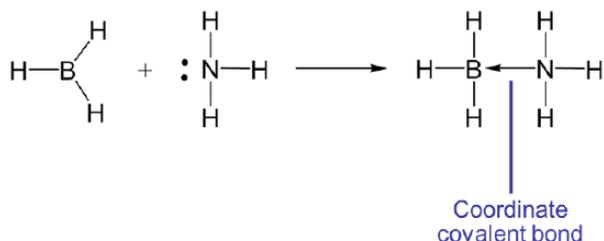
The arrow notation for the coordinate covalent bond is really just a convenient formalism - a bookkeeping tool to help keep track of where the electrons came from and where they might return if the reverse reaction occurs.

For example, in Brønsted acid base reactions the hydrogen ion is an acid because it accepts an electron pair from the Brønsted base. Consequently under the Lewis acid-base concept in Brønsted acid base reactions involve the formation of an adduct between H^+ and a base.
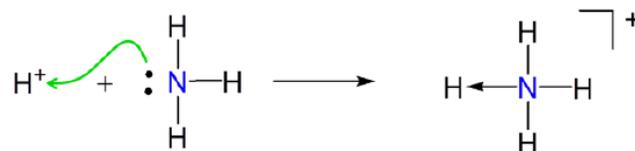
$$(9.3.1)$$

The Lewis acid base concept nicely explains ionization reactions involving nonaqueous solvents. For instance, the autoionization of $SOCl_2$ as an acid-base reaction between two $SOCl_2$ molecules.
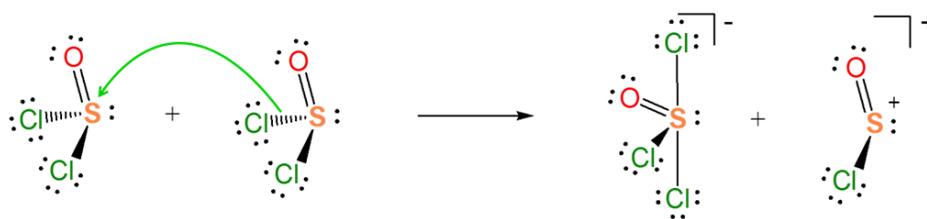
$$(9.3.2)$$

Example 9.3.1

Explain how the autoionization of SOCl$_2$ is a Lewis acid-base displacement reaction.

Solution

In the autoionization of SOCl$_2$ the pair of electrons donated comes from the S-Cl bond and the S-Cl bond is broken to give a lone pair bearing Cl$^-$ base and a SOCl$^+$ Lewis acid fragment. If you are having trouble seeing how this works it can be instructive to consider the reverse of this process. It is a Lewis acid-base reaction to give a Lewis acid-base adduct:
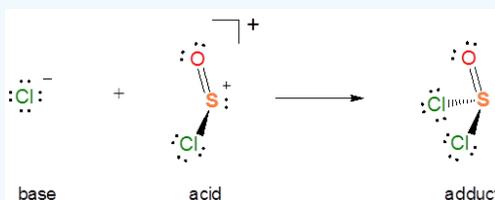
From the autoionization reaction it is also apparent that $SOCl_2$ itself acts as a Lewis acid towards the liberated Cl^-. So the autoionization reaction involves a transfer of the base Cl^- base between the two Lewis acids - a Lewis acid-base displacement reaction.
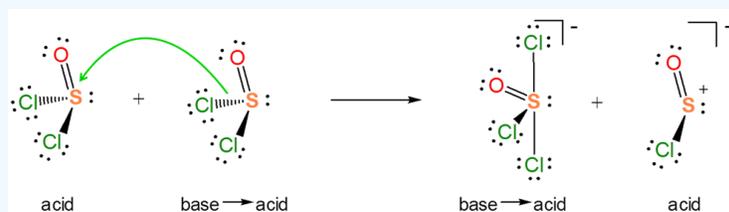
Lewis acid-base model and chemical reactions

It can be helpful to keep several distinctions in mind when using the Lewis acid-base concept to describe chemical reactions.

1. Many Lewis-Acid base reactions are displacement reactions. This is because the hydrogen ion is usually bound to something at the start of the reaction. In such cases the Lewis acid H^+ unit is transferred from one Lewis base and another. Such acid-base reactions are sometimes called displacement reactions since the base group in the initial Lewis acid-base complex is displaced by the incoming Lewis base to generate another complex.
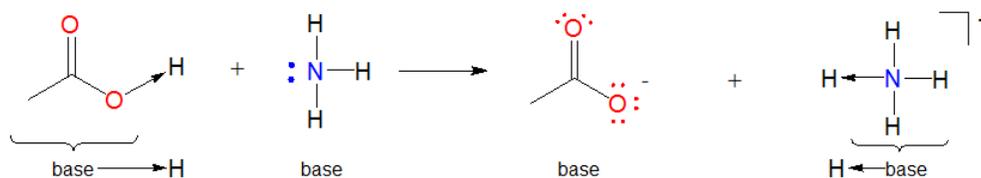
$$(9.3.3)$$

2. Substances are sometimes considered amphoteric because they exhibit Lewis acidity and basicity at different types of atomic centers. The classic example is aluminum hydroxide, $Al(OH)_3$. In water $Al(OH)_3$ can act as a Lewis acid towards OH$^-$ ion. The reaction occurs by formation of an adduct at $Al(OH)_3$'s Al^{3+} center:

$$Al(OH)_3 + OH^- \rightarrow Al(OH)_4^- \tag{9.3.4}$$

Notice that in addition to acting as a Lewis acid, in this reaction $Al(OH)_3$

- does not act as a Brønsted acid or base since no H$^+$ ion transfer occurs
- but does act as an Arhennius acid since OH$^-$ ion is consumed from solution, decreasing [OH$^-$] and increasing [H$^+$]

In water $Al(OH)_3$ also acts as a Lewis base towards H$^+$ through the lone pairs on its hydroxide ligands.

$$Al(OH)_3 + 3H^+ + 3H_2O \rightarrow Al(H_2O)_6^{3+} \tag{9.3.5}$$
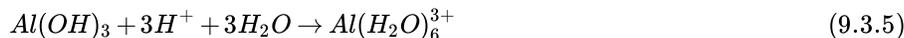
Notice that in addition to acting as a Lewis base, in this reaction $Al(OH)_3$ also acts as a

- Brønsted base since a H$^+$ ion is transferred onto the OH$^-$ ligand
- Arhennius base since H$^+$ ion is consumed from solution, decreasing [H$^+$]
- Lewis acid at its Al^{3+} center since Al-O metal-ligand bonds are formed

Frontier Orbitals

Another way the Lewis acid-base concept is widely employed for understanding chemical reactivity is through the frontier orbital approach to chemical reactions. The frontier orbital concept is a simplified version of molecular orbital theory where chemical bonding and reactivity are visualized in terms of the interactions between frontier molecular orbitals on the chemical species undergoing an interaction (*e.g.* molecules, atoms, ions, or groups as they interact to form a bond or undergo a reaction). Frontier orbitals are those at the frontier between occupied and unoccupied. They are often taken to be the <u>h</u>ighest energy <u>o</u>ccupied and <u>l</u>owest energy <u>u</u>noccupied molecular orbitals, called the HOMO and LUMO levels. However, it can sometimes be more convenient to think about them as atomic orbitals or Valence Bond approach-derived orbitals. When developing rough qualitative frontier orbital descriptions of the orbital interactions involved in a given system the choice of what types of orbitals to use is often a matter of what is the most informative and convenient.

In particular the frontier orbital concept envisions a Lewis acid-base interaction as involving an interaction between some of the frontier orbitals of the Lewis acid and base, specifically the donation of electrons from the bases' HOMO level into the acid's LUMO level. For example, in the frontier orbital approach adduct formation between NH_3 and BH_3 involves the donation of electrons from ammonia's HOMO into BH$_3$'s LUMO level.
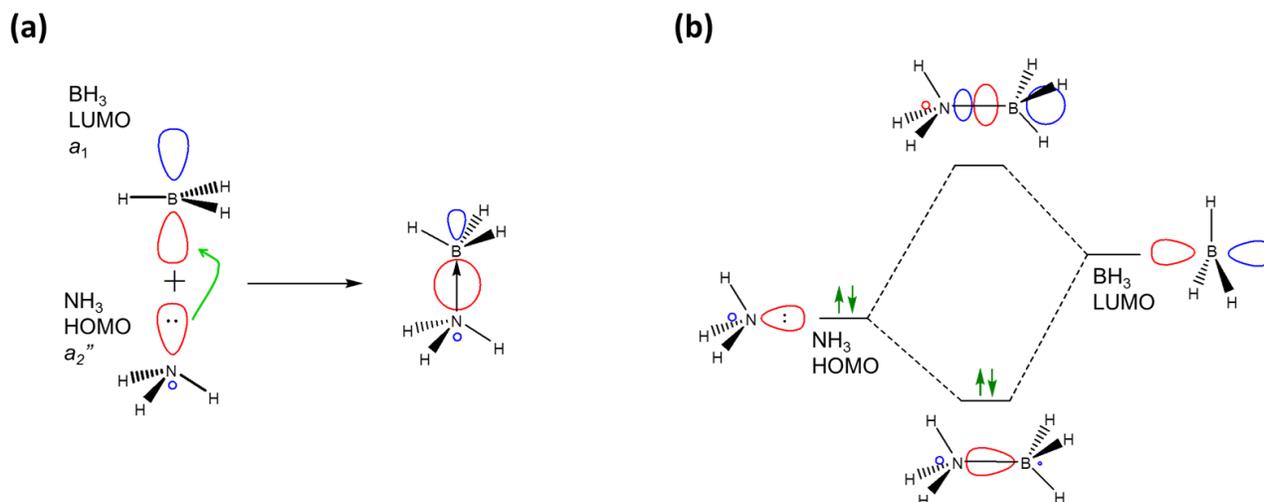
Figure 9.3.1: Frontier orbital picture of adduct formation between ammonia and borane. (a) As NH_3 and BH_3 approach one another interaction between the NH_3 HOMO (lone pair on N) and BH_3 LUMO (unoccupied, non-bonding 2p orbital) gives a bonding MO. (b) Partial molecular orbital diagram for $NH_3 \rightarrow BH_3$ showing the stabilization of the base (NH_3) lone pair in a sigma bonding MO on adduct formation.

As expected when two orbitals of the appropriate symmetry combine, the result of the interaction is the formation of a lower energy bonding orbital between the acid and base (Figure 9.3.1). Since it is occupied by an electron the net result of the interaction is the lowering of the base's lone pair as it interacts with the Lewis acid. In this case the interaction just follows the general pattern for Lewis-Acid base adduct formation, which is shown in Figure 9.3.2.
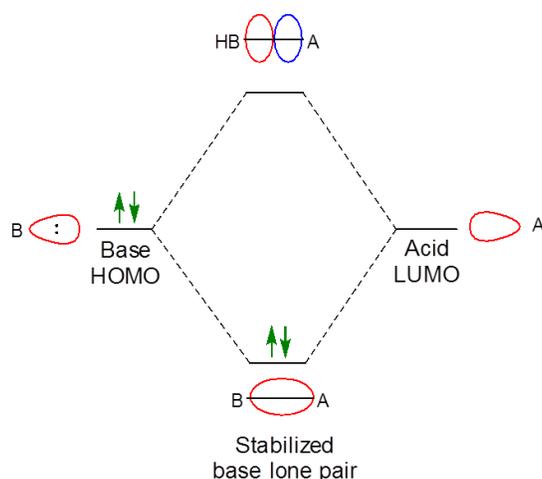
Figure 9.3.2: Generalized frontier orbital picture for adduct formation between a Lewis base (B) and a Lewis acid (A) involving stabilization of the lone pair of the base HOMO by formation of a bonding orbital with the acid LUMO. The relative energies of the acid LUMO and base HOMO affect the character of the bonding and antibonding MOs but are otherwise unimportant in determining the general features of the interaction. In some cases the base HOMO is higher in energy; in others the acid LUMO is higher in energy; in still others they are equal in energy. In any case the net result is the stabilization of the base lone pair.

The frontier orbital concept illuminates the orbital interactions involved in reactions. For instance, from a frontier orbital perspective the alkyl halide substitution reaction between hydroxide and CH_3Cl via the S_N2 mechanism involves a Lewis acid-base interaction:
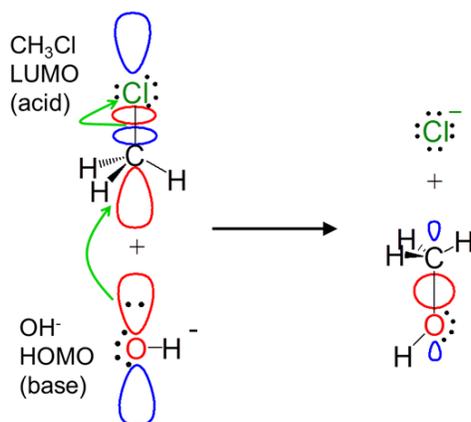
Notice how the frontier orbital approach even explains the displacement of the chloride leaving group. The donation of electrons from the hydroxide HOMO populates the antibonding CH_3Cl LUMO, breaking the C-Cl bond.

Using the frontier orbital approach it becomes apparent that pericyclic reactions are Lewis acid-base reactions. For example, in the Diels-Alder reaction the dienophile acts as a Lewis base and the diene as a Lewis acid.
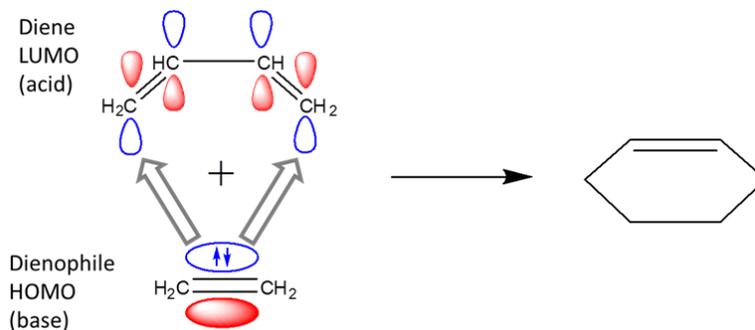
The orbital interactions involved in a given reaction can include both reactants acting as both an acid and base. In these cases the HOMO of each reactant interacts with the LUMO of the other. A good example of this involves Π-type interactions between a metal ion with occupied d orbitals and a pi-acceptor ligand. The ligand acts as a base and the metal as an acid to give a M-CO single bond.

Metal LUMO (d_{z^2})
acts as an acid

Carbon monoxide
HOMO
acts as a base
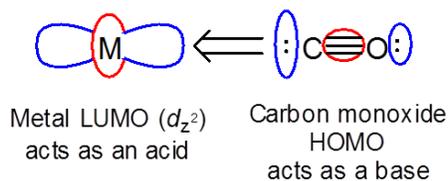
However, the metal can also act as a base towards the ligand LUMO (π^*) orbitals. Bonding between metals and ligands will be discussed further in chapter 9

Metal HOMO (d_{xz}, d_{xz})
acts as a base

Carbon monoxide
LUMO (π^*)
acts as an acid
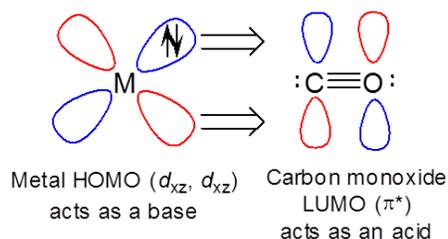
Substituent Effects

The electrons donated from a Lewis base to a Lewis acid in a Lewis acid-base reaction are donated and accepted at particular atomic centers. For instance, the formation of an adduct between ammonia and BF_3 involves the donation of the lone pair on the ammonia nitrogen atom to the Lewis acid site on BF_3.
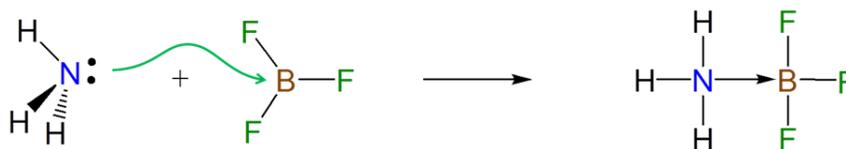
Because Lewis acid-base reactions involve electron donation and acceptance at particular sites subsistent groups which alter the electron density at a site through inductively donating or withdrawing electron density will affect the Lewis acid-base properties of that site. For instance, the BF_3 affinities of 4-substituted pyridines increase slightly as the substituent on the aromatic ring is changed from electron donating Me to electron withdrawing CF_3.

BF_3 Affinity (kJ/mol)[a]
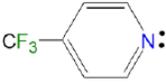
115.7 ± 0.4
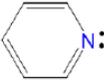
128.1 ± 0.5
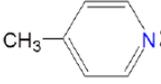
134.1 ± 0.6

a) Data from Laurence, C.; Gal, J.-F. o., *Lewis basicity and Affinity Scales: Data and Measurement.* John Wiley: Chichester, West Sussex, U.K., 2010; pp. 91-101.

Substituent inductive effects are much as one might predict. Since Lewis bases donate electron pairs and Lewis acids accept them:

- electron withdrawing substituents tend to decrease the Lewis basicity of basic sites while electron donating substituents increase site Lewis basicity by making them more electron rich.
- electron withdrawing substituents increase the Lewis acidity of acidic sites by making those sites more electron deficient while electron donating substituents tend decrease Lewis acidity by making sites less electron deficient.

Nevertheless it can be difficult to predict substituent-based trends in Lewis acidity and basicity by inductive effects alone. This is because inductive effects are modest and often exists in competition with other substituent effects, such as

- Steric effects
- Hardness effects
- π-donation and acceptance effects, which can increase or decrease electron density at a given site as well as create an energy barrier for any structural distortions that might occur on adduct formation.

π Donation and Acceptance and Lewis Acid-Base Affinity

As with σ-based induction effects π-donation tends to increase Lewis basicity and decrease Lewis acditiy while π-withdrawal tends to decrease Lewis basicity and increase Lewis acidity. However, care needs to be taken in assessing the effect of π-donation effects on Lewis acidity and basicity. For example, some textbooks claim that the Lewis acidity of boron trihalides is dominated by the reduction of boron acidity through π-donation from the halide substituents:
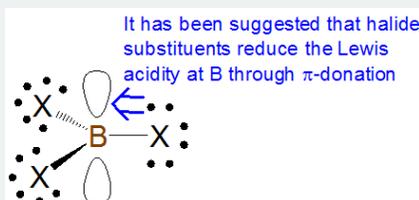
According to this explanation the extent of this π-donation decreases down the halogen group as the boron-halogen bond distance decreases. This is consistent with the observed trend in Lewis acidity of the boron trihalides towards most bases, which runs counter to that suggested by inductive effects alone:

$$BI_3 > BBr_3 > BCl_3 >> BF_3$$

However, computation work suggests that this explanation is incorrect since

- atomic size effects are important mainly for substituents in which the connected atom is row 3+ or higher
- atomic size effects mainly involve changes in the extent of σ-overlap. In other words the larger halogens are less able to reduce the electron deficiency at the boron center through σ interactions while π-interactions play little or no role.
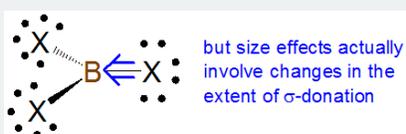
References:

1. Plumley, J. A.; Evanseck, J. D., Periodic Trends and Index of Boron Lewis Acidity. *The Journal of Physical Chemistry A* 2009, 113 (20), 5985-5992.
2. Jupp, A. R.; Johnstone, T. C.; Stephan, D. W., Improving the Global Electrophilicity Index (GEI) as a Measure of Lewis Acidity. *Inorganic Chemistry* 2018, 57 (23), 14764-14771.

Conjugate Bases of Brønsted Superacids

The nonreactivity of Brønsted superacids' conjugate bases towards hydrogen ions is often mirrored in nonreactivity towards other Lewis Acids/electrophiles, most notably metals. This makes these substances useful as inert or noncoordinating ions, although since all are reactive towards a suitably electrophilic centers they are perhaps better understood as weakly coordinating.

A number of noncoordinating anions are commonly used in synthetic and other applications. The conjugate base of perchloric acid, perchlorate, was a common noncoordinating inert anion in classical coordination chemistry and continues to be used

widely in electrochemistry. However metal perchlorate salts can be explosive, so synthesis of metal salts with perchlorate anions, especially on large scales is much less common in modern inorganic chemistry. In contrast, the conjugate bases of triflic acid, hexaflouroboric acid, and tetrafloroboric acid are now more commonly used as counterions for when isolating reactive cations.

triflate   hexaflourophosphate   tetraflouroborate
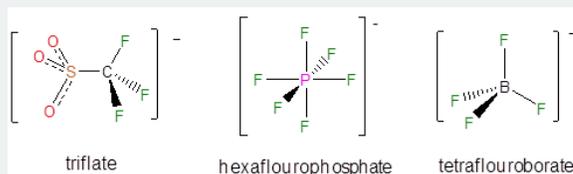
Even less reactive noncoordinating anions include derivatives of tetraphenylborate, particularly those with electron withdrawing substituents.

tetraphenylborate   perflourotetraphenylborate   tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BARF)
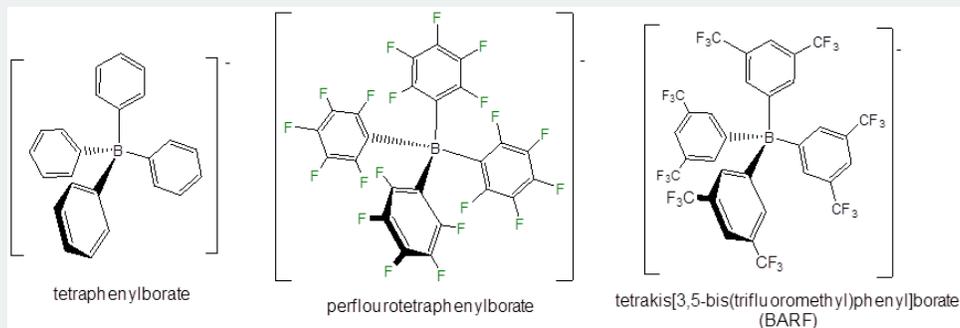
Other classes of noncoordinating ions include floroantimonate clusters, derivatives of the carborane anion ($CB_{11}H_{11}^{-}$), and flourinated aluminum tetraalkoxides.

References:

1. Engesser, T. A.; Lichtenthaler, M. R.; Schleep, M.; Krossing, I., Reactive p-block cations stabilized by weakly coordinating anions. *Chemical Society Reviews* **2016**, *45 (4)*, 789-899.

Lewis Acid-Base Adducts

When a Lewis acid-base adduct is formed electron density and negative charge is transferred from the Lewis base to the acid.

$$(9.3.6)$$

For example, the formation of an adduct between borane and ammonia involves the transfer of a small amount of electron density, as shown by the movement of negative charge from NH_3 to BH_3 depicted in Figure 9.3.3.
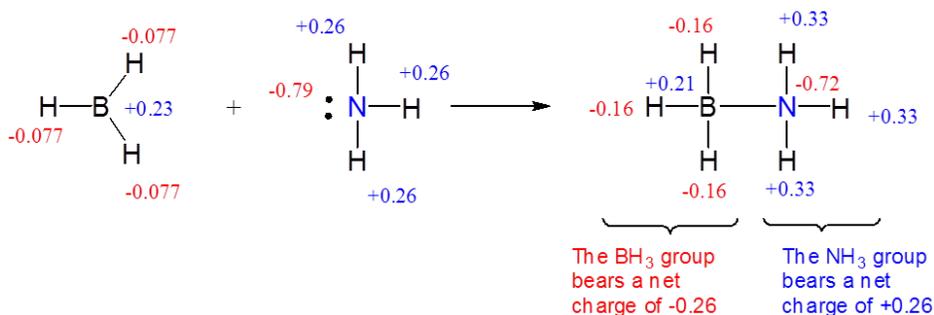
Figure 9.3.3: Calculated change in atomic charge distribution on formation of an adduct between BH_3 and NH_3 in the gas phase. All partial charges were calculated for geometry optimized molecules at the 6-31G** level.

In many weakly bound Lewis acid-base complexes the transfer of electron density and consequently, charge, from the base group to the acid group is only partial:

$$A + B \rightleftharpoons A^{\delta-}B^{\delta+} \tag{9.3.7}$$

Such Lewis acid-base adducts are commonly called **charge transfer complexes (CT complexes)** or **donor-acceptor complexes (DA complexes)**. In these

- the base is called the **donor (D)** since it is a net donor of electrons and, consequently, their negative charge
- the acid is called the **acceptor (A)** since it is a net acceptor of electrons and, consequently, their negative charge

A particularly well-known class of charge transfer complexes are the iodine charge transfer complexes. In iodine charge transfer complexes the I_2 acts as a Lewis acid. This is possible since iodine is a Row 3+ element and so is capable of forming hypervalent complexes on reaction with a Lewis base. For example, I_2 reacts with I^- to give the triiodide ion.

$$\tag{9.3.8}$$
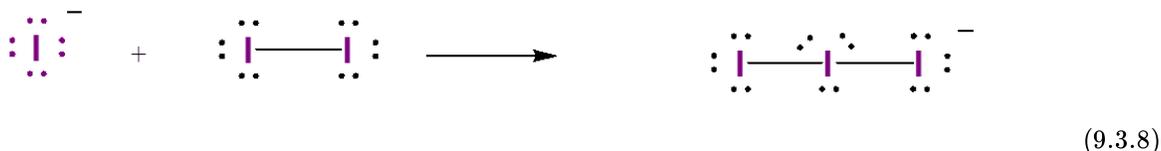
Triiodie is well-known from introductory chemistry from the bright blue color that appears when the triiodie is complexes with starch to give the dark blue starch-iodide complex.

In contrast to stable triiodide anion, iodine charge transfer complexes are only weakly associated. Complexes between iodine and amines are a well known example:

$$\tag{9.3.9}$$
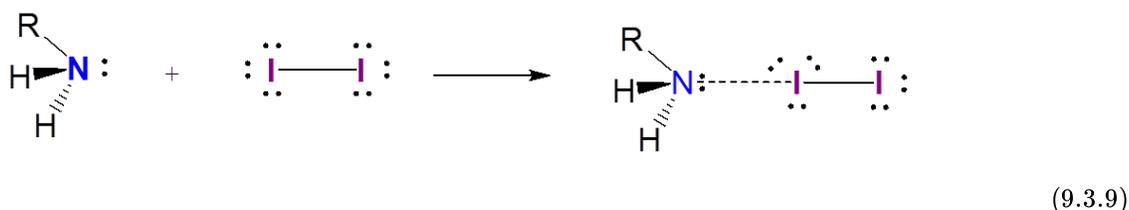
Iodine also forms weakly-associated charge transfer complexes with many solvents. For instance, iodine can weakly associate with both acetone and benzene:
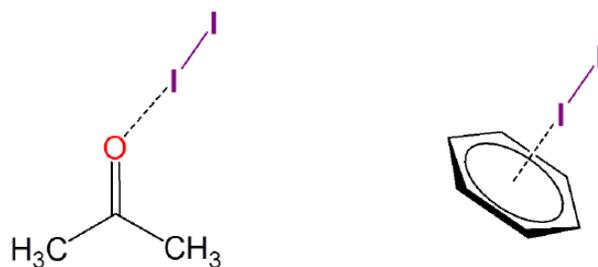
Steric Effects

Steric effects can influence the ability of a Lewis acid or base to form adducts by introducing:

- **front strain (F-strain)** whereby bulky groups make it difficult for the Lewis acid and Lewis base centers to approach and interact.
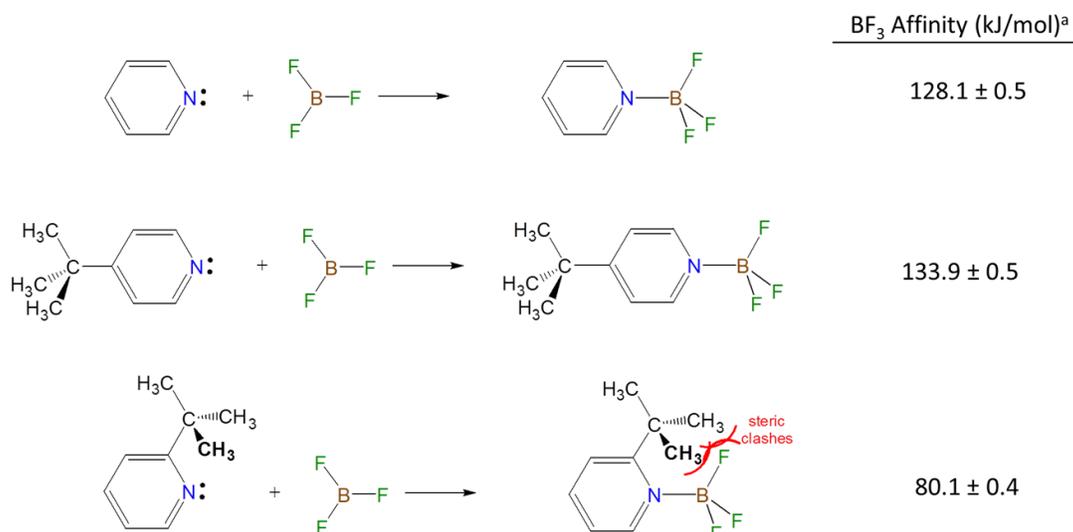
	BF$_3$ Affinity (kJ/mol)[a]
	128.1 ± 0.5
	133.9 ± 0.5
	80.1 ± 0.4

a) Data from Laurence, C.; Gal, J.-F. o., *Lewis basicity and Affinity Scales: Data and Measurement*. John Wiley: Chichester, West Sussex, U.K., 2010; pp. 91-101.

- **back strain (B-strain)** associated with steric interactions that do not directly impede the Lewis acid and base centers from interacting but instead occur as the acid and base rearrange on adduct formation. For instance, when trivalent boron compounds form adducts with amines the boron center changes from a more open trigonal pyramidal geometry to a more hindered tetrahedral one:
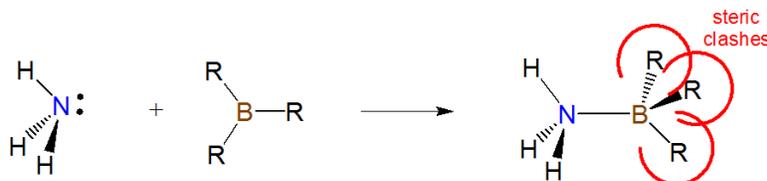
- **internal strain (I-strain)** is also associated with the geometry changes incident on adduct formation. However, while B-strain involves direct steric clashes that occur on adduct formation I-strain is the strain involved in deforming bond and torsional angles away from more stable local geometries. Thus it is more important for Lewis base centers embedded in rings or clusters.

References

1. Alder, R. W., Strain effects on amine basicities. *Chemical Reviews* 1989, 89 (5), 1215-1223.

Contributors and Attributions

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- **6.4.2: All other things being equal, electron withdrawing groups tend to make Lewis acids stronger and bases weaker while electron donating groups tend to make Lewis bases stronger and acids weaker** by Stephen M. Contakes has no license indicated.
- **6.4.3: The electronic spectra of charge transfer complexes illustrate the impact of frontier orbital interactions on the electronic structure of Lewis acid-base adducts** by Stephen M. Contakes is licensed CC BY-NC 4.0.
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9.4: Hard and Soft Acids and Bases

Origin of the Hard-Soft Acid-Base Principle

One of the strengths of the Lewis acid-base concept is the readiness with which it illuminates the role that covalent and electrostatic interactions in acid base behavior, specifically through its ability to explain chemical interactions in terms of frontier orbitals and the interactions between charged groups as electrons are donated from a base to an acid. However, simply acknowledging the presence of such interactions does little to illuminate the degree to which each mode of explanation best explains the bonding in a given system? To what extent is a given adduct better described as held together by covalent bonds as opposed to ionic ones - *e.g.* better described as a molecule rather than an ion pair? Moreover, does it even matter, given that the orbitals of quantum mechanics result from the combination of electrons' wavelike behavior with their electrostatic attraction to nuclei in either case? These questions and more are addressed by one of the most important conceptual tools in contemporary inorganic chemistry, the hard-soft acid-base principle.

The hard-soft acid-base (HSAB) principle stems from the recognition that some Lewis acids and bases seem to have a natural affinity for one another.* Consider the following:

- Some metals are commonly found in nature as salts of chloride or as oxide ores while others are found in combination with sulfur. Geochemists even use the Goldschmidtt classification scheme to classify the halide and oxide formers as lithophiles and the sulfide formers as chalcophiles.
- In living systems small highly charged metals ions like Fe^{3+} are usually found bound to N and O atoms while larger metals with lower charges such as Zn^{2+} are often found attached to at least one S atom. Similarly, metals prefer to bind to one coordination site over the other when forming complexes with ambidentate ligands. The most well-known instances involve complexes of cyanate and thiocyanate, which can coordinate metals through either the N or chalcogen atom. For instance, Cu^{2+} and Zn^{2+} form *N*-thiocyanato complexes in species like $[Cu(NCS)_2(py)_2]$ and $[Zn(NCS)_4]^{2-}$ while their larger cogeners Au^{3+} and Hg^{2+} preferentially forms *S*-thiocyanato complexes, giving speciles like $[Hg(SCN)_4]^{2-}$.

> **Ambidentate ligands**
>
> Ambidentate ligands possess multiple coordination sites through which a metal may bind. For instance, thiocyanate may coordinate metals (M) at either the S or N to give *S*-thiocyanato or *N*-thiocyanato complexes.
>
>
>
> S-thiocyanato   N-thiocyanato
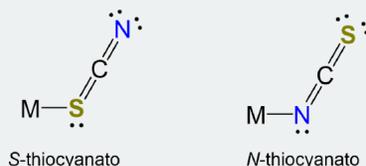
- The solubility trends for the alklai metal halides and silver halides are opposite, even though both involve salts of formula M^+X^- (salts can be thought of as involving Lewis acid-base adduct formation between the anions and cations). Specifically, although the silver halides are all relatively insoluble in water, the very modest solubility they possess follows the order:

$$X = F >> Cl > Br > I \text{ (for the solubility of AgX)}$$
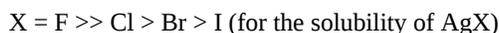
In contrast, the much more ample solubility of the alkali metal halides** follows the opposite order. For example, the order for the lithium halides is
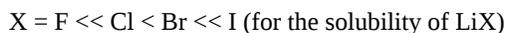
$$X = F << Cl < Br << I \text{ (for the solubility of LiX)}$$

Notes

* Despite the fruitfulness of this observation, in general it is important to reduce the potential for observer bias by checking observations like these against compounds reported in the chemical literature and databases like the Inorganic Crystal Structure and Cambridge Crystallographic Databases.

** These are very soluble in water, to the point where some solutions are perhaps better described as solutions of water in the halide.

Qualitative HSAB Principle

The hard-soft acid-base principle is a conceptual tool for thinking about patterns of Lewis acid base reactivity. The explanation of the trends in metal distribution, halide salt solubility, and preferred metal coordination patterns is rooted in Arland, Chatt, and Davies' observation that *Lewis acids and bases could be classified into two groups based on their propensity to form stable compounds with one another* (*e.g.* acids in a class tend to form more stable adducts with bases in the same class than they did with bases in the other).[1] Arland, Chatt, and Davies somewhat boringly termed these groups class a and class b but today they are known by Ralph Pearson's name for them. Pearson called the class a acids and bases hard and class b acids and bases soft. These terms reflect how "soft" these substance's electron clouds are towards distortion or, in other words, their polarizability (Figure 9.4.1). Pearson terms acids and bases which are relatively polarizable **soft** and those which are difficult to polarize **hard.**
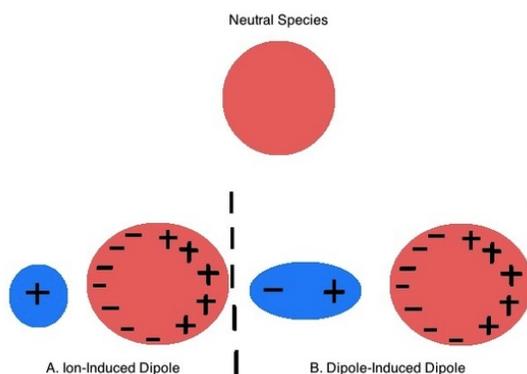
Figure 9.4.1: Polarizability refers to the ease with which a substance's electron cloud may be distorted under the action of an electric field. An fragment's polarizability determines the degree to which its electron cloud is distorted by A.) an Ion and B.) a polar molecule to induce a dipole moment. The figure is taken from (and the caption expanded from) Cox, Kelly and Dana Reusser "Polarizability" in https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Physical_Properties_of_Matter/Atomic_and_Molecular_Properties/Intermolecular_Forces/Specific_Interactions/Polarizability

Recognizing Hard and Soft Acids and Bases

Hard acids and bases come in two varieties:

1. hard acid and base sites which possess few valence electrons and for which polarization therefore involves distorting core electrons, which are difficult to distort because they are close to the nucleus and experience a high nuclear charge. The most common examples of such substances are Lewis acids hard acids towards the left of the periodic table.
2. hard acids and base sites with a high charge density (highly charged relative to size) and/or which are electron deficient. In these cases polarization involves distorting electrons that already experience strong unshielded electrostatic interactions.

Soft acids and bases also come in two varieties

1. soft acids and bases which posses many valence electrons and so are more readily polarized. In consequence, all other tings being equal, soft acids and bases are more likely to be found towards the middle or right of the periodic table.
2. soft acids and bases with little charge density and/or which are relatively electron rich.

Note that the hard-soft classification should not be thought of as if all hard acids and bases are equally hard and all soft acids and bases equally soft. There is a graduation in hardness and softness and a number of intermediate acids and bases which do not fit neatly in either category. With this caveat in mind, representative **hard, soft, and borderline acids** are given below. Notice how they illustrate the trends just outlined.

Selected Hard Acids (Class a)

H^+

Be^{2+}

Na^+ Mg^{2+}

K^+ Ca^{2+} Sc^{3+} Ti^{4+} Cr^{3+} Fe^{3+} Co^{3+}

Zr^{4+} Mo^{3+}

Ce^{3+} U^{4+}

BF_3 $C^{IV}O_2$ $N^VO_2^+$ $S^{VI}O_3$

Al^{3+}

AlF_3

AlH_3

Tl^{3+} Sn^{4+}

Selected Borderline Acids

BR_3

$S^{IV}O_2$

Fe^{2+} Co^{2+} Ni^{2+} Cu^{2+} Zn^{2+}

Pb^{2+}

Selected Soft Acids (Class b)

BH_3 $Cl^{I/II}R_n$ (Electron poor atomatics) HO^+

Cu^+ RS^+

$C^{II}R_2$ (Fischer Carbene) RSe^+

Pd^{2+} Ag^+ Cd^{2+}

Pt^{2+} Au^+ Hg_2^{2+} Tl^+

Hg^{2+}

Br^+ & Br_2

I^+ & I_2

As expected, hard acids tend to be found towards the left side of the periodic table and involve higher oxidation states and/or electron donating substituents while soft acids are more common to the right of the periodic table and involve lower oxidation states and/or electron donating substituents.

Illustrative hard, soft, and borderline bases are given below. Again, notice how these substances illustrate the general trends.

Selected Hard Bases (Class a)

Nitrogen bases	Oxygen bases		small halides
NH_2^-	OH^-	CO_3^{2-}	F^-
NH_3	H_2O	RCO_2^-	Cl^-
RNH_2	ROH	NO_3^-	
NH_2NH_2	ROR	PO_4^{3-}	
		SO_4^{2-}	

Selected Borderline Bases

electron-poor Nitrogen bases		low oxidation state element oxyanions	intermediate halides
N_3^-	N (pyridine)		
NO_2^-		NO_2^-	
SCN^-	NH_2 (aniline)	SO_3^{2-}	Br^-
N_2			

Selected Soft Bases (Class b)

Carbon bases	P and As bases	Sulfur bases	large halides & pseudohalides
R^-	PR_3	RS^-	H^-
CO	$P(OR)_3$	RSH	I^-
CN^-	AsR_3	RSR	
RNC		SCN^-	
$R_2C=CR_2$ (alkenes)			

(electron-rich aromatics)

Qualitative Estimation of the Relative Hardness and Softness of Lewis Acids and Bases

As can be seen from the examples above, **hard acids are relatively electron-poor and hard bases electron-rich** since they have comparatively

- small frontier orbitals, reflective of their relatively small atom/ion/fragment sizes
- high (for acids) or low (for bases) oxidation states on the base atom, reflected in a large positive formal charge (for acids) or negative formal charge (for bases)
- low polarizability, due to loss or gain of substantial numbers of electrons, or the localization of
  - positive charge on an electropositive element or an atom bearing electron-withdrawing substituents
  - negative charge on an electronegative element or an atom bearing electron-donating substituents

In contrast to hard acids and bases **soft acids are relatively electron-rich and soft bases larger and more electron poor** since they have comparatively

- large frontier orbitals, reflective of their relatively large atom/ion/fragment sizes
- low oxidation states, often resulting in small or nonexistent atomic charges
- high polarizability, as might be expected of species in which electron-electron repulsions are lower and electrons are spread over a large volume. Sometimes this is indicated by
  - positive charge on an electronegative element or an atom bearing electron-donating substituents
  - negative charge on an electropositive element or an atom bearing electron-withdrawing substituents

Exercise 9.4.1

Rank the acid or bases in each set in increasing order of expected hardness?

(a) Cr^{2+} and Cr^{3+}

(b) H^+, Cs^+, and Tl^+

(c) SCN^- (acting as a base at N) and SCN^- (acting as a base at S)

(d) AlF_3, AlH_3, $AlMe_3$

(e) The side chains of the following proteinogenic amino acids

Serine, Ser or S   cysteine, Cys or C   selenocysteine, Sec or U
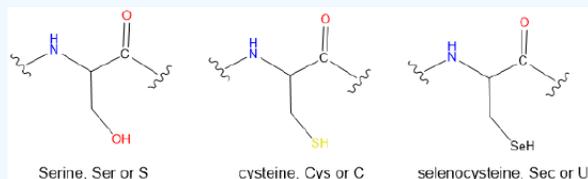
Answer

(a) $Cr^{2+} < Cr^{3+}$ All other things being equal, hardness increases with oxidation state.

(b) $Tl^+ < Cs^+ < H^+$ The order reflects Cs^+ and Tl^+'s larger size relative to H^+ (which doesn't possess any electrons that can be polarized anyway) and that Tl^+ still possesses two valence electrons while Cs^+ possesses none.

(c) SCN^- (acting as a base at S) < SCN^- (acting as a base at N) The order reflects that N is more elctronegative than S and possesses a more negative formal charge of -1.

(d) $AlH_3 < AlMe_3$, AlF_3 The hardness increases as the substituents on the Lewis acid Al center become less electron donating and more electron withdrawing (and, incidentally, harder bases) as their electronegativity increases in the order $H^- < CH_3^- < F^-$. Note that the order of electron donating ability for H^- and CH_3^- is the opposite observed for carbocations, for which hyperconjugation plays a larger role.

(e) Sec < Cys < Ser The hardness increases as the electronegativity of the Lewis base chalcogen increases on going from a selenol to a thiol to an alcohol.

Applications of HSAB Principle

The Hard-Soft acid-base principle (HSAB Principle) explains patterns in Lewis acid-base reactivity in terms of a *like reacts with like preference*. Both thermodynamically and kinetically hard acids prefer hard bases and soft acids soft bases. Specifically,

- Thermodynamically, hard acids form stronger acid-base complexes with hard bases while soft acids form stronger complexes with soft bases.
- Kinetically, hard acids/electrophiles react more quickly with hard bases/nucleophiles while soft acids/electrophiles react more quickly with soft bases/neucleophiles

Applications of the HSAB principle include

1. Predicting the equilibrium or speed of *Lewis acid-base metathesis and displacement reactions*. In a Lewis acid-base *metathesis reaction* the acids and bases swap partners

$$A_1{:}B_1 + A_2{:}B_2 \xrightleftharpoons{k_1,\ K_{eq}} A_1B_2 + A_2{:}B_1$$
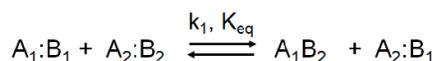
(9.4.1)

For example, the equilibrium position of the metathesis reaction between TlF and K_2S favors the products:

$$2TlF + K_2S \rightleftharpoons Tl_2S + 2KF$$

$$(9.4.2)$$

consistent with the HSAB's hard-hard and soft-soft preference.

$$2\ Tl^+\ F^-\ + (K^+)_2\,S^{2-} \longrightarrow (Tl^+)_2\ S^{2-}\ +\ 2\,K^+F^-$$

soft hard   hard soft   soft soft   hard hard

$$(9.4.3)$$
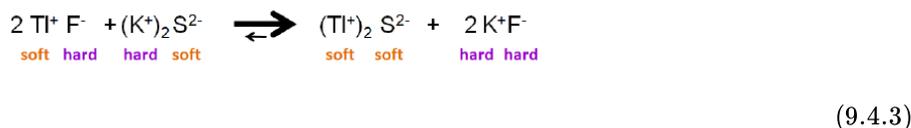
The HSAB principle also allows for prediction of the position of displacement reactions, in which a Lewis acid or base forms an adduct using a base or acid from an existing Lewis acid-base complex. In these reactions, the displacement of acid or base from the reactant complex to may be thought of as a sort of metathesis reaction, one in which in the unbound acid or base switches places with one in the complex. For example, the reaction between HI and methylmercury cation

$$HI + HgSCH_3{}^+ \rightleftharpoons CH_3SHgI + H^+$$

$$(9.4.4)$$

involves displacement of an iodide from HI to give CH_3HgI. The position of the equilibrium favors CH_3HgI since both CH_3Hg^+ and I^- are both soft, while H^+ is a hard acid.

$$H\text{-}I +\ CH_3Hg^+ \longrightarrow CH_3Hg\text{-}I\ +\ H^+$$

hard-soft   soft   soft -soft   hard

$$(9.4.5)$$
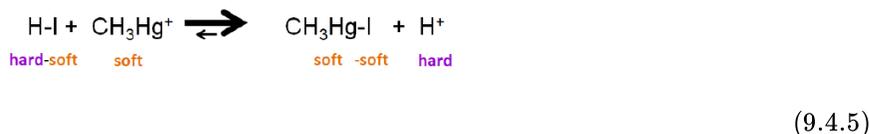
Exercise 9.4.2

Predict the position of equilibrium for the following reaction.

$$Fe_2O_3 + 3Ag_2S \rightleftharpoons Fe_2S_3 + 3Ag_2O$$

Answer

The equilibrium will favor the reactants (K<1) since the hard-hard and soft-soft interactions in the reactants are more stable than the hard-soft interactions in the products.

$$(Fe^{3+})_2\,(O^{2-})_3 +\ 3\,(Ag^+)_2S^{2-} \longrightarrow (Fe^{3+})_2\,(S^{2-})_3 +\ 3\,(Ag^+)_2O^{2-}$$

hard   hard   soft soft   hard   soft   soft hard

Exercise 9.4.3

Predict whether K for the following equilibria will be <<1, ~1, or >>1.

a. $2HF + (CH_3Hg)_2S \rightleftharpoons 2CH_3HgF + H_2S$

b. $Ag(NH_3)_2^+ + 2PH_3 \rightleftharpoons Ag(PH_3)_2^+ + 2NH_3$

c. $Ag(PH_3)_2^+ + 2H_3B-SH_2 \rightleftharpoons 2H_3B-PH_3 + Ag(SH_2)_2^+$

d. $H_3B-NH_3 + F_3B-SH_2 \rightleftharpoons H_3B-SH_2 + F_3B-NH_3$

Answer

a. K< < 1 since the reactant adducts are hard-hard and soft-soft while the products involve hard-soft interactions

b. K>>1 since the reactant complex, diamine silver(I) is a complex of a hard base, NH_3, with the soft acid, Ag^+, while the product is a complex of the same soft acid with the soft base phosphine.

c. K~1 since all the adducts amongst the reactants and products involve soft acids and bases

d. K>>1 since BH_3 is a softer acid than BF_3 so it will form a stronger complex with the softer base H_2S while the harder BF_3 forms a stronger complex with the harder base NH_3.

2. Predicting the relative strengths of a given set of *Lewis acids or bases towards a particular substrate*. Consider, for example, the relative strengths of a BH_3, BMe_3, and BF_3 towards group 15 hydrides like NH_3, PH_3, and AsH_3. Of the boranes listed, the hardest acid BF_3 is the strongest acid towards the hard base NH_3 while BH_3 is the strongest towards AsH_3.[†]

Exercise 9.4.4

Which acid will form the most stable complex with CO - BH_3, BF_3, or BMe_3?

Answer

BH_3. Since CO forms complexes primarily through its carbon lone pair it is a soft base and so will form the strongest complex with the softest Lewis acid.

Exercise 9.4.5

When lactones react with nucleophiles they can undergo ring opening reactions to give either an alcohol or carboxylic acid, as shown for propiolactone below:
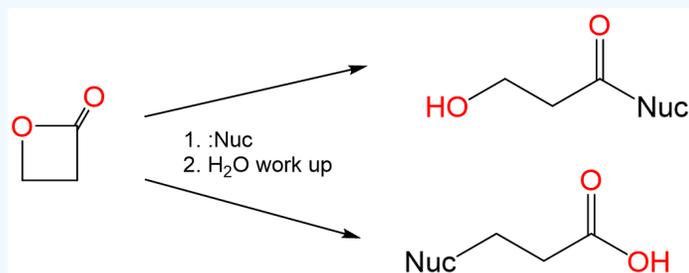
In the reaction above, sterically unhindered alkoxides give one product and sterically unhindered thioalkoxides the other. Explain why this is the case and predict the products of the reaction between propiolactone and the sodium salts of ethoxide and thioethoxide.

Answer

The two reaction products correspond to nucleophilic attack at the lactones two electrophilic carbon centers. Specifically, the acid is produced by attack at the softer C^I center of the CH_2 directly attached to the ester oxygen and the alcohol by nucleophilic attack at the harder C^{III} center of the ester carbonyl.
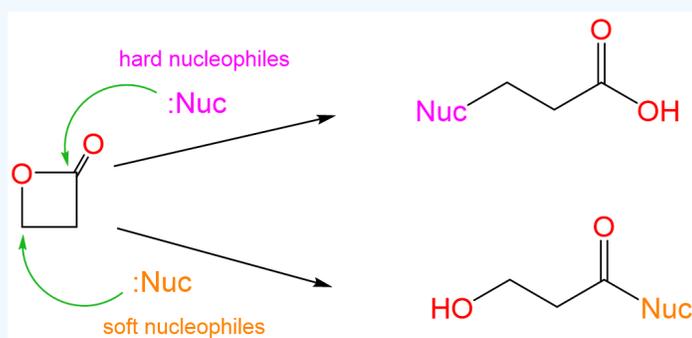
Consequently, it is reasonable to expect that the harder base ethoxide will nucleophilically attack the harder carbonyl carbon while the softer thioethoxide will attack the softer methylene carbon.
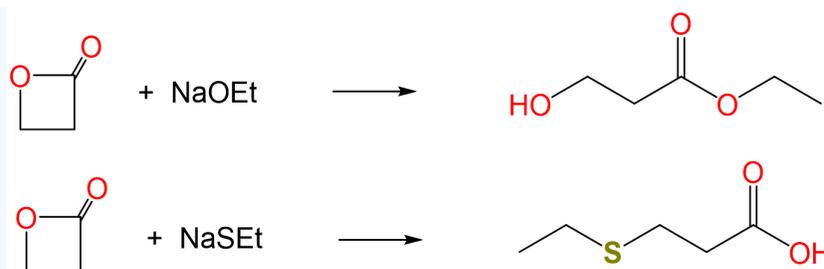
Theoretical Interpretation of the Hard Soft Acid-Base Principle

The Theoretical Interpretation of the Hard Soft Acid-Base Principle is that hard-hard preferences reflect superior electrostatic stabilization while soft-soft preferences reflect superior covalent stabilization. The hard-hard and soft-soft preferences in Lewis acid-base interactions reflect that

- The lone pair of a hard base is strongly stabilized electrostatically by a hard acid
- The lone pair of a soft base is strongly stabilized by forming a covalent bond with a soft acid
- The lone pair of a hard or soft base is comparatively weakly stabilized by an acid opposite to it in hardness or softness since the overall electrostatic and covalent stabilization of the adduct is comparatively weak.

To see why this is the case it is helpful to divide the contributions to the interaction energy between an acid and a base as follows:

$$
\begin{array}{ccc}
\text{Interaction Energy} = & \underbrace{\begin{array}{c}\text{Electrostatic attractions and repulsions of partial atomic charges}\end{array}}_{\text{Ionic term}} + & \underbrace{\begin{array}{c}\text{Interactions between filled orbitals on one fragment and unfilled orbitals on the other}\end{array}}_{\text{Covalent term}} + \underbrace{\begin{array}{c}\text{Electrostatic repulsions between filled orbitals on the two fragments}\end{array}}_{\text{Steric term}}
\end{array}
$$

$$(9.4.6)$$

Of the three contributions to the interaction energy, only the ionic and covalent terms directly relate to the hardness of the interacting acid and base. One approach to thinking about how hardness influences the ionic and covalent contributions is to consider the frontier orbitals involved in the acid-base interaction. This is sometimes done through the use of the Salem-Klopman equation,[1,*] although in the treatment which follows a more qualitative approach will be employed.

Both hard acids and bases will have comparatively low energy HOMO levels and high energy LUMO levels, with a correspondingly high HOMO-LUMO gap. In contrast, soft acids and bases will have comparatively high-energy HOMO levels and low-energy LUMO levels, giving a comparatively smaller HOMO-LUMO gap.
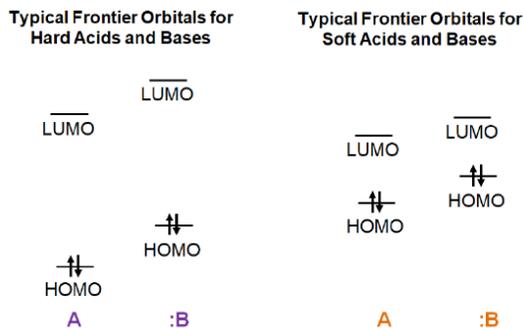
Given this, consider the frontier orbital interactions involved in the formation of an acid-base complex for the possible cases, as illustrated schematically below.

Hard-Hard Interactions are mainly electrostatic

There is little covalent stabilization of the base lone pair

LUMO

LUMO

HOMO

HOMO

A $^{δ+}$A-B$^{δ-}$:B

$δ+$ $δ-$ **strong**

⬇ weak

There is much electrostatic stabilization of the base lone pair by the highly charged acid center

Soft-Soft Interactions are mainly covalent

There is significant covalent stabilization of the base lone pair

LUMO

LUMO

HOMO

HOMO

A   A-B   :B

$δ+$ $δ-$ weak

strong

There is little electrostatic stabilization of the diffuse base lone pair by the electron rich acid center

The large gap in energy between hard bases' highly stabilized HOMO lone pairs and the high energy LUMO of hard acids ensures that in **hard acid-hard base adducts the dominant stabilizing interaction will involve electrostatic attraction between the base lone pair and the electropositive Lewis acid center**. Fortunately, since the electron clouds in hard bases are relatively dense and electron rich while hard Lewis acids are highly charged and small these electrostatic interactions are strong.

In contrast, in **soft acid-soft base adducts the dominant stabilizing interaction will be covalent.** This is because the small gap in energy between a soft base HOMO and soft acid LUMO enables the formation of a well-stabilized bonding orbital with significant electron density between the acid and base.

The orbitals interactions between hard acids and soft bases and soft acids and hard bases are intermediate between the hard acid-hard base and soft acid-soft base cases.

Hard-soft Interactions are stabilizing but involve mediocre covalent and electrostatic stabilization

Soft bases' electron pairs are more weakly stabilized covalently by orbital overlap with the high energy LUMO of hard acids

LUMO

LUMO

HOMO

HOMO

A $^{δ+}$A-B$^{δ-}$:B

$δ+$ $δ-$ mediocre

⬇ mediocre

The diffuse lone pair of soft bases is more weakly stabilized electrostatically by hard acids

Hard Bases' electron pairs are more weakly stabilized covalently by orbital overlap between the low lying base HOMO and acid LUMO

LUMO

LUMO

HOMO

HOMO

A $^{δ+}$A-B$^{δ-}$:B

$δ+$ $δ-$ mediocre

⬇ mediocre

Hard bases are more weakly stabilized electrostatically by electron rich soft acids

This means that the adducts are stable relative to free acid and base – just not as well stabilized as in the hard acid and hard base case. In the case of hard acids and soft bases the hard acids are less able to stabilize the soft bases' relatively diffuse electron pair electrostatically and there isn't as much covalent stabilization as in adducts of soft acids and bases due to hard acid's high energy.

Notes

* Despite the fruitfulness of this observation, in general it is important to reduce the potential for observer bias by checking observations like these against compounds reported in the chemical literature and databases like the Inorganic Crystal Structure and

Cambridge Crystallographic Databases.

** These are very soluble in water, to the point where some solutions are perhaps better described as solutions of water in the halide.

† This can be predicted based on the relative hardness of BF_3, BR_3, and BH_3 in the list of hard and soft acids. However, for those of you who may be confused as to why H is considered a better electron donor for the purposes of softening a Lewis acid center while alkyl groups are better electron donors for the purposes of stabilizing carbocations in organic chemistry, the dominant effect is the lower electronegativity of H relative to carbon (in CH_3). The effect of electron donation due to hyperconjugation isn't as great for thermodynamically stable bases like BX_3/BR_3.

†† For more on the Salem-Klopman equation see Fleming, I., Molecular orbitals and organic chemical reactions. Reference ed.; Wiley: Hoboken, N.J., 2010; pp. 138-143.

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1. Ahrland, S.; Chatt, J.; Davies, N. R., The relative affinities of ligand atoms for acceptor molecules and ions. Quarterly Reviews, Chemical Society 1958, 12 (3), 265-276.

2. Pearson, R. G., Hard and Soft Acids and Bases. Journal of the American Chemical Society 1963, 85 (22), 3533-3539.

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Contributors and Attributions

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9.5: Exercises

1. Explain why HF is a weaker acid than HCl despite fluorine being more electronegative than chlorine.

2. Rank the following bases in order of increasing basicity: NH_3, OH^-, CH_3O^-, F^-.

3. **:** Rank the following acids in order of increasing acidity: H_2O, HCl, HF, H_2S.

4. Explain why BF_3 is a Lewis acid but not a Bronsted-Lowry acid.

5. For the following compounds, identify the site that will act as the Lewis base: CH_3CN, CH_3OH, and CH_3NH_2.

6. Predict which molecule is the stronger Bronsted-Lowry acid: HNO_3 or HNO_2. Explain your choice.

7. Determine which compound is a stronger acid, phenol or cyclohexanol and explain why.

8. Rank the following anions in order of increasing basicity: NO_3^-, CH_3COO^-, OH^-, F^-. Provide an explanation based on their structures and resonance effects.

9. Rank the following ligands in order of increasing preference for binding to Pt^{2+}: NH_3, Cl^-, PPh_3, and CN^-.

10. Explain why Zn^{2+} can form stable complexes with both NH_3 and S^{2-}.

11. Explain why phosphine ligands (PR_3) form more stable complexes with gold (Au^+) compared to amine ligands (NR_3)

12. Explain the difference in reactivity between phenoxide ion ($C_6H_5O^-$) and methoxide ion (CH_3O^-) in nucleophilic substitution reactions with benzyl chloride ($C_6H_5CH_2Cl$). Use Lewis acid-base theory to support your explanation.

13. Predict the outcome of the reaction between borane (BH_3) and tetrahydrofuran (THF). Identify the Lewis acid and base and describe the nature of the bonding interaction.

14. Aniline has a $pK_b = 9.40$ and cyclohexylamine has a $pK_b = 3.30$. Explain these values using electronic and structural effects.
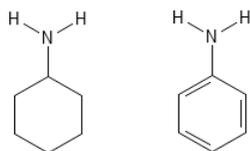
15. Rank the following aromatic amines based on their strength as Lewis bases. Explain your reasoning.
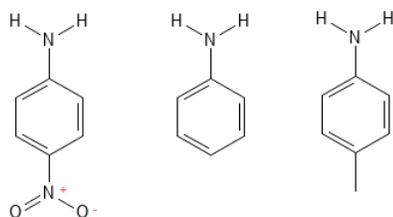
CHAPTER OVERVIEW

10: Reduction and Oxidation Chemistry

> **◧ Learning Objectives**
>
> - Balance a redox reaction in acidic or basic solution
> - Calculate the cell potential and free energy of an electrochemical cell under standard and non-standard conditions
> - Use Latimer diagrams to determine unknown reduction potential values and to quickly identify stable and unstable species
> - Use Frost diagrams to determine which oxidation states of a species are stable and which are unstable
> - Use Porbaix diagrams to determine which species will be present in solution under given conditions

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10.1: Review of Redox Chemistry

> ◑ **Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Describe defining traits of redox chemistry
> - Identify the oxidant and reductant of a redox reaction
> - Balance chemical equations for redox reactions using the half-reaction method

Since reactions involving electron transfer are essential to the topic of electrochemistry, a brief review of redox chemistry is provided here that summarizes and extends the content of an earlier text chapter (see chapter on reaction stoichiometry). Readers wishing additional review are referred to the text chapter on reaction stoichiometry.

Oxidation Numbers

By definition, a redox reaction is one that entails changes in *oxidation number* (or *oxidation state*) for one or more of the elements involved. The oxidation number of an element in a compound is essentially an assessment of how the electronic environment of its atoms is different in comparison to atoms of the pure element. By this description, *the oxidation number of an atom in an element is equal to zero*. For an atom in a compound, *the oxidation number is equal to the charge the atom would have in the compound if the compound were ionic*. Consequential to these rules, *the sum of oxidation numbers for all atoms in a molecule is equal to the charge on the molecule*. To illustrate this formalism, examples from the two compound classes, ionic and covalent, will be considered.

Simple ionic compounds present the simplest examples to illustrate this formalism, since by definition the elements' oxidation numbers are numerically equivalent to ionic charges. Sodium chloride, NaCl, is comprised of Na^+ cations and Cl^- anions, and so oxidation numbers for sodium and chlorine are, +1 and −1, respectively. Calcium fluoride, CaF_2, is comprised of Ca^{2+} cations and F^- anions, and so oxidation numbers for calcium and fluorine are, +2 and −1, respectively.

Covalent compounds require a more challenging use of the formalism. Water is a covalent compound whose molecules consist of two H atoms bonded separately to a central O atom via polar covalent O−H bonds. The shared electrons comprising an O−H bond are more strongly attracted to the more electronegative O atom, and so it acquires a partial negative charge in the water molecule (relative to an O atom in elemental oxygen). Consequently, H atoms in a water molecule exhibit partial positive charges compared to H atoms in elemental hydrogen. The sum of the partial negative and partial positive charges for each water molecule is zero, and the water molecule is neutral.

Imagine that the polarization of shared electrons within the O−H bonds of water were 100% complete—the result would be *transfer* of electrons from H to O, and water would be an ionic compound comprised of O^{2-} anions and H^+ cations. And so, the oxidations numbers for oxygen and hydrogen in water are −2 and +1, respectively. Applying this same logic to carbon tetrachloride, CCl_4, yields oxidation numbers of +4 for carbon and −1 for chlorine. In the nitrate ion, NO_3^-, the oxidation number for nitrogen is +5 and that for oxygen is −2, summing to equal the 1− charge on the molecule:

$$(1N \text{ atom}) \left(\frac{+5}{N \text{ atom}} \right) + (3O \text{ atoms}) \left(\frac{-2}{O \text{ atom}} \right) = +5 + -6 = -1$$

Balancing Redox Equations

The unbalanced equation below describes the decomposition of molten sodium chloride:

$$NaCl(l) \longrightarrow Na(l) + Cl_2(g) \hspace{3cm} \text{(unbalanced)}$$

This reaction satisfies the criterion for redox classification, since the oxidation number for Na is decreased from +1 to 0 (it undergoes *reduction*) and that for Cl is increased from −1 to 0 (it undergoes *oxidation*). The equation in this case is easily balanced by inspection, requiring stoichiometric coefficients of 2 for the NaCl and Na:

$$2\,NaCl(l) \longrightarrow 2\,Na(l) + Cl_2(g) \hspace{3cm} \text{(balanced)}$$

Redox reactions that take place in aqueous solutions are commonly encountered in electrochemistry, and many involve water or its characteristic ions, $H^+(aq)$ and $OH^-(aq)$, as reactants or products. In these cases, equations representing the redox reaction can be

very challenging to balance by inspection, and the use of a systematic approach called the *half-reaction method* is helpful.

📌 Balancing REDOX reactions via the half-reaction Method

This approach involves the following steps:

1. Write skeletal equations for the oxidation and reduction half-reactions.
2. Balance each half-reaction for all elements except H and O.
3. Balance each half-reaction for O by adding H_2O.
4. Balance each half-reaction for H by adding H^+.
5. Balance each half-reaction for charge by adding electrons.
6. If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.
7. Add the two half-reactions and simplify.
8. If the reaction takes place in a basic medium, add OH^- ions the equation obtained in step 7 to neutralize the H^+ ions (add in equal numbers to both sides of the equation) and simplify.

The examples below demonstrate the application of this method to balancing equations for aqueous redox reactions.

✔ Example 10.1.1: Balancing Equations for Redox Reactions in Acidic Solutions

Write the balanced equation representing reaction between solid copper and nitric acid to yield aqueous copper(II) ions and nitrogen monoxide gas.

Solution

Following the steps of the half-reaction method:

Step 1: Write skeletal equations for the oxidation and reduction half-reactions.

$$\text{oxidation:} \quad Cu(s) \longrightarrow Cu^{2+}(aq)$$
$$\text{reduction:} \quad HNO_3(aq) \longrightarrow NO(g)$$

Step 2: Balance each half-reaction for all elements except H and O.

$$\text{oxidation:} \quad Cu(s) \longrightarrow Cu^{2+}(aq)$$
$$\text{reduction:} \quad HNO_3(aq) \longrightarrow NO(g)$$

Step 3: Balance each half-reaction for O by adding H_2O.

$$\text{oxidation:} \quad Cu(s) \longrightarrow Cu^{2+}(aq)$$
$$\text{reduction:} \quad HNO_3(aq) \longrightarrow NO(g) + \mathbf{2\,H_2O(l)}$$

Step 4: Balance each half-reaction for H by adding H^+.

$$\text{oxidation:} \quad Cu(s) \longrightarrow Cu^{2+}(aq)$$
$$\text{reduction:} \quad \mathbf{3\,H^+(aq)} + HNO_3(aq) \longrightarrow NO(g) + 2\,H_2O(l)$$

Step 5: Balance each half-reaction for charge by adding electrons.

$$\text{oxidation:} \quad Cu(s) \longrightarrow Cu^{2+}(aq) + \mathbf{2\,e^-}$$
$$\text{reduction:} \quad \mathbf{3\,e^-} + 3\,H^+(aq) + HNO_3(aq) \longrightarrow NO(g) + 2\,H_2O(l)$$

Step 6: If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.

$$\text{oxidation } (\times 3): \quad \mathbf{3}\,Cu(s) \longrightarrow \mathbf{3}\,Cu^{2+}(aq) + \mathbf{6}\;\cancel{2}e^-$$
$$\text{reduction } (\times 2): \quad \mathbf{6}\;\cancel{3}e^- + \mathbf{6}\;\cancel{3}H^+(aq) + \mathbf{2}\,HNO_3(aq) \longrightarrow \mathbf{2}\,NO(g) + \mathbf{4}\;\cancel{2}H_2O(l)$$

Step 7: Add the two half-reactions and simplify.

$$3\,\mathrm{Cu(s)} + \cancel{6\,\mathrm{e^-}} + 6\,\mathrm{H^+(aq)} + 2\,\mathrm{HNO_3(aq)} \longrightarrow 3\,\mathrm{Cu^{2+}(aq)} + \cancel{6\,\mathrm{e^-}} + 2\,\mathrm{NO(g)} + 4\,\mathrm{H_2O(l)}$$

$$3\,\mathrm{Cu(s)} + 6\,\mathrm{H^+(aq)} + 2\,\mathrm{HNO_3(aq)} \longrightarrow 3\,\mathrm{Cu^{2+}(aq)} + 2\,\mathrm{NO(g)} + 4\,\mathrm{H_2O(l)}$$
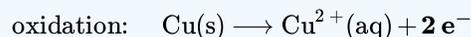
Step 8: If the reaction takes place in a basic medium, add $\mathrm{OH^-}$ ions the equation obtained in step 7 to neutralize the $\mathrm{H^+}$ ions (add in equal numbers to both sides of the equation) and simplify.

This step not necessary since the solution is stipulated to be acidic.

The balanced equation for the reaction in an acidic solution is then

$$3\,\mathrm{Cu(s)} + 6\,\mathrm{H^+(aq)} + 2\,\mathrm{HNO_3(aq)} \longrightarrow 3\,\mathrm{Cu^{2+}(aq)} + 2\,\mathrm{NO(g)} + 4\,\mathrm{H_2O(l)}$$
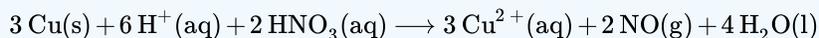
? Exercise 10.1.1

The reaction above results when using relatively diluted nitric acid. If concentrated nitric acid is used, nitrogen dioxide is produced instead of nitrogen monoxide. Write a balanced equation for this reaction.

Answer

$$\mathrm{Cu(s)} + 2\,\mathrm{H^+(aq)} + 2\,\mathrm{HNO_3(aq)} \longrightarrow \mathrm{Cu^{2+}(aq)} + 2\,\mathrm{NO_2(g)} + 2\,\mathrm{H_2O(l)}$$
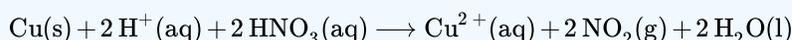
✔ Example 10.1.2: Balancing Equations for Redox Reactions in Basic Solutions

Write the balanced equation representing reaction between aqueous permanganate ion, , and solid chromium(III) hydroxide, $\mathrm{Cr(OH)_3}$, to yield solid manganese(IV) oxide, $\mathrm{MnO_2}$, and aqueous chromate ion, The reaction takes place in a basic solution.

Solution

Step 1: Write skeletal equations for the oxidation and reduction half-reactions.
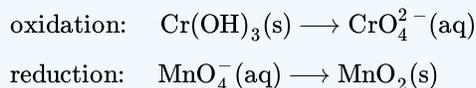
$$\text{oxidation:} \quad \mathrm{Cr(OH)_3(s)} \longrightarrow \mathrm{CrO_4^{2-}(aq)}$$
$$\text{reduction:} \quad \mathrm{MnO_4^-(aq)} \longrightarrow \mathrm{MnO_2(s)}$$

Step 2: Balance each half-reaction for all elements except H and O.

$$\text{oxidation:} \quad \mathrm{Cr(OH)_3(s)} \longrightarrow \mathrm{CrO_4^{2-}(aq)}$$
$$\text{reduction:} \quad \mathrm{MnO_4^-(aq)} \longrightarrow \mathrm{MnO_2(s)}$$

Step 3: Balance each half-reaction for O by adding $\mathrm{H_2O}$.

$$\text{oxidation:} \quad \mathbf{H_2O(l)} + \mathrm{Cr(OH)_3(s)} \longrightarrow \mathrm{CrO_4^{2-}(aq)}$$
$$\text{reduction:} \quad \mathrm{MnO_4^-(aq)} \longrightarrow \mathrm{MnO_2(s)} + \mathbf{2\,H_2O(l)}$$

Step 4: Balance each half-reaction for H by adding $\mathrm{H^+}$.

$$\text{oxidation:} \quad \mathrm{H_2O(l)} + \mathrm{Cr(OH)_3(s)} \longrightarrow \mathrm{CrO_4^{2-}(aq)} + \mathbf{5\,H^+(aq)}$$
$$\text{reduction:} \quad \mathbf{4\,H^+(aq)} + \mathrm{MnO_4^-(aq)} \longrightarrow \mathrm{MnO_2(s)} + 2\,\mathrm{H_2O(l)}$$

Step 5: Balance each half-reaction for charge by adding electrons.

$$\text{oxidation:} \quad \mathrm{H_2O(l)} + \mathrm{Cr(OH)_3(s)} \longrightarrow \mathrm{CrO_4^{2-}(aq)} + 5\,\mathrm{H^+(aq)} + \mathbf{3\,e^-}$$
$$\text{reduction:} \quad \mathbf{3\,e^-} + 4\,\mathrm{H^+(aq)} + \mathrm{MnO_4^-(aq)} \longrightarrow \mathrm{MnO_2(s)} + 2\,\mathrm{H_2O(l)}$$
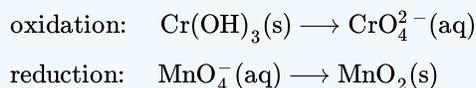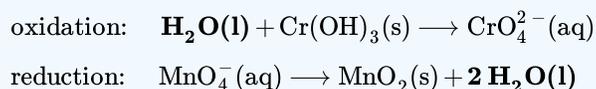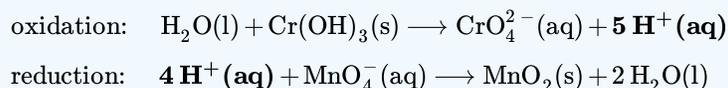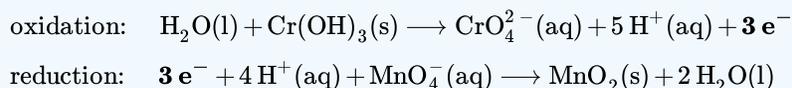
Step 6: If necessary, multiply one or both half-reactions so that the number of electrons consumed in one is equal to the number produced in the other.

This step is not necessary since the number of electrons is already in balance.

Step 7: Add the two half-reactions and simplify.
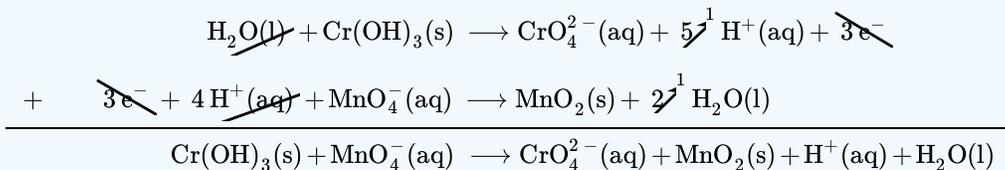
$$H_2O(l) + Cr(OH)_3(s) \longrightarrow CrO_4^{2-}(aq) + 5\overset{1}{\cancel{7}} \, H^+(aq) + \cancel{3e^-}$$

$$+ \quad \cancel{3e^-} + 4\,H^+(aq) + MnO_4^-(aq) \longrightarrow MnO_2(s) + \overset{1}{\cancel{2}} \, H_2O(l)$$

$$\overline{Cr(OH)_3(s) + MnO_4^-(aq) \longrightarrow CrO_4^{2-}(aq) + MnO_2(s) + H^+(aq) + H_2O(l)}$$

Step 8: If the reaction takes place in a basic medium, add OH^- ions the equation obtained in step 7 to neutralize the H^+ ions (add in equal numbers to both sides of the equation) and simplify.

$$OH^-(aq) + Cr(OH)_3(s) + MnO_4^-(aq) \longrightarrow CrO_4^{2-}(aq) + MnO_2(s) + \cancel{H^+(aq)} + H_2O(l) + \cancel{OH^-(aq)}$$
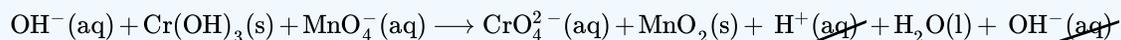
after neutralizing the H^+, we get the balanced equation for the reaction in a basic solution

$$OH^-(aq) + Cr(OH)_3(s) + MnO_4^-(aq) \longrightarrow CrO_4^{2-}(aq) + MnO_2(s) + 2\,H_2O(l)$$
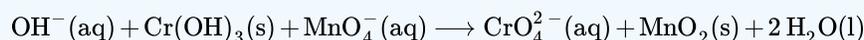
? Exercise 10.1.2

Aqueous permanganate ion may also be reduced using aqueous bromide ion, Br^-, the products of this reaction being solid manganese(IV) oxide and aqueous bromate ion, BrO_3^-. Write the balanced equation for this reaction occurring in a basic medium.

Answer

$$H_2O(l) + 2\,MnO_4^-(aq) + Br^-(aq) \longrightarrow 2\,MnO_2(s) + BrO_3^-(aq) + 2\,OH^-(aq)$$
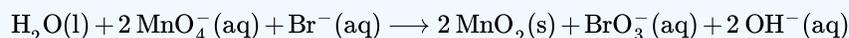
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10.2: Oxidation States of Transition Metals

The oxidation state of an element is related to the number of electrons that an atom loses, gains, or appears to use when joining with another atom in compounds. It also determines the ability of an atom to oxidize (to lose electrons) or to reduce (to gain electrons) other atoms or species. Almost all of the transition metals have multiple oxidation states experimentally observed.

Introduction

Filling atomic orbitals requires a set number of electrons. The s-block is composed of elements of Groups I and II, the alkali and alkaline earth metals (sodium and calcium belong to this block). Groups XIII through XVIII comprise of the p-block, which contains the nonmetals, halogens, and noble gases (carbon, nitrogen, oxygen, fluorine, and chlorine are common members). Transition metals reside in the d-block, between Groups III and XII. If the following table appears strange, or if the orientations are unclear, please review the section on atomic orbitals.

Table 10.2.1

s Orbital	p Orbitals	d Orbitals
1 orbital, 2 electrons	3 orbitals: p_x, p_y, p_z; 6 electrons	5 orbitals: $d_{x^2-y^2}$, d_{z^2}, d_{xy}, d_{yz}, d_{xz}; 10 electrons
	Highest energy orbital for a given quantum number n	Degenerate with s-orbital of quantum number n+1

The key thing to remember about electronic configuration is that the most stable noble gas configuration is ideal for any atom. Forming bonds are a way to approach that configuration. In particular, the transition metals form more lenient bonds with anions, cations, and neutral complexes in comparison to other elements. This is because the d orbital is rather diffused (the f orbital of the lanthanide and actinide series more so).

Neutral-Atom Electron Configurations

Counting through the periodic table is an easy way to determine which electrons exist in which orbitals. As mentioned before, by counting protons (atomic number), you can tell the number of electrons in a neutral atom. Organizing by block quickens this process. For example, if we were interested in determining the electronic organization of **Vanadium** (atomic number 23), we would start from hydrogen and make our way down the the the Periodic Table).

1s (H, He), 2s (Li, Be), 2p (B, C, N, O, F, Ne), 3s (Na, Mg), 3p (Al, Si, P, S, Cl, Ar), 4s (K, Ca), 3d (Sc, Ti, V).

If you do not feel confident about this counting system and how electron orbitals are filled, please see the section on electron configuration.

Figure 10.2.1: Periodic Table (Public Domain; PubChem)

Referring to the periodic table below confirms this organization. We have three elements in the 3d orbital. Therefore, we write in the order the orbitals were filled.

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

or
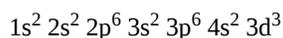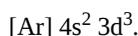
$$[Ar] \, 4s^2 \, 3d^3.$$

The neutral atom configurations of the fourth period transition metals are in Table 10.2.2

Table 10.2.2

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
[Ar] $4s^2 3d^1$	[Ar] $4s^2 3d^2$	[Ar] $4s^2 3d^3$	[Ar] ~~$4s^2 3d^4$~~	[Ar] $4s^2 3d^5$	[Ar] $4s^2 3d^6$	[Ar] $4s^2 3d^7$	[Ar] $4s^2 3d^8$	[Ar] ~~$4s^2 3d^9$~~	[Ar] $4s^2 3d^{10}$
			[Ar] $4s^1 3d^5$					[Ar] $4s^1 3d^{10}$	

Chromium and copper appear anomalous. Take a brief look at where the element **Chromium** (atomic number 24) lies on the Periodic Table (Figure 10.2.1). The electronic configuration for chromium is not [Ar] $4s^2 3d^4$ but instead it is [Ar] $4s^1 3d^5$. This is because the half-filled 3d manifold (with one 4s electron) is more stable than a partially filled d-manifold (and a filled 4s manifold). You will notice from Table 10.2.2 that the copper exhibits a similar phenomenon, although with a fully filled d-manifold.

Oxidation States of Transition Metal Ions

When considering ions, we add or subtract negative charges from an atom. Keeping the atomic orbitals when assigning oxidation numbers in mind helps in recognizing that transition metals pose a special case, but not an exception to this convenient method. An atom that accepts an electron to achieve a more stable configuration is assigned an oxidation number of -1. The donation of an electron is then +1. When a transition metal loses electrons, it tends to lose it's s orbital electrons before any of its d orbital electrons. For more discussion of these compounds form, see formation of coordination complexes.

> ✔ **Example 10.2.1**
>
> Write the electronic configurations of:
>
> a. neutral iron,
> b. iron(II) ion, and
> c. iron(III) ion.
>
> **Answer**
>
> The atomic number of iron is 26 so there are 26 protons in the species.
>
> a. Fe: $[Ar]\ 4s^2\ 3d^6$
> b. Fe^{2+}: $[Ar]\ 3d^6$
> c. Fe^{3+}: $[Ar]\ 3d^5$
>
> Note that the s-orbital electrons are lost **first**, then the d-orbital electrons.

> ✔ **Example 10.2.2**
>
> Determine the more stable configuration between the following pair:
>
> a. $[Kr]\ 5s^2\ 4d^6$ vs. $[Kr]\ 5s^1\ 4d^7$
> b. Ag^{1+} vs. Ag^{2+}
>
> **Answer**
>
> a. This describes Ruthenium. There is only one 5s electron.
> b. Once-oxidized silver ($[Kr]\ 4d^{10}$) is more stable than twice- ($[Kr]\ 4d^9$).

Multiple Oxidation States

Most transition metals have multiple oxidation states, since it is relatively easy to lose electron(s) for transition metals compared to the alkali metals and alkaline earth metals. Alkali metals have one electron in their valence s-orbital and their ions almost always have oxidation states of +1 (from losing a single electron). Similarly, alkaline earth metals have two electrons in their valences s-orbitals, resulting in ions with a +2 oxidation state (from losing both). However, transitions metals are more complex and exhibit a range of observable oxidation states due primarily to the removal of d-orbital electrons. The following chart describes the most common oxidation states of the period 3 elements.

Element Name and Symbol	Atomic Number	Common Oxidation States	Electron Configuration	
Scandium (Sc)	21	+3	Sc: [Ar] $4s^2 3d^1$	Sc: [Ar] ↑↓(4s) ↑ _ _ _ _ (3d)
Titanium (Ti)	22	+4	Ti: [Ar] $4s^2 3d^2$	Ti: [Ar] ↑↓(4s) ↑ ↑ _ _ _ (3d)
Vanadium (V)	23	+2, +3, +4, +5	V: [Ar] $4s^2 3d^3$	V: [Ar] ↑↓(4s) ↑ ↑ ↑ _ _ (3d)
Chromium (Cr)	24	+2, +3, +6	Cr: [Ar] $4s^1 3d^5$	Cr: [Ar] ↑(4s) ↑ ↑ ↑ ↑ ↑ (3d)
Manganese (Mn)	25	+2, +3, +4, +6, +7	Mn: [Ar] $4s^2 3d^5$	Mn: [Ar] ↑↓(4s) ↑ ↑ ↑ ↑ ↑ (3d)
Iron (Fe)	26	+2, +3	Fe: [Ar] $4s^2 3d^6$	Fe: [Ar] ↑↓(4s) ↑↓ ↑ ↑ ↑ ↑ (3d)
Cobalt (Co)	27	+2, +3	Co: [Ar] $4s^2 3d^7$	Co: [Ar] ↑↓(4s) ↑↓ ↑↓ ↑ ↑ ↑ (3d)
Nickel (Ni)	28	+2	Ni: [Ar] $4s^2 3d^8$	Ni: [Ar] ↑↓(4s) ↑↓ ↑↓ ↑↓ ↑ ↑ (3d)
Copper (Cu)	29	+1, +2	Cu: [Ar] $4s^1 3d^{10}$	Cu: [Ar] ↑(4s) ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ (3d)
Zinc (Zn)	30	+2	Zn: [Ar] $4s^2 3d^{10}$	Zn: [Ar] ↑↓(4s) ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ (3d)

Scandium is one of the two elements in the first transition metal period which has only one oxidation state (zinc is the other, with an oxidation state of +2). All the other elements have at least two different oxidation states. Manganese, which is in the middle of the period, has the highest number of oxidation states, and indeed the highest oxidation state in the whole period since it has five unpaired electrons (see table below).

To help remember the stability of higher oxidation states for transition metals it is important to know the trend: the stability of the higher oxidation states progressively increases down a group. For example, in group 6, (chromium) Cr is most stable at a +3 oxidation state, meaning that you will not find many stable forms of Cr in the +4 and +5 oxidation states. By contrast, there are many stable forms of molybdenum (Mo) and tungsten (W) at +4 and +5 oxidation states.

✔ Example 10.2.3

What makes zinc stable as Zn^{2+}? What makes scandium stable as Sc^{3+}?

Answer

Zinc has the neutral configuration $[Ar]4s^2 3d^{10}$. Losing 2 electrons does not alter the complete d orbital. Neutral scandium is written as $[Ar]4s^2 3d^1$. Losing 3 electrons brings the configuration to the noble state with valence $3p^6$.

✔ Example 10.2.4

Why is iron almost always Fe^{2+} or Fe^{3+}?

Answer

Iron is written as $[Ar]4s^2 3d^6$. Losing 2 electrons from the s-orbital ($3d^6$) or 2 s- and 1 d-orbital ($3d^5$) electron are fairly stable oxidation states.

> ### ✔ Example 10.2.5
>
> Write manganese oxides in a few different oxidation states. Which ones are possible and/or reasonable?
>
> **Answer**
>
> Although Mn^{+2} is the most stable ion for manganese, the d-orbital can be made to remove 0 to 7 electrons. Compounds of manganese therefore range from Mn(0) as $Mn_{(s)}$, Mn(II) as MnO, Mn(II,III) as Mn_3O_4, Mn(IV) as MnO_2, or manganese dioxide, Mn(VII) in the permanganate ion MnO_4^-, and so on.

Oxidation State of Transition Metals in Compounds

When given an ionic compound such as $AgCl$, you can easily determine the oxidation state of the transition metal. In this case, you would be asked to determine the oxidation state of silver (Ag). Since we know that chlorine (Cl) is in the halogen group of the periodic table, we then know that it has a charge of -1, or simply Cl^-. In addition, by seeing that there is no overall charge for $AgCl$, (which is determined by looking at the top right of the compound, i.e., $AgCl^{\#}$, where # represents the overall charge of the compound) we can conclude that silver (Ag) has an oxidation state of +1. This gives us Ag^+ and Cl^-, in which the positive and negative charge cancels each other out, resulting with an overall neutral charge; therefore +1 is verified as the oxidation state of silver (Ag).

> ### ✔ Example 10.2.6
>
> Determine the oxidation state of cobalt in $CoBr_2$.
>
> **Answer**
>
> Similar to chlorine, bromine (Br) is also a halogen with an oxidation charge of -1 (Br^-). Since there are two bromines each with a charge of -1. In addition, we know that $CoBr_2$ has an overall neutral charge, therefore we can conclude that the cation (cobalt), Co must have an oxidation state of +2 to neutralize the -2 charge from the two bromine anions.

> ### ✔ Example 10.2.7
>
> What is the oxidation state of zinc in $ZnCO_3$. (Note: the CO_3 anion has a charge state of -2)
>
> **Answer**
>
> Knowing that CO_3 has a charge of -2 and knowing that the overall charge of this compound is neutral, we can conclude that zinc has an oxidation state of +2. This gives us Zn^{2+} and CO_3^{-2}, in which the positive and negative charges from zinc and carbonate will cancel with each other, resulting in an overall neutral charge expected of a compound.

Polyatomic Transition Metal Ions

Consider the manganese (Mn) atom in the permanganate (MnO_4^-) ion. Since oxygen has an oxidation state of -2 and we know there are four oxygen atoms. In addition, this compound has an overall charge of -1; therefore the overall charge is not neutral in this example. Thus, since the oxygen atoms in the ion contribute a total oxidation state of -8, and since the overall charge of the ion is -1, the sole manganese atom must have an oxidation state of +7. This gives us Mn^{7+} and $4\,O^{2-}$, which will result as MnO_4^-.

> *This example also shows that manganese atoms can have an oxidation state of +7, which is the highest possible oxidation state for the fourth period transition metals.*

> ### 📌 Manganese: A Case Study
>
> Manganese is widely studied because it is an important reducing agent in chemical analysis and is also studied in biochemistry for catalysis and in metallurgy in fortifying alloys. In plants, manganese is required in trace amounts; stronger doses begin to react with enzymes and inhibit some cellular function. Due to manganese's flexibility in accepting many oxidation states, it becomes a good example to describe general trends and concepts behind electron configurations.

Figure 10.2.2: (left) A rough fragment of lustrous silvery metal (CC BY-SA 3.0; Tomihahndorf via Wikipedia) (right) Some of the Lascaux cave paintings use manganese-based pigments. (Public Domain; Prof saxx via Wikipedia)

Electron configurations of unpaired electrons are said to be **paramagnetic** and respond to the proximity of magnets. Fully paired electrons are **diamagnetic** and do not feel this influence. Manganese, in particular, has paramagnetic and diamagnetic orientations depending on what its oxidation state is.

Mn_2O_3 is manganese(III) oxide with manganese in the +3 state. 4 unpaired electrons means this complex is paramagnetic.

$$[Ar]4s^0 3d^4$$
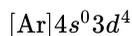
MnO_2 is manganese(IV) oxide, where manganese is in the +4 state. 3 unpaired electrons means this complex is less paramagnetic than Mn^{3+}.

$$[Ar]4s^0 3d^3$$
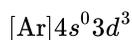
$KMnO_4$ is potassium permanganate, where manganese is in the +7 state with no electrons in the 4s and 3d orbitals.

$$[Ar]4s^0 3d^0$$
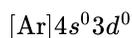
Since the 3p orbitals are all paired, this complex is diamagnetic.

Summary

Oxidation states of transition metals follow the general rules for most other ions, except for the fact that the d orbital is degenerated with the s orbital of the higher quantum number. Transition metals achieve stability by arranging their electrons accordingly and are oxidized, or they lose electrons to other atoms and ions. These resulting cations participate in the formation of coordination complexes or synthesis of other compounds.

Questions

Determine the oxidation states of the transition metals found in these neutral compounds. Note: The transition metal is underlined in the following compounds.

(A) Copper(I) Chloride: CuCl	(B) Copper(II) Nitrate: $Cu(NO_3)_2$	(C) Gold(V) Fluoride: AuF_5
(D) Iron(II) Oxide: FeO	(E) Iron(III) Oxide: Fe_2O_3	(F) Lead(II) Chloride: $PbCl_2$
(G) Lead(II) Nitrate: $Pb(NO_3)_2$	(H) Manganese(II) Chloride: $MnCl_2$	(I) Molybdenum trioxide: MoO_3
(J) Nickel(II) Hydroxide: $Ni(OH)_2$	(K) Platinum(IV) Chloride: $PtCl_4$	(L) Silver Sulfide: Ag_2S
(M) Tungsten(VI) Fluoride: WF_6	(N) Vanadium(III) Nitride: VN	(O) Zirconium Hydroxide: $Zr(OH)_4$

1. Determine the oxidation state of the transition metal for an overall non-neutral compound: Manganate (MnO_4^{2-})
2. Why do transition metals have a greater number of oxidation states than main group metals (i.e. alkali metals and alkaline earth metals)?
3. Which transition metal has the most number of oxidation states?
4. Why does the number of oxidation states for transition metals increase in the middle of the group?

5. What two transition metals have only one oxidation state?

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Contributors and Attributions

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10.3: Electrochemical Potentials

In electrochemical cells, or in redox reactions that happen in solution, the thermodynamic driving force can be measured as the **cell potential**. Chemical reactions are spontaneous in the direction of -ΔG, which is also the direction in which the cell potential (defined as $E_{cathode}$ - E_{anode}) is positive. A cell operating in the **spontaneous** direction (for example, a battery that is discharging) is called a **galvanic cell**. A cell that is being driven in the **non-spontaneous** direction is called an **electrolytic cell**. For example, let us consider the reaction of hydrogen and oxygen to make water:

$$2\,H_{2(g)} + O_{2(g)} = 2\,H_2O_{(l)} \tag{10.3.1}$$

Thermodynamically, this reaction is spontaneous in the direction shown and has an overall standard free energy change (ΔG°) of -237 kJ per mole of water produced.

When this reaction occurs electrochemically in the spontaneous direction (e.g., in a hydrogen-air fuel cell), the two half cell reactions that occur are:

Anode: $H_{2(g)} \longrightarrow 2\,H^{+}_{(aq)} + 2\,e^{-}$

Cathode: $O_{2(g)} + 4\,H^{+}_{(aq)} + 4\,e^{-} \longrightarrow 2\,H_2O_{(l)}$
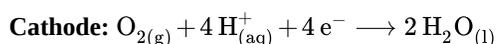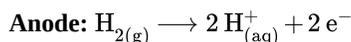
Here the anode is the negative electrode and the cathode is the positive electrode; under conditions of very low current density (where there are minimal resistive losses and kinetic overpotentials), the potential difference we would measure between the two electrodes would be 1.229 V.

In an **electrolytic cell**, this reaction is run in reverse. That is, we put in electrical energy to split water into hydrogen and oxygen molecules. In this case, the half reactions (and their standard potentials) reverse. O_2(g) bubbles form at the anode and H_2(g) is formed at the cathode. Now the **anode** is the **positive** electrode and the **cathode** is **negative**. Electrons are extracted from the substance at the anode (water) and pumped into the solution at the cathode to make hydrogen. An animation of the cathode half reaction is shown below.
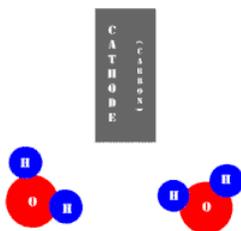
In both galvanic and electrolytic cells, **oxidation** occurs at the **anode** and **reduction** occurs at the **cathode**.

Half-cell potentials

As noted above, the equilibrium voltage of an electrochemical cell is proportional to the free energy change of the reaction. Because electrochemical reactions can be broken up into two half-reactions, it follows that the potentials of half reactions (like free energies) can be added and subtracted to give an overall value for the reaction. If we take the **standard hydrogen electrode** as our reference, i.e., if we assign it a value of zero volts, we can measure all the other half cells against it and thus obtain the voltage of each one. This allows us to rank redox couples according to their **standard reduction potentials** (or more simply their **standard potentials**), as shown in the table below.

Half Reaction					Standard Potential (V)
F_2	+	$2e^-$	$\rightleftharpoons$	$2F^-$	+2.87
Pb^{4+}	+	$2e^-$	$\rightleftharpoons$	Pb^{2+}	+1.67
Cl_2	+	$2e^-$	$\rightleftharpoons$	$2Cl^-$	+1.36
$O_2 + 4H^+$	+	$4e-$	$\rightleftharpoons$	$2H_2O$	+1.23
Ag^+	+	$1e^-$	$\rightleftharpoons$	Ag	+0.80
Fe^{3+}	+	$1e^-$	$\rightleftharpoons$	Fe^{2+}	+0.77
Cu^{2+}	+	$2e^-$	$\rightleftharpoons$	Cu	+0.34
$2H^+$	+	$2e^-$	$\rightleftharpoons$	H_2	0.00
Pb^{2+}	+	$2e^-$	$\rightleftharpoons$	Pb	-0.13
Fe^{2+}	+	$2e^-$	$\rightleftharpoons$	Fe	-0.44
Zn^{2+}	+	$2e^-$	$\rightleftharpoons$	Zn	-0.76
Al^{3+}	+	$3e^-$	$\rightleftharpoons$	Al	-1.66
Mg^{2+}	+	$2e^-$	$\rightleftharpoons$	Mg	-2.36
Li^+	+	$1e^-$	$\rightleftharpoons$	Li	-3.05

stronger oxidizing agent

stronger reducing agent

Note that when we construct an electrochemical cell and calculate the voltage, we simply take the difference between the half cell potentials and do not worry about the number of electrons in the reaction. For example, for the displacement reaction in which silver ions are reduced by copper metal, the reaction is:

$2\,Ag^+_{(aq)} + Cu_{(s)} = 2\,Ag_{(s)} + Cu^{2+}_{(aq)}$

The two half-cell reactions are:

$Ag^+_{(aq)} + e^- = Ag_{(s)} \quad +0.80V$

$Cu^{2+}_{(aq)} + 2e^- = Cu_{(s)} \quad +0.34V$
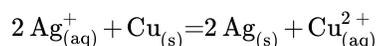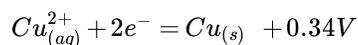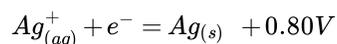
and the standard potential $E^o = +0.80 - 0.34V = +0.46V$

The reason we don't need to multiply the Ag potential by 2 is that E^o is a measure of the free energy change **per electron**. Dividing the free energy change by the number of electrons (see below) makes E^o an **intensive property** (like pressure, temperature, etc.).

Relationship between E and ΔG. For systems that are in equilibrium, $\Delta G^o = -nFE^o_{cell}$, where n is number of moles of electrons per mole of products and F is the Faraday constant, ~96485 C/mol. Here the ^{o} symbol indicates that the substances involved in the reaction are in their standard states. For example, for the water electrolysis reaction, the standard states would be pure liquid water, H$^+$ at 1M concentration (or more precisely, at unit activity), and O$_2$ and H$_2$(g) at 1 atmosphere pressure.

More generally (at any concentration or pressure), $\Delta G = -nFE$, where

$$E = E^o - \frac{RT}{nF} * lnQ \tag{10.3.2}$$

,

or at 298 K

$$E = E^o - \frac{0.0592}{n} * \log Q \tag{10.3.3}$$

where Q is the concentration ratio of products over reactants, raised to the powers of their coefficients in the reaction. **This equation (in either form) is called the Nernst equation.** The second term in the equation, when multiplied by -nF, is RT*lnQ. This is the free energy difference between ΔG and ΔG°. We can think of this as an entropic term that takes into account the positive entropy change of dilution, or the negative entropy change of concentrating a reactant or product, relative to its standard state.

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10.4: Latimer Diagrams

Latimer diagrams helpfully summarize elements' redox chemistry in a compact format.

Latimer diagrams helpfully summarize elements' redox chemistry in a compact format.To see how Latimer diagrams work and why they are so useful it is helpful to start with an example. A selection of the redox reactions nitrogen is known to undergo in 1.0 M aqueous acid are given in Scheme 10.4.1a.

> **Scheme 10.4.1.** (a) Full and (b) compact presentation of selected standard reduction half reactions for nitrogenous species in aqueous solution at pH 0.
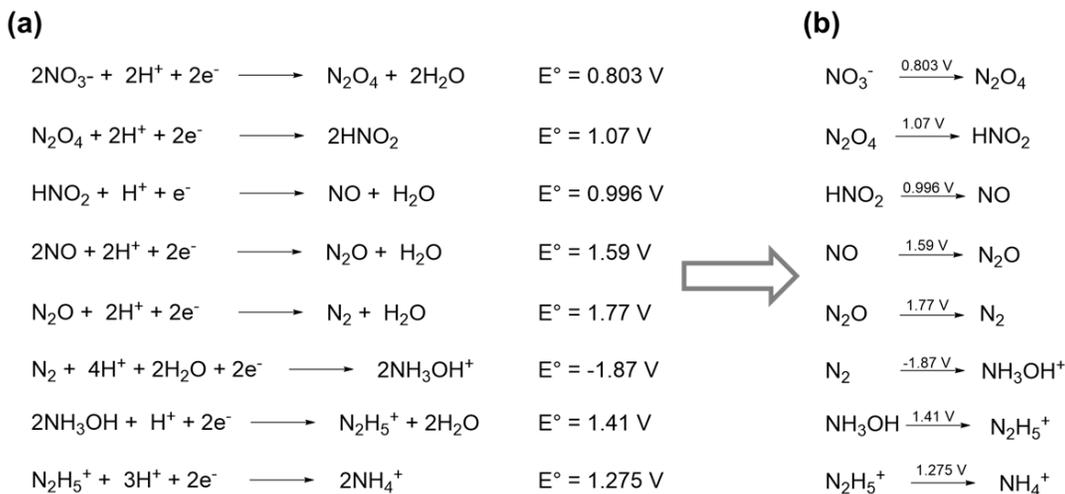
The most important information in Scheme 10.4.1a are the redox potentials and the identity of each nitrogen containing species. In fact, if the latter are known the number of electrons-, water molecules, and any H^+ (in acid) or OH^- (in base) involved in the reduction may be deduced by from the stoichiometry of the reaction. Consequently, the information in scheme 10.4.1a may be presented more compactly by only giving the nitrogen-containing species and by writing the associated redox potential for each reaction above its reaction arrow, as is shown in Scheme 10.4.1b Notice that in Scheme 10.4.1$b$the product of each half reaction is the reactant in the succeeding one. Because of this it is possible to represent the entire sequence of redox reactions even more compactly by writing out the reactions on a single line, as shown in Scheme 10.4.2

Scheme 10.4.2. Simplified acidic Latimer diagram for nitrogen.
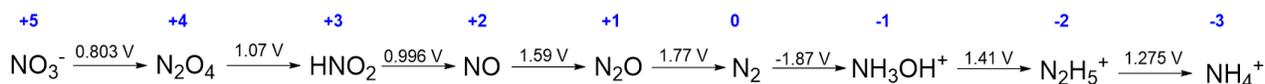
The type of diagram shown in Scheme 10.4.II is called a **Latimer diagram**.

When interpreting Latimer diagrams it can be helpful to look for two pieces of information.

1. Whether the diagram corresponds to acidic (pH 0), basic (pH 14), or other solution conditions should be specified. In cases where it is not it is customary to assume the diagram refers to behavior in pH 0 aqueous solution. As redox chemistry can be pH dependent, a Latimer diagram is only valid at the specified pH.
2. The element's oxidation state, which makes it easier to keep track of the number of electrons involved in each reduction and to compare the redox behavior of related species. Oxidation states are commonly written above each chemical species, as is done in blue in Scheme 10.4.2

When multiple pathways are available for interconverting two species in a Latimer diagram, these can be included by adding reaction arrows above and below the line. This is evident from the full pH 0 Latimer diagram for nitrogen given in Scheme 10.4.3

Scheme 10.4.3. Latimer diagram for nitrogen at pH 0. Redrawn from reference 1.
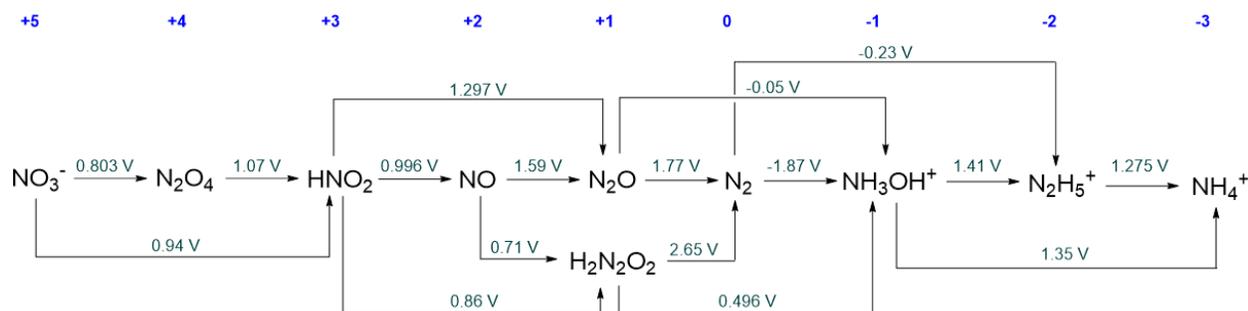
The diagram in Scheme $10.4.\text{III}$ presents a large number of possible interconversions. However, every possible interconversion is not represented. For example, the reduction potential for the reduction of N_2O_4 to NO is not presented. This type of selectivity is common in Latimer diagrams but it does not necessarily mean that the missing conversions are not possible or that the potential has not been measured experimentally. Since $\Delta G^\circ = -nFE^\circ$ the potentials in Latimer diagrams are thermodynamic quantities and may always be calculated from solution thermodynamic parameters. In fact, some redox potentials reported in Latimer diagrams have been only determined that way. An example is the reduction potential of flourine,

$$F_2(g) \ + \ 2H^+ \ 2e^- \ \rightarrow \ 2HF \ \ E^\circ \ = \ 3.053 \ V \ in \ acid \tag{10.4.1}$$

This potential has not been experimentally measured since F_2 is unstable in aqueous solution, reacting rapidly to give HF and O_2.

$$2\,F_2 \ + \ 2\,H_2O \ \xrightarrow{\text{fast}} \ 4\,HF \ + O_2 \tag{10.4.2}$$

When a potential is missing from a Latimer diagram it may always be calculated by constructing a thermodynamic cycle involving the known and unknown potentials, as explained in Note $10.4.1$ at the bottom of this page.

Latimer Diagrams and Disproportionation.

Latimer diagrams permit are also useful for comparing elements' redox properties and determining whether a substance is stable to disproportionation. Latimer diagrams not only provide a compact summary of an element's redox chemistry, they also are useful for

1. Determining whether a species is thermodynamically unstable with respect to disproprotionation.

Disproprotionation occurs when a species reacts with itself to produce two or more stable products. For instance, in basic solution ReO_3 can undergo disproprotionation to ReO_4^- and $ReO_2 \cdot 2H_2O$.

$$2Re^{VI}O_3 + 2H_2O \rightarrow Re^{VII}O_4^- + Re^VO_2 \cdot 2H_2O \tag{10.4.3}$$
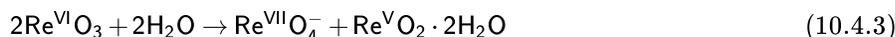
As with all redox reactions, disproprotionation reactions are thermodynamically favored when they possess a positive reaction potential. To see when this will be the case it is helpful to separate the disproprotionation reaction into its half reactions:

$$\text{Reduction} : Re^{VI}O_3 + H_2O + 2H^+e^- \rightarrow Re^VO_2 \cdot 2H_2O \qquad\qquad E^\circ = -0.446V \tag{10.4.4}$$

$$\text{Oxidation} : Re^{VI}O_3 + H_2O \rightarrow Re^{VII}O_4^- + 2H^+ + e^- \qquad\qquad E^\circ = +0.889V \tag{10.4.5}$$

$$\text{Sum} : 2Re^{VI}O_3 + 2H_2O \rightarrow Re^{VII}O_4^- + Re^VO_2 \cdot 2H_2O \qquad E^\circ = -0.446V + 0.889V = +0.443V \tag{10.4.6}$$
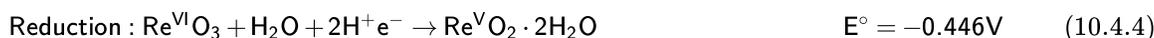
Notice that the disproprotionation of ReO_3 in basic solution is favored because the favorable reaction potential for ReO_3 oxidation is larger in magnitude than negative oxidation potential for ReO_3 reduction.

The ReO_3 disproportionation reaction is a specific instance of a general case. Any species possessing a standard reduction potential that is more positive than the standard reduction potential leading to their formation is thermodynamically unstable with respect to disproportionation. This situation is easy to recognize using a Latimer diagram; **species are unstable to disproportionation if the potential on their right is more positive than that on their left**.

Example 10.4.1

The Latimer diagram that has been reported for Cr in pH 14 aqueous solution is given below. Which, if any, species are unstable with respect to disproprotionation?

$$+6 \qquad\qquad +3 \qquad\qquad 0$$

$$CrO_4{}^{2-} \xrightarrow{-0.11\ V} Cr(OH)_3(s) \xrightarrow{-1.33\ V} Cr$$

$$\xrightarrow{+0.72\ V} Cr(OH)_4{}^{-} \xrightarrow{-1.33\ V}$$

Solution

All of the species are stable with respect to disproprotionation since all the potentials on the right of all the Cr^{3+} intermediates are less than those on their left.

Example 10.4.2

The Latimer diagram for Cr in pH 0 aqueous solution is given below. Which, if any, species are unstable with respect to disproprotionation?

$$+6 \qquad +5 \qquad +4 \qquad +3 \qquad +2 \qquad 0$$

$$0.95\ V \qquad\qquad\qquad -0.74\ V$$

$$Cr^{6+} \xrightarrow{0.55\ V} Cr^{5+} \xrightarrow{1.34\ V} Cr^{4+} \xrightarrow{2.10\ V} Cr^{3+} \xrightarrow{-0.424\ V} Cr^{2+} \xrightarrow{-0.90\ V} Cr$$

$$1.72\ V$$

$$1.38\ V$$

Solution

Both Cr^{5+} and Cr^{4+} are unstable towards disproportionation since the potentials on their right (for their reduction) are greater than the potentials on their left (for their formation by reduction).

Example 10.4.3

Which manganese species are unstable with respect to disproportionation in aqueous solution under acidic and basic conditions? What will each of these metastable species give on sidproportionation? The Latimer diagrams for manganese are given below.

	+7	+6	+5	+4	+3	+2	+1	0

pH 0

$MnO_4^- \xrightarrow{0.56\ V} MnO_4^{2-} \xrightarrow{0.27\ V} MnO_4^{3-} \xrightarrow{4.27\ V} MnO_2 \xrightarrow{0.95\ V} Mn^{3+} \xrightarrow{1.5\ V} Mn^{2+} \xrightarrow{-1.18\ V} Mn$

- $MnO_4^{2-} \xrightarrow{2.27V} MnO_2$
- $MnO_4^{3-} \xrightarrow{1.70\ V} MnO_2$
- $MnO_2 \xrightarrow{1.23\ V} Mn^{2+}$
- $MnO_4^- \xrightarrow{1.51\ V} Mn^{2+}$

pH 14

$MnO_4^- \xrightarrow{0.56\ V} MnO_4^{2-} \xrightarrow{0.27\ V} MnO_4^{3-} \xrightarrow{0.96\ V} MnO_2 \xrightarrow{0.15\ V} Mn_2O_3 \xrightarrow{-0.25\ V} Mn(OH)_2 \xrightarrow{-1.56\ V} Mn$

- $MnO_4^{2-} \xrightarrow{0.62\ V} MnO_2$
- $MnO_2 \xrightarrow{-0.05\ V} Mn(OH)_2$
- $MnO_4^{3-} \xrightarrow{0.60\ V} MnO_2$
- $MnO_4^- \xrightarrow{0.34\ V} MnO_2$

Solution

Under acidic conditions the following species are unstable with respect to disproprtionation:

- MnO_4^{2-} is unstable with respect to disproprtionation to MnO_4^- and MnO_2.
- MnO_4^{3-} is unstable with respect to MnO_4^{2-} and MnO_2. However, since MnO_4^{2-} is unstable with respect to disproprtionation the ultimate poducts of the disproprtionation will be MnO_4^- and MnO_2.
- Mn^{3+} is unstable towards disproprtionation to MnO_2 and Mn^{2+}.

Under basic conditions the following species are unstable with respect to disproprtionation:

- MnO_4^{2-} is unstable with respect to disproprtionation to MnO_4^- and MnO_2.
- MnO_4^{3-} is unstable with respect to MnO_4^{2-} and MnO_2. However, since MnO_4^{2-} is unstable with respect to disproprtionation the ultimate poducts of the disproprtionation will be MnO_4^- and MnO_2.

Notice that the +3 oxidation state of Mn is stable under basic conditions but not acidic ones.

Exercise 10.4.1, part a

Which, if any of the species in nitrogen's Latimer diagram (Scheme $10.4.III$, which for convenience is reproduced below) are unstable with respect to disproportionation?

+5	+4	+3	+2	+1	0	-1	-2	-3

$NO_3^- \xrightarrow{0.803\ V} N_2O_4 \xrightarrow{1.07\ V} HNO_2 \xrightarrow{0.996\ V} NO \xrightarrow{1.59\ V} N_2O \xrightarrow{1.77\ V} N_2 \xrightarrow{-1.87\ V} NH_3OH^+ \xrightarrow{1.41\ V} N_2H_5^+ \xrightarrow{1.275\ V} NH_4^+$

- $N_2 \xrightarrow{-0.23\ V} N_2H_5^+$
- $N_2O \xrightarrow{-0.05\ V} NH_3OH^+$
- $N_2O_4 \xrightarrow{1.297\ V} NO$
- $NO_3^- \xrightarrow{0.94\ V} HNO_2$
- $NO \xrightarrow{0.71\ V} H_2N_2O_2$
- $H_2N_2O_2 \xrightarrow{2.65\ V} N_2$
- $HNO_2 \xrightarrow{0.86\ V} H_2N_2O_2$
- $H_2N_2O_2 \xrightarrow{0.496\ V} N_2$
- $NH_3OH^+ \xrightarrow{1.35\ V} NH_4^+$
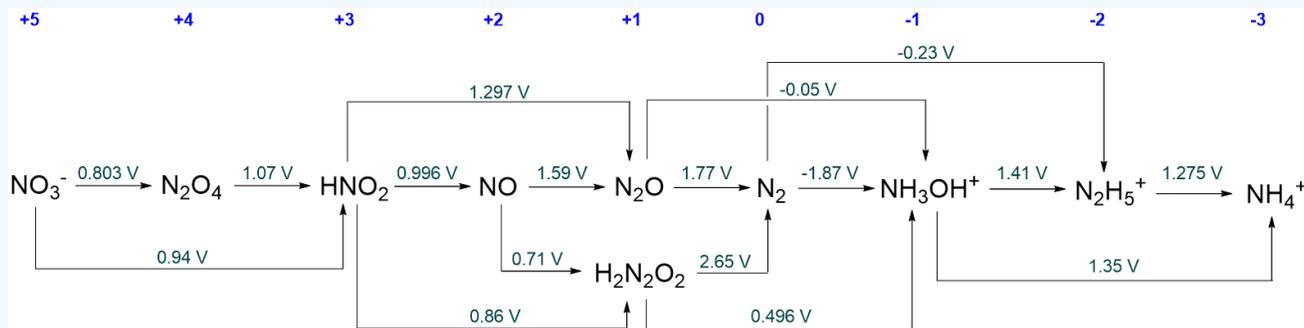
Answer

They will be all the intermediate species for which the redox potential on their right is more positive than that on their left. These are N_2O_4, HNO_2, NO, N_2O, $H_2N_2O_2$, and NH_3OH^+.

As far as you are able, determine what each metastable nitrogen speices will disproprtionate to at pH 0.

Answer

Initially the metastable species will disproprtionate to give their immediate neighbors in the Latimer diagram.

However, many of these neighbors are themselves metastable with respect to disproprtionation and so ultimately disproprtionation will only stop when species that are stable towards disproprtionation are reached.

In the case of N_2O_4, HNO_2, NO, N_2O, and $H_2N_2O_2$ disproprtionation will ultimately give NO_3^- and N_2.

For NH_3OH^+ disproprtionation will give N_2 and N_2H_5.

2. Comparing the redox chemistry of an element under different conditions (typically pH 0 and pH 14). This is well-illustrated by the Latimer diagrams of Chromium explored in Examples 10.4.1 and 10.4.2 A simple instance involves the acidic and basic Latimer diagrams of mercury shown in Scheme 10.4.IV.

Scheme 10.4.IV. Latimer diagrams for mercury in aqueous solution.
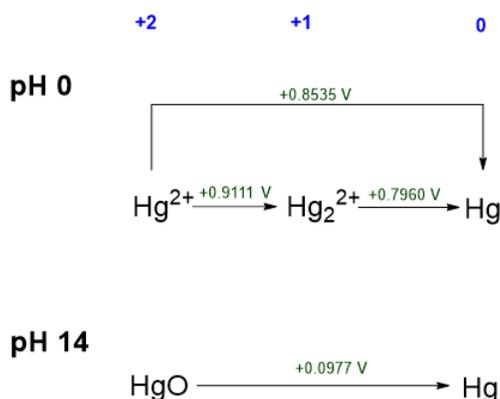
From Scheme 10.4.IV several things are clear about mercury's redox chemistry under acidic and basic conditions:

- Mercury(I) ion, Hg_2^{2+}, is thermodynamically stable under acidic conditions, but it is not likely stable under basic conditions. This may be inferred from its absence in the pH 14 diagram, which suggests that it is not readily formed under basic conditions.
- Elemental mercury is the thermodynamically most stable form of the element under both acidic and basic conditions. This may be inferred that the standard reduction potential for all mercury +2 and +1 species is positive.
- In both its +1 and +2 oxidation states (Hg^{2+} and Hg_2^{2+} ions) mercury is a fairly powerful oxidant under acidic conditions (with $\boxed{\sf{E^{\circ}}}$ 0.796 - 0.9111 V). In contrast, under basic conditions the +2 form of mercury (HgO) is only a weak oxidant (E°) = 0.0977 V.
- All of the mercury species represented are thermodynamically stable towards disproprtionation.

3. Comparing the redox chemistry of different elements under similar conditions. For instance, the redox behavior of mercury and its cogeners in acid solution may be easily compared using the Latimer diagrams (Scheme 10.4.V.

Scheme 10.4.V. Latimer diagrams for the group 12 elements in pH 0 aqueous solution.

$$+2 \qquad\qquad +1 \qquad\qquad 0$$

$$Zn^{2+} \xrightarrow{\text{-0.7626 V}} Zn$$

$$Cd^{2+} \xrightarrow{\text{-0.4025 V}} Cd$$

$$Hg^{2+} \xrightarrow{\text{0.9111 V}} Hg_2^{2+} \xrightarrow{\text{+0.7960 V}} Hg$$
(with +0.8535 V spanning from Hg^{2+} to Hg)
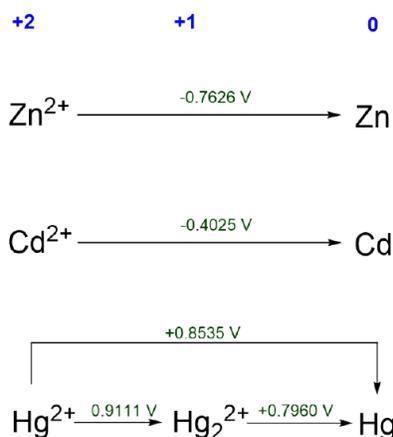
From Scheme $10.4.V$ it is clear that Zn and Cd exhibit similar redox behavior. Both should dissolve at pH 0 to give dications. In contrast, elemental mercury should be stable towards acid. Mercury is also the only group 12 element for which the +1 oxidation state is stable.

As the examples above indicate Latimer diagrams are helpful summaries of elements' redox chemistry but it still requires a fair bit of careful reading to use them to make sense of trends in elements redox chemistry or to trace out the disproprtionation products of a given redox state. The published diagrams also tend to be limited to describing the redox chemistry of the elements under conditions of extreme pH. Fortunately, a variety of graphical representations of elements' redox chemistry have been developed that are particularly useful for estimating the dominant form of an element under a given set of conditions and for making sense of trends in elements' redox chemistry. These graphical methods will be described in the next two sections.

Note 10.4.1.

Potentials that are not shown in a Latimer diagram may always be calculated by constructing a **thermodynamic cycle**. Consider the interconversion of N_2O_4 to NO, $E^{\circ}_{IV/II}$, the value of which is not given in the standard Nitrogen Latimer diagram presented in Scheme $10.4.sfII$. Part of that diagram is reproduced as Scheme $10.4.VI$ below.

Scheme 10.4.VI. Partial Latimer diagram for nitrogen in acid.

$$+4 \qquad\qquad +3 \qquad\qquad +2$$

$$E^{\circ}_{IV/II} = ?? \text{ V}$$

$$N_2O_4 \xrightarrow{\text{1.07 V}} HNO_2 \xrightarrow{\text{0.996 V}} NO$$
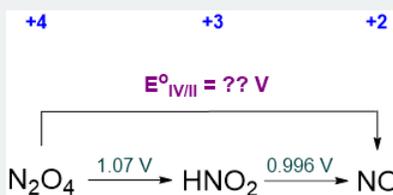
The relevant thermodynamic cycle that may be used to calculate the unknown potential involves the free energies and is depicted in Scheme $10.4.VII$

Scheme 10.4.VII. Thermodynamic cycle that may be used to determine $E^{\circ}_{N_2O_4 \rightarrow NO}$.

$$+4 \qquad\qquad +3 \qquad\qquad +2$$

$$\Delta G^{\circ}_{IV/II}$$

$$N_2O_4 \xrightarrow{\Delta G^{\circ}_{IV/III}} HNO_2 \xrightarrow{\Delta G^{\circ}_{III/II}} NO$$
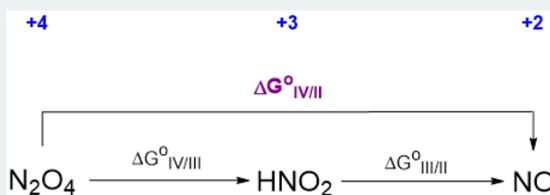
The free energies for each conversion step in the cycle is related to the corresponding potential by the relationship

$$\Delta G^{\circ} = nFE^{\circ} \tag{10.4.7}$$

where n is the number of electrons involved in each step. Making this substitution the thermodynamic cycle above may be converted to the one shown in Scheme $10.4.VIII$

Scheme 10.4.VIII. Thermodynamic cycle expressed in terms of standard potentials.
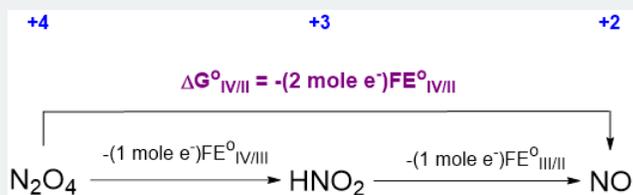
From Scheme 10.4.VIII it may be seen that

$$\Delta G^\circ_{IV/II} \;=\; -(2 \text{ mol } e^-)FE^\circ_{IV/II} \;=\; -(1 \text{ mol } e^-)FE^\circ_{IV/III} - (1 \text{ mol } e^-)FE^\circ_{III/II} \tag{10.4.8}$$

Cancelling the constant F and replacing the unknown potentials with the values in Scheme 10.4.VI gives

$$-(2 \text{ mol } e^-)E^\circ_{IV/II} \;=\; -(1 \text{ mol } e^-)(1.07 \text{ V}) \;-\; (1 \text{ mol } e^-)(0.996 \text{ V}) \tag{10.4.9}$$

from which $E^\circ_{IV/II}$ may be calculated, giving $E^\circ_{IV/II}$ = +1.033 V.

References

1. All standard reduction potentials are taken from Bard, A. J.; Parsons, R.; Jordan, J. Standard potentials in aqueous solution. M. Dekker: New York, 1985.

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10.5: Frost Diagrams

Frost diagrams show how stable an element's redox states are relative to the free element

Frost diagrams represent how stable an element's redox states are relative to the free element. In a Frost diagram, a proxy for the free energy relative to that of the free element (oxidation state zero) is plotted as a function of oxidation state. To avoid ambiguity, sometimes the points are labeled with the identity of the chemical species involved.

The proxy used in place of the free energy is NE°, sometimes expressed as nE°. On this page N will be used in place of n to avoid confusion with the common use of n in redox chemistry to denote the number of electrons involved in individual oxidation or reduction reaction steps.

In Frost diagrams the quantity NE° is used since it is proportional to the standard free energy change for conversion of the free element to that oxidation state.

In NE°

- N is the oxidation state.
- E° is the standard *reduction potential* associated with *interconversion between the free element and that oxidation state*.

For a proof that NE° is proportional to the free energy of an element's oxidation state and more information on how NE° may be calculated, see Note $10.5.1$ at the end of this page.

Frost diagrams allow for rapid estimation of the relative stability of elements' redox states.

Because Frost diagrams directly show oxidation states' relative stabilities, they enable the rapid assessment of the following:

1. *The relative stability of an element's oxidation states under a given set of conditions.* Since NE° is a measure of thermodynamic stability, the lower its value the more stable the state. Moreover, since NE° measures stability relative to the free element, negative values of NE° indicate that a state is more stable than the element, while positive values indicate that the state is less stable.

Consider the Frost diagram for copper at pH 0 shown in Figure $10.5.1$.
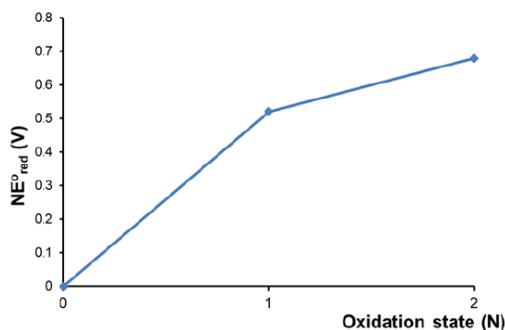
Figure 10.5.1. Frost diagram for copper in aqueous acid. (CC BY-SA 4.0 International; Stephen Contakes)

As can be seen in Figure $10.5.1$, Cu$^+$ and Cu^{2+} are both higher in free energy ($\propto NE^\circ$) than free Cu. This is consistent with copper's status as a noble metal that can only be dissolved in acid with the aid of oxidizing agents like O_2, H_2O_2, or NO_3^- (*e.g.*, as in HNO_3).

The acidic Frost diagram of Nickel shown in Figure $10.5.2$ provides an example of a metal which dissolves in acid under otherwise nonoxidizing conditions (*i.e.*, without the aid of oxidants like O_2 or H_2O_2).
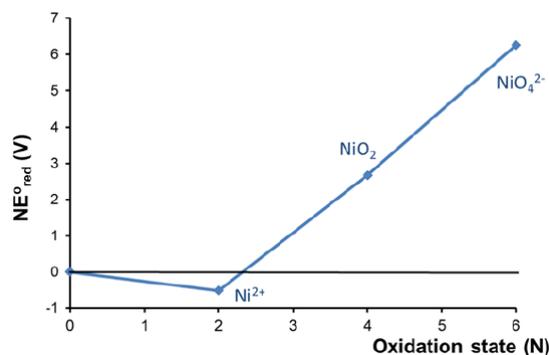
Figure 10.5.2. Frost diagram for nickel in aqueous acid. (CC BY-SA 4.0 International; Stephen Contakes)

In this case the diagram shows that the Ni^{2+} oxidation state is lower in free energy than the free element, indicating that Ni spontaneously dissolves in acid to give Ni^{2+}. The diagram also reveals that higher nickel oxidation states (+4 and +6) are known but unstable with respect to both Ni^{2+} and free nickel.

✔ Example 10.5.1. Interpreting a Frost Diagram

Consider the Frost diagram of Cr in acid shown in Figure $10.5.3$. What can be determined about the relative stability of chromium's oxidation states in acid?
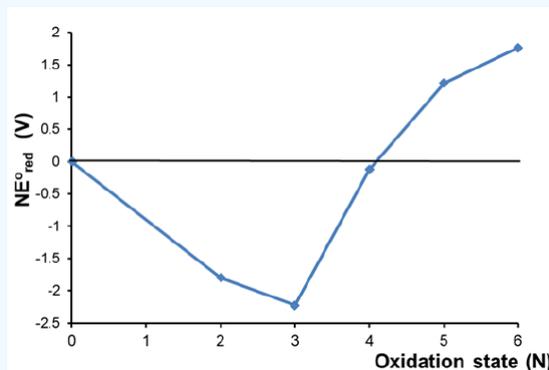
Figure 10.5.3. Frost diagram for Cr in acidic solution. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Solution

A cursory glance at the diagram reveals that

- The +3 oxidation state is the most stable since it has the lowest NE°.
- The +2, +3, and +4 oxidation states are all more stable than the free element while the +5 and +6 oxidaton states are less stable.
- The diagram also reveals information about the susceptibility of the chromium species to undergo disproportionation and comproportionation reactions. For details see example 2.

---

2. *The redox behavior of an element under different conditions.* Consider the Frost diagrams of sulfur at pH 0 and 14 shown in Figure $10.5.4$.
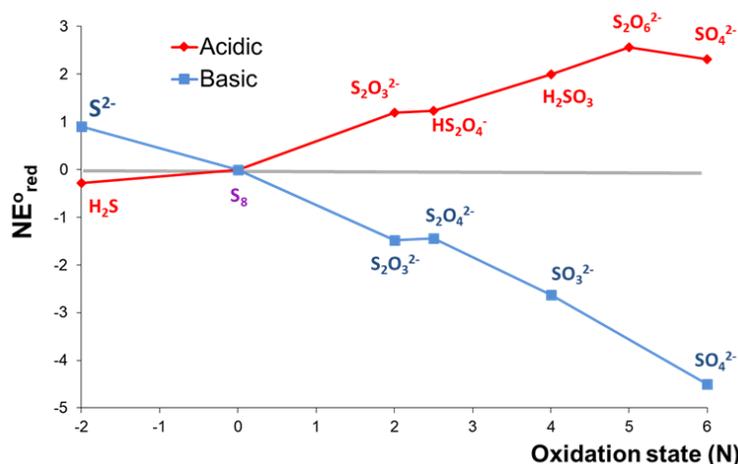
Figure 10.5.4. Frost diagrams for sulfur at pH 0 and 14. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

As can be seen in Figure 10.5.4, the relative stabilities of high and low sulfur oxidation states are roughly inverted between acidic and basic conditions. Under basic conditions, the oxidized forms of sulfur are all more stable than the free element, with sulfate most stable overall. In contrast, H_2S is the most stable form of sulfur under acidic conditions, while all the oxidized forms of sulfur are less stable than the free element.

3. *Comparison of the redox behavior of a series of elements.* Consider the pH 0 Frost diagrams of the group 6 elements shown in Figure 10.5.5.
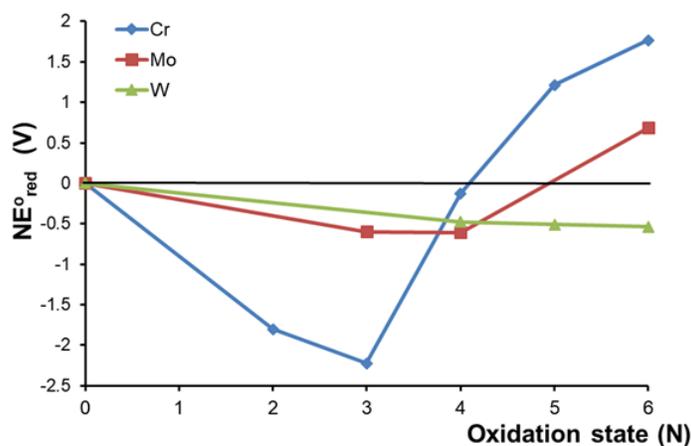
Figure 10.5.5. Frost diagrams for the group 6 elements at pH 0. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Several trends may be noted from the data in Figure 10.5.5. First, on moving down the group from Cr to W, there is an increasing preference for higher oxidation states, with the most stable forms being Cr^{4+}, Mo^{4+}, and W^{6+}. Second, the coincidentally low stabilization of Cr^{4+} aside, the stabilization or destabilization of oxidation states relative to the free element decreases down a group - *i.e.*, Cr^{4+} is stabilized relative to Cr more so than Mo^{4+} is relative to Mo, and W^{6+} is stabilized relative to W even less so.

One of the most striking examples of the utility of Frost diagrams for comparing the empirical redox behavior of a series of elements involves the first row transition elements, the pH 0 Frost diagrams for which are shown in Figure 10.5.6.[2,3] A number of trends may be noted. For example, as in the case of the group 6 elements, a shift in the most stable oxidation state may be observed, with Sc through Cr exhibiting a preference for the +3 oxidation state and Mn through Cu the +2 oxidation state. The diagram also shows that Sc through Mn lose all their valence electrons to form d^0 species, while similar species have not been observed for later members of the series (although an iron(VII) complex has been isolated[4] and iron's heavier cogeners, Ru and Os, do form d^0 species, RuO_4 and OsO_4).
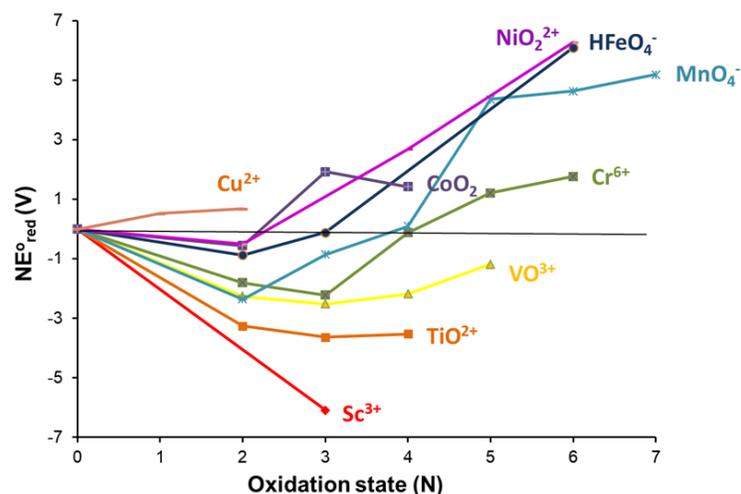
Figure 10.5.6. Frost diagrams for the first transition series at pH 0. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

4. *Whether a redox state is unstable towards disproportionation* may be determined from the relative positions of that state and the states on either side of it on the diagram.[5] Remember that in **disproportionation** a species reacts with itself to produce two or more stable products. For example, NO can in principle undergo disproportionation in aqueous acid to give nitrate and N_2.

$$10\, NO\, +\, 2H_2O \rightarrow 3\, N_2 + 4\, NO_3^- + 4H^+$$
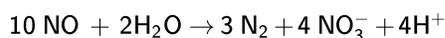
A Frost diagram can be used to determine when a redox state is unstable with respect to such disproportionation because the slope of a line between any two points is equal to the standard *reduction* potential interconverting the species involved. This means that *if a line is drawn between any two redox states then any states above the line will be unstable towards disproportionation to those states.* This is because in that case the potential for the reduction half reaction in the disproportionation will be more positive than the potential for the oxidation half reaction, rendering the overall reaction potential positive and so spontaneous. For proof of a specific example see Exercise 1.

To see how a disproportionation analysis may be performed using a Frost diagram, it can be helpful to examine the pH 0 Frost diagram for Cr more carefully. In this case the instability of Cr^{4+} and Cr^{5+} towards disproportionation may be revealed by placing a tie line drawn between the Cr^{3+} and Cr^{6+} states, as shown in Figure 10.5.7a.
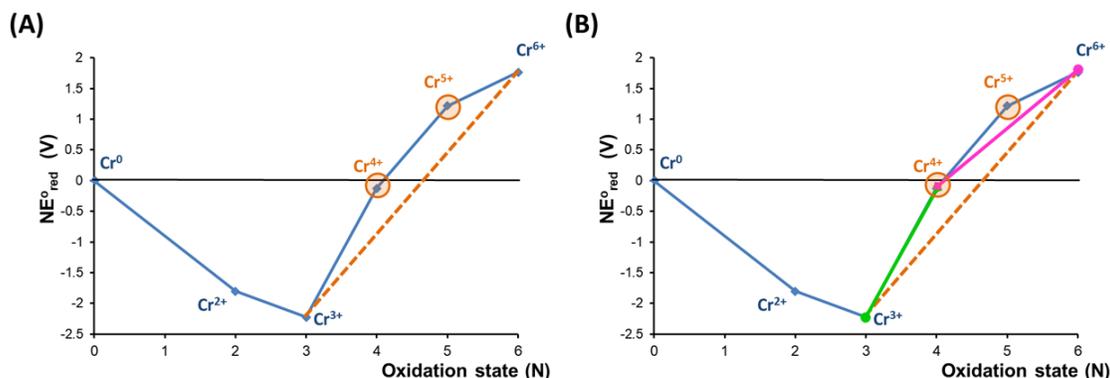
Figure 10.5.7. (a) Frost diagram for Cr in acidic solution showing that the Cr^{4+} and Cr^{5+} states lie above a tie-line between the Cr^{3+} and Cr^{6+} states. (b) In the case of Cr^{4+}, disproportionation is favored because the $Cr^{4/3+}$ potential (slope of the green tie-line connecting the Cr^{4+} and Cr^{3+} states) is larger than the $Cr^{6/4+}$ potential (slope of the pink tie-line connecting Cr^{6+} and Cr^{4+}). This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

As shown in Figure 10.5.7a, the Cr^{4+} and Cr^{5+} states are unstable towards disproportionation because they lie above a tie-line between the Cr^{3+} and Cr^{6+} states. This is because the potential for Cr^{4+} reduction to Cr^{3+}, represented by the tie-line connecting those species in Figure 10.5.7b, is larger than the potential for Cr^{6+} reduction to Cr^{4+}, as indicated by the lower slope of the tie-line connecting Cr^{6+} and Cr^{4+}.

Sometimes states which are unstable towards disproportionation correspond to concave down points on the Frost diagram. However, as this is not always the case, a systematic approach for finding metastable redox states is recommended. An example of such an approach is given in Example 10.5.2

> ✔ **Example 10.5.2. Systematic identification of Mn redox states that are unstable towards disproportionation in acid.**
>
> Consider the Frost diagram of Mn in acid shown in Figure 10.5.8 Which, if any, of manganese's oxidation states are unstable towards disproportionation at pH 0?
>
>
>
> Figure 10.5.8. Frost diagram for Mn at pH 0. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.
>
> **Solution**
>
> States that are unstable towards disproportionation may be identified by drawing all the possible tie-lines between nonadjacent states spanning the lowest and highest oxidation states in the diagram, which in this case are Mn^0 and Mn^7. The possible permutations beginning with Mn^0 are given below
>
>
>
> In the figure above the states that are thermodynamically unstable towards disproportionation (circled) are +3, +5, and +6.
>
> The figure above by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.
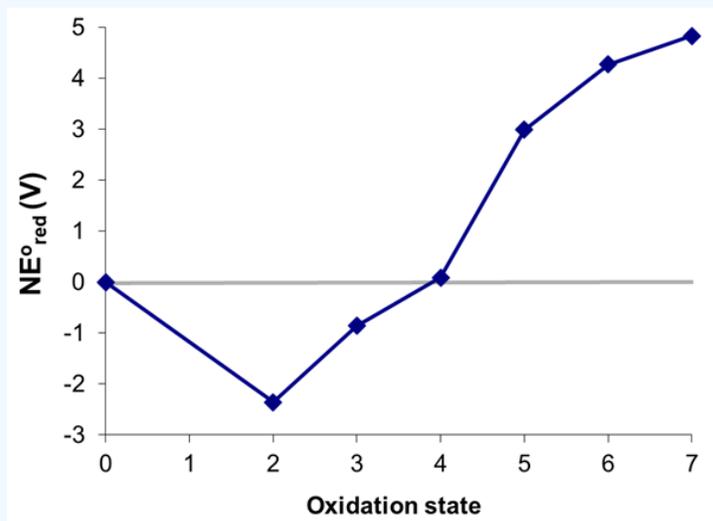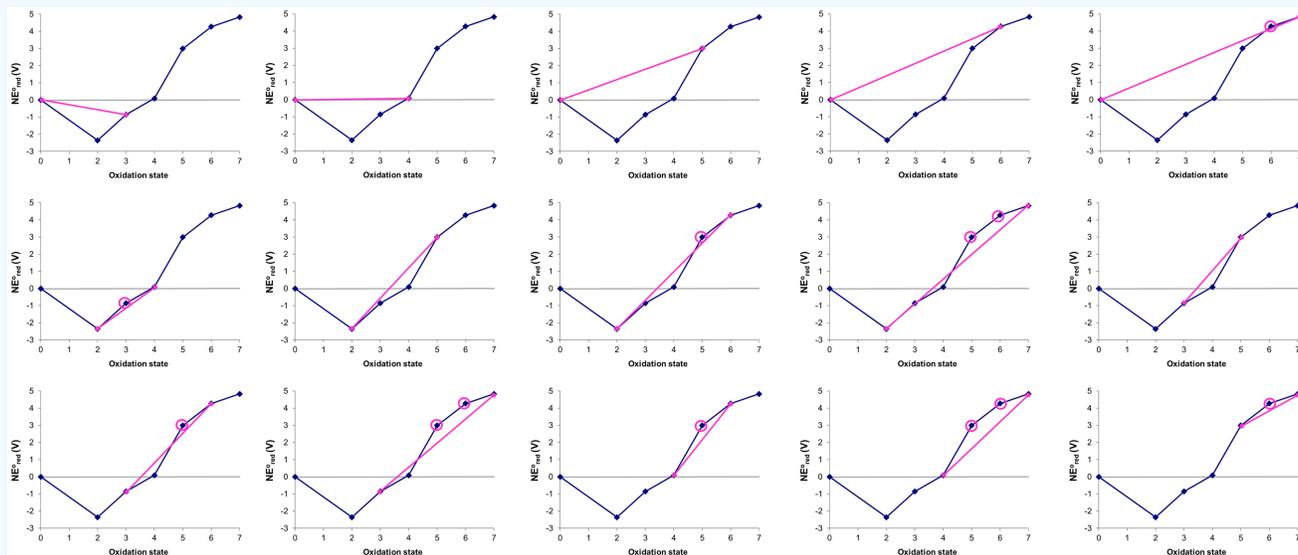
4. Whether *two species are unstable towards comproportionation* may be assessed from the relative positions of the two species and all intervening species on the diagram. In **comproportionation,** two related species react to give a more stable product. For example, NO and hydrazinium ion can in principle undergo comproportionation in aqueous acid to give N_2.

$$2\,NO \;+\; N_2H_5^+ \;\rightarrow 2\,N_2 \;+\; 2\,H_2O \;+\; H^+$$

A Frost diagram may be used to determine when two species are thermodynamically favored to undergo comproportionation. *Draw a line between the two species on the diagram. If there are states below the line then the two species are unstable towards forming those states by comproportionation.* Again, it can be helpful to examine the acidic condition Frost diagram for Cr to see how this works. In this case consider a tie line drawn between the Cr^{4+} and Cr^{2+} states, as shown in Figure $10.5.9a$.
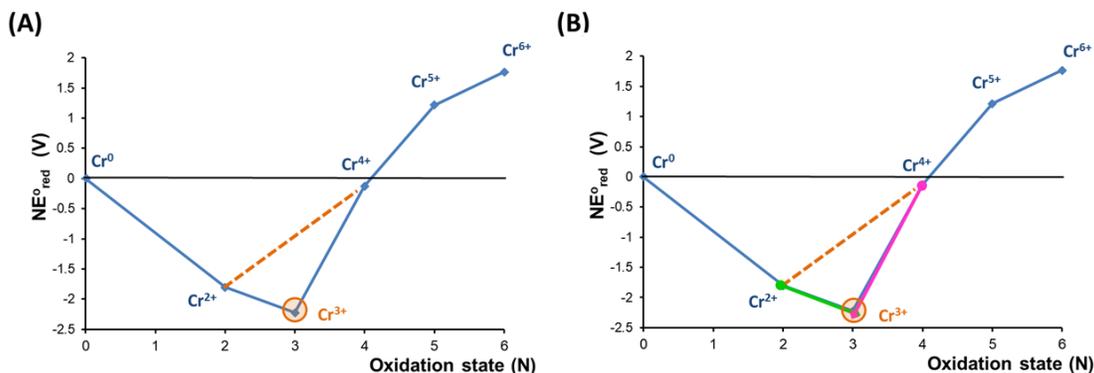
Figure 10.5.9. (a) Frost diagram for Cr in acidic solution showing that the Cr^{3+} redox state lies below a tie-line between the Cr^{2+} and Cr^{4+} states. (b) The slope of the green line connecting the Cr^{2+} and Cr^{3+} states is less than that of the pink line connecting the Cr^{3+} and Cr^{4+} states. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

As shown in Figure $10.5.9a$, a mixture of Cr^{2+} and Cr^{4+} is unstable towards comproportionation because on the Frost diagram Cr^{3+} lies below the tie-line between Cr^{2+} and Cr^{4+}. This shows that the standard potential for reduction of Cr^{3+} to Cr^{2+} (equal to the slope of the line connecting those states) is less than that for the reduction of Cr^{4+} to Cr^{3+} (again, equal to that of the line connecting the states), in consequence of which the potential for comproportionation will be positive.

The analysis of a Frost diagram for all favorable comproportionations is similar to the analysis used to detect species that are unstable towards disproportion. The products of thermodynamically favored comproportionations are sometimes concave up points but since this is not always the case a systematic approach should be used. An example is given in Example $10.5.3$.

✔ Example $10.5.3$. Systematic identification of pairs of Mn redox states that are unstable towards comproportionation in acid.

Consider the Frost diagram of Mn at pH 0 in Figure $10.5.8$ of Example $10.5.2$, which for convenience is reproduced below. Which, if any, pairs of manganese species are unstable towards comproportionation under these conditions and what products could they form?
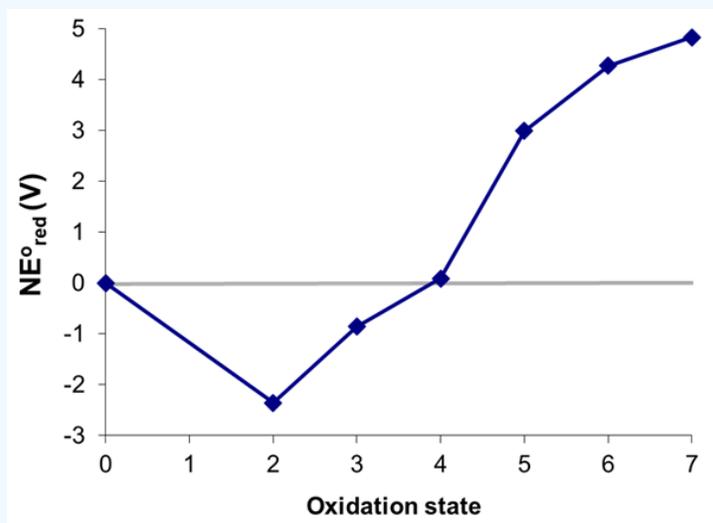
Solution

The possible tie-lines were already identified in Exercise $10.5.2$
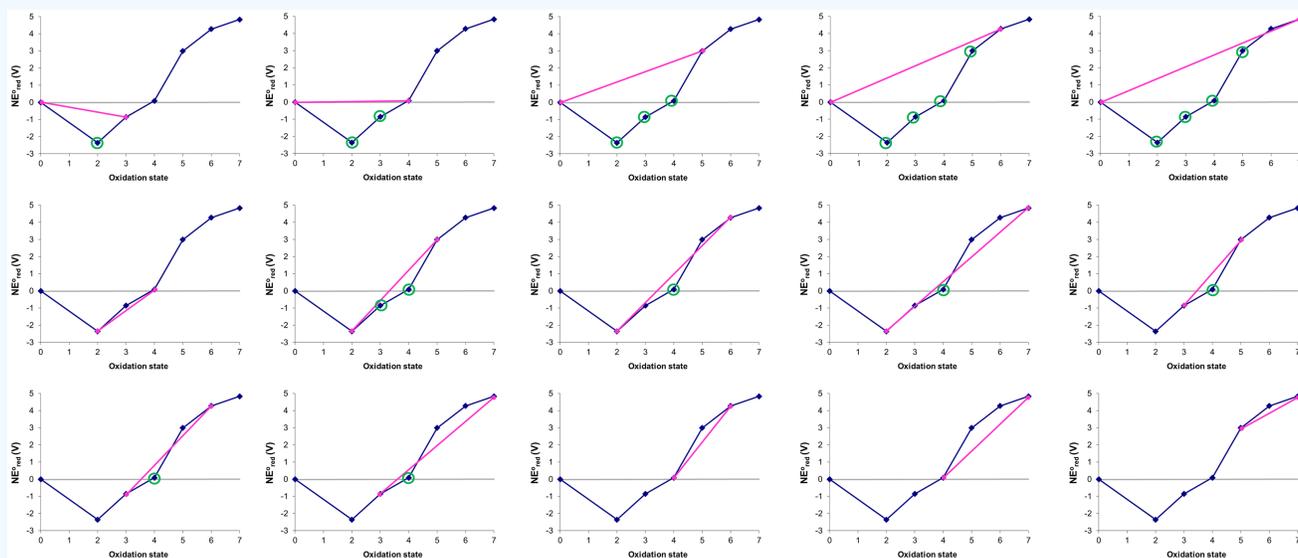
Figure above: the lower energy comproportionation products that species form are circled in green. The comproportionations identified involve the following pairs of oxidation states:

- 0 and +3 → +2
- 0 and +4 → +2 or +3
- 0 and +5 → +2 or +3 or +4
- 0 and +6 → +2 or +3 or +4 or +5
- 0 and +7 → +2 or +3 or +4 or +5
- +2 and +5 → +3 or +4
- +2 and +6 → +4
- +2 and +7 → +4
- +3 and +5 → +4
- +3 and +6 → +4
- +3 and +7 → +4

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Additional analysis is needed to determined the thermodynamic product of many comproportionation reactions - but fortunately such an analysis is not necessary to understand the descriptive chemistry of the elements.

This list of possible comproportionation reactions identified in Example $10.5.3$ raises several interesting questions:

1. When more than one comproportionation product is possible, which one(s) will be formed?

In this case the answer is that all species can be formed in thermodynamically favored comproportionation reactions. However, the system still only possesses one state of lowest free energy. For example, depending on the stoichiometry of the reactants, the lowest energy products that can be formed from a mixture of Mn^0 and Mn^{VII} might be a mixture of Mn^{II} and Mn^{IV}. The identification of this state in a given case is complicated and involves minimizing the system energy subject to the constraints of a mass and charge balance. Fortunately, such an analysis is not needed to make sense of the chemistry of the elements.

What should be noted is that if a comproportionation product can itself undergo a comproportionation reaction with one or more reactants, then that reaction can take place in solution. For instance, if the case of the comproportionation between Mn^0 and Mn^{IV} produces Mn^{III}, then that Mn^{III} can undergo an additional comproportionation reaction with Mn^0 to give Mn^{II}.

2. What happens if a species formed by comproportionation is susceptible to disproportionation?

If the conditions allow, then that species will undergo disproportionation. Again, thermodynamic measures like those shown on Frost diagrams describe what can happen, not what will occur under a given set of conditions.

Exercises

? Exercise 10.5.1

Using the simplified Latimer diagram for Cr in aqueous acid, reproduced below, verify that the disproportionation of Cr^{4+} to Cr^{3+} and Cr^{6+} is thermodynamically spontaneous.

$$+6 \qquad\qquad +5 \qquad\qquad +4 \qquad\qquad +3 \qquad\qquad +2 \qquad\qquad 0$$
$$Cr^{6+} \xrightarrow{0.55\ V} Cr^{5+} \xrightarrow{1.34\ V} Cr^{4+} \xrightarrow{2.10\ V} Cr^{3+} \xrightarrow{-0.424\ V} Cr^{2+} \xrightarrow{-0.90\ V} Cr$$

Answer

The disproportionation of Cr^{4+} to Cr^{3+} and Cr^{6+} is the sum of two processes:

$$Cr^{4+}\text{reduction}: \qquad Cr^{4+} + e^- \to Cr^{3+} \qquad\qquad E^{\circ}_{Cr^{4/3+}} = 2.10\ V$$

$$Cr^{4+}\text{oxidation}: \quad Cr^{4+} \to Cr^{6+} + 2e^- \qquad E^{\circ} = -E^{\circ}_{Cr^{6/4+}}$$

_____

$$\text{Sum}: \ 3Cr^{4+} + \to Cr^{6+} + 2Cr^{3+} \qquad E^{\circ}_{\text{disproportionation}} = E^{\circ}_{Cr^{4/3+}} - E^{\circ}_{Cr^{6/4+}}$$
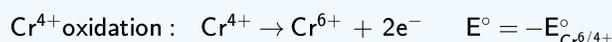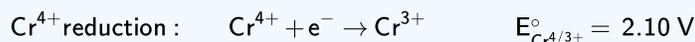
The value of $E^{\circ}_{Cr^{6/4+}}$ is just the sum of the $Cr^{6/5+}$ and $Cr^{5/4+}$ reduction potentials (+0.55 V + 1.34 V) or +1.89 V. Consequently,

$$E^{\circ}_{\text{disproportionation}} = E^{\circ}_{Cr^{4/3+}} \quad E^{\circ}_{Cr^{6/4+}} = 2.10\ V - 1.89\ V = +0.21\ V$$

which is spontaneous.

? Exercise 10.5.2

Using the simplified Latimer diagram for Cr in aqueous acid, reproduced below, verify that the comproportionation of Cr^{2+} and Cr^{4+} to Cr^{3+} is thermodynamically spontaneous.

$$+6 \qquad\qquad +5 \qquad\qquad +4 \qquad\qquad +3 \qquad\qquad +2 \qquad\qquad 0$$
$$Cr^{6+} \xrightarrow{0.55\ V} Cr^{5+} \xrightarrow{1.34\ V} Cr^{4+} \xrightarrow{2.10\ V} Cr^{3+} \xrightarrow{-0.424\ V} Cr^{2+} \xrightarrow{-0.90\ V} Cr$$

Answer

The comproportionation of Cr^{2+} and Cr^{4+} to Cr^{3+} is the sum of two processes:

$$Cr^{4+}\text{reduction}: \qquad Cr^{4+} + e^- \to Cr^{3+} \qquad\qquad E^{\circ}_{Cr^{4/3+}} = +2.10\ V$$

$$Cr^{2+}\text{oxidation}: \quad Cr^{2+} \to Cr^{3+} + e^- \qquad E^{\circ} = -E^{\circ}_{Cr^{3/2+}} = -(-0.424\ V) = = +0.424\ V$$

_____

$$\text{Sum}: \ Cr^{2+} + Cr^{4+} \to 2Cr^{3+} \qquad E^{\circ}_{\text{comproportionation}} = +2.10\ V + 0.424\ V = +2.524\ V$$
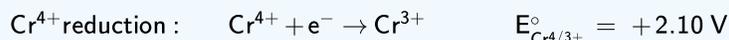
Since $E^{\circ}_{\text{comproportionation}}$ is positive, the comproportionation is spontaneous.

? Exercise 10.5.3. Identifying thermodynamically favored comproportionation and disproportionation reactions.

The Frost diagrams for acidic and basic solutions of sulfur are given below.

(A) Acidic — plot of NE°red vs Oxidation state (N) showing H₂S, S₈, S₂O₃²⁻, HS₂O₄⁻, H₂SO₃, S₂O₆²⁻, SO₄²⁻

(B) Basic — plot of NE°red vs Oxidation state (N) showing S²⁻, S₈, S₂O₃²⁻, S₂O₄²⁻, SO₃²⁻, SO₄²⁻
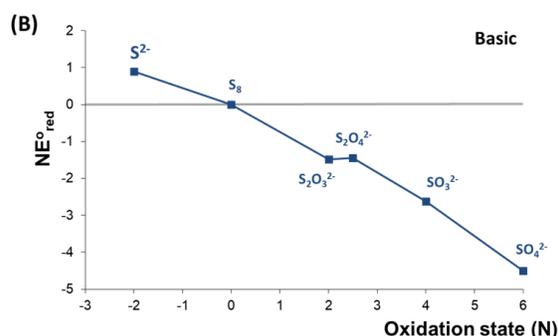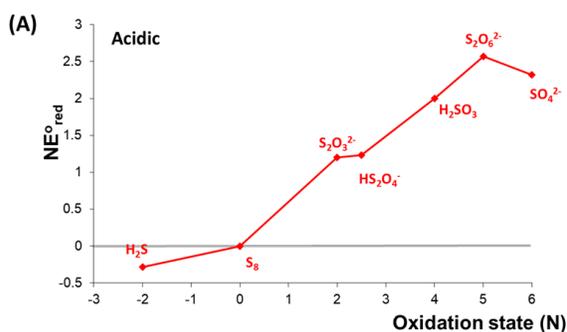
a. Identify any species that are unstable towards disproportionation under acidic or basic conditions.

b. Identify any species that can be formed by comproportionation under acidic or basic conditions.

Answer

The species that are unstable towards *disproportionation* and *comproportionation* may be identified by constructing tie-lines between nonadjacent redox states and identifying any that fall above and below these lines. Species that are unstable to *disproportionation* will lie above a line; those that will be formed by *comproportionation* will lie below a line. Note that some species may be both capable of being formed by *comproportionation* and thermodynamically susceptible to *disproportionation.*

The possible tie-lines for acidic conditions are as follows:
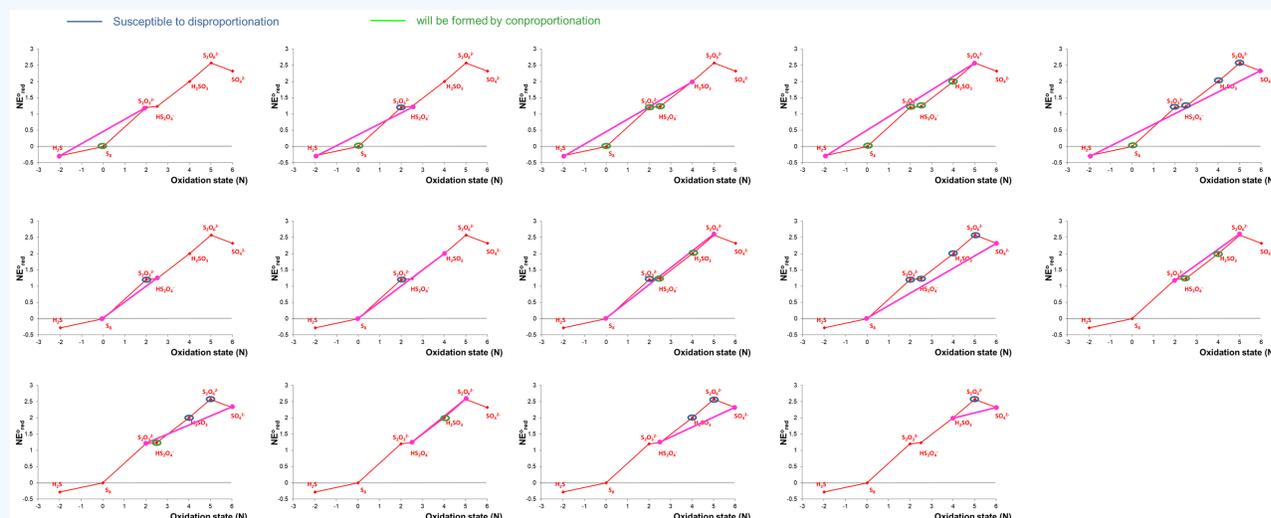
Notice that in some cases it can be difficult to tell whether a point lies above or below a tie-line based on inspection alone. In these cases the relevant redox potential should be calculated to determine whether disproportionation or comproportionation is thermodynamically favored or even if the process is free energy neutral.

The possibilities for basic conditions are left as an exercise for the reader. To check your work the species that are susceptible to disproportionation and those which can be formed by comproportionation are summarized below.
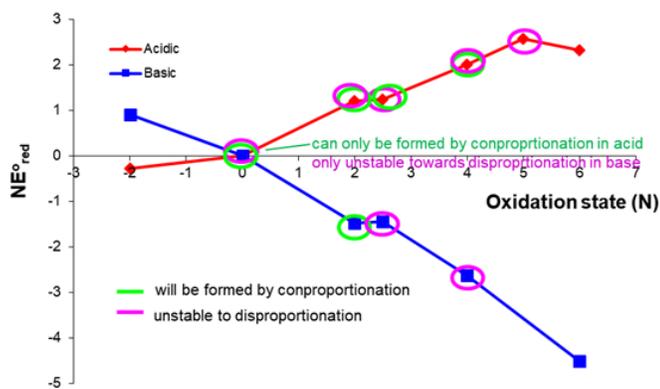
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Appendix

📌 Note 10.5.1. Construction of a Frost Diagram.

Since Frost diagrams use NE° as a proxy for oxidation free energy, the construction of a Frost diagram is a matter of calculating NE° for each oxidation state, where E° is the standard potential for the *formation of that oxidation state (O.S.)* from the free element. To see why this quantity is a useful proxy for oxidation state free energy, it is helpful to recognize that the oxidation state, N, is formally equal to the number of electrons that are *removed* from the free element when the oxidation state is formed. From this perspective the formation of negative oxidation states by adding electrons to the free element may be thought of as involving the removal of a negative number of electrons.

The free energy for formation of each oxidation state is determined as follows:

1. For free elements the free energy of formation, E°, and consequently NE°, are all by definition zero.

2. Negative oxidation states are formed by reduction of the free element

$$E + ne^- \rightarrow E^{O.S.} \qquad E^\circ = E^\circ_{red}$$

so that

$$\Delta G^\circ = -nFE^\circ_{red}$$

in which F is the Faraday constant.

In this case the oxidation state, N, is equal to $-n$ and the expression above becomes

$$\Delta G^\circ_{red} = F \times (NE^\circ)$$

from which it can also be seen why NE° is a useful proxy for free energy. It is proportional to ΔG°:

$$NE^\circ = \frac{1}{F}\Delta G^\circ_{red}$$

3. Positive oxidation states are formed by oxidation of the element:

$$E \rightarrow E^{O.S.} + ne^- \qquad E^\circ_{ox} = E^\circ = -E^\circ_{red}$$

in which the number of electrons, n, is equal to the oxidation state, N and

$$E^\circ_{ox} = E^\circ = -E^\circ_{red}$$

So that for positive oxidation states,

$$\Delta G^\circ_{ox} = -\Delta G^\circ_{red} = -(-nFE^\circ_{red}) = F(NE^\circ)$$

This is the same expression obtained for the negative oxidation states in which NE° is proportional to ΔG°.

From considering these cases, it is clear that as long as N is taken as the oxidation state and E° the associated standard reduction potential, the quantity NE° is proportional to the free energy.

In many cases the relevant standard reduction potentials are neither tabulated nor listed in the element's Latimer diagram. For example, in nickel's acidic Latimer diagram, the standard reduction potentials for formation of elemental Ni from NiO_4^{2-} or NiO_2 are not given.
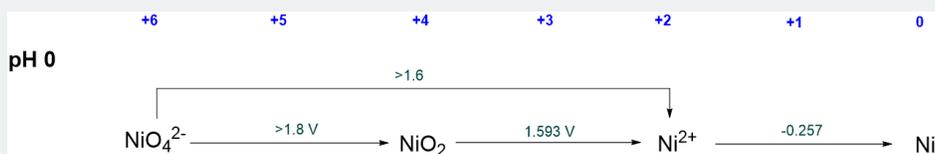
In such cases the relevant reduction potential should be calculated by taking into account the fact that since free energy is a state function, the free energy for formation of that oxidation state is the sum of the free energies of the steps described in the Latimer diagram. For example, to calculate NE° for the formation of NiO_2, the following relationship may be used:

$$\Delta G^\circ_{NiO_2 \to Ni} = \Delta G^\circ_{NiO_2 \to Ni^{2+}} + \Delta G^\circ_{Ni^{2+} \to Ni}$$

But since $\Delta G = -nFE^\circ$, where n is the number of electrons involved in each reduction, then the above expression may be rewritten as

$$-n_{e^-,NiO_2 \to Ni} FE^\circ_{NiO_2 \to Ni} = -n_{e^-,NiO_2 \to Ni^{2+}} FE^\circ_{NiO_2 \to Ni^{2+}} + -n_{e^-,Ni^{2+} \to Ni} FE^\circ_{Ni^{2+} \to Ni}$$

which may be further simplified by cancelling the Faraday constant, F, from both sides, giving an expression for the desired value of NE°:

$$-n_{e^-,NiO_2 \to Ni} E^\circ_{NiO_2 \to Ni} = NE^\circ_{Ni \to NiO_2} = -n_{e^-,NiO_2 \to Ni^{2+}} E^\circ_{NiO_2 \to Ni^{2+}} + -n_{e^-,Ni^{2+} \to Ni} E^\circ_{Ni^{2+} \to Ni}$$

From this expression the value of $NE^\circ_{Ni \to NiO_2}$ may be calculated by inserting the relevant reduction potentials and number of electrons:

$$NE^\circ_{Ni \to NiO_2} = 2 \times (+1.593V) + 2 \times (-0.257V) = +2.672V$$

For complex cases it can be helpful to tabulate the calculations, as is done in the following example.

✔ **Example 10.5.1: Calculating the Frost Diagram for nitrogen in aqueous acid**

Calculate the acidic Frost diagram of nitrogen from the information given in the simplified acidic Latimer diagram for nitrogen given below.
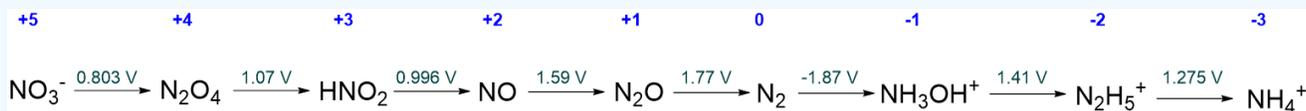
Solution

The value of NE° for each oxidation state is calculated as described in Table 10.5.1. The calculations follow the procedure:

1. Set $NE^\circ = 0$ for the free element.
2. Use $NE^\circ = $ O.S. $\times$ associated E° to calculate NE° for the lowest positive and negative oxidation states.
3. Iteratively use $NE^\circ = NE^\circ_{last\ step} + NE^\circ_{one\ lower\ oxidation\ state}$ to calculate NE° for all higher oxidation states.

Table 10.5.1: Calculation of NE° for each oxidation state of nitrogen.

Oxidation State	Step	$NE^\circ =$	Calculated as the sum of the steps	Notes

Oxidation State	Step	$NE° =$	Calculated as the sum of the steps	Notes
5	$N_2 \rightarrow NO_3^-$	$5 \times \left(E°_{NO_3^- \rightarrow N_2}\right)$	$N_2 \rightarrow N_2O_4 \rightarrow NO_3^-$ $NE° = 1 \times E°_{NO_3^- \rightarrow N_2O_4}$ $NE° = 1 \times E°_{NO_3^- \rightarrow N_2O_4}$ $NE° = 1 \times 0.803V + 5.426V = 6.229V$	Calculate $NE°$ for the +4 oxidation state, NO, first. Then use it in this calculation.
4	$N_2 \rightarrow N_2O_4$	$4 \times \left(E°_{N_2O_4 \rightarrow N_2}\right)$	$N_2 \rightarrow HNO_2 \rightarrow N_2O_4$ $NE° = 1 \times E°_{HNO_2 \rightarrow NO}$ $NE° = 1 \times E°_{N_2O_4 \rightarrow HNO_2}$ $NE° = 1 \times 1.07V + 4.356V = 5.426V$	Calculate $NE°$ for the +3 oxidation state, NO, first. Then use it in this calculation.
3	$N_2 \rightarrow HNO_2$	$3 \times \left(E°_{HNO_2 \rightarrow N_2}\right)$	$N_2 \rightarrow NO \rightarrow HNO_2$ $NE° = 1 \times E°_{HNO_2 \rightarrow NO}$ $NE° = 1 \times E°_{NO \rightarrow N_2O} + NE°$ $NE° = 1 \times 0.996V + 3.36V = 4.356V$	Calculate $NE°$ for the +2 oxidation state, NO, first. Then use it in this calculation.
2	$N_2 \rightarrow NO$	$2 \times \left(E°_{NO \rightarrow N_2}\right)$	$N_2 \rightarrow N_2O \rightarrow NO$ $NE° = 1 \times E°_{NO \rightarrow N_2O} + 1 \times E°_{N_2O \rightarrow N_2}$ $NE° = 1 \times E°_{NO \rightarrow N_2O} + NE°$ $NE° = 1 \times 1.59V + 1.77V = 3.36V$	Calculate $NE°$ for the +1 oxidation state, NO, first. Then use it in this calculation.
1	$N_2 \rightarrow N_2O$	$1 \times E°_{N_2O \rightarrow N_2}$	$N_2 \rightarrow N_2O$ $NE° = 1 \times E°_{N_2O \rightarrow N_2}$ $NE° = 1 \times +1.77V = +1.77V$	
0	None	0 V	$NE° = 0V$ by definition.	Defined as 0 V
-1	$N_2 \rightarrow NH_3OH^+$	$(-1) \times E°_{N_2 \rightarrow NH_3OH^+}$	$N_2 \rightarrow NH_3OH^+$ $NE° = (-1)E°_{N_2 \rightarrow NH_3OH^+}$ $NE° = (-1) \times (-1.87V) = +1.87V$	
-2	$N_2 \rightarrow N_2H_5^+$	$(-2) \times E°_{N_2 \rightarrow N_2H_5^+}$	$N_2 \rightarrow NH_3OH^+ \rightarrow N_2H_5^+$ $NE° = (-1) \times E°_{N_2 \rightarrow NH_3OH^+} + (-1)E°_{NH_3OH^+ \rightarrow N_2H_5^+}$ $NE° = NE°_{-1 O.S.} + (-1)E°_{NH_3OH^+ \rightarrow N_2H_5^+}$ $NE° = +1.87V + (-1) \times 1.41V = 0.46V$	Calculate $NE°$ for the -1 oxidation state, NO, first. Then use it in this calculation.
-3	$N_2 \rightarrow NH_4^+$	$(-3) \times E°_{N_2 \rightarrow NH_4^+}$	$N_2 \rightarrow N_2H_5^+ \rightarrow NH_4^+$ $NE° = (-1)E°_{N_2 \rightarrow N_2H_5^+} + (-1)E°_{N_2H_5^+ \rightarrow NH_4^+}$ $NE° = NE°_{-2 O.S.} + (-1)E°_{N_2H_5^+ \rightarrow NH_4^+}$ $NE° = +0.46V + (-1) \times 1.275V = -0.815V$	Calculate $NE°$ for the -2 oxidation state, NO, first. Then use it in this calculation.

The resulting Frost diagram for acidic aqueous nitrogen is given below.
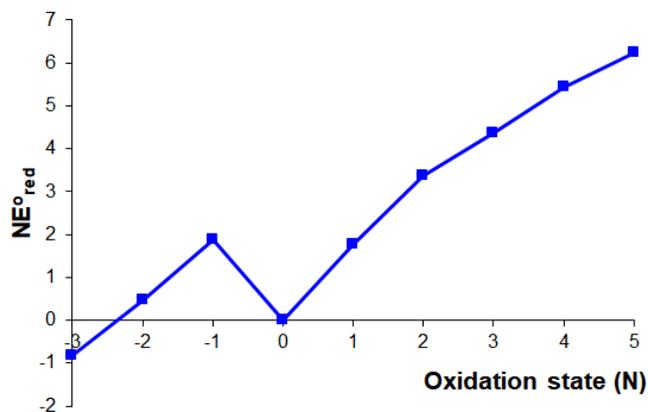
The figure above by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

References

1. Unless otherwise noted all potentials are for strongly acidic solutions and taken from Bard, A. J.; Parsons, R.; Jordan, J. Standard potentials in aqueous solution. M. Dekker: New York, 1985.
2. This diagram is inspired by the similar diagram given in M. Gerken Chemistry 2810 Lecture Notes. Posted on classes.uleth.ca/200501/chem2...lecture_20.pdf
3. The estimated $Fe^{6/3+}$ reduction potential of +2.07 V used to construct the Frost diagram for the first row transition metals is taken from Huheey, J. E.; Keiter, E. A.; Keiter, R. L., Inorganic chemistry : principles of structure and reactivity. 4th ed.; HarperCollins College Publishers: New York, NY, 1993; pg. 596.
4. Lu, J.-B.; Jian, J.; Huang, W.; Lin, H.; Li, J.; Zhou, M., Experimental and theoretical identification of the Fe(vii) oxidation state in FeO4−. Physical Chemistry Chemical Physics 2016, 18 (45), 31125-31131.
5. In some pedagogical applications only the adjoining states are considered.

Contributors and Attributions

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- **8.1.4.2: Frost Diagrams show how stable element's redox states are relative to the free element** has no license indicated.

10.6: Pourbaix Diagrams

Pourbaix Diagrams plot electrochemical stability for different redox states of an element as a function of pH.[3] As noted above, these diagrams are essentially phase diagrams that map the conditions of potential and pH (most typically in aqueous solutions) where different redox species are stable. We saw a simple example of such a diagram in section 4.2 for H_2O. Typically, the water redox reactions are plotted as dotted lines on these more complicated diagrams for other elements.

The lines in Pourbaix diagrams represent redox and acid-base reactions, and are the parts of the diagram where two species can exist in equilibrium. For example, in the Pourbaix diagram for Fe below, the horizontal line between the Fe^{3+} and Fe^{2+} regions represents the reaction $Fe^{3+}_{(aq)} + e^- = Fe^{2+}_{(aq)}$, which has a standard potential of +0.77 V. While we could use standard potentials for all these lines, in practice Pourbaix diagrams are usually plotted for lower ion concentrations (often 1 mM) that are more relevant to corrosion and electrochemical experiments.

Example: Iron Pourbaix diagram

Areas in the Pourbaix diagram mark regions where a single species (Fe^{2+}(aq), Fe_3O_4(s), etc.) is stable. More stable species tend to occupy larger areas.

Lines mark places where two species exist in equilibrium.

- **Pure redox** reactions are **horizontal** lines - these reactions are not pH-dependent
- **Pure acid-base** reactions are **vertical** lines - these do not depend on potential
- Reactions that are **both** acid-base and redox have a slope of -0.0592 V/pH x # H^+/# e^-)
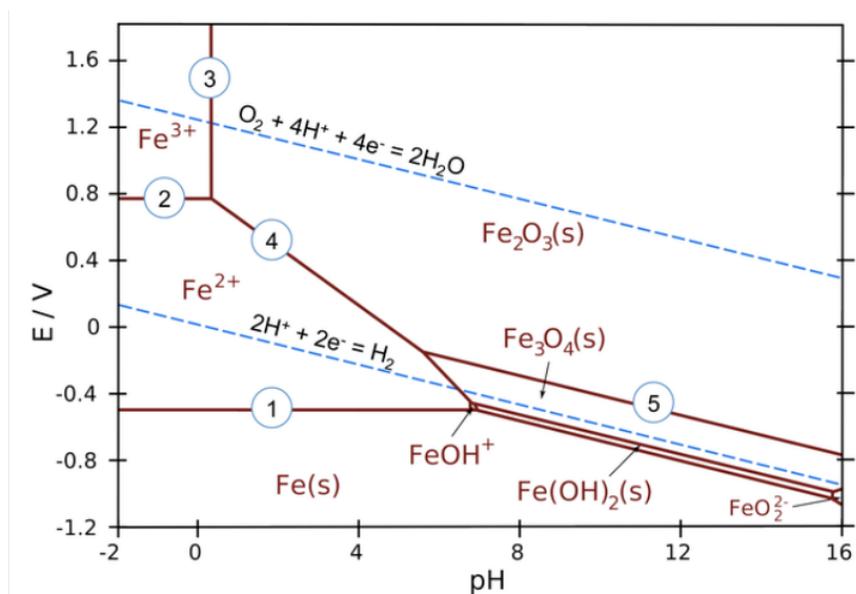
Figure 10.6.1: Pourbaix diagram for iron at ionic concentrations of 1.0 mM. (CC BY-SA 3.0 Unported; Metallos via Wikipedia)

Examples of equilibria in the iron Pourbaix diagram (numbered on the plot):

1. $Fe^{2+} + 2\,e^- \longrightarrow Fe_{(s)}$ (pure redox reaction - no pH dependence)

2. $Fe^{3+} + e^- \longrightarrow Fe^{2+}$ (pure redox reaction - no pH dependence)

3. $2\,Fe^{3+} + 3\,H_2O \longrightarrow Fe_2O_{3(s)} + 6\,H^+$ (pure acid-base, no redox)

4. $2\,Fe^{2+} + 3\,H_2O \longrightarrow Fe_2O_{3(s)} + 6\,H^+ + 2\,e^-$ (slope = -59.2 x 6/2 = -178 mV/pH)

5. $2\,Fe_3O_{4(s)} + H_2O \longrightarrow 2\,H^+ + 2\,e^-$ (slope = -59.2 x 2/2 = -59.2 mV/pH)

The water redox lines have special significance on a Pourbaix diagram for an element such as iron. Recall that liquid water is stable *only* in the region between the dotted lines. Below the H_2 line, water is unstable relative to hydrogen gas, and above the O_2 line, water is unstable with respect to oxygen. For active metals such as Fe, the region where the pure element is stable is typically below the H_2 line. This means that iron metal is unstable in contact with water, undergoing reactions:

$$Fe_{(s)} + 2\,H^+ \longrightarrow Fe^{2+}_{(aq)} + H_2 \quad \text{(in acid)}$$

$$fe_{(s)} + 2\,H_2O \longrightarrow Fe(OH)_{2(s)} + H_2 \quad \text{(in base)}$$
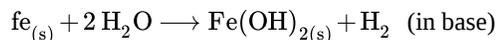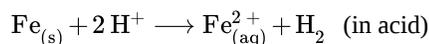
Iron (and most other metals) are also thermodynamically unstable in air-saturated water, where the potential of the solution is close to the O_2 line in the Pourbaix diagram. Here the spontaneous reactions are:

$$4\,Fe_{(s)} + 3\,O_2 + 12\,H^+ \longrightarrow 4\,Fe^{3+} + 6\,H_2O \quad \text{(in acid)}$$

\(\ce{4Fe_{(s)} + 3O2 -> 2Fe2O3_{(s)}} (in base)
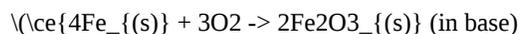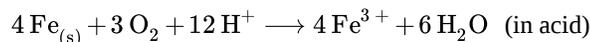
Corrosion and passivation. It certainly sounds bad for our friend Fe: unstable in water, no matter what the pH or potential. Given enough time, it will all turn into rust. But iron (and other active metals) can corrode, or can be stabilized against corrosion, depending on the conditions. Because our civilization is dependent on the use of active metals such as Fe, Al, Zn, Ti, Cr... for practically everything, it is important to understand this, and we can do so by referring to the Pourbaix diagram.

The **corrosion** of iron (and other active metals such as Al) is indeed rapid in parts of the Pourbaix diagram where the element is oxidized to a soluble, ionic product such as Fe^{3+}(aq) or Al^{3+}(aq). However, solids such as Fe_2O_3, and especially Al_2O_3, form a protective coating on the metal that greatly impedes the corrosion reaction. This phenomenon is called **passivation.**

Draw a vertical line through the iron Pourbaix diagram at the pH of tap water (about 6) and you will discover something interesting: at slightly acidic pH, iron is quite unstable with respect to corrosion by the reaction:

$$Fe_{(s)} + 2\,H^+ \longrightarrow Fe^{2+}_{(aq)} + H_2 \tag{10.6.1}$$

but *only in water that contains relatively little oxygen,* i.e., in solutions where the potential is near the H_2 line. Saturating the water with air or oxygen moves the system closer to the O_2 line, where the most stable species is Fe_2O_3 and the corrosion reaction is:

$$4\,Fe_{(s)} + 3\,O_2 \longrightarrow 2\,Fe_2O_{3(s)} \tag{10.6.2}$$

This oxidation reaction is orders of magnitude slower because the oxide that is formed *passivates* the surface. Therefore iron corrodes much more slowly in oxygenated solutions.

More generally, iron (and other active metals) are passivated whenever they oxidize to produce a solid product, and corrode whenever the product is ionic and soluble. This behavior can be summed up on the color-coded Pourbaix diagram below. The red and green regions represent conditions under which oxidation of iron produces soluble and insoluble products, respectively.
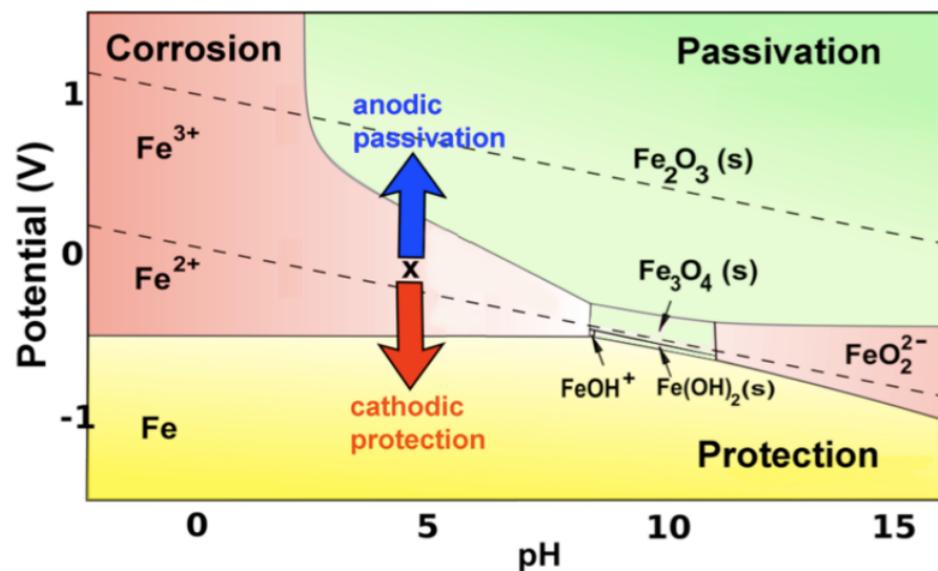
In the yellow part of the diagram, an active metal such as iron can be **protected** by a second mechanism, which is to bias it so that its potential is below the oxidation potential of the metal. This **cathodic protection** strategy is most frequently carried out by

connecting a more active metal such as Mg or Zn to the iron or steel object (e.g., the hull of a ship, or an underground gas pipeline) that is being protected. The active metal (which must be higher than Fe in the activity series) is also in contact with the solution and slowly corrodes, so it must eventually be replaced. In some cases a battery or DC power supply - the anode of which oxidizes water to oxygen in the solution - is used instead to apply a negative bias.

The white patches visible on the ship's hull are zinc block sacrificial anodes.

Another common mode of corrosion of iron and carbon steel is **differential aeration.** In this case, part of the iron object - e.g., the base of a bridge, or the drill in an oil rig - is under water or in an anoxic environment such as mud or soil. The potential of the solution is close to the H_2 line in the Pourbaix diagram, where Fe can corrode to Fe^{2+} (aq). Another part of the iron object is in the air, or near the surface where water is well oxygenated. At that surface oxygen can be reduced to water, $O_2 + 4H^+ + 4e^- = 2\ H_2O$. The conductive iron object completes the circuit, carrying electrons from the anode (where Fe is oxidized) to the cathode (where O_2 is reduced). Corrosion by differential aeration can be rapid because soluble ions are produced, and the reaction has a driving force of over 1 V. Iron or carbon steel that is subjected to frequent weathering, such as the cast iron bridge and lamppost shown below, is corroded on the surface by differential aeration.

Rusty cast iron bridge and lamppost, North Ayrshire, Scotland

Differential aeration is involved in the formation of a rust ring around wet areas of cast iron, e.g., an iron frying pan left partially submerged in water for a day or more. (You may have seen this mechanism of corrosion in action when you did not get to the dirty dishes right away). Under the water, Fe is oxidized to soluble Fe^{2+}, and at the water line O_2 is reduced to H_2O. As Fe^{2+} ions diffuse towards the water surface, they encounter oxygen molecules and are oxidized to Fe^{3+}. However Fe^{3+} is insoluble at neutral pH and deposits as rust, typically just below the water line, forming the rust ring.

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10.7: Exercises

1.

Identify each half-reaction below as either oxidation or reduction.

(a) $Fe^{3+} + 3e^- \longrightarrow Fe$

(b) $Cr \longrightarrow Cr^{3+} + 3e^-$

(c) $MnO_4^{2-} \longrightarrow MnO_4^- + e^-$

(d) $Li^+ + e^- \longrightarrow Li$

2.

Identify each half-reaction below as either oxidation or reduction.

(a) $Cl^- \longrightarrow Cl_2$

(b) $Mn^{2+} \longrightarrow MnO_2$

(c) $H_2 \longrightarrow H^+$

(d) $NO_3^- \longrightarrow NO$
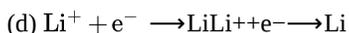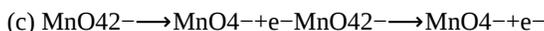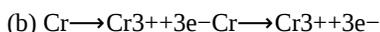
3.

Assuming each pair of half-reactions below takes place in an acidic solution, write a balanced equation for the overall reaction.

(a) $Ca \longrightarrow Ca^{2+} + 2e^-$, $F_2 + 2e^- \longrightarrow 2F^-$

(b) $Li \longrightarrow Li^+ + e^-$, $Cl_2 + 2e^- \longrightarrow 2Cl^-$

(c) $Fe \longrightarrow Fe^{3+} + 3e^-$, $Br_2 + 2e^- \longrightarrow 2Br^-$

(d) $Ag \longrightarrow Ag^+ + e^-$, $MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O$
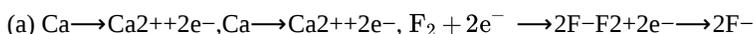
4.

Balance the equations below assuming they occur in an acidic solution.

(a) $H_2O_2 + Sn^{2+} \longrightarrow H_2O + Sn^{4+}$

(b) $PbO_2 + Hg \longrightarrow Hg_2^{2+} + Pb^{2+}$

(c) $Al + Cr_2O_7^{2-} \longrightarrow Al^{3+} + Cr^{3+}$

5.
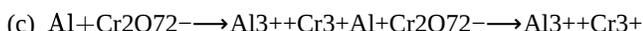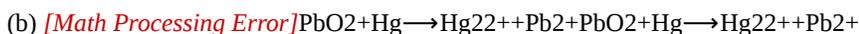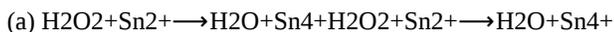
Identify the oxidant and reductant of each reaction of the previous exercise.

6.

Balance the equations below assuming they occur in a basic solution.

(a) $SO_3^{2-}(aq) + Cu(OH)_2(s) \longrightarrow SO_4^{2-}(aq) + Cu(OH)(s)$

(b) $O_2(g) + Mn(OH)_2(s) \longrightarrow MnO_2(s)$

(c) $NO_3^-(aq) + H_2(g) \longrightarrow NO(g)$

(d) $Al(s) + CrO_4^{2-}(aq) \longrightarrow Al(OH)_3(s) + Cr(OH)_4^-(aq)$
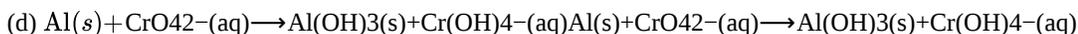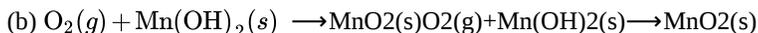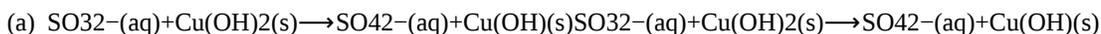
7.

Identify the oxidant and reductant of each reaction of the previous exercise.

8.

Why don't hydroxide ions appear in equations for half-reactions occurring in acidic solution?

9.

Why don't hydrogen ions appear in equations for half-reactions occurring in basic solution?

10.

Why must the charge balance in oxidation-reduction reactions?

11.

Write cell schematics for the following cell reactions, using platinum as an inert electrode as needed.

(a) *[Math Processing Error]*$Mg(s) + Ni^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Ni(s)$

(b) $2Ag^+(aq) + Cu(s) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$

(c) $Mn(s) + Sn(NO_3)_2(aq) \longrightarrow Mn(NO_3)_2(aq) + Sn(s)$

(d) $3CuNO_3(aq) + Au(NO_3)_3(aq) \longrightarrow 3Cu(NO_3)_2(aq) + Au(s)$
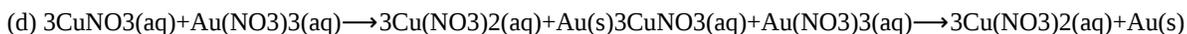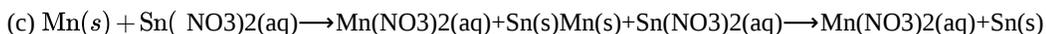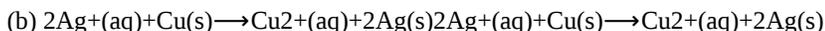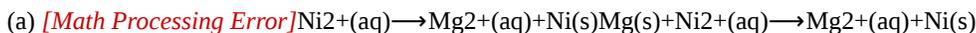
12.

Assuming the schematics below represent galvanic cells as written, identify the half-cell reactions occurring in each.

(a) *[Math Processing Error]*$Mg(s) \mid Mg^{2+}(aq) \parallel Cu^{2+}(aq) \mid Cu(s)$

(b) *[Math Processing Error]*$Ni(s) \mid Ni^{2+}(aq) \parallel Ag^+(aq) \mid Ag(s)$
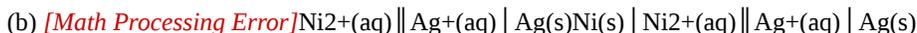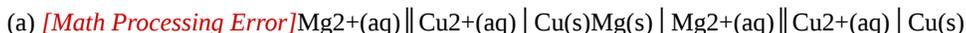
13.

Write a balanced equation for the cell reaction of each cell in the previous exercise.

14.

Balance each reaction below, and write a cell schematic representing the reaction as it would occur in a galvanic cell.

(a) *[Math Processing Error]*$Al(s) + Zr^{4+}(aq) \longrightarrow Al^{3+}(aq) + Zr(s)$

(b) $Ag^+(aq) + NO(g) \longrightarrow Ag(s) + NO_3^-(aq)$ (acidic solution)

(c) $SiO_3^{2-}(aq) + Mg(s) \longrightarrow Si(s) + Mg(OH)_2(s)$ (basic solution)

(d) *[Math Processing Error]*$ClO_3^-(aq) + MnO_2(s) \longrightarrow Cl^-(aq) + MnO_4^-(aq)$ (basic solution)
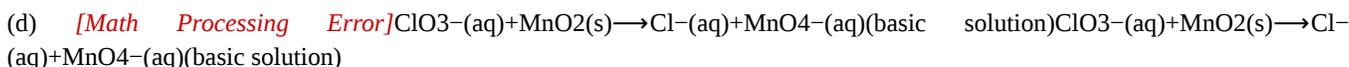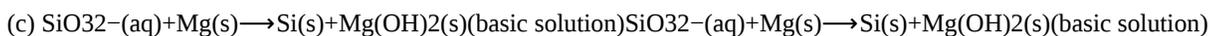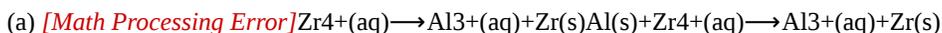
15.

Identify the oxidant and reductant in each reaction of the previous exercise.

16.

From the information provided, use cell notation to describe the following systems:

(a) In one half-cell, a solution of $Pt(NO_3)_2$ forms Pt metal, while in the other half-cell, Cu metal goes into a $Cu(NO_3)_2$ solution with all solute concentrations 1 M.

(b) The cathode consists of a gold electrode in a 0.55 M $Au(NO_3)_3$ solution and the anode is a magnesium electrode in 0.75 M $Mg(NO_3)_2$ solution.

(c) One half-cell consists of a silver electrode in a 1 M $AgNO_3$ solution, and in the other half-cell, a copper electrode in 1 M $Cu(NO_3)_2$ is oxidized.

17.

Why is a salt bridge necessary in galvanic cells like the one in Figure 16.3?

18.

An active (metal) electrode was found to gain mass as the oxidation-reduction reaction was allowed to proceed. Was the electrode an anode or a cathode? Explain.

19.

An active (metal) electrode was found to lose mass as the oxidation-reduction reaction was allowed to proceed. Was the electrode an anode or a cathode? Explain.

20.

The masses of three electrodes (A, B, and C), each from three different galvanic cells, were measured before and after the cells were allowed to pass current for a while. The mass of electrode A increased, that of electrode B was unchanged, and that of electrode C decreased. Identify each electrode as active or inert, and note (if possible) whether it functioned as anode or cathode.

21.

Calculate the standard cell potential for each reaction below, and note whether the reaction is spontaneous under standard state conditions.

(a) *[Math Processing Error]*Ni2+(aq)⟶Mg2+(aq)+Ni(s)Mg(s)+Ni2+(aq)⟶Mg2+(aq)+Ni(s)

(b) 2Ag+(aq)+Cu(s)⟶Cu2+(aq)+2Ag(s)2Ag+(aq)+Cu(s)⟶Cu2+(aq)+2Ag(s)

(c) $\mathrm{Mn}(s) + \mathrm{Sn}($ NO3)2(aq)⟶Mn(NO3)2(aq)+Sn(s)Mn(s)+Sn(NO3)2(aq)⟶Mn(NO3)2(aq)+Sn(s)

(d) 3Fe(NO3)2(aq)+Au(NO3)3(aq)⟶3Fe(NO3)3(aq)+Au(s)3Fe(NO3)2(aq)+Au(NO3)3(aq)⟶3Fe(NO3)3(aq)+Au(s)

22.

Calculate the standard cell potential for each reaction below, and note whether the reaction is spontaneous under standard state conditions.

(a) *[Math Processing Error]*Ni2+(aq)⟶Mn2+(aq)+Ni(s)Mn(s)+Ni2+(aq)⟶Mn2+(aq)+Ni(s)

(b) 3Cu2+(aq)+2Al(s)⟶2Al3+(aq)+3Cu(s)3Cu2+(aq)+2Al(s)⟶2Al3+(aq)+3Cu(s)

(c) *[Math Processing Error]*LiNO3(aq)⟶NaNO3(aq)+Li(s)Na(s)+LiNO3(aq)⟶NaNO3(aq)+Li(s)
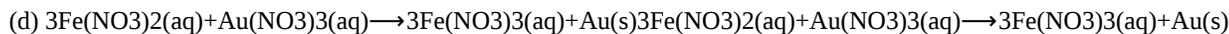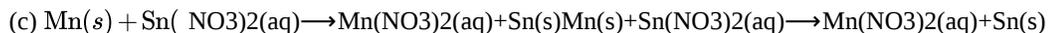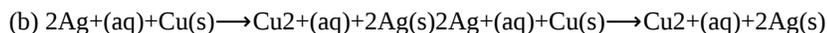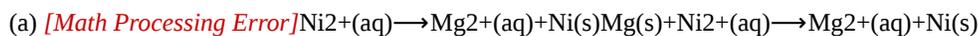
(d) Ca(NO3)2(aq)+Ba(s)⟶Ba(NO3)2(aq)+Ca(s)Ca(NO3)2(aq)+Ba(s)⟶Ba(NO3)2(aq)+Ca(s)
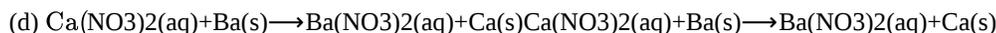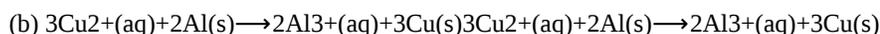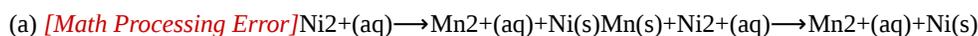
23.

Write the balanced cell reaction for the cell schematic below, calculate the standard cell potential, and note whether the reaction is spontaneous under standard state conditions.

$$\mathrm{Cu}(s) \,|\, \mathrm{Cu}^{2+}(aq) \,\|\, \mathrm{Au}^{3+}(aq) \,|\, \mathrm{Au}(s)$$
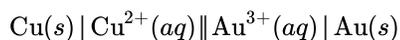
24.

Determine the cell reaction and standard cell potential at 25 °C for a cell made from a cathode half-cell consisting of a silver electrode in 1 *M* silver nitrate solution and an anode half-cell consisting of a zinc electrode in 1 *M* zinc nitrate. Is the reaction spontaneous at standard conditions?

25.

Determine the cell reaction and standard cell potential at 25 °C for a cell made from an anode half-cell containing a cadmium electrode in 1 *M* cadmium nitrate and a cathode half-cell consisting of an aluminum electrode in 1 *M* aluminum nitrate solution. Is the reaction spontaneous at standard conditions?

26.

Write the balanced cell reaction for the cell schematic below, calculate the standard cell potential, and note whether the reaction is spontaneous under standard state conditions.
*[Math Processing Error]*Br2(aq),Br−(aq)│Pt(s)Pt(s)│H2(g)│H+(aq)‖Br2(aq),Br−(aq)│Pt(s)
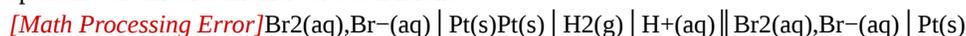
27.

For each pair of standard cell potential and electron stoichiometry values below, calculate a corresponding standard free energy change (kJ).

(a) 0.000 V, n = 2

(b) +0.434 V, n = 2

(c) −2.439 V, n = 1

28.

For each pair of standard free energy change and electron stoichiometry values below, calculate a corresponding standard cell potential.

(a) 12 kJ/mol, n = 3

(b) −45 kJ/mol, n = 1

29.

Determine the standard cell potential and the cell potential under the stated conditions for the electrochemical reactions described here. State whether each is spontaneous or nonspontaneous under each set of conditions at 298.15 K.

(a) $Hg(l) + S^{2-}(aq, 0.10\ M) + 2Ag+(aq, 0.25M) \longrightarrow 2Ag(s) + HgS(s)$Hg(l)+S2−(aq, 0.10M)+2Ag+(aq, 0.25M)⟶2Ag(s)+HgS(s)

(b) The cell made from an anode half-cell consisting of an aluminum electrode in 0.015 *M* aluminum nitrate solution and a cathode half-cell consisting of a nickel electrode in 0.25 *M* nickel(II) nitrate solution.

(c) The cell comprised of a half-cell in which aqueous bromide ion (1.0 *M*) is being oxidized to aqueous bromine (0.11 *M*) and a half-cell in which Al^{3+} (0.023 *M*) is being reduced to aluminum metal.

30.

Determine Δ*G* and Δ*G*° for each of the reactions in the previous problem.

31.

Use the data in Appendix L to calculate equilibrium constants for the following reactions. Assume 298.15 K if no temperature is given.

(a) $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

(b) *[Math Processing Error]*Cd2+(aq)+S2−(aq)at 377 KCdS(s)⇌Cd2+(aq)+S2−(aq)at 377 K

(c) *[Math Processing Error]*Hg2+(aq)+4Br−(aq)⇌[HgBr4]2−(aq)Hg2+(aq)+4Br−(aq)⇌[HgBr4]2−(aq)

(d) H2O(l)⇌H+(aq)+OH−(aq)at 25°CH2O(l)⇌H+(aq)+OH−(aq)at 25°C
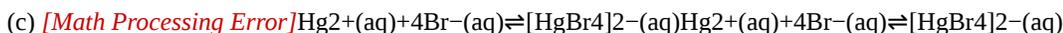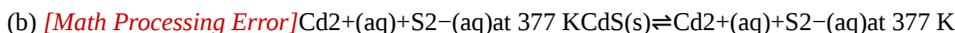
32.

Consider a battery made from one half-cell that consists of a copper electrode in 1 *M* $CuSO_4$ solution and another half-cell that consists of a lead electrode in 1 *M* $Pb(NO_3)_2$ solution.

(a) What is the standard cell potential for the battery?

(b) What are the reactions at the anode, cathode, and the overall reaction?

(c) Most devices designed to use dry-cell batteries can operate between 1.0 and 1.5 V. Could this cell be used to make a battery that could replace a dry-cell battery? Why or why not.

(d) Suppose sulfuric acid is added to the half-cell with the lead electrode and some $PbSO_4(s)$ forms. Would the cell potential increase, decrease, or remain the same?

33.

Consider a battery with the overall reaction: $Cu(s) + 2Ag+(aq) \longrightarrow 2Ag(s) + Cu2+(aq).$Cu(s)+2Ag+(aq)⟶2Ag(s)+Cu2+(aq).

(a) What is the reaction at the anode and cathode?

(b) A battery is "dead" when its cell potential is zero. What is the value of *Q* when this battery is dead?

(c) If a particular dead battery was found to have $[Cu^{2+}]$ = 0.11 *M*, what was the concentration of silver ion?

34.

Why do batteries go dead, but fuel cells do not?

35.

Use the Nernst equation to explain the drop in voltage observed for some batteries as they discharge.

36.

Using the information thus far in this chapter, explain why battery-powered electronics perform poorly in low temperatures.

37.

Which member of each pair of metals is more likely to corrode (oxidize)?

(a) Mg or Ca

(b) Au or Hg

(c) Fe or Zn

(d) Ag or Pt

38.

Consider the following metals: Ag, Au, Mg, Ni, and Zn. Which of these metals could be used as a sacrificial anode in the cathodic protection of an underground steel storage tank? Steel is an alloy composed mostly of iron, so use −0.447 V as the standard reduction potential for steel.

39.

Aluminum *[Math Processing Error]*EAl3+/Al°=−2.07 V)(EAl3+/Al°=−2.07 V) is more easily oxidized than iron *[Math Processing Error]*EFe3+/Fe°=−0.477 V),(EFe3+/Fe°=−0.477 V), and yet when both are exposed to the environment, untreated aluminum has very good corrosion resistance while the corrosion resistance of untreated iron is poor. What might explain this observation?

40.

If a sample of iron and a sample of zinc come into contact, the zinc corrodes but the iron does not. If a sample of iron comes into contact with a sample of copper, the iron corrodes but the copper does not. Explain this phenomenon.

41.

Suppose you have three different metals, A, B, and C. When metals A and B come into contact, B corrodes and A does not corrode. When metals A and C come into contact, A corrodes and C does not corrode. Based on this information, which metal corrodes and which metal does not corrode when B and C come into contact?

42.

Why would a sacrificial anode made of lithium metal be a bad choice

43.

If a 2.5 A current flows through a circuit for 35 minutes, how many coulombs of charge moved through the circuit?

44.

For the scenario in the previous question, how many electrons moved through the circuit?

45.

Write the half-reactions and cell reaction occurring during electrolysis of each molten salt below.

(a) $CaCl_2$

(b) LiH

(c) $AlCl_3$

(d) $CrBr_3$

46.

What mass of each product is produced in each of the electrolytic cells of the previous problem if a total charge of 3.33×10^5 C passes through each cell?

47.

How long would it take to reduce 1 mole of each of the following ions using the current indicated?

(a) Al^{3+}, 1.234 A

(b) Ca^{2+}, 22.2 A

(c) Cr^{5+}, 37.45 A

(d) Au^{3+}, 3.57 A

48.

A current of 2.345 A passes through the cell shown in Figure 16.19 for 45 minutes. What is the volume of the hydrogen collected at room temperature if the pressure is exactly 1 atm? (Hint: Is hydrogen the only gas present above the water?)

49.

An irregularly shaped metal part made from a particular alloy was galvanized with zinc using a $Zn(NO_3)_2$ solution. When a current of 2.599 A was used, it took exactly 1 hour to deposit a 0.01123-mm layer of zinc on the part. What was the total surface area of the part? The density of zinc is 7.140 g/cm^3.

Certainly! Latimer diagrams, also known as reduction potential diagrams, are helpful in understanding the redox stability of various oxidation states of an element. Here are five questions for college students that involve the use of Latimer diagrams to analyze the chemical stability of inorganic compounds:

50.
Using the Latimer diagram for manganese in acidic solution, determine if Mn^{3+} is a stable intermediate or if it will disproportionate. If it is not stable, write the disproportionation reaction.
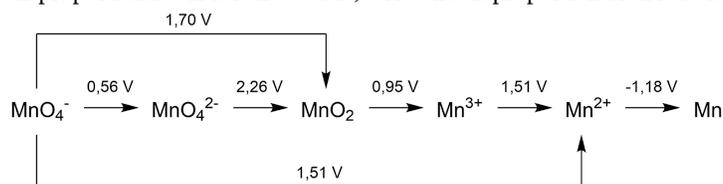
Image by Ptjackyll, CC0, via Wikimedia Commons

51.
Given the Latimer diagram for chlorine in acidic solution, predict if ClO_3^- will disproportionate in acidic solution. Justify your answer with calculations.

Image by Ptjackyll, CC0, via Wikimedia Commons

52.
Analyze the Latimer diagram for copper in neutral or basic solution:

$$Cu^+ \rightarrow Cu \rightarrow Cu^{2+} \tag{10.7.1}$$

with reduction potentials:

$$E^\circ(Cu/Cu^+) = 0.52\,V \tag{10.7.2}$$

$$E^\circ(Cu^{2+}/Cu) = -0.34\,V \tag{10.7.3}$$

Determine if Cu^+ is stable in neutral or basic solution or if it will disproportionate. If disproportionation occurs, provide the balanced reaction.

53.
For the Latimer diagram of nitrogen in acidic solution:

$$N_2 \rightarrow NO \rightarrow NO_2^- \rightarrow NO_3^- \tag{10.7.4}$$
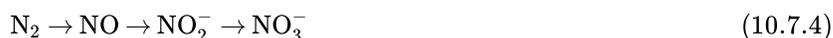
with reduction potentials:

$$E^\circ(NO/N_2) = 0.76\,V \tag{10.7.5}$$

$$E^\circ(NO_2^-/NO) = 1.52\,V \tag{10.7.6}$$

$$E^\circ(\mathrm{NO_3^-/NO_2^-}) = 0.40\,\mathrm{V} \tag{10.7.7}$$

Is NO a stable intermediate in this series, or will it undergo disproportionation? Provide calculations and the balanced equation if disproportionation is predicted.

54.

Given the Latimer diagram for iron in acidic solution:

$$\mathrm{Fe^{2+}} \rightarrow \mathrm{Fe^{3+}} \rightarrow \mathrm{FeO_4^{2-}} \tag{10.7.8}$$

with reduction potentials:

$$E^\circ(\mathrm{Fe^{3+}/Fe^{2+}}) = 0.77\,\mathrm{V} \tag{10.7.9}$$

$$E^\circ(\mathrm{FeO_4^{2-}/Fe^{3+}}) = 2.20\,\mathrm{V} \tag{10.7.10}$$

Assess the stability of $\mathrm{Fe^{3+}}$. Will $\mathrm{Fe^{3+}}$ disproportionate under these conditions? Show your work and the disproportionation reaction if applicable.

55.

Use the Frost diagram for manganese (Mn) in acidic solution to determine which oxidation state is the most stable.
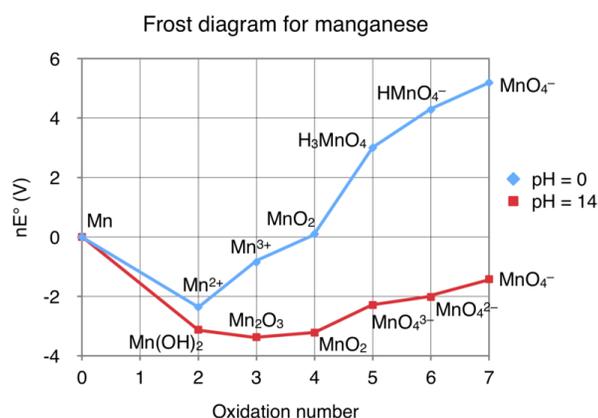
Image by Albris, CC BY-SA 4.0, via Wikimedia commons

56.

Based on the Frost diagram for sulfur in basic solution, identify which oxidation state of sulfur is the least stable. Also, determine which species can act as a good reducing agent.
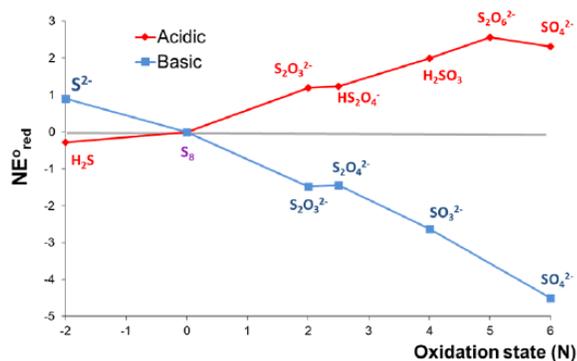
Frost diagrams for sulfur at pH 0 (red) and 14 (blue). This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

57.

Refer to the Frost diagram for chlorine in acidic solution (pH=0 – red line; and pH=14 – blue line), determine which chlorine species is most likely to undergo disproportionation. Explain your reasoning.
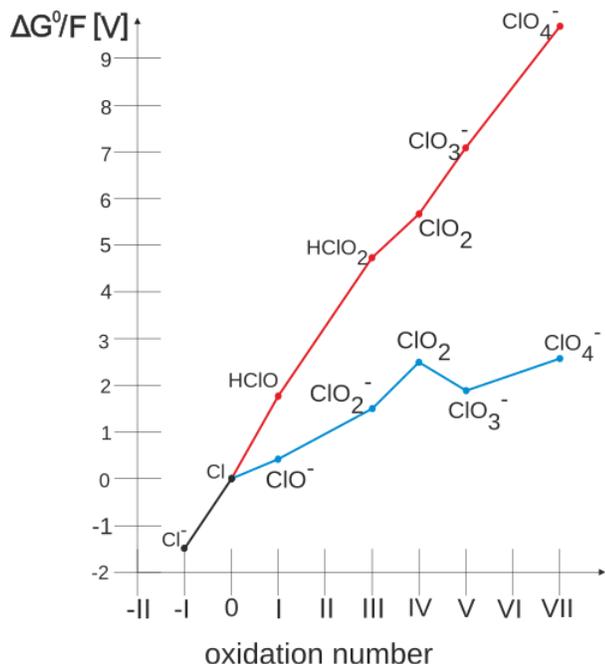
Image by Ptjackyll, CC0, via Wikimedia Commons

58.

Using the Pourbaix diagram for chromium (Cr), how does chromium behave in solutions with pH 1 and pH 9 at potential of 0.7 V? Identify the predominant oxidation states and compounds of chromium at these conditions.
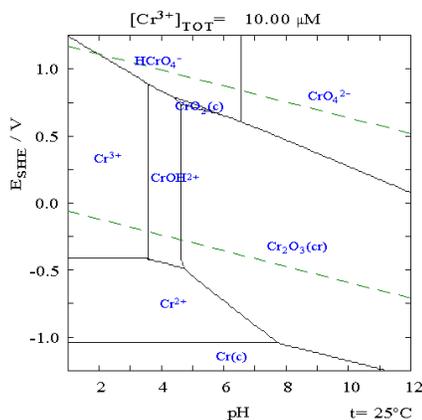
Image by Cadmium (talk) (Uploads), Public domain, via Wikimedia Commons

59.

You are studying the behavior of copper (Cu) in natural water using its Pourbaix diagram. Determine the stability of copper at a pH of 8 and a potential of 0.2 V. Will copper corrode, form a passivating oxide layer, or remain as a solid metal?
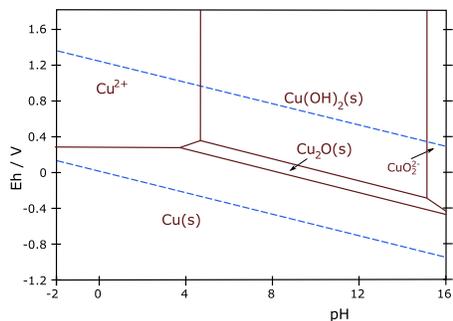
Image by Metallos, GNU Free Documentation License on Wikipedia

60.

You are using a Pourbaix diagram to understand the electroplating process of nickel (Ni). For nickel electroplating, the potential is set to -0.5 V. What should be the pH of the solution to ensure that nickel is deposited as a solid metal rather than forming soluble ions?

$[Ni^{2+}]_{TOT} = 10.00\ \mu M$
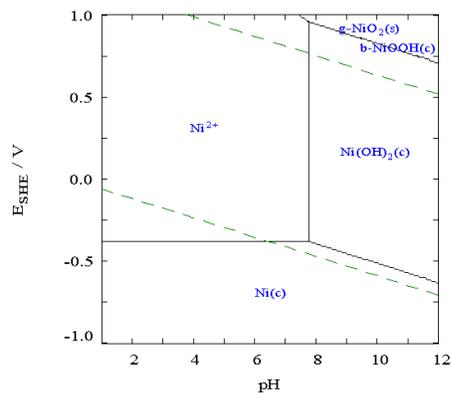
t= 25°C

Image by Cadmium, Public Domain, via Wikimedia

11: Representative Metals, Metalloids, and Nonmetals

The development of the periodic table in the mid-1800s came from observations that there was a periodic relationship between the properties of the elements. Chemists, who have an understanding of the variations of these properties, have been able to use this knowledge to solve a wide variety of technical challenges. For example, silicon and other semiconductors form the backbone of modern electronics because of our ability to fine-tune the electrical properties of these materials. This chapter explores important properties of representative metals, metalloids, and nonmetals in the periodic table.

11.1: Introduction

The development of the periodic table in the mid-1800s came from observations that there was a periodic relationship between the properties of the elements. Chemists, who have an understanding of the variations of these properties, have been able to use this knowledge to solve a wide variety of technical challenges. For example, silicon and other semiconductors form the backbone of modern electronics because of our ability to fine-tune the electrical properties of these materials. This chapter explores important properties of representative metals, metalloids, and nonmetals in the periodic table.
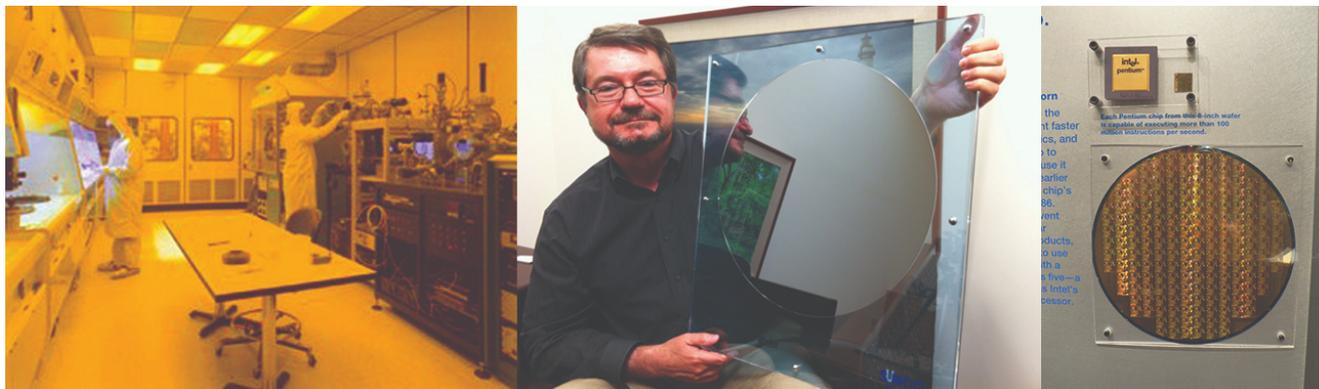
Figure 11.1.1: Purity is extremely important when preparing silicon wafers. Technicians in a cleanroom prepare silicon without impurities (left). The CEO of VLSI Research, Don Hutcheson, shows off a pure silicon wafer (center). A silicon wafer covered in Pentium chips is an enlarged version of the silicon wafers found in many electronics used today (right). (credit middle: modification of work by "Intel Free Press"/Flickr; credit right: modification of work by Naotake Murayama)

11.2: Periodicity

> **◑ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Classify elements
> - Make predictions about the periodicity properties of the representative elements

We begin this section by examining the behaviors of representative metals in relation to their positions in the periodic table. The primary focus of this section will be the application of periodicity to the representative metals.

It is possible to divide elements into groups according to their electron configurations. The **representative elements** are elements where the *s* and *p* orbitals are filling. The transition elements are elements where the *d* orbitals (groups 3–11 on the periodic table) are filling, and the inner transition metals are the elements where the *f* orbitals are filling. The *d* orbitals fill with the elements in group 11; therefore, the elements in group 12 qualify as representative elements because the last electron enters an *s* orbital. Metals among the representative elements are the **representative metals**. Metallic character results from an element's ability to lose its outer valence electrons and results in high thermal and electrical conductivity, among other physical and chemical properties. There are 20 nonradioactive representative metals in groups 1, 2, 3, 12, 13, 14, and 15 of the periodic table (the elements shaded in yellow in Figure 11.2.1). The radioactive elements copernicium, flerovium, polonium, and livermorium are also metals but are beyond the scope of this chapter.

In addition to the representative metals, some of the representative elements are metalloids. A **metalloid** is an element that has properties that are between those of metals and nonmetals; these elements are typically semiconductors.

The remaining representative elements are nonmetals. Unlike metals, which typically form cations and ionic compounds (containing ionic bonds), nonmetals tend to form anions or molecular compounds. In general, the combination of a metal and a nonmetal produces a salt. A salt is an ionic compound consisting of cations and anions.

Figure 11.2.1: The location of the representative metals is shown in the periodic table. Nonmetals are shown in green, metalloids in purple, and the transition metals and inner transition metals in blue.

Most of the representative metals do not occur naturally in an uncombined state because they readily react with water and oxygen in the air. However, it is possible to isolate elemental beryllium, magnesium, zinc, cadmium, mercury, aluminum, tin, and lead from their naturally occurring minerals and use them because they react very slowly with air. Part of the reason why these elements react slowly is that these elements react with air to form a protective coating. The formation of this protective coating is passivation. The coating is a nonreactive film of oxide or some other compound. Elemental magnesium, aluminum, zinc, and tin are important in the fabrication of many familiar items, including wire, cookware, foil, and many household and personal objects. Although beryllium, cadmium, mercury, and lead are readily available, there are limitations in their use because of their toxicity.

Group 1: The Alkali Metals

The alkali metals lithium, sodium, potassium, rubidium, cesium, and francium constitute group 1 of the periodic table. Although hydrogen is in group 1 (and also in group 17), it is a nonmetal and deserves separate consideration later in this chapter. The name alkali metal is in reference to the fact that these metals and their oxides react with water to form very basic (alkaline) solutions.

The properties of the alkali metals are similar to each other as expected for elements in the same family. The alkali metals have the largest atomic radii and the lowest first ionization energy in their periods. This combination makes it very easy to remove the single electron in the outermost (valence) shell of each. The easy loss of this valence electron means that these metals readily form stable cations with a charge of 1+. Their reactivity increases with increasing atomic number due to the ease of losing the lone valence electron (decreasing ionization energy). Since oxidation is so easy, the reverse, reduction, is difficult, which explains why it is hard

to isolate the elements. The solid alkali metals are very soft; lithium, shown in Figure 11.2.2, has the lowest density of any metal (0.5 g/cm^3).

The alkali metals all react vigorously with water to form hydrogen gas and a basic solution of the metal hydroxide. This means they are easier to oxidize than is hydrogen. As an example, the reaction of lithium with water is:

$$2\,\mathrm{Li(s)} + 2\,\mathrm{H_2O(l)} \longrightarrow 2\,\mathrm{LiOH(aq)} + \mathrm{H_2(g)}$$
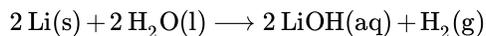
Figure 11.2.2: Lithium floats in paraffin oil because its density is less than the density of paraffin oil.

Alkali metals react directly with all the nonmetals (except the noble gases) to yield binary ionic compounds containing 1+ metal ions. These metals are so reactive that it is necessary to avoid contact with both moisture and oxygen in the air. Therefore, they are stored in sealed containers under mineral oil, as shown in Figure 11.2.3, to prevent contact with air and moisture. The pure metals never exist free (uncombined) in nature due to their high reactivity. In addition, this high reactivity makes it necessary to prepare the metals by electrolysis of alkali metal compounds.

Figure 11.2.3: To prevent contact with air and water, potassium for laboratory use comes as sticks or beads stored under kerosene or mineral oil, or in sealed containers. (credit: http://images-of-elements.com/potassium.php)

Unlike many other metals, the reactivity and softness of the alkali metals make these metals unsuitable for structural applications. However, there are applications where the reactivity of the alkali metals is an advantage. For example, the production of metals such as titanium and zirconium relies, in part, on the ability of sodium to reduce compounds of these metals. The manufacture of many organic compounds, including certain dyes, drugs, and perfumes, utilizes reduction by lithium or sodium.

Sodium and its compounds impart a bright yellow color to a flame, as seen in Figure 11.2.4. Passing an electrical discharge through sodium vapor also produces this color. In both cases, this is an example of an emission spectrum as discussed in the chapter on electronic structure. Streetlights sometime employ sodium vapor lights because the sodium vapor penetrates fog better

than most other light. This is because the fog does not scatter yellow light as much as it scatters white light. The other alkali metals and their salts also impart color to a flame. Lithium creates a bright, crimson color, whereas the others create a pale, violet color.

Figure 11.2.4: Dipping a wire into a solution of a sodium salt and then heating the wire causes emission of a bright yellow light, characteristic of sodium.

📌 Link to Learning

This video demonstrates the reactions of the alkali metals with water.

Group 2: The Alkaline Earth Metals

The **alkaline earth metals** (beryllium, magnesium, calcium, strontium, barium, and radium) constitute group 2 of the periodic table. The name alkaline metal comes from the fact that the oxides of the heavier members of the group react with water to form alkaline solutions. The nuclear charge increases when going from group 1 to group 2. Because of this charge increase, the atoms of the alkaline earth metals are smaller and have higher first ionization energies than the alkali metals within the same period. The higher ionization energy makes the alkaline earth metals less reactive than the alkali metals; however, they are still very reactive elements. Their reactivity increases, as expected, with increasing size and decreasing ionization energy. In chemical reactions, these metals readily lose both valence electrons to form compounds in which they exhibit an oxidation state of 2+. Due to their high reactivity, it is common to produce the alkaline earth metals, like the alkali metals, by electrolysis. Even though the ionization energies are low, the two metals with the highest ionization energies (beryllium and magnesium) do form compounds that exhibit some covalent characters. Like the alkali metals, the heavier alkaline earth metals impart color to a flame. As in the case of the alkali metals, this is part of the emission spectrum of these elements. Calcium and strontium produce shades of red, whereas barium produces a green color.

Magnesium is a silver-white metal that is malleable and ductile at high temperatures. Passivation decreases the reactivity of magnesium metal. Upon exposure to air, a tightly adhering layer of magnesium oxycarbonate forms on the surface of the metal and

inhibits further reaction. (The carbonate comes from the reaction of carbon dioxide in the atmosphere.) Magnesium is the lightest of the widely used structural metals, which is why most magnesium production is for lightweight alloys.

Magnesium (shown in Figure 11.2.5), calcium, strontium, and barium react with water and air. At room temperature, barium shows the most vigorous reaction. The products of the reaction with water are hydrogen and the metal hydroxide. The formation of hydrogen gas indicates that the heavier alkaline earth metals are better reducing agents (more easily oxidized) than is hydrogen. As expected, these metals react with both acids and nonmetals to form ionic compounds. Unlike most salts of the alkali metals, many of the common salts of the alkaline earth metals are insoluble in water because of the high lattice energies of these compounds, containing a divalent metal ion.

Figure 11.2.5: From left to right: Mg(s), warm water at pH 7, and the resulting solution with a pH greater than 7, as indicated by the pink color of the phenolphthalein indicator. (credit: modification of work by Sahar Atwa)

The potent reducing power of hot magnesium is useful in preparing some metals from their oxides. Indeed, magnesium's affinity for oxygen is so great that burning magnesium reacts with carbon dioxide, producing elemental carbon:

$$2\,\mathrm{Mg(s)} + \mathrm{CO_2(g)} \longrightarrow 2\,\mathrm{MgO(s)} + \mathrm{C(s)}$$

For this reason, a CO_2 fire extinguisher will not extinguish a magnesium fire. Additionally, the brilliant white light emitted by burning magnesium makes it useful in flares and fireworks.

Group 12

The elements in group 12 are transition elements; however, the last electron added is not a d electron, but an s electron. Since the last electron added is an s electron, these elements qualify as representative metals, or post-transition metals. The group 12 elements behave more like the alkaline earth metals than transition metals. Group 12 contains the four elements zinc, cadmium, mercury, and copernicium. Each of these elements has two electrons in its outer shell (ns^2). When atoms of these metals form cations with a charge of 2+, where the two outer electrons are lost, they have pseudo-noble gas electron configurations. Mercury is sometimes an exception because it also exhibits an oxidation state of 1+ in compounds that contain a diatomic ion. In their elemental forms and in compounds, cadmium and mercury are both toxic.

Zinc is the most reactive in group 12, and mercury is the least reactive. (This is the reverse of the reactivity trend of the metals of groups 1 and 2, in which reactivity increases down a group. The increase in reactivity with increasing atomic number only occurs for the metals in groups 1 and 2.) The decreasing reactivity is due to the formation of ions with a pseudo-noble gas configuration and to other factors that are beyond the scope of this discussion. The chemical behaviors of zinc and cadmium are quite similar to each other but differ from that of mercury.

Zinc and cadmium have lower reduction potentials than hydrogen, and, like the alkali metals and alkaline earth metals, they will produce hydrogen gas when they react with acids. The reaction of zinc with hydrochloric acid, shown in Figure 11.2.6, is:

$$\mathrm{Zn(s)} + 2\,\mathrm{H_3O^+(aq)} + 2\,\mathrm{Cl^-(aq)} \longrightarrow \mathrm{H_2(g)} + \mathrm{Zn^{2+}(aq)} + 2\,\mathrm{Cl^-(aq)} + 2\,\mathrm{H_2O(l)}$$
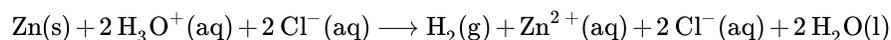
Figure 11.2.6: Zinc is an active metal. It dissolves in hydrochloric acid, forming a solution of colorless Zn^{2+} ions, Cl^- ions, and hydrogen gas.

Zinc is a silvery metal that quickly tarnishes to a blue-gray appearance. This change in color is due to an adherent coating of a basic carbonate, $Zn_2(OH)_2CO_3$, which passivates the metal to inhibit further corrosion. Dry cell and alkaline batteries contain a zinc anode. Brass (Cu and Zn) and some bronze (Cu, Sn, and sometimes Zn) are important zinc alloys. About half of zinc production serves to protect iron and other metals from corrosion. This protection may take the form of a sacrificial anode (also known as a galvanic anode, which is a means of providing cathodic protection for various metals) or as a thin coating on the protected metal. Galvanized steel is steel with a protective coating of zinc.

📌 Chemistry in Everyday Life: Sacrificial Anodes

A sacrificial anode, or galvanic anode, is a means of providing cathodic protection of various metals. Cathodic protection refers to the prevention of corrosion by converting the corroding metal into a cathode. As a cathode, the metal resists corrosion, which is an oxidation process. Corrosion occurs at the sacrificial anode instead of at the cathode.

The construction of such a system begins with the attachment of a more active metal (more negative reduction potential) to the metal needing protection. Attachment may be direct or via a wire. To complete the circuit, a *salt bridge* is necessary. This salt bridge is often seawater or ground water. Once the circuit is complete, oxidation (corrosion) occurs at the anode and not the cathode.

The commonly used sacrificial anodes are magnesium, aluminum, and zinc. Magnesium has the most negative reduction potential of the three and serves best when the salt bridge is less efficient due to a low electrolyte concentration such as in freshwater. Zinc and aluminum work better in saltwater than does magnesium. Aluminum is lighter than zinc and has a higher capacity; however, an oxide coating may passivate the aluminum. In special cases, other materials are useful. For example, iron will protect copper.

Mercury is very different from zinc and cadmium. Mercury is the only metal that is liquid at 25 °C. Many metals dissolve in mercury, forming solutions called amalgams (see the feature on Amalgams), which are alloys of mercury with one or more other metals. Mercury, shown in Figure 11.2.7, is a nonreactive element that is more difficult to oxidize than hydrogen. Thus, it does not displace hydrogen from acids; however, it will react with strong oxidizing acids, such as nitric acid:

$$Hg(l) + HCl(aq) \longrightarrow \text{ no reaction}$$

$$3\,Hg(l) + 8\,HNO_3(aq) \longrightarrow 3\,Hg(NO_3)_2(aq) + 4\,H_2O(l) + 2\,NO(g)$$
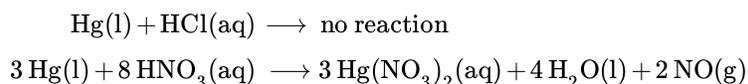
The clear NO initially formed quickly undergoes further oxidation to the reddish brown NO_2.
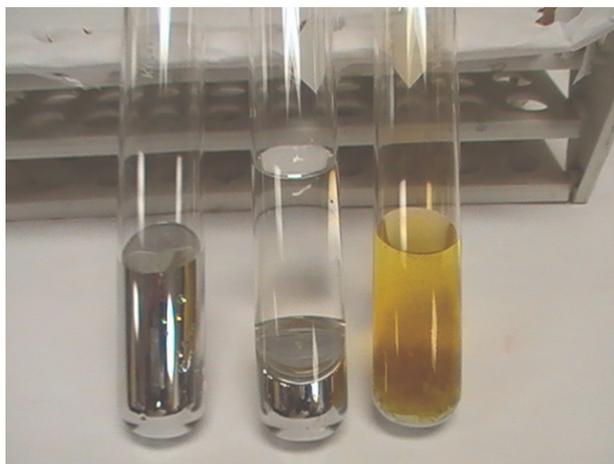
Figure 11.2.7: From left to right: Hg(*l*), Hg + concentrated HCl, Hg + concentrated HNO$_3$. (credit: Sahar Atwa)

Most mercury compounds decompose when heated. Most mercury compounds contain mercury with a 2+-oxidation state. When there is a large excess of mercury, it is possible to form compounds containing the ion. All mercury compounds are toxic, and it is necessary to exercise great care in their synthesis.

📌 Chemistry in Everyday Life: Amalgams

An amalgam is an alloy of mercury with one or more other metals. This is similar to considering steel to be an alloy of iron with other metals. Most metals will form an amalgam with mercury, with the main exceptions being iron, platinum, tungsten, and tantalum.

Due to toxicity issues with mercury, there has been a significant decrease in the use of amalgams. Historically, amalgams were important in electrolytic cells and in the extraction of gold. Amalgams of the alkali metals still find use because they are strong reducing agents and easier to handle than the pure alkali metals.

Prospectors had a problem when they found finely divided gold. They learned that adding mercury to their pans collected the gold into the mercury to form an amalgam for easier collection. Unfortunately, losses of small amounts of mercury over the years left many streams in California polluted with mercury.

Dentists use amalgams containing silver and other metals to fill cavities. There are several reasons to use an amalgam including low cost, ease of manipulation, and longevity compared to alternate materials. Dental amalgams are approximately 50% mercury by weight, which, in recent years, has become a concern due to the toxicity of mercury.

After reviewing the best available data, the Food and Drug Administration (FDA) considers amalgam-based fillings to be safe for adults and children over six years of age. Even with multiple fillings, the mercury levels in the patients remain far below the lowest levels associated with harm. Clinical studies have found no link between dental amalgams and health problems. Health issues may not be the same in cases of children under six or pregnant women. The FDA conclusions are in line with the opinions of the Environmental Protection Agency (EPA) and Centers for Disease Control (CDC). The only health consideration noted is that some people are allergic to the amalgam or one of its components.

Group 13

Group 13 contains the metalloid boron and the metals aluminum, gallium, indium, and thallium. The lightest element, boron, is semiconducting, and its binary compounds tend to be covalent and not ionic. The remaining elements of the group are metals, but their oxides and hydroxides change characters. The oxides and hydroxides of aluminum and gallium exhibit both acidic and basic behaviors. A substance, such as these two, that will react with both acids and bases is amphoteric. This characteristic illustrates the combination of nonmetallic and metallic behaviors of these two elements. Indium and thallium oxides and hydroxides exhibit only basic behavior, in accordance with the clearly metallic character of these two elements. The melting point of gallium is unusually low (about 30 °C) and will melt in your hand.

Aluminum is amphoteric because it will react with both acids and bases. A typical reaction with an acid is:

$$2\,\text{Al(s)} + 6\,\text{HCl(aq)} \longrightarrow 2\,\text{AlCl}_3\text{(aq)} + 3\,\text{H}_2\text{(g)}$$
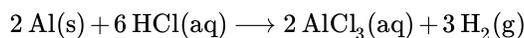
The products of the reaction of aluminum with a base depend upon the reaction conditions, with the following being one possibility:

$$2\,\text{Al(s)} + 2\,\text{NaOH(aq)} + 6\,\text{H}_2\text{O(l)} \longrightarrow 2\,\text{Na[Al(OH)}_4\text{](aq)} + 3\,\text{H}_2\text{(g)}$$
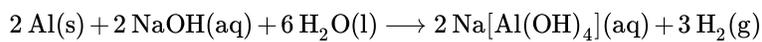
With both acids and bases, the reaction with aluminum generates hydrogen gas.

The group 13 elements have a valence shell electron configuration of ns^2np^1. Aluminum normally uses all of its valence electrons when it reacts, giving compounds in which it has an oxidation state of 3+. Although many of these compounds are covalent, others, such as AlF_3 and $Al_2(SO_4)_3$, are ionic. Aqueous solutions of aluminum salts contain the cation $[\text{Al(H}_2\text{O)}_6]^{3+}$ abbreviated as Al^{3+} (*aq*). Gallium, indium, and thallium also form ionic compounds containing M^{3+} ions. These three elements exhibit not only the expected oxidation state of 3+ from the three valence electrons but also an oxidation state (in this case, 1+) that is two below the expected value. This phenomenon, the inert pair effect, refers to the formation of a stable ion with an oxidation state two lower than expected for the group. The pair of electrons is the valence *s* orbital for those elements. In general, the inert pair effect is important for the lower *p*-block elements. In an aqueous solution, the Tl^+(*aq*) ion is more stable than is Tl^{3+}(*aq*). In general, these metals will react with air and water to form 3+ ions; however, thallium reacts to give thallium(I) derivatives. The metals of group 13 all react directly with nonmetals such as sulfur, phosphorus, and the halogens, forming binary compounds.

The metals of group 13 (Al, Ga, In, and Tl) are all reactive. However, passivation occurs as a tough, hard, thin film of the metal oxide forms upon exposure to air. Disruption of this film may counter the passivation, allowing the metal to react. One way to disrupt the film is to expose the passivated metal to mercury. Some of the metal dissolves in the mercury to form an amalgam, which sheds the protective oxide layer to expose the metal to further reaction. The formation of an amalgam allows the metal to react with air and water.

📌 Link to Learning

> Although easily oxidized, the passivation of aluminum makes it very useful as a strong, lightweight building material. Because of the formation of an amalgam, mercury is corrosive to structural materials made of aluminum. This video demonstrates how the integrity of an aluminum beam can be destroyed by the addition of a small amount of elemental mercury.

The most important uses of aluminum are in the construction and transportation industries, and in the manufacture of aluminum cans and aluminum foil. These uses depend on the lightness, toughness, and strength of the metal, as well as its resistance to corrosion. Because aluminum is an excellent conductor of heat and resists corrosion, it is useful in the manufacture of cooking utensils.

Aluminum is a very good reducing agent and may replace other reducing agents in the isolation of certain metals from their oxides. Although more expensive than reduction by carbon, aluminum is important in the isolation of Mo, W, and Cr from their oxides.

Group 14

The metallic members of group 14 are tin, lead, and flerovium. Carbon is a typical nonmetal. The remaining elements of the group, silicon and germanium, are examples of semimetals or metalloids. Tin and lead form the stable divalent cations, Sn^{2+} and Pb^{2+}, with oxidation states two below the group oxidation state of 4+. The stability of this oxidation state is a consequence of the inert pair effect. Tin and lead also form covalent compounds with a formal 4+-oxidation state. For example, $SnCl_4$ and $PbCl_4$ are low-boiling covalent liquids.
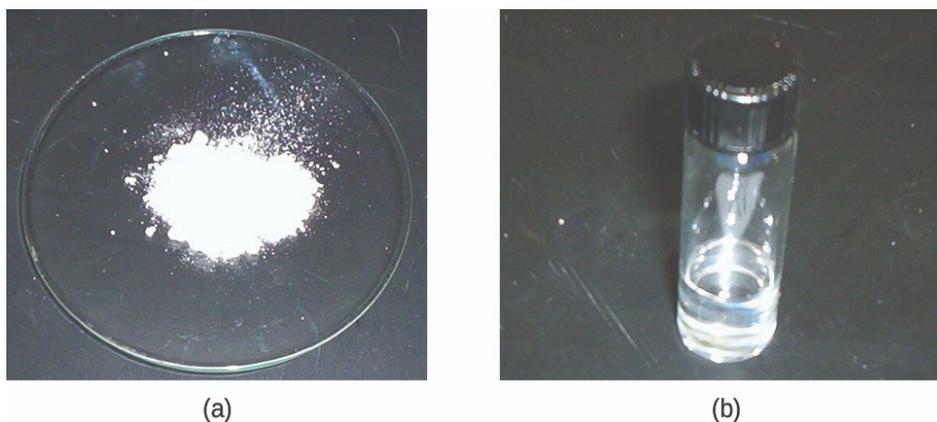
Figure 11.2.8: (a) Tin(II) chloride is an ionic solid; (b) tin(IV) chloride is a covalent liquid.

Tin reacts readily with nonmetals and acids to form tin(II) compounds (indicating that it is more easily oxidized than hydrogen) and with nonmetals to form either tin(II) or tin(IV) compounds (shown in Figure 11.2.8), depending on the stoichiometry and reaction conditions. Lead is less reactive. It is only slightly easier to oxidize than hydrogen, and oxidation normally requires a hot concentrated acid.

Many of these elements exist as allotropes. **Allotropes** are two or more forms of the same element in the same physical state with different chemical and physical properties. There are two common allotropes of tin. These allotropes are grey (brittle) tin and white tin. As with other allotropes, the difference between these forms of tin is in the arrangement of the atoms. White tin is stable above 13.2 °C and is malleable like other metals. At low temperatures, gray tin is the more stable form. Gray tin is brittle and tends to break down to a powder. Consequently, articles made of tin will disintegrate in cold weather, particularly if the cold spell is lengthy. The change progresses slowly from the spot of origin, and the gray tin that is first formed catalyzes further change. In a way, this effect is similar to the spread of an infection in a plant or animal body, leading people to call this process tin disease or tin pest.

The principal use of tin is in the coating of steel to form tin plate-sheet iron, which constitutes the tin in tin cans. Important tin alloys are bronze (Cu and Sn) and solder (Sn and Pb). Lead is important in the lead storage batteries in automobiles.

Group 15

Bismuth, the heaviest member of group 15, is a less reactive metal than the other representative metals. It readily gives up three of its five valence electrons to active nonmetals to form the tri-positive ion, Bi^{3+}. It forms compounds with the group oxidation state of 5+ only when treated with strong oxidizing agents. The stability of the 3+-oxidation state is another example of the inert pair effect.

11.3: Occurrence and Preparation of the Representative Metals

> **◑ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Identify natural sources of representative metals
> - Describe electrolytic and chemical reduction processes used to prepare these elements from natural sources

Because of their reactivity, we do not find most representative metals as free elements in nature. However, compounds that contain ions of most representative metals are abundant. In this section, we will consider the two common techniques used to isolate the metals from these compounds—electrolysis and chemical reduction.

These metals primarily occur in minerals, with lithium found in silicate or phosphate minerals, and sodium and potassium found in salt deposits from evaporation of ancient seas and in silicates. The alkaline earth metals occur as silicates and, with the exception of beryllium, as carbonates and sulfates. Beryllium occurs as the mineral beryl, $Be_3Al_2Si_6O_{18}$, which, with certain impurities, may be either the gemstone emerald or aquamarine. Magnesium is in seawater and, along with the heavier alkaline earth metals, occurs as silicates, carbonates, and sulfates. Aluminum occurs abundantly in many types of clay and in bauxite, an impure aluminum oxide hydroxide. The principle tin ore is the oxide cassiterite, SnO_2, and the principle lead and thallium ores are the sulfides or the products of weathering of the sulfides. The remaining representative metals occur as impurities in zinc or aluminum ores.

Electrolysis

Ions of metals in of groups 1 and 2, along with aluminum, are very difficult to reduce; therefore, it is necessary to prepare these elements by electrolysis, an important process discussed in the chapter on electrochemistry. Briefly, electrolysis involves using electrical energy to drive unfavorable chemical reactions to completion; it is useful in the isolation of reactive metals in their pure forms. Sodium, aluminum, and magnesium are typical examples.

The Preparation of Sodium

The most important method for the production of sodium is the electrolysis of molten sodium chloride; the set-up is a Downs cell, shown in Figure 11.3.1. The reaction involved in this process is:

$$2\,NaCl(l) \xrightarrow[600°C]{electrolysis} 2\,Na(l) + Cl_2(g)$$
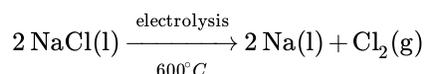
The electrolysis cell contains molten sodium chloride (melting point 801 °C), to which calcium chloride has been added to lower the melting point to 600 °C (a colligative effect). The passage of a direct current through the cell causes the sodium ions to migrate to the negatively charged cathode and pick up electrons, reducing the ions to sodium metal. Chloride ions migrate to the positively charged anode, lose electrons, and undergo oxidation to chlorine gas. The overall cell reaction comes from adding the following reactions:

at the cathode:	$2\,Na^+ + 2\,e^- \longrightarrow 2\,Na(l)$
at the anode:	$2\,Cl^- \longrightarrow Cl_2(g) + 2\,e^-$
overall change:	$2\,Na^+ + 2\,Cl^- \longrightarrow 2\,Na(l) + Cl_2(g)$
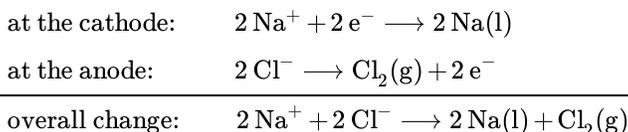
Separation of the molten sodium and chlorine prevents recombination. The liquid sodium, which is less dense than molten sodium chloride, floats to the surface and flows into a collector. The gaseous chlorine goes to storage tanks. Chlorine is also a valuable product.
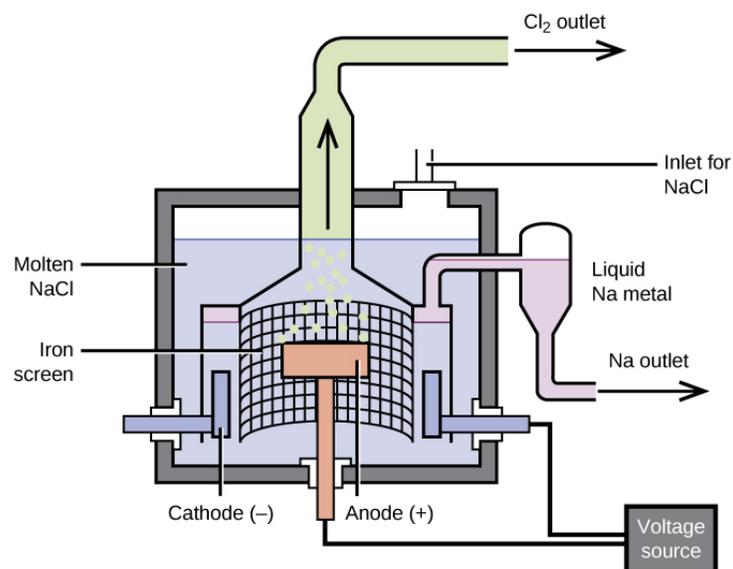
Figure 11.3.1: Pure sodium metal is isolated by electrolysis of molten sodium chloride using a Downs cell. It is not possible to isolate sodium by electrolysis of aqueous solutions of sodium salts because hydrogen ions are more easily reduced than are sodium ions; as a result, hydrogen gas forms at the cathode instead of the desired sodium metal. The high temperature required to melt NaCl means that liquid sodium metal forms.

The Preparation of Aluminum

The preparation of aluminum utilizes a process invented in 1886 by Charles M. Hall, who began to work on the problem while a student at Oberlin College in Ohio. Paul L. T. Héroult discovered the process independently a month or two later in France. In honor to the two inventors, this electrolysis cell is known as the Hall–Héroult cell. The Hall–Héroult cell is an electrolysis cell for the production of aluminum. Figure $11.3.2$ illustrates the Hall–Héroult cell.

The production of aluminum begins with the purification of bauxite, the most common source of aluminum. The reaction of bauxite, AlO(OH), with hot sodium hydroxide forms soluble sodium aluminate, while clay and other impurities remain undissolved:

$$\mathrm{AlO(OH)(s) + NaOH(aq) + H_2O(l) \longrightarrow Na[Al(OH)_4](aq)}$$
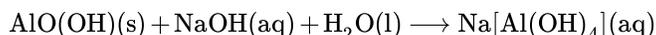
After the removal of the impurities by filtration, the addition of acid to the aluminate leads to the reprecipitation of aluminum hydroxide:

$$\mathrm{Na[Al(OH)_4](aq) + H_3O^+(aq) \longrightarrow Al(OH)_3(s) + Na^+(aq) + 2\,H_2O(l)}$$
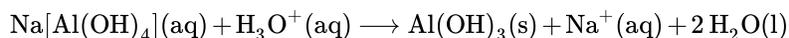
The next step is to remove the precipitated aluminum hydroxide by filtration. Heating the hydroxide produces aluminum oxide, $\mathrm{Al_2O_3}$, which dissolves in a molten mixture of cryolite, $\mathrm{Na_3AlF_6}$, and calcium fluoride, $\mathrm{CaF_2}$. Electrolysis of this solution takes place in a cell like that shown in Figure $11.3.2$ Reduction of aluminum ions to the metal occurs at the cathode, while oxygen, carbon monoxide, and carbon dioxide form at the anode.
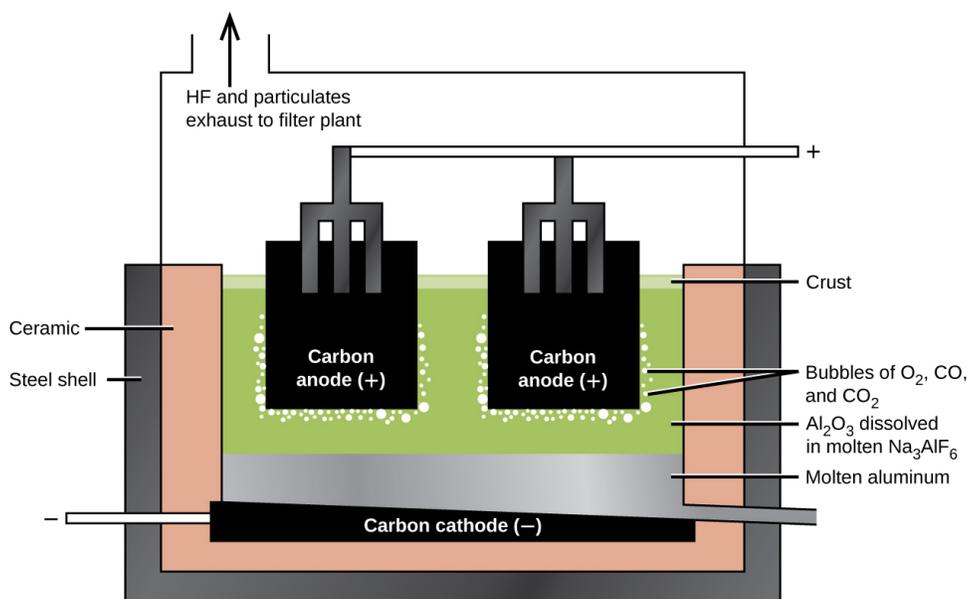
Figure 11.3.2: An electrolytic cell is used for the production of aluminum. The electrolysis of a solution of cryolite and calcium fluoride results in aluminum metal at the cathode, and oxygen, carbon monoxide, and carbon dioxide at the anode.

The Preparation of Magnesium

Magnesium is the other metal that is isolated in large quantities by electrolysis. Seawater, which contains approximately 0.5% magnesium chloride, serves as the major source of magnesium. Addition of calcium hydroxide to seawater precipitates magnesium hydroxide. The addition of hydrochloric acid to magnesium hydroxide, followed by evaporation of the resultant aqueous solution, leaves pure magnesium chloride. The electrolysis of molten magnesium chloride forms liquid magnesium and chlorine gas:

$$\text{MgCl}_2(\text{aq}) + \text{Ca(OH)}_2(\text{aq}) \longrightarrow \text{Mg(OH)}_2(\text{s}) + \text{CaCl}_2(\text{aq})$$

$$\text{Mg(OH)}_2(\text{s}) + 2\,\text{HCl}(\text{aq}) \longrightarrow \text{MgCl}_2(\text{aq}) + 2\,\text{H}_2\text{O}(\text{l})$$

$$\text{MgCl}_2(\text{l}) \longrightarrow \text{Mg}(\text{l}) + \text{Cl}_2(\text{g})$$
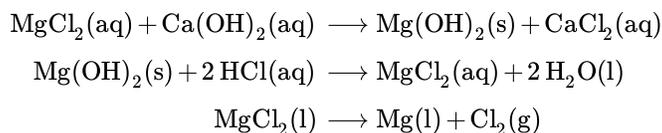
Some production facilities have moved away from electrolysis completely. In the next section, we will see how the Pidgeon process leads to the chemical reduction of magnesium.

Chemical Reduction

It is possible to isolate many of the representative metals by chemical reduction using other elements as reducing agents. In general, chemical reduction is much less expensive than electrolysis, and for this reason, chemical reduction is the method of choice for the isolation of these elements. For example, it is possible to produce potassium, rubidium, and cesium by chemical reduction, as it is possible to reduce the molten chlorides of these metals with sodium metal. This may be surprising given that these metals are more reactive than sodium; however, the metals formed are more volatile than sodium and can be distilled for collection. The removal of the metal vapor leads to a shift in the equilibrium to produce more metal (see how reactions can be driven in the discussions of Le Chatelier's principle in the chapter on fundamental equilibrium concepts).

The production of magnesium, zinc, and tin provide additional examples of chemical reduction.

The Preparation of Magnesium

The Pidgeon process involves the reaction of magnesium oxide with elemental silicon at high temperatures to form pure magnesium:

$$\text{Si}(\text{s}) + 2\,\text{MgO}(\text{s}) \xrightarrow{\Delta} \text{SiO}_2(\text{s}) + 2\,\text{Mg}(\text{g})$$
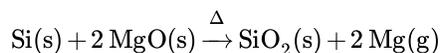
Although this reaction is unfavorable in terms of thermodynamics, the removal of the magnesium vapor produced takes advantage of Le Chatelier's principle to continue the forward progress of the reaction. Over 75% of the world's production of magnesium, primarily in China, comes from this process.

The Preparation of Zinc

Zinc ores usually contain zinc sulfide, zinc oxide, or zinc carbonate. After separation of these compounds from the ores, heating in air converts the ore to zinc oxide by one of the following reactions:

$$2\,ZnS(s) + 3\,O_2(g) \xrightarrow{\Delta} 2\,ZnO(s) + 2\,SO_2(g)$$

$$ZnCO_3(s) \xrightarrow{\Delta} ZnO(s) + CO_2(g)$$
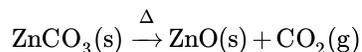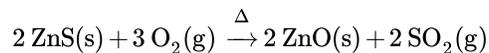
Carbon, in the form of coal, reduces the zinc oxide to form zinc vapor:

$$ZnO(s) + C(s) \longrightarrow Zn(g) + CO(g)$$
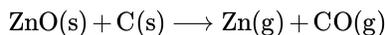
The zinc can be distilled (boiling point 907 °C) and condensed. This zinc contains impurities of cadmium (767 °C), iron (2862 °C), lead (1750 °C), and arsenic (613 °C). Careful redistillation produces pure zinc. Arsenic and cadmium are distilled from the zinc because they have lower boiling points. At higher temperatures, the zinc is distilled from the other impurities, mainly lead and iron.

The Preparation of Tin

The ready reduction of tin(IV) oxide by the hot coals of a campfire accounts for the knowledge of tin in the ancient world. In the modern process, the roasting of tin ores containing SnO_2 removes contaminants such as arsenic and sulfur as volatile oxides. Treatment of the remaining material with hydrochloric acid removes the oxides of other metals. Heating the purified ore with carbon at temperature above 1000 °C produces tin:

$$SnO_2(s) + 2\,C(s) \xrightarrow{\Delta} Sn(s) + 2\,CO(g)$$
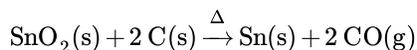
The molten tin collects at the bottom of the furnace and is drawn off and cast into blocks.

11.4: Structure and General Properties of the Metalloids

> **◆ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Describe the general preparation, properties, and uses of the metalloids
> - Describe the preparation, properties, and compounds of boron and silicon

A series of six elements called the metalloids separate the metals from the nonmetals in the periodic table. The metalloids are boron, silicon, germanium, arsenic, antimony, and tellurium. These elements look metallic; however, they do not conduct electricity as well as metals so they are semiconductors. They are semiconductors because their electrons are more tightly bound to their nuclei than are those of metallic conductors. Their chemical behavior falls between that of metals and nonmetals. For example, the pure metalloids form covalent crystals like the nonmetals, but like the metals, they generally do not form monatomic anions. This intermediate behavior is in part due to their intermediate electronegativity values. In this section, we will briefly discuss the chemical behavior of metalloids and deal with two of these elements—boron and silicon—in more detail.

The metalloid boron exhibits many similarities to its neighbor carbon and its diagonal neighbor silicon. All three elements form covalent compounds. However, boron has one distinct difference in that its $2s^2 2p^1$ outer electron structure gives it one less valence electron than it has valence orbitals. Although boron exhibits an oxidation state of 3+ in most of its stable compounds, this electron deficiency provides boron with the ability to form other, sometimes fractional, oxidation states, which occur, for example, in the boron hydrides.

Silicon has the valence shell electron configuration $3s^2 3p^2$, and it commonly forms tetrahedral structures in which it is sp^3 hybridized with a formal oxidation state of 4+. The major differences between the chemistry of carbon and silicon result from the relative strength of the carbon-carbon bond, carbon's ability to form stable bonds to itself, and the presence of the empty $3d$ valence-shell orbitals in silicon. Silicon's empty d orbitals and boron's empty p orbital enable tetrahedral silicon compounds and trigonal planar boron compounds to act as Lewis acids. Carbon, on the other hand, has no available valence shell orbitals; tetrahedral carbon compounds cannot act as Lewis acids. Germanium is very similar to silicon in its chemical behavior.

Arsenic and antimony generally form compounds in which an oxidation state of 3+ or 5+ is exhibited; however, arsenic can form arsenides with an oxidation state of 3−. These elements tarnish only slightly in dry air but readily oxidize when warmed.

Tellurium combines directly with most elements. The most stable tellurium compounds are the tellurides—salts of Te^{2-} formed with active metals and lanthanides—and compounds with oxygen, fluorine, and chlorine, in which tellurium normally exhibits an oxidation state 2+ or 4+. Although tellurium(VI) compounds are known (for example, TeF_6), there is a marked resistance to oxidation to this maximum group oxidation state.

Structures of the Metalloids

Covalent bonding is the key to the crystal structures of the metalloids. In this regard, these elements resemble nonmetals in their behavior.

Elemental silicon, germanium, arsenic, antimony, and tellurium are lustrous, metallic-looking solids. Silicon and germanium crystallize with a diamond structure. Each atom within the crystal has covalent bonds to four neighboring atoms at the corners of a regular tetrahedron. Single crystals of silicon and germanium are giant, three-dimensional molecules. There are several allotropes of arsenic with the most stable being layer like and containing puckered sheets of arsenic atoms. Each arsenic atom forms covalent bonds to three other atoms within the sheet. The crystal structure of antimony is similar to that of arsenic, both shown in Figure 11.4.1. The structures of arsenic and antimony are similar to the structure of graphite, covered later in this chapter. Tellurium forms crystals that contain infinite spiral chains of tellurium atoms. Each atom in the chain bonds to two other atoms.

> **📌 Link to Learning**
>
> Explore a cubic diamond crystal structure.
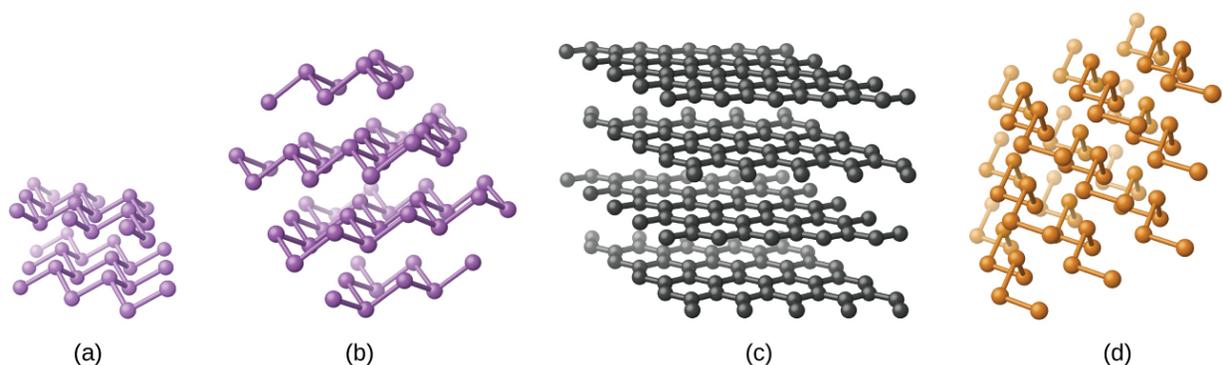
Figure 11.4.1: (a) Arsenic and (b) antimony have a layered structure similar to that of (c) graphite, except that the layers are puckered rather than planar. (d) Elemental tellurium forms spiral chains.

Pure crystalline boron is transparent. The crystals consist of icosahedra, as shown in Figure 11.4.2, with a boron atom at each corner. In the most common form of boron, the icosahedra pack together in a manner similar to the cubic closest packing of spheres. All boron-boron bonds within each icosahedron are identical and are approximately 176 pm in length. In the different forms of boron, there are different arrangements and connections between the icosahedra.
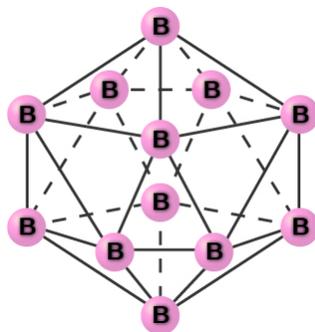
Figure 11.4.2: An icosahedron is a symmetrical, solid shape with 20 faces, each of which is an equilateral triangle. The faces meet at 12 corners.

The name silicon is derived from the Latin word for flint, *silex*. The metalloid silicon readily forms compounds containing Si-O-Si bonds, which are of prime importance in the mineral world. This bonding capability is in contrast to the nonmetal carbon, whose ability to form carbon-carbon bonds gives it prime importance in the plant and animal worlds.

Occurrence, Preparation, and Compounds of Boron and Silicon

Boron constitutes less than 0.001% by weight of the earth's crust. In nature, it only occurs in compounds with oxygen. Boron is widely distributed in volcanic regions as boric acid, $B(OH)_3$, and in dry lake regions, including the desert areas of California, as borates and salts of boron oxyacids, such as borax, $Na_2B_4O_7 \cdot 10H_2O$.

Elemental boron is chemically inert at room temperature, reacting with only fluorine and oxygen to form boron trifluoride, BF_3, and boric oxide, B_2O_3, respectively. At higher temperatures, boron reacts with all nonmetals, except tellurium and the noble gases, and with nearly all metals; it oxidizes to B_2O_3 when heated with concentrated nitric or sulfuric acid. Boron does not react with nonoxidizing acids. Many boron compounds react readily with water to give boric acid, $B(OH)_3$ (sometimes written as H_3BO_3).

Reduction of boric oxide with magnesium powder forms boron (95–98.5% pure) as a brown, amorphous powder:

$$B_2O_3(s) + 3\,Mg(s) \longrightarrow 2\,B(s) + 3\,MgO(s)$$

An amorphous substance is a material that appears to be a solid, but does not have a long-range order like a true solid. Treatment with hydrochloric acid removes the magnesium oxide. Further purification of the boron begins with conversion of the impure boron into boron trichloride. The next step is to heat a mixture of boron trichloride and hydrogen:

$$2\,BCl_3(g) + 3\,H_2(g) \xrightarrow{1500\,^\circ C} 2\,B(s) + 6\,HCl(g) \qquad \Delta H^\circ = 253.7 kJ$$
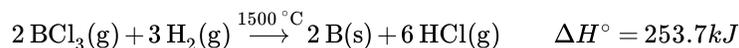
Silicon makes up nearly one-fourth of the mass of the earth's crust—second in abundance only to oxygen. The crust is composed almost entirely of minerals in which the silicon atoms are at the center of the silicon-oxygen tetrahedron, which connect in a variety

of ways to produce, among other things, chains, layers, and three-dimensional frameworks. These minerals constitute the bulk of most common rocks, soil, and clays. In addition, materials such as bricks, ceramics, and glasses contain silicon compounds.

It is possible to produce silicon by the high-temperature reduction of silicon dioxide with strong reducing agents, such as carbon and magnesium:

$$\mathrm{SiO_2(s) + 2\,C(s) \xrightarrow{\Delta} Si(s) + 2\,CO(g)}$$

$$\mathrm{SiO_2(s) + 2\,Mg(s) \xrightarrow{\Delta} Si(s) + 2\,MgO(s)}$$
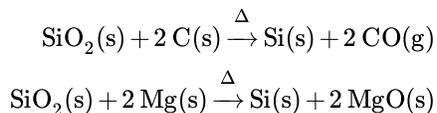
Extremely pure silicon is necessary for the manufacture of semiconductor electronic devices. This process begins with the conversion of impure silicon into silicon tetrahalides, or silane (SiH_4), followed by decomposition at high temperatures. Zone refining, illustrated in Figure 11.4.3, completes the purification. In this method, a rod of silicon is heated at one end by a heat source that produces a thin cross-section of molten silicon. Slowly lowering the rod through the heat source moves the molten zone from one end of the rod to other. As this thin, molten region moves, impurities in the silicon dissolve in the liquid silicon and move with the molten region. Ultimately, the impurities move to one end of the rod, which is then cut off.
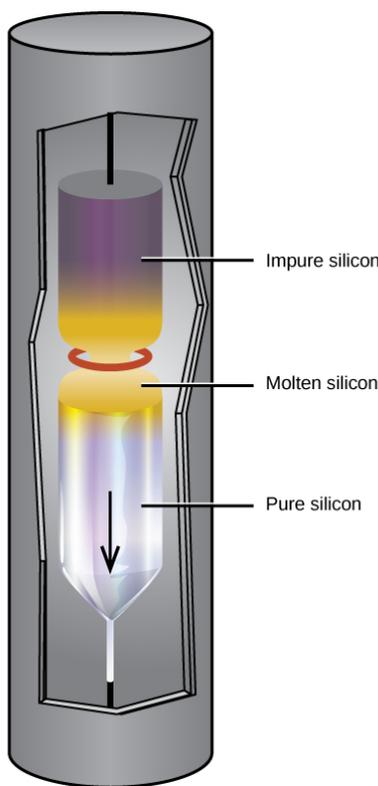
Figure 11.4.3: A zone-refining apparatus used to purify silicon.

This highly purified silicon, containing no more than one part impurity per million parts of silicon, is the most important element in the computer industry. Pure silicon is necessary in semiconductor electronic devices such as transistors, computer chips, and solar cells.

Like some metals, passivation of silicon occurs due the formation of a very thin film of oxide (primarily silicon dioxide, SiO_2). Silicon dioxide is soluble in hot aqueous base; thus, strong bases destroy the passivation. Removal of the passivation layer allows the base to dissolve the silicon, forming hydrogen gas and silicate anions. For example:

$$\mathrm{Si(s) + 4\,OH^-(aq) \longrightarrow SiO_4^{4-}(aq) + 2\,H_2(g)}$$
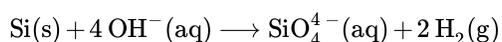
Silicon reacts with halogens at high temperatures, forming volatile tetrahalides, such as SiF_4.

Unlike carbon, silicon does not readily form double or triple bonds. Silicon compounds of the general formula SiX_4, where X is a highly electronegative group, can act as Lewis acids to form six-coordinate silicon. For example, silicon tetrafluoride, SiF_4, reacts with sodium fluoride to yield $Na_2[SiF_6]$, which contains the octahedral ion in which silicon is sp^3d^2 hybridized:

$$2\,\mathrm{NaF(s)} + \mathrm{SiF_4(g)} \longrightarrow \mathrm{Na_2SiF_6(s)}$$
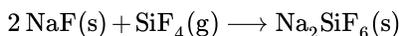
Antimony reacts readily with stoichiometric amounts of fluorine, chlorine, bromine, or iodine, yielding trihalides or, with excess fluorine or chlorine, forming the pentahalides SbF_5 and $SbCl_5$. Depending on the stoichiometry, it forms antimony(III) sulfide, Sb_2S_3, or antimony(V) sulfide when heated with sulfur. As expected, the metallic nature of the element is greater than that of arsenic, which lies immediately above it in group 15.

Boron and Silicon Halides

Boron trihalides—BF_3, BCl_3, BBr_3, and BI_3—can be prepared by the direct reaction of the elements. These nonpolar molecules contain boron with sp^2 hybridization and a trigonal planar molecular geometry. The fluoride and chloride compounds are colorless gasses, the bromide is a liquid, and the iodide is a white crystalline solid.

Except for boron trifluoride, the boron trihalides readily hydrolyze in water to form boric acid and the corresponding hydrohalic acid. Boron trichloride reacts according to the equation:

$$\mathrm{BCl_3(g)} + 3\,\mathrm{H_2O(l)} \longrightarrow \mathrm{B(OH)_3(aq)} + 3\,\mathrm{HCl(aq)}$$
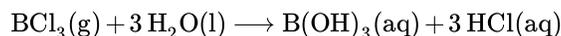
Boron trifluoride reacts with hydrofluoric acid, to yield a solution of fluoroboric acid, HBF_4:

$$\mathrm{BF_3(aq)} + \mathrm{HF(aq)} + \mathrm{H_2O(l)} \longrightarrow \mathrm{H_3O^+(aq)} + \mathrm{BF_4^-(aq)}$$
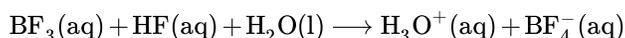
In this reaction, the BF_3 molecule acts as the Lewis acid (electron pair acceptor) and accepts a pair of electrons from a fluoride ion:
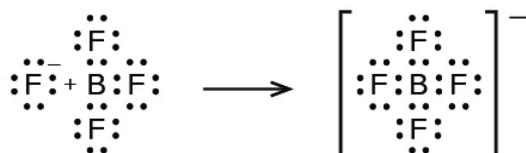
All the tetrahalides of silicon, SiX_4, have been prepared. Silicon tetrachloride can be prepared by direct chlorination at elevated temperatures or by heating silicon dioxide with chlorine and carbon:

$$\mathrm{SiO_2(s)} + 2\,\mathrm{C(s)} + 2\,\mathrm{Cl_2(g)} \xrightarrow{\Delta} \mathrm{SiCl_4(g)} + 2\,\mathrm{CO(g)} \tag{11.4.1}$$
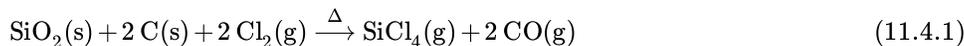
Silicon tetrachloride is a covalent tetrahedral molecule, which is a nonpolar, low-boiling (57 °C), colorless liquid.

It is possible to prepare silicon tetrafluoride by the reaction of silicon dioxide with hydrofluoric acid:

$$\mathrm{SiO_2(s)} + 4\,\mathrm{HF(g)} \longrightarrow \mathrm{SiF_4(g)} + 2\,\mathrm{H_2O(l)} \qquad \Delta H^\circ = -191.2\ \mathrm{kJ}$$
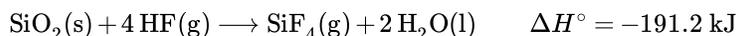
Hydrofluoric acid is the only common acid that will react with silicon dioxide or silicates. This reaction occurs because the silicon-fluorine bond is the only bond that silicon forms that is stronger than the silicon-oxygen bond. For this reason, it is possible to store all common acids, other than hydrofluoric acid, in glass containers.

Except for silicon tetrafluoride, silicon halides are extremely sensitive to water. Upon exposure to water, $SiCl_4$ reacts rapidly with hydroxide groups, replacing all four chlorine atoms to produce unstable orthosilicic acid, $Si(OH)_4$ or H_4SiO_4, which slowly decomposes into SiO_2.

Boron and Silicon Oxides and Derivatives

Boron burns at 700 °C in oxygen, forming boric oxide, B_2O_3. Boric oxide is necessary for the production of heat-resistant borosilicate glass, like that shown in Figure 11.4.4 and certain optical glasses. Boric oxide dissolves in hot water to form boric acid, $B(OH)_3$:

$$\mathrm{B_2O_3(s)} + 3\,\mathrm{H_2O(l)} \longrightarrow 2\,\mathrm{B(OH)_3(aq)}$$
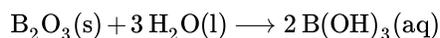
Figure 11.4.4: Laboratory glassware, such as Pyrex and Kimax, is made of borosilicate glass because it does not break when heated. The inclusion of borates in the glass helps to mediate the effects of thermal expansion and contraction. This reduces the likelihood of thermal shock, which causes silicate glass to crack upon rapid heating or cooling. (credit: "Tweenk"/Wikimedia Commons)

The boron atom in $B(OH)_3$ is sp^2 hybridized and is located at the center of an equilateral triangle with oxygen atoms at the corners. In solid $B(OH)_3$, hydrogen bonding holds these triangular units together. Boric acid, shown in Figure 11.4.5, is a very weak acid that does not act as a proton donor but rather as a Lewis acid, accepting an unshared pair of electrons from the Lewis base OH^-:

$$B(OH)_3(aq) + 2\,H_2O(l) \rightleftharpoons B(OH)_4^-(aq) + H_3O^+(aq) \qquad K_a = 5.8 \times 10^{-10}$$
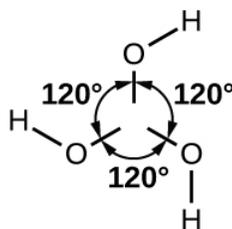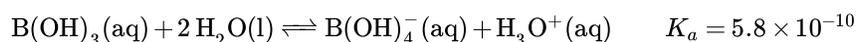
Figure 11.4.5: Boric acid has a planar structure with three –OH groups spread out equally at 120° angles from each other.

Heating boric acid to 100 °C causes molecules of water to split out between pairs of adjacent –OH groups to form metaboric acid, HBO_2. At about 150 °C, additional B-O-B linkages form, connecting the BO_3 groups together with shared oxygen atoms to form tetraboric acid, $H_2B_4O_7$. Complete water loss, at still higher temperatures, results in boric oxide.

Borates are salts of the oxyacids of boron. Borates result from the reactions of a base with an oxyacid or from the fusion of boric acid or boric oxide with a metal oxide or hydroxide. Borate anions range from the simple trigonal planar $_2[B_4O_5(OH)_4]\cdot 8H_2O$, which is an important component of some laundry detergents. Most of the supply of borax comes directly from dry lakes, such as Searles Lake in California, or is prepared from kernite, $Na_2B_4O_7\cdot 4H_2O$.
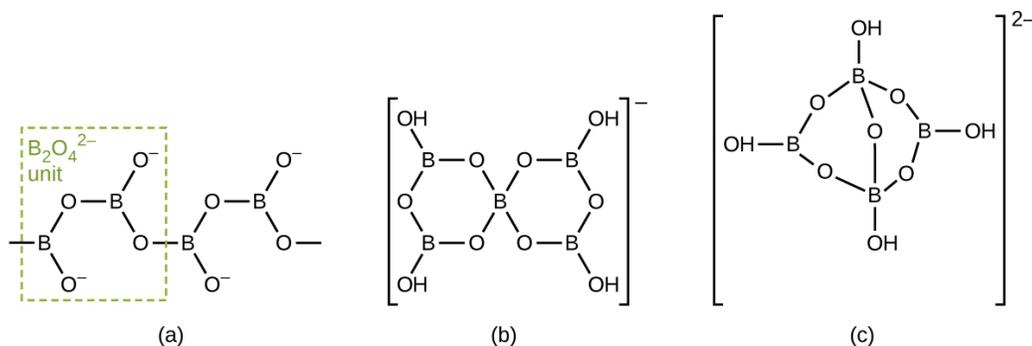
Figure 11.4.6: The borate anions are (a) CaB_2O_4, (b) $KB_5O_8\cdot 4H_2O$, and (c) $Na_2B_4O_7\cdot 10H_2O$. The anion in CaB_2O_4 is an "infinite" chain.

Silicon dioxide, silica, occurs in both crystalline and amorphous forms. The usual crystalline form of silicon dioxide is quartz, a hard, brittle, clear, colorless solid. It is useful in many ways—for architectural decorations, semiprecious jewels, and frequency control in radio transmitters. Silica takes many crystalline forms, or **polymorphs**, in nature. Trace amounts of Fe^{3+} in quartz give

amethyst its characteristic purple color. The term *quartz* is also used for articles such as tubing and lenses that are manufactured from amorphous silica. Opal is a naturally occurring form of amorphous silica.

The contrast in structure and physical properties between silicon dioxide and carbon dioxide is interesting, as illustrated in Figure 11.4.7. Solid carbon dioxide (dry ice) contains single CO_2 molecules with each of the two oxygen atoms attached to the carbon atom by double bonds. Very weak intermolecular forces hold the molecules together in the crystal. The volatility of dry ice reflect these weak forces between molecules. In contrast, silicon dioxide is a covalent network solid. In silicon dioxide, each silicon atom links to four oxygen atoms by single bonds directed toward the corners of a regular tetrahedron, and SiO_4 tetrahedra share oxygen atoms. This arrangement gives a three dimensional, continuous, silicon-oxygen network. A quartz crystal is a macromolecule of silicon dioxide. The difference between these two compounds is the ability of the group 14 elements to form strong π bonds. Second-period elements, such as carbon, form very strong π bonds, which is why carbon dioxide forms small molecules with strong double bonds. Elements below the second period, such as silicon, do not form π bonds as readily as second-period elements, and when they do form, the π bonds are weaker than those formed by second-period elements. For this reason, silicon dioxide does not contain π bonds but only σ bonds.

dry ice

quartz

silicon
oxygen

CO_2

SiO_2

(a)

(b)
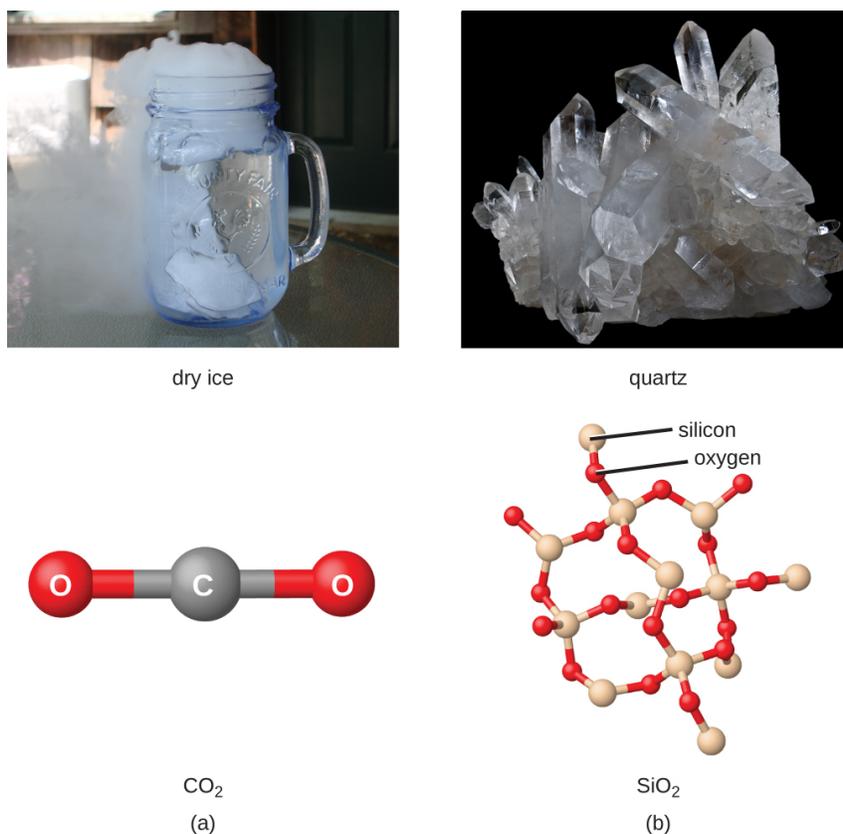
Figure 11.4.7: Because carbon tends to form double and triple bonds and silicon does not, (a) carbon dioxide is a discrete molecule with two C=O double bonds and (b) silicon dioxide is an infinite network of oxygen atoms bridging between silicon atoms with each silicon atom possessing four Si-O single bonds. (credit a photo: modification of work by Erica Gerdes; credit b photo: modification of work by Didier Descouens)

At 1600 °C, quartz melts to yield a viscous liquid. When the liquid cools, it does not crystallize readily but usually supercools and forms a glass, also called silica. The SiO_4 tetrahedra in glassy silica have a random arrangement characteristic of supercooled liquids, and the glass has some very useful properties. Silica is highly transparent to both visible and ultraviolet light. For this reason, it is important in the manufacture of lamps that give radiation rich in ultraviolet light and in certain optical instruments that operate with ultraviolet light. The coefficient of expansion of silica glass is very low; therefore, rapid temperature changes do not cause it to fracture. CorningWare and other ceramic cookware contain amorphous silica.

Silicates are salts containing anions composed of silicon and oxygen. In nearly all silicates, sp^3-hybridized silicon atoms occur at the centers of tetrahedra with oxygen at the corners. There is a variation in the silicon-to-oxygen ratio that occurs because silicon-oxygen tetrahedra may exist as discrete, independent units or may share oxygen atoms at corners in a variety of ways. In addition, the presence of a variety of cations gives rise to the large number of silicate minerals.

Many ceramics are composed of silicates. By including small amounts of other compounds, it is possible to modify the physical properties of the silicate materials to produce ceramics with useful characteristics.

11.5: Structure and General Properties of the Nonmetals

> **◐ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Describe structure and properties of nonmetals

The nonmetals are elements located in the upper right portion of the periodic table. Their properties and behavior are quite different from those of metals on the left side. Under normal conditions, more than half of the nonmetals are gases, one is a liquid, and the rest include some of the softest and hardest of solids. The nonmetals exhibit a rich variety of chemical behaviors. They include the most reactive and least reactive of elements, and they form many different ionic and covalent compounds. This section presents an overview of the properties and chemical behaviors of the nonmetals, as well as the chemistry of specific elements. Many of these nonmetals are important in biological systems.

In many cases, trends in electronegativity enable us to predict the type of bonding and the physical states in compounds involving the nonmetals. We know that electronegativity decreases as we move down a given group and increases as we move from left to right across a period. The nonmetals have higher electronegativities than do metals, and compounds formed between metals and nonmetals are generally ionic in nature because of the large differences in electronegativity between them. The metals form cations, the nonmetals form anions, and the resulting compounds are solids under normal conditions. On the other hand, compounds formed between two or more nonmetals have small differences in electronegativity between the atoms, and covalent bonding—sharing of electrons—results. These substances tend to be molecular in nature and are gases, liquids, or volatile solids at room temperature and pressure.

In normal chemical processes, nonmetals do not form monatomic positive ions (cations) because their ionization energies are too high. All monatomic nonmetal ions are anions; examples include the chloride ion, Cl^-, the nitride ion, N^{3-}, and the selenide ion, Se^{2-}.

The common oxidation states that the nonmetals exhibit in their ionic and covalent compounds are shown in Figure 11.5.1. Remember that an element exhibits a positive oxidation state when combined with a more electronegative element and that it exhibits a negative oxidation state when combined with a less electronegative element.

H	C	N	O	F	
1+	4+	5+	1–	1–	
1–	To	To	2–		
	4–	3–			
		P, As	**S, Se**	**Cl, Br, I**	**Xe**
		5+	6+	7+	8+
		3+	4+	5+	6+
		3–	2–	3+	4+
				1+	2+
				1–	

Figure 11.5.1: Nonmetals exhibit these common oxidation states in ionic and covalent compounds.

The first member of each nonmetal group exhibits different behaviors, in many respects, from the other group members. The reasons for this include smaller size, greater ionization energy, and (most important) the fact that the first member of each group has only four valence orbitals (one 2s and three 2p) available for bonding, whereas other group members have empty d orbitals in their valence shells, making possible five, six, or even more bonds around the central atom. For example, nitrogen forms only NF_3, whereas phosphorus forms both PF_3 and PF_5.

Another difference between the first group member and subsequent members is the greater ability of the first member to form π bonds. This is primarily a function of the smaller size of the first member of each group, which allows better overlap of atomic orbitals. Nonmetals, other than the first member of each group, rarely form π bonds to nonmetals that are the first member of a group. For example, sulfur-oxygen π bonds are well known, whereas sulfur does not normally form stable π bonds to itself.

The variety of oxidation states displayed by most of the nonmetals means that many of their chemical reactions involve changes in oxidation state through oxidation-reduction reactions. There are five general aspects of the oxidation-reduction chemistry:

1. Nonmetals oxidize most metals. The oxidation state of the metal becomes positive as it undergoes oxidation and that of the nonmetal becomes negative as it undergoes reduction. For example:

$$\overset{0}{4\mathrm{Fe}}(s) + \overset{0}{3\mathrm{O}_2}(g) \longrightarrow \overset{+3\ -2}{2\mathrm{Fe}_2\mathrm{O}_3}(s)$$
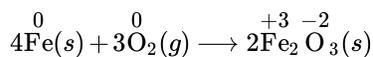
2. With the exception of nitrogen and carbon, which are poor oxidizing agents, a more electronegative nonmetal oxidizes a less electronegative nonmetal or the anion of the nonmetal:

$$\overset{0}{\mathrm{S}}(s) + \overset{0}{3\mathrm{O}_2}(g) \longrightarrow 2\ \overset{+4-2}{\mathrm{S}\ \mathrm{O}_2}(s)$$

$$\overset{0}{\mathrm{Cl}_2}(s) + 2\mathrm{I}^-(aq) \longrightarrow \overset{0}{\mathrm{I}_2}(s) + 2\mathrm{Cl}^-(aq)$$
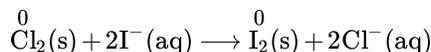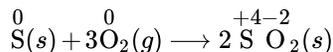
3. Fluorine and oxygen are the strongest oxidizing agents within their respective groups; each oxidizes all the elements that lie below it in the group. Within any period, the strongest oxidizing agent is in group 17. A nonmetal often oxidizes an element that lies to its left in the same period. For example:

$$\overset{0}{2\mathrm{As}}(s) + \overset{0}{3\mathrm{Br}_2}(l) \longrightarrow \overset{+3\ -1}{2\mathrm{As}_2\mathrm{Br}_3}(s)$$
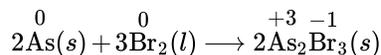
4. The stronger a nonmetal is as an oxidizing agent, the more difficult it is to oxidize the anion formed by the nonmetal. This means that the most stable negative ions are formed by elements at the top of the group or in group 17 of the period.
5. Fluorine and oxygen are the strongest oxidizing elements known. Fluorine does not form compounds in which it exhibits positive oxidation states; oxygen exhibits a positive oxidation state only when combined with fluorine. For example:

$$\overset{0}{2\mathrm{F}_2}(s) + 2\mathrm{OH}^-(aq) \longrightarrow \overset{+2}{\mathrm{O}}\overset{-1}{\mathrm{F}_2}(s) + 2\mathrm{F}^-(aq) + \mathrm{H}_2\mathrm{O}(l)$$
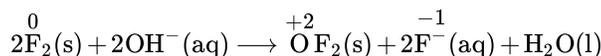
With the exception of most of the noble gases, all nonmetals form compounds with oxygen, yielding covalent oxides. Most of these oxides are acidic, that is, they react with water to form oxyacids. Recall from the acid-base chapter that an oxyacid is an acid consisting of hydrogen, oxygen, and some other element. Notable exceptions are carbon monoxide, CO, nitrous oxide, N_2O, and nitric oxide, NO. There are three characteristics of these acidic oxides:

1. Oxides such as SO2 and N2O5, in which the nonmetal exhibits one of its common oxidation states, are acid anhydrides and react with water to form acids with no change in oxidation state. The product is an oxyacid. For example:
2. Those oxides such as NO_2 and ClO_2, in which the nonmetal does not exhibit one of its common oxidation states, also react with water. In these reactions, the nonmetal is both oxidized and reduced. For example:
Reactions in which the same element is both oxidized and reduced are called disproportionation reactions.
3. The acid strength increases as the electronegativity of the central atom increases. To learn more, see the discussion in the chapter on acid-base chemistry.

The binary hydrogen compounds of the nonmetals also exhibit an acidic behavior in water, although only HCl, HBr, and HI are strong acids. The acid strength of the nonmetal hydrogen compounds increases from left to right across a period and down a group. For example, ammonia, NH_3, is a weaker acid than is water, H_2O, which is weaker than is hydrogen fluoride, HF. Water, H_2O, is also a weaker acid than is hydrogen sulfide, H_2S, which is weaker than is hydrogen selenide, H_2Se. Weaker acidic character implies greater basic character.

Structures of the Nonmetals

The structures of the nonmetals differ dramatically from those of metals. Metals crystallize in closely packed arrays that do not contain molecules or covalent bonds. Nonmetal structures contain covalent bonds, and many nonmetals consist of individual molecules. The electrons in nonmetals are localized in covalent bonds, whereas in a metal, there is delocalization of the electrons throughout the solid.

The noble gases are all monatomic, whereas the other nonmetal gases—hydrogen, nitrogen, oxygen, fluorine, and chlorine—normally exist as the diatomic molecules H_2, N_2, O_2, F_2, and Cl_2. The other halogens are also diatomic; Br_2 is a liquid and I_2 exists as a solid under normal conditions. The changes in state as one moves down the halogen family offer excellent examples of the increasing strength of intermolecular London forces with increasing molecular mass and increasing polarizability.

Oxygen has two allotropes: O_2, dioxygen, and O_3, ozone. Phosphorus has three common allotropes, commonly referred to by their colors: white, red, and black. Sulfur has several allotropes. There are also many carbon allotropes. Most people know of diamond, graphite, and charcoal, but fewer people know of the recent discovery of fullerenes, carbon nanotubes, and graphene.

Descriptions of the physical properties of three nonmetals that are characteristic of molecular solids follow.

Carbon

Carbon occurs in the uncombined (elemental) state in many forms, such as diamond, graphite, charcoal, coke, carbon black, graphene, and fullerene.

Diamond, shown in Figure 11.5.2, is a very hard crystalline material that is colorless and transparent when pure. Each atom forms four single bonds to four other atoms at the corners of a tetrahedron (sp^3 hybridization); this makes the diamond a giant molecule. Carbon-carbon single bonds are very strong, and, because they extend throughout the crystal to form a three-dimensional network, the crystals are very hard and have high melting points (~4400 °C).

(a)   (b)   (c)   (d)
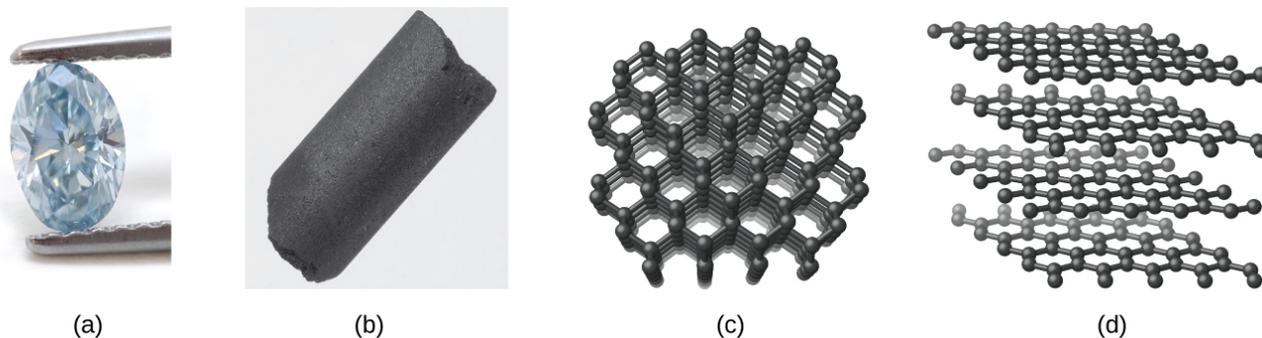
Figure 11.5.2: (a) Diamond and (b) graphite are two forms of carbon. (c) In the crystal structure of diamond, the covalent bonds form three-dimensional tetrahedrons. (d) In the crystal structure of graphite, each planar layer is composed of six-membered rings. (credit a: modification of work by "Fancy Diamonds"/Flickr; credit b: modification of work from http://images-of-elements.com/carbon.php)

Graphite, also shown in Figure 11.5.2, is a soft, slippery, grayish-black solid that conducts electricity. These properties relate to its structure, which consists of layers of carbon atoms, with each atom surrounded by three other carbon atoms in a trigonal planar arrangement. Each carbon atom in graphite forms three σ bonds, one to each of its nearest neighbors, by means of sp^2-hybrid orbitals. The unhybridized p orbital on each carbon atom will overlap unhybridized orbitals on adjacent carbon atoms in the same layer to form π bonds. Many resonance forms are necessary to describe the electronic structure of a graphite layer; Figure 11.5.3 illustrates two of these forms.

(a)   (b)
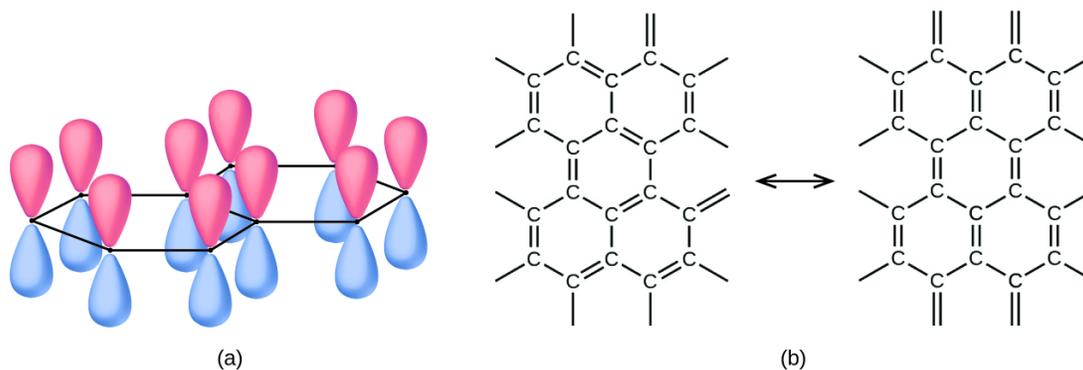
Figure 11.5.3: (a) Carbon atoms in graphite have unhybridized p orbitals. Each p orbital is perpendicular to the plane of carbon atoms. (b) These are two of the many resonance forms of graphite necessary to describe its electronic structure as a resonance hybrid.

Atoms within a graphite layer are bonded together tightly by the σ and π bonds; however, the forces between layers are weak. London dispersion forces hold the layers together. To learn more, see the discussion of these weak forces in the chapter on liquids and solids. The weak forces between layers give graphite the soft, flaky character that makes it useful as the so-called "lead" in pencils and the slippery character that makes it useful as a lubricant. The loosely held electrons in the resonating π bonds can move throughout the solid and are responsible for the electrical conductivity of graphite.

Other forms of elemental carbon include carbon black, charcoal, and coke. Carbon black is an amorphous form of carbon prepared by the incomplete combustion of natural gas, CH_4. It is possible to produce charcoal and coke by heating wood and coal, respectively, at high temperatures in the absence of air.

Recently, new forms of elemental carbon molecules have been identified in the soot generated by a smoky flame and in the vapor produced when graphite is heated to very high temperatures in a vacuum or in helium. One of these new forms, first isolated by Professor Richard Smalley and coworkers at Rice University, consists of icosahedral (soccer-ball-shaped) molecules that contain 60 carbon atoms, C_{60}. This is buckminsterfullerene (often called bucky balls) after the architect Buckminster Fuller, who designed domed structures, which have a similar appearance (Figure 11.5.4).
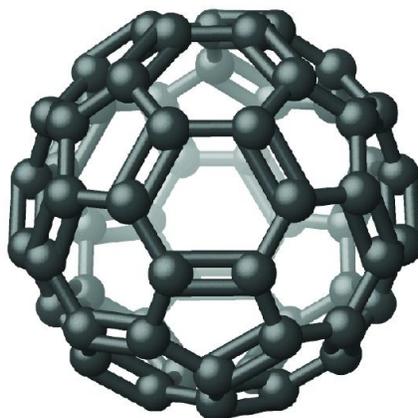
Figure 11.5.4: The molecular structure of C_{60}, buckminsterfullerene, is icosahedral.

📌 Chemistry in Everyday Life: Nanotubes and Graphene

Graphene and carbon nanotubes are two recently discovered allotropes of carbon. Both of the forms bear some relationship to graphite. Graphene is a single layer of graphite (one atom thick), as illustrated in Figure 11.5.5, whereas carbon nanotubes roll the layer into a small tube, as illustrated in Figure 11.5.5.

(a)   (b)
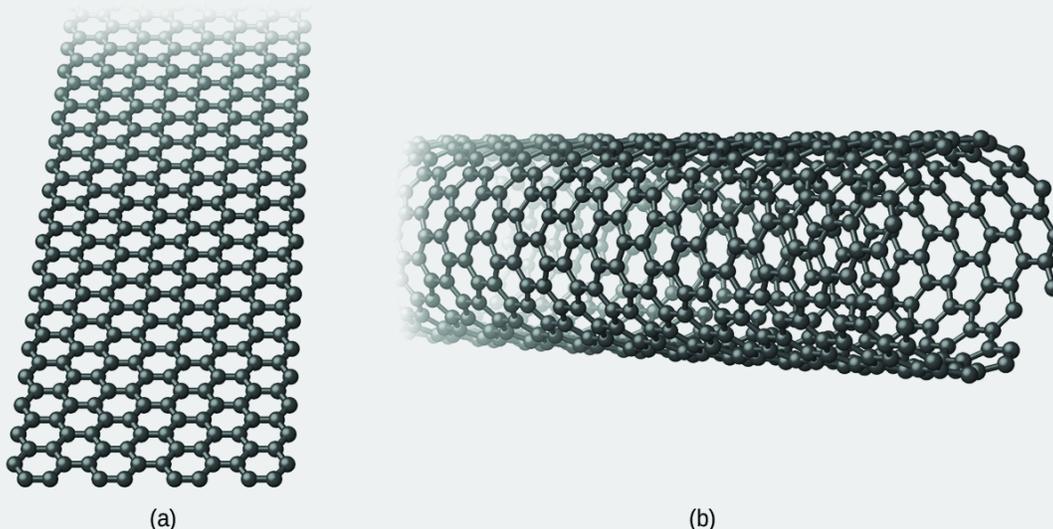
Figure 11.5.5: (a) Graphene and (b) carbon nanotubes are both allotropes of carbon.

Graphene is a very strong, lightweight, and efficient conductor of heat and electricity discovered in 2003. As in graphite, the carbon atoms form a layer of six-membered rings with sp^2-hybridized carbon atoms at the corners. Resonance stabilizes the system and leads to its conductivity. Unlike graphite, there is no stacking of the layers to give a three-dimensional structure. Andre Geim and Kostya Novoselov at the University of Manchester won the 2010 Nobel Prize in Physics for their pioneering work characterizing graphene.

The simplest procedure for preparing graphene is to use a piece of adhesive tape to remove a single layer of graphene from the surface of a piece of graphite. This method works because there are only weak London dispersion forces between the layers in graphite. Alternative methods are to deposit a single layer of carbon atoms on the surface of some other material (ruthenium, iridium, or copper) or to synthesize it at the surface of silicon carbide via the sublimation of silicon.

There currently are no commercial applications of graphene. However, its unusual properties, such as high electron mobility and thermal conductivity, should make it suitable for the manufacture of many advanced electronic devices and for thermal management applications.

Carbon nanotubes are carbon allotropes, which have a cylindrical structure. Like graphite and graphene, nanotubes consist of rings of sp^2-hybridized carbon atoms. Unlike graphite and graphene, which occur in layers, the layers wrap into a tube and bond together to produce a stable structure. The walls of the tube may be one atom or multiple atoms thick.

Carbon nanotubes are extremely strong materials that are harder than diamond. Depending upon the shape of the nanotube, it may be a conductor or semiconductor. For some applications, the conducting form is preferable, whereas other applications utilize the semiconducting form.

The basis for the synthesis of carbon nanotubes is the generation of carbon atoms in a vacuum. It is possible to produce carbon atoms by an electrical discharge through graphite, vaporization of graphite with a laser, and the decomposition of a carbon compound.

The strength of carbon nanotubes will eventually lead to some of their most exciting applications, as a thread produced from several nanotubes will support enormous weight. However, the current applications only employ bulk nanotubes. The addition of nanotubes to polymers improves the mechanical, thermal, and electrical properties of the bulk material. There are currently nanotubes in some bicycle parts, skis, baseball bats, fishing rods, and surfboards.

Phosphorus

The name *phosphorus* comes from the Greek words meaning *light bringing*. When phosphorus was first isolated, scientists noted that it glowed in the dark and burned when exposed to air. Phosphorus is the only member of its group that does not occur in the uncombined state in nature; it exists in many allotropic forms. We will consider two of those forms: white phosphorus and red phosphorus.

White phosphorus is a white, waxy solid that melts at 44.2 °C and boils at 280 °C. It is insoluble in water (in which it is stored—see Figure 11.5.6), is very soluble in carbon disulfide, and bursts into flame in air. As a solid, as a liquid, as a gas, and in solution, white phosphorus exists as P_4 molecules with four phosphorus atoms at the corners of a regular tetrahedron, as illustrated in Figure 11.5.6. Each phosphorus atom covalently bonds to the other three atoms in the molecule by single covalent bonds. White phosphorus is the most reactive allotrope and is very toxic.

(a)	(b)	(c)	(d)
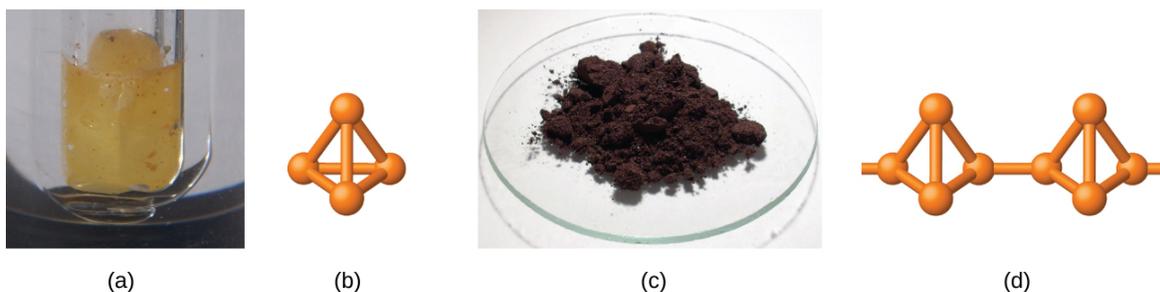
Figure 11.5.6: (a) Because white phosphorus bursts into flame in air, it is stored in water. (b) The structure of white phosphorus consists of P_4 molecules arranged in a tetrahedron. (c) Red phosphorus is much less reactive than is white phosphorus. (d) The structure of red phosphorus consists of networks of P_4 tetrahedra joined by P-P single bonds. (credit a: modification of work from http://images-of-elements.com/phosphorus.php)

Heating white phosphorus to 270–300 °C in the absence of air yields red phosphorus. Red phosphorus (shown in Figure 11.5.6) is denser, has a higher melting point (~600 °C), is much less reactive, is essentially nontoxic, and is easier and safer to handle than is white phosphorus. Its structure is highly polymeric and appears to contain three-dimensional networks of P_4 tetrahedra joined by P-P single bonds. Red phosphorus is insoluble in solvents that dissolve white phosphorus. When red phosphorus is heated, P_4 molecules sublime from the solid.

Sulfur

The allotropy of sulfur is far greater and more complex than that of any other element. Sulfur is the brimstone referred to in the Bible and other places, and references to sulfur occur throughout recorded history—right up to the relatively recent discovery that it is a component of the atmospheres of Venus and of Io, a moon of Jupiter. The most common and most stable allotrope of sulfur is

yellow, rhombic sulfur, so named because of the shape of its crystals. Rhombic sulfur is the form to which all other allotropes revert at room temperature. Crystals of rhombic sulfur melt at 113 °C. Cooling this liquid gives long needles of monoclinic sulfur. This form is stable from 96 °C to the melting point, 119 °C. At room temperature, it gradually reverts to the rhombic form.

Both rhombic sulfur and monoclinic sulfur contain S_8 molecules in which atoms form eight-membered, puckered rings that resemble crowns, as illustrated in Figure 11.5.7. Each sulfur atom is bonded to each of its two neighbors in the ring by covalent S-S single bonds.

(a)   (b)

(c)   (d)
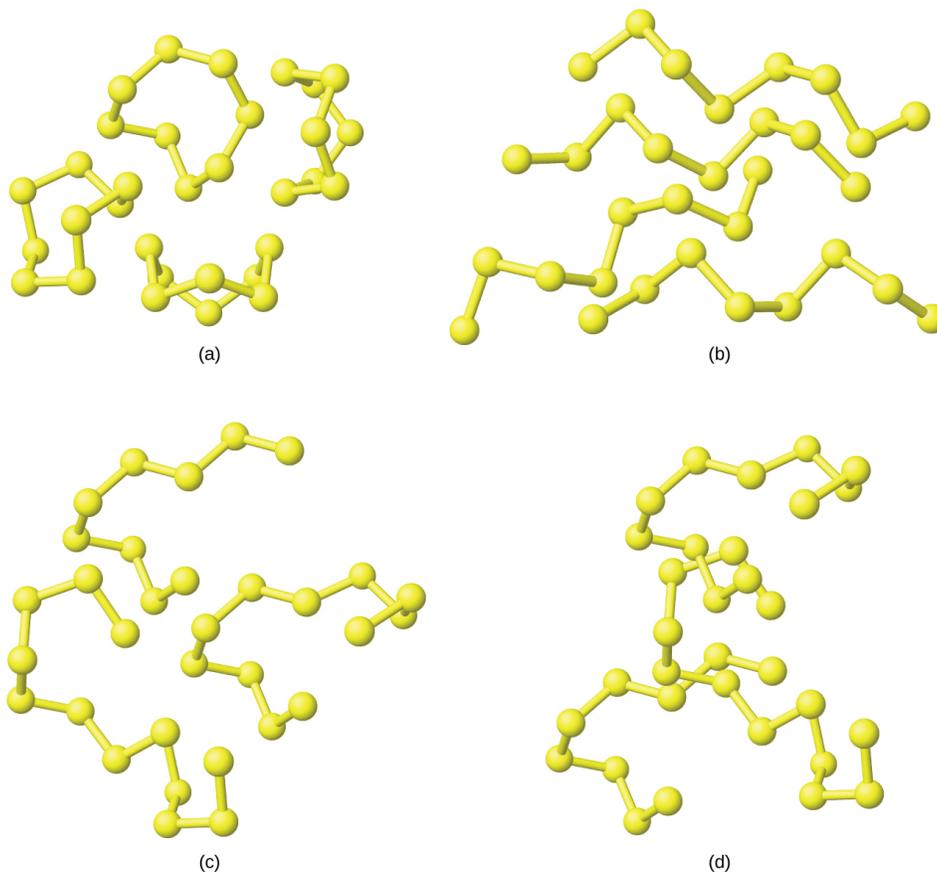
Figure 11.5.7: These four sulfur allotropes show eight-membered, puckered rings. Each sulfur atom bonds to each of its two neighbors in the ring by covalent S-S single bonds. Here are (a) individual S_8 rings, (b) S_8 chains formed when the rings open, (c) longer chains formed by adding sulfur atoms to S_8 chains, and (d) part of the very long sulfur chains formed at higher temperatures.

When rhombic sulfur melts, the straw-colored liquid is quite mobile; its viscosity is low because S_8 molecules are essentially spherical and offer relatively little resistance as they move past each other. As the temperature rises, S-S bonds in the rings break, and polymeric chains of sulfur atoms result. These chains combine end to end, forming still longer chains that tangle with one another. The liquid gradually darkens in color and becomes so viscous that finally (at about 230 °C) it does not pour easily. The dangling atoms at the ends of the chains of sulfur atoms are responsible for the dark red color because their electronic structure differs from those of sulfur atoms that have bonds to two adjacent sulfur atoms. This causes them to absorb light differently and results in a different visible color. Cooling the liquid rapidly produces a rubberlike amorphous mass, called plastic sulfur.

Sulfur boils at 445 °C and forms a vapor consisting of S_2, S_6, and S_8 molecules; at about 1000 °C, the vapor density corresponds to the formula S_2, which is a paramagnetic molecule like O_2 with a similar electronic structure and a weak sulfur-sulfur double bond.

As seen in this discussion, an important feature of the structural behavior of the nonmetals is that the elements usually occur with eight electrons in their valence shells. If necessary, the elements form enough covalent bonds to supplement the electrons already present to possess an octet. For example, members of group 15 have five valence electrons and require only three additional electrons to fill their valence shells. These elements form three covalent bonds in their free state: triple bonds in the N_2 molecule or single bonds to three different atoms in arsenic and phosphorus. The elements of group 16 require only two additional electrons. Oxygen forms a double bond in the O_2 molecule, and sulfur, selenium, and tellurium form two single bonds in various rings and chains. The halogens form diatomic molecules in which each atom is involved in only one bond. This provides the electron

required necessary to complete the octet on the halogen atom. The noble gases do not form covalent bonds to other noble gas atoms because they already have a filled outer shell.

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11.6: Occurrence, Preparation, and Compounds of Hydrogen

> **◐ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Describe the properties, preparation, and compounds of hydrogen

Hydrogen is the most abundant element in the universe. The sun and other stars are composed largely of hydrogen. Astronomers estimate that 90% of the atoms in the universe are hydrogen atoms. Hydrogen is a component of more compounds than any other element. Water is the most abundant compound of hydrogen found on earth. Hydrogen is an important part of petroleum, many minerals, cellulose and starch, sugar, fats, oils, alcohols, acids, and thousands of other substances.

At ordinary temperatures, hydrogen is a colorless, odorless, tasteless, and nonpoisonous gas consisting of the diatomic molecule H_2. Hydrogen is composed of three isotopes, and unlike other elements, these isotopes have different names and chemical symbols: protium, ^1H, deuterium, ^2H(or "D"), and tritium ^3H(or "T"). In a naturally occurring sample of hydrogen, there is one atom of deuterium for every 7000 H atoms and one atom of radioactive tritium for every 10^{18} H atoms. The chemical properties of the different isotopes are very similar because they have identical electron structures, but they differ in some physical properties because of their differing atomic masses. Elemental deuterium and tritium have lower vapor pressure than ordinary hydrogen. Consequently, when liquid hydrogen evaporates, the heavier isotopes are concentrated in the last portions to evaporate. Electrolysis of heavy water, D_2O, yields deuterium. Most tritium originates from nuclear reactions.

Preparation of Hydrogen

Elemental hydrogen must be prepared from compounds by breaking chemical bonds. The most common methods of preparing hydrogen follow.

From Steam and Carbon or Hydrocarbons

Water is the cheapest and most abundant source of hydrogen. Passing steam over coke(an impure form of elemental carbon) at 1000 °C produces a mixture of carbon monoxide and hydrogen known as water gas:

$$C(s) + H_2O(g) \xrightarrow{1000°\,C} \underset{\text{water gas}}{CO(g) + H_2(g)}$$
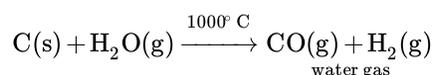
Water gas is as an industrial fuel. It is possible to produce additional hydrogen by mixing the water gas with steam in the presence of a catalyst to convert the CO to CO_2. This reaction is the water gas shift reaction.

It is also possible to prepare a mixture of hydrogen and carbon monoxide by passing hydrocarbons from natural gas or petroleum and steam over a nickel-based catalyst. Propane is an example of a hydrocarbon reactant:

$$C_3H_8(g) + 3\,H_2O(g) \xrightarrow[\text{catalyst}]{900°\,C} 3\,CO(g) + 7\,H_2(g)$$
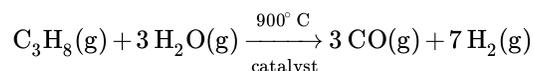
Electrolysis

Hydrogen forms when direct current electricity passes through water containing an electrolyte such as H_2SO_4, as illustrated in Figure 11.6.1. Bubbles of hydrogen form at the cathode, and oxygen evolves at the anode. The net reaction is:

$$2\,H_2O(l) + electrical\,energy \longrightarrow 2\,H_2(g) + O_2(g)$$
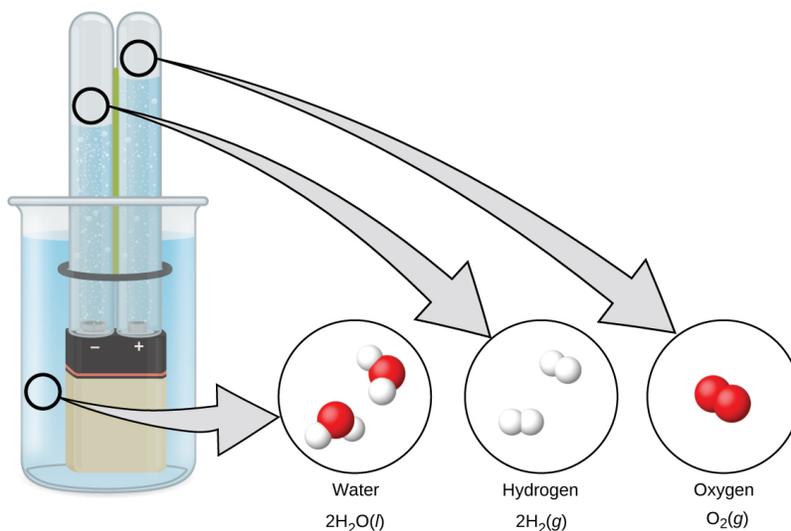
Figure 11.6.1: The electrolysis of water produces hydrogen and oxygen. Because there are twice as many hydrogen atoms as oxygen atoms and both elements are diatomic, there is twice the volume of hydrogen produced at the cathode as there is oxygen produced at the anode.

Reaction of Metals with Acids

This is the most convenient laboratory method of producing hydrogen. Metals with lower reduction potentials reduce the hydrogen ion in dilute acids to produce hydrogen gas and metal salts. For example, as shown in Figure 11.6.2, iron in dilute hydrochloric acid produces hydrogen gas and iron(II) chloride:

$$\mathrm{Fe(s) + 2\,H_3O^+(aq) + 2\,Cl^-(aq) \longrightarrow Fe^{2+}(aq) + 2\,Cl^-(aq) + H_2(g) + 2\,H_2O(l)}$$
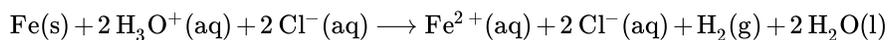
Figure 11.6.2: The reaction of iron with an acid produces hydrogen. Here, iron reacts with hydrochloric acid.(credit: Mark Ott)

Reaction of Ionic Metal Hydrides with Water

It is possible to produce hydrogen from the reaction of hydrides of the active metals, which contain the very strongly basic $\mathrm{H^-}$ anion, with water:

$$\mathrm{CaH_2(s) + 2\,H_2O(l) \longrightarrow Ca^{2+}(aq) + 2\,OH^-(aq) + 2\,H_2(g)}$$
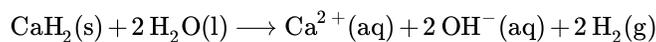
Metal hydrides are expensive but convenient sources of hydrogen, especially where space and weight are important factors. They are important in the inflation of life jackets, life rafts, and military balloons.

Reactions

Under normal conditions, hydrogen is relatively inactive chemically, but when heated, it enters into many chemical reactions.

Two thirds of the world's hydrogen production is devoted to the manufacture of ammonia, which is a fertilizer and used in the manufacture of nitric acid. Large quantities of hydrogen are also important in the process of **hydrogenation**, discussed in the chapter on organic chemistry.

It is possible to use hydrogen as a nonpolluting fuel. The reaction of hydrogen with oxygen is a very exothermic reaction, releasing 286 kJ of energy per mole of water formed. Hydrogen burns without explosion under controlled conditions. The oxygen-hydrogen torch, because of the high heat of combustion of hydrogen, can achieve temperatures up to 2800 °C. The hot flame of this torch is useful in cutting thick sheets of many metals. Liquid hydrogen is also an important rocket fuel (Figure 11.6.3).

Figure 11.6.3: Before the fleet's retirement in 2011, liquid hydrogen and liquid oxygen were used in the three main engines of a space shuttle. Two compartments in the large tank held these liquids until the shuttle was launched.(credit: "reynermedia"/Flickr)

An uncombined hydrogen atom consists of a nucleus and one valence electron in the $1s$ orbital. The $n = 1$ valence shell has a capacity for two electrons, and hydrogen can rightfully occupy two locations in the periodic table. It is possible to consider hydrogen a group 1 element because hydrogen can lose an electron to form the cation, H^+. It is also possible to consider hydrogen to be a group 17 element because it needs only one electron to fill its valence orbital to form a hydride ion, H^-, or it can share an electron to form a single, covalent bond. In reality, hydrogen is a unique element that almost deserves its own location in the periodic table.

Reactions with Elements

When heated, hydrogen reacts with the metals of group 1 and with Ca, Sr, and Ba(the more active metals in group 2). The compounds formed are crystalline, ionic hydrides that contain the hydride anion, H^-, a strong reducing agent and a strong base, which reacts vigorously with water and other acids to form hydrogen gas.

The reactions of hydrogen with nonmetals generally produce *acidic* hydrogen compounds with hydrogen in the 1+ oxidation state. The reactions become more exothermic and vigorous as the electronegativity of the nonmetal increases. Hydrogen reacts with nitrogen and sulfur only when heated, but it reacts explosively with fluorine(forming HF) and, under some conditions, with chlorine(forming HCl). A mixture of hydrogen and oxygen explodes if ignited. Because of the explosive nature of the reaction, it is necessary to exercise caution when handling hydrogen(or any other combustible gas) to avoid the formation of an explosive mixture in a confined space. Although most hydrides of the nonmetals are acidic, ammonia and phosphine(PH_3) are very, very weak acids and generally function as bases. There is a summary of these reactions of hydrogen with the elements in Table 11.6.1.

Table 11.6.1: Chemical Reactions of Hydrogen with Other Elements

General Equation	Comments
MH or $MH_2 \longrightarrow MOH$ or $M(OH)_2 + H2$	ionic hydrides with group 1 and Ca, Sr, and Ba
$H_2 + C \longrightarrow (no\,reaction)$	
$3\,H_2 + N_2 \longrightarrow 2\,NH_3$	requires high pressure and temperature; low yield
$2\,H_2 + O_2 \longrightarrow 2\,H_2O$	exothermic and potentially explosive
\[\ce{H2 + S \longrightarrow H2S}\)	requires heating; low yield
$H_2^+ X_2 \longrightarrow 2\,HX$	X = F, Cl, Br, and I; explosive with F_2; low yield with I_2

Reaction with Compounds

Hydrogen reduces the heated oxides of many metals, with the formation of the metal and water vapor. For example, passing hydrogen over heated CuO forms copper and water.

Hydrogen may also reduce the metal ions in some metal oxides to lower oxidation states:

$$H_2(g) + MnO_2(s) \xrightarrow{\Delta} MnO(s) + H_2O(g)$$
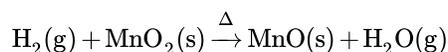
Hydrogen Compounds

Other than the noble gases, each of the nonmetals forms compounds with hydrogen. For brevity, we will discuss only a few hydrogen compounds of the nonmetals here.

Nitrogen Hydrogen Compounds

Ammonia, NH_3, forms naturally when any nitrogen-containing organic material decomposes in the absence of air. The laboratory preparation of ammonia is by the reaction of an ammonium salt with a strong base such as sodium hydroxide. The acid-base reaction with the weakly acidic ammonium ion gives ammonia, illustrated in Figure 11.6.4 Ammonia also forms when ionic nitrides react with water. The nitride ion is a much stronger base than the hydroxide ion:

$$Mg_3N_2(s) + 6\,H_2O(l) \longrightarrow 3\,Mg(OH)_2(s) + 2\,NH_3(g)$$
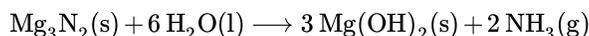
The commercial production of ammonia is by the direct combination of the elements in the **Haber process**:

$$N_2(g) + 3\,H_2(g) \xrightarrow{catalyst} 2\,NH_3(g) \qquad \Delta H° = -92 \text{ kJ}$$
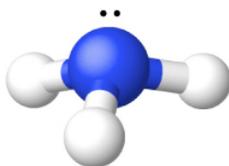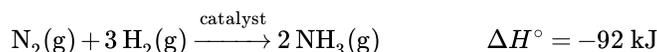
Figure 11.6.4: The structure of ammonia is shown with a central nitrogen atom and three hydrogen atoms.

Ammonia is a colorless gas with a sharp, pungent odor. Smelling salts utilize this powerful odor. Gaseous ammonia readily liquefies to give a colorless liquid that boils at −33 °C. Due to intermolecular hydrogen bonding, the enthalpy of vaporization of liquid ammonia is higher than that of any other liquid except water, so ammonia is useful as a refrigerant. Ammonia is quite soluble in water(658 L at STP dissolves in 1 L H_2O).

The chemical properties of ammonia are as follows:

1. Ammonia acts as a Brønsted base, as discussed in the chapter on acid-base chemistry. The ammonium ion is similar in size to the potassium ion; compounds of the two ions exhibit many similarities in their structures and solubilities.
2. Ammonia can display acidic behavior, although it is a much weaker acid than water. Like other acids, ammonia reacts with metals, although it is so weak that high temperatures are necessary. Hydrogen and(depending on the stoichiometry) amides(salts of NH_2^-), imides(salts of NH^{2-}), or nitrides(salts of N^{3-}) form.
3. The nitrogen atom in ammonia has its lowest possible oxidation state(3−) and thus is not susceptible to reduction. However, it can be oxidized. Ammonia burns in air, giving NO and water. Hot ammonia and the ammonium ion are active reducing agents. Of particular interest are the oxidations of ammonium ion by nitrite ion, to yield pure nitrogen and by nitrate ion to yield nitrous oxide, N_2O.
4. There are a number of compounds that we can consider derivatives of ammonia through the replacement of one or more hydrogen atoms with some other atom or group of atoms. Inorganic derivations include chloramine, NH_2Cl, and hydrazine, N_2H_4:
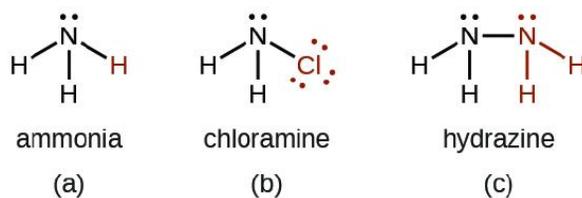
Chloramine, NH_2Cl, results from the reaction of sodium hypochlorite, NaOCl, with ammonia in basic solution. In the presence of a large excess of ammonia at low temperature, the chloramine reacts further to produce hydrazine, N_2H_4:

$$NH_3(aq) + OCl^-(aq) \longrightarrow NH_2Cl(aq) + OH^-(aq)$$

$$[4pt]NH_2Cl(aq) + NH_3(aq) + OH^-(aq) \longrightarrow N_2H_4(aq) + Cl^-(aq) + H_2O(l)$$
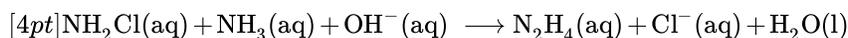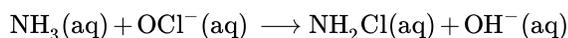
Anhydrous hydrazine is relatively stable in spite of its positive free energy of formation:

$$N_2(g) + 2\,H_2(g) \longrightarrow N_2H_4(l) \qquad \Delta G_f^\circ = 149.2\,kJmol^{-1}$$
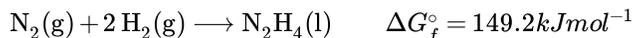
Hydrazine is a fuming, colorless liquid that has some physical properties remarkably similar to those of H_2O(it melts at 2 °C, boils at 113.5 °C, and has a density at 25 °C of 1.00 g/mL). It burns rapidly and completely in air with substantial evolution of heat:

$$N_2H_4(l) + O_2(g) \longrightarrow N_2(g) + 2\,H_2O(l) \qquad \Delta H^\circ = -621.5\,kJmol^{-1}$$

Like ammonia, hydrazine is both a Brønsted base and a Lewis base, although it is weaker than ammonia. It reacts with strong acids and forms two series of salts that contain the and ions, respectively. Some rockets use hydrazine as a fuel.

Phosphorus Hydrogen Compounds

The most important hydride of phosphorus is phosphine, PH_3, a gaseous analog of ammonia in terms of both formula and structure. Unlike ammonia, it is not possible to form phosphine by direct union of the elements. There are two methods for the preparation of phosphine. One method is by the action of an acid on an ionic phosphide. The other method is the disproportionation of white phosphorus with hot concentrated base to produce phosphine and the hydrogen phosphite ion:

$$AlP(s) + 3\,H_3O^+(aq) \longrightarrow PH_3(g) + Al^{3+}(aq) + 3\,H_2O(l)$$

$$[4pt]P_4(s) + 4\,OH^-(aq) + 2\,H_2O(l) \longrightarrow 2\,HPO_3^{2-}(aq) + 2\,PH_3(g)$$
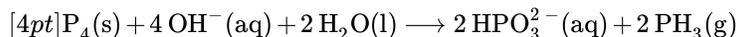
Phosphine is a colorless, very poisonous gas, which has an odor like that of decaying fish. Heat easily decomposes phosphine ($4\,PH_3 \longrightarrow P_4 + 6\,H_2$) and the compound burns in air. The major uses of phosphine are as a fumigant for grains and in semiconductor processing. Like ammonia, gaseous phosphine unites with gaseous hydrogen halides, forming phosphonium compounds like PH_4Cl and PH_4I. Phosphine is a much weaker base than ammonia; therefore, these compounds decompose in water, and the insoluble PH_3 escapes from solution.

Sulfur Hydrogen Compounds

Hydrogen sulfide, H_2S, is a colorless gas that is responsible for the offensive odor of rotten eggs and of many hot springs. Hydrogen sulfide is as toxic as hydrogen cyanide; therefore, it is necessary to exercise great care in handling it. Hydrogen sulfide is particularly deceptive because it paralyzes the olfactory nerves; after a short exposure, one does not smell it.

The production of hydrogen sulfide by the direct reaction of the elements(H_2 + S) is unsatisfactory because the yield is low. A more effective preparation method is the reaction of a metal sulfide with a dilute acid. For example:

$$FeS(s) + 2\,H_3O^+(aq) \longrightarrow Fe^{2+}(aq) + H_2S(g) + 2\,H_2O(l)$$
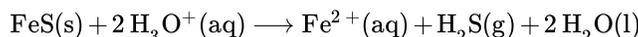
It is easy to oxidize the sulfur in metal sulfides and in hydrogen sulfide, making metal sulfides and H_2S good reducing agents. In acidic solutions, hydrogen sulfide reduces Fe^{3+} to Fe^{2+}, to Mn^{2+}, to Cr^{3+}, and HNO_3 to NO_2. The sulfur in H_2S usually oxidizes to elemental sulfur, unless a large excess of the oxidizing agent is present. In which case, the sulfide may oxidize to or(or to SO_2 or SO_3 in the absence of water):

$$2\,H_2S(g) + O_2(g) \longrightarrow 2\,S(s) + 2\,H_2O(l)$$

This oxidation process leads to the removal of the hydrogen sulfide found in many sources of natural gas. The deposits of sulfur in volcanic regions may be the result of the oxidation of H_2S present in volcanic gases.

Hydrogen sulfide is a weak diprotic acid that dissolves in water to form hydrosulfuric acid. The acid ionizes in two stages, yielding hydrogen sulfide ions, HS^-, in the first stage and sulfide ions, S^{2-}, in the second. Since hydrogen sulfide is a weak acid, aqueous solutions of soluble sulfides and hydrogen sulfides are basic:

$$S^{2-}(aq) + H_2O(l) \rightleftharpoons HS^-(aq) + OH^-(aq)$$

$$[4pt]HS^-(aq) + H_2O(l) \rightleftharpoons H_2S(g) + OH^-(aq)$$
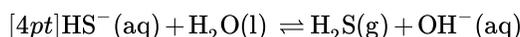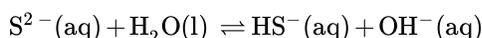
Halogen Hydrogen Compounds

Binary compounds containing only hydrogen and a halogen are **hydrogen halides**. At room temperature, the pure hydrogen halides HF, HCl, HBr, and HI are gases.

In general, it is possible to prepare the halides by the general techniques used to prepare other acids. Fluorine, chlorine, and bromine react directly with hydrogen to form the respective hydrogen halide. This is a commercially important reaction for preparing hydrogen chloride and hydrogen bromide.

The acid-base reaction between a nonvolatile strong acid and a metal halide will yield a hydrogen halide. The escape of the gaseous hydrogen halide drives the reaction to completion. For example, the usual method of preparing hydrogen fluoride is by heating a mixture of calcium fluoride, CaF_2, and concentrated sulfuric acid:

$$CaF_2(s) + H_2SO_4(aq) \longrightarrow CaSO_4(s) + 2\,HF(g)$$
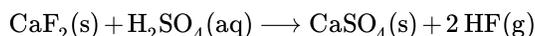
Gaseous hydrogen fluoride is also a by-product in the preparation of phosphate fertilizers by the reaction of fluoroapatite, $Ca_5(PO_4)_3F$, with sulfuric acid. The reaction of concentrated sulfuric acid with a chloride salt produces hydrogen chloride both commercially and in the laboratory.

In most cases, sodium chloride is the chloride of choice because it is the least expensive chloride. Hydrogen bromide and hydrogen iodide cannot be prepared using sulfuric acid because this acid is an oxidizing agent capable of oxidizing both bromide and iodide. However, it is possible to prepare both hydrogen bromide and hydrogen iodide using an acid such as phosphoric acid because it is a weaker oxidizing agent. For example:

$$H_3PO_4(l) + Br^-(aq) \longrightarrow HBr(g) + H_2PO_4^-(aq)$$
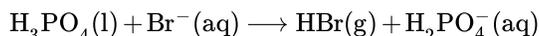
All of the hydrogen halides are very soluble in water, forming hydrohalic acids. With the exception of hydrogen fluoride, which has a strong hydrogen-fluoride bond, they are strong acids. Reactions of hydrohalic acids with metals, metal hydroxides, oxides, or carbonates produce salts of the halides. Most chloride salts are soluble in water. $AgCl$, $PbCl_2$, and Hg_2Cl_2 are the commonly encountered exceptions.

The halide ions give the substances the properties associated with $X^-(aq)$. The heavier halide ions(Cl^-, Br^-, and I^-) can act as reducing agents, and the lighter halogens or other oxidizing agents will oxidize them:

$$Cl_2(aq) + 2\,e^- \rightleftharpoons 2\,Cl^-(aq) \qquad E^\circ = 1.36V$$
$$[4pt]Br_2(aq) + 2\,e^- \rightleftharpoons 2\,Br^-(aq) \qquad E^\circ = 1.09V$$
$$[4pt]I_2(aq) + 2\,e^- \rightleftharpoons 2\,I^-(aq) \qquad E^\circ = 0.54V$$
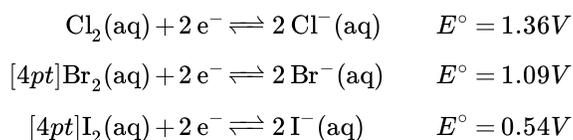
For example, bromine oxidizes iodine:

$$Br_2(aq) + 2\,HI(aq) \longrightarrow 2\,HBr(aq) + I_2(aq) \qquad E^\circ = 0.55V$$
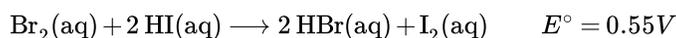
Hydrofluoric acid is unique in its reactions with sand(silicon dioxide) and with glass, which is a mixture of silicates:

$$SiO_2(s) + 4\,HF(aq) \longrightarrow SiF_4(g) + 2\,H_2O(l)$$
$$[4pt]CaSiO_3(s) + 6\,HF(aq) \longrightarrow CaF_2(s) + SiF_4(g) + 3\,H_2O(l)$$
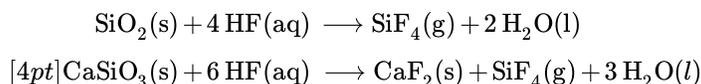
The volatile silicon tetrafluoride escapes from these reactions. Because hydrogen fluoride attacks glass, it can frost or etch glass and is used to etch markings on thermometers, burets, and other glassware.

The largest use for hydrogen fluoride is in production of hydrochlorofluorocarbons for refrigerants, in plastics, and in propellants. The second largest use is in the manufacture of cryolite, Na_3AlF_6, which is important in the production of aluminum. The acid is also important in the production of other inorganic fluorides(such as BF_3), which serve as catalysts in the industrial synthesis of certain organic compounds.

Hydrochloric acid is relatively inexpensive. It is an important and versatile acid in industry and is important for the manufacture of metal chlorides, dyes, glue, glucose, and various other chemicals. A considerable amount is also important for the activation of oil wells and as pickle liquor—an acid used to remove oxide coating from iron or steel that is to be galvanized, tinned, or enameled. The amounts of hydrobromic acid and hydroiodic acid used commercially are insignificant by comparison.

11.7: Occurrence, Preparation, and Properties of Carbonates

> 🧠 **Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Describe the preparation, properties, and uses of some representative metal carbonates

The chemistry of carbon is extensive; however, most of this chemistry is not relevant to this chapter. The other aspects of the chemistry of carbon will appear in the chapter covering organic chemistry. In this chapter, we will focus on the carbonate ion and related substances. The metals of groups 1 and 2, as well as zinc, cadmium, mercury, and lead(II), form ionic **carbonates**—compounds that contain the carbonate anions, The metals of group 1, magnesium, calcium, strontium, and barium also form **hydrogen carbonates**—compounds that contain the hydrogen carbonate anion, HCO_3^-, also known as the **bicarbonate anion**.

With the exception of magnesium carbonate, it is possible to prepare carbonates of the metals of groups 1 and 2 by the reaction of carbon dioxide with the respective oxide or hydroxide. Examples of such reactions include:

$$Na_2O(s) + CO_2(g) \longrightarrow Na_2CO_3(s)$$
$$[4pt]Ca(OH)_2(s) + CO_2(g) \longrightarrow CaCO_3(s) + H_2O(l)$$
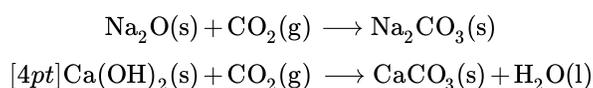
The carbonates of the alkaline earth metals of group 12 and lead(II) are not soluble. These carbonates precipitate upon mixing a solution of soluble alkali metal carbonate with a solution of soluble salts of these metals. Examples of net ionic equations for the reactions are:

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow CaCO_3(s)$$
$$[4pt]Pb^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow PbCO_3(s)$$
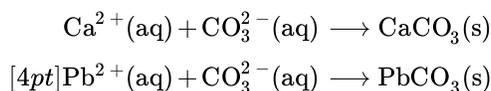
Pearls and the shells of most mollusks are calcium carbonate. Tin(II) or one of the trivalent or tetravalent ions such as Al^{3+} or Sn^{4+} behave differently in this reaction as carbon dioxide and the corresponding oxide form instead of the carbonate.

Alkali metal hydrogen carbonates such as $NaHCO_3$ and $CsHCO_3$ form by saturating a solution of the hydroxides with carbon dioxide. The net ionic reaction involves hydroxide ion and carbon dioxide:

$$OH^-(aq) + CO_2(aq) \longrightarrow HCO_3^-(aq)$$
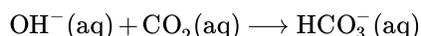
It is possible to isolate the solids by evaporation of the water from the solution.

Although they are insoluble in pure water, alkaline earth carbonates dissolve readily in water containing carbon dioxide because hydrogen carbonate salts form. For example, caves and sinkholes form in limestone when $CaCO_3$ dissolves in water containing dissolved carbon dioxide:

$$CaCO_3(s) + CO_2(aq) + H_2O(l) \longrightarrow Ca^{2+}(aq) + 2\,HCO_3^-(aq)$$
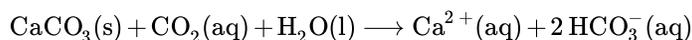
Hydrogen carbonates of the alkaline earth metals remain stable only in solution; evaporation of the solution produces the carbonate. Stalactites and stalagmites, like those shown in Figure 11.7.1: , form in caves when drops of water containing dissolved calcium hydrogen carbonate evaporate to leave a deposit of calcium carbonate.
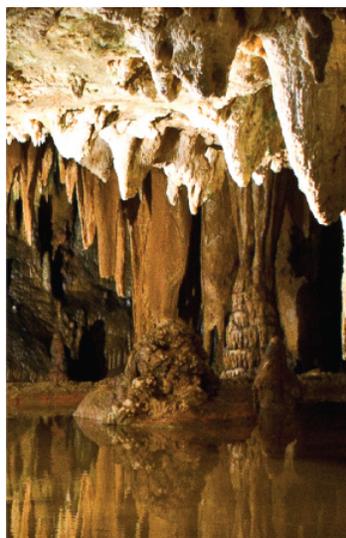
Figure 11.7.1:(a) Stalactites and(b) stalagmites are cave formations of calcium carbonate.(credit a: modification of work by Arvind Govindaraj; credit b: modification of work by the National Park Service.)

The two carbonates used commercially in the largest quantities are sodium carbonate and calcium carbonate. In the United States, sodium carbonate is extracted from the mineral trona, $Na_3(CO_3)(HCO_3)(H_2O)_2$. Following recrystallization to remove clay and other impurities, heating the recrystallized trona produces Na_2CO_3:

$$2\,Na_3(CO_3)(HCO_3)(H_2O)_2(s) \longrightarrow 3\,Na_2CO_3(s) + 5\,H_2O(l) + CO_2(g)$$
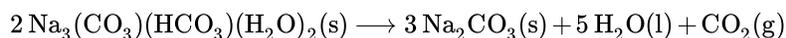
Carbonates are moderately strong bases. Aqueous solutions are basic because the carbonate ion accepts hydrogen ion from water in this reversible reaction:

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$
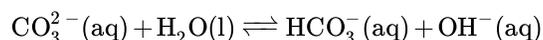
Carbonates react with acids to form salts of the metal, gaseous carbon dioxide, and water. The reaction of calcium carbonate, the active ingredient of the antacid Tums, with hydrochloric acid(stomach acid), as shown in Figure 11.7.2, illustrates the reaction:

$$CaCO_3(s) + 2\,HCl(aq) \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$
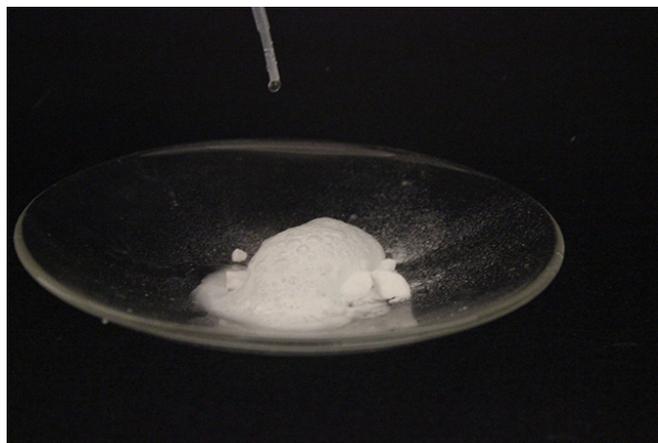
Figure 11.7.2: The reaction of calcium carbonate with hydrochloric acid is shown.(credit: Mark Ott)

Other applications of carbonates include glass making—where carbonate ions serve as a source of oxide ions—and synthesis of oxides.

Hydrogen carbonates are amphoteric because they act as both weak acids and weak bases. Hydrogen carbonate ions act as acids and react with solutions of soluble hydroxides to form a carbonate and water:

$$\mathrm{KHCO_3(aq) + KOH(aq) \longrightarrow K_2CO_3(aq) + H_2O(l)}$$
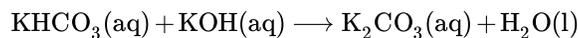
With acids, hydrogen carbonates form a salt, carbon dioxide, and water. Baking soda(bicarbonate of soda or sodium bicarbonate) is sodium hydrogen carbonate. Baking powder contains baking soda and a solid acid such as potassium hydrogen tartrate(cream of tartar), $\mathrm{KHC_4H_4O_6}$. As long as the powder is dry, no reaction occurs; immediately after the addition of water, the acid reacts with the hydrogen carbonate ions to form carbon dioxide:

$$\mathrm{HC_4H_4O_6^-(aq) + HCO_3^-(aq) \longrightarrow C_4H_4O_6^{2-}(aq) + CO_2(g) + H_2O(l)}$$
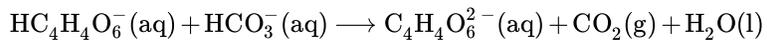
Dough will trap the carbon dioxide, causing it to expand during baking, producing the characteristic texture of baked goods.

11.8: Occurrence, Preparation, and Properties of Nitrogen

> **◖ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Describe the properties, preparation, and uses of nitrogen

Most pure nitrogen comes from the fractional distillation of liquid air. The atmosphere consists of 78% nitrogen by volume. This means there are more than 20 million tons of nitrogen over every square mile of the earth's surface. Nitrogen is a component of proteins and of the genetic material (DNA/RNA) of all plants and animals.

Under ordinary conditions, nitrogen is a colorless, odorless, and tasteless gas. It boils at 77 K and freezes at 63 K. Liquid nitrogen is a useful coolant because it is inexpensive and has a low boiling point. Nitrogen is very unreactive because of the very strong triple bond between the nitrogen atoms. The only common reactions at room temperature occur with lithium to form Li_3N, with certain transition metal complexes, and with hydrogen or oxygen in nitrogen-fixing bacteria. The general lack of reactivity of nitrogen makes the remarkable ability of some bacteria to synthesize nitrogen compounds using atmospheric nitrogen gas as the source one of the most exciting chemical events on our planet. This process is one type of nitrogen fixation. In this case, nitrogen fixation is the process where organisms convert atmospheric nitrogen into biologically useful chemicals. Nitrogen fixation also occurs when lightning passes through air, causing molecular nitrogen to react with oxygen to form nitrogen oxides, which are then carried down to the soil.

> **⚷ Chemistry in Everyday Life: Nitrogen Fixation**
>
> All living organisms require nitrogen compounds for survival. Unfortunately, most of these organisms cannot absorb nitrogen from its most abundant source—the atmosphere. Atmospheric nitrogen consists of N_2 molecules, which are very unreactive due to the strong nitrogen-nitrogen triple bond. However, a few organisms can overcome this problem through a process known as nitrogen fixation, illustrated in Figure 11.8.1.
>
>
>
> Figure 11.8.1: All living organisms require nitrogen. A few microorganisms are able to process atmospheric nitrogen using nitrogen fixation. (credit "roots": modification of work by the United States Department of Agriculture; credit "root nodules": modification of work by Louisa Howard)
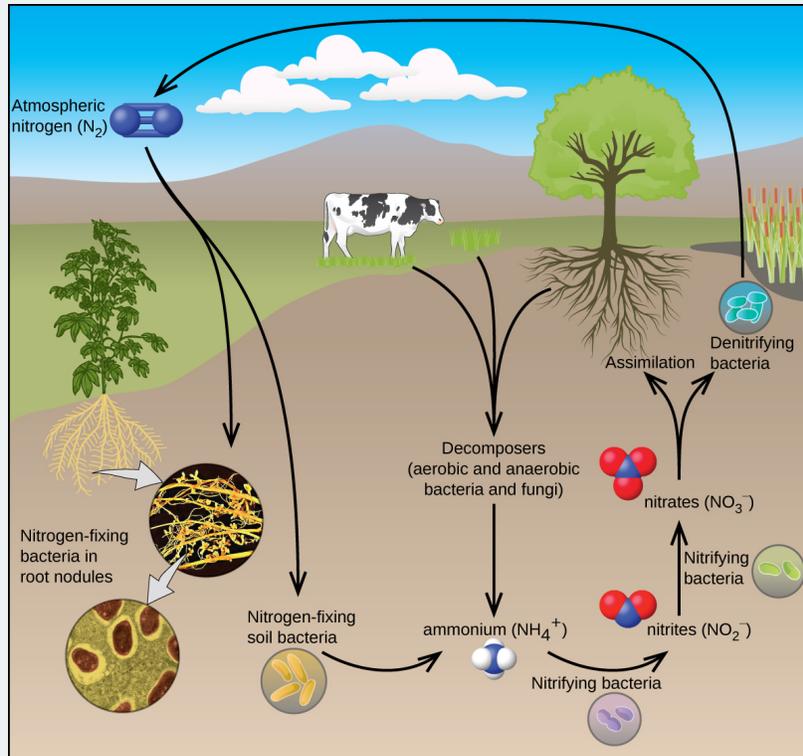
Nitrogen fixation is the process where organisms convert atmospheric nitrogen into biologically useful chemicals. To date, the only known kind of biological organisms capable of nitrogen fixation are microorganisms. These organisms employ enzymes called nitrogenases, which contain iron and molybdenum. Many of these microorganisms live in a symbiotic relationship with plants, with the best-known example being the presence of rhizobia in the root nodules of legumes.

Large volumes of atmospheric nitrogen are necessary for making ammonia—the principal starting material used for preparation of large quantities of other nitrogen-containing compounds. Most other uses for elemental nitrogen depend on its inactivity. It is helpful when a chemical process requires an inert atmosphere. Canned foods and luncheon meats cannot oxidize in a pure nitrogen atmosphere, so they retain a better flavor and color, and spoil less rapidly, when sealed in nitrogen instead of air. This technology allows fresh produce to be available year-round, regardless of growing season.

There are compounds with nitrogen in all of its oxidation states from 3− to 5+. Much of the chemistry of nitrogen involves oxidation-reduction reactions. Some active metals (such as alkali metals and alkaline earth metals) can reduce nitrogen to form metal nitrides. In the remainder of this section, we will examine nitrogen-oxygen chemistry.

There are well-characterized nitrogen oxides in which nitrogen exhibits each of its positive oxidation numbers from 1+ to 5+. When ammonium nitrate is carefully heated, nitrous oxide (dinitrogen oxide) and water vapor form. Stronger heating generates nitrogen gas, oxygen gas, and water vapor. No one should ever attempt this reaction—it can be very explosive. In 1947, there was a major ammonium nitrate explosion in Texas City, Texas, and, in 2013, there was another major explosion in West, Texas. In the last 100 years, there were nearly 30 similar disasters worldwide, resulting in the loss of numerous lives. In this oxidation-reduction reaction, the nitrogen in the nitrate ion oxidizes the nitrogen in the ammonium ion. Nitrous oxide, shown in Figure 11.8.2 , is a colorless gas possessing a mild, pleasing odor and a sweet taste. It finds application as an anesthetic for minor operations, especially in dentistry, under the name "laughing gas."
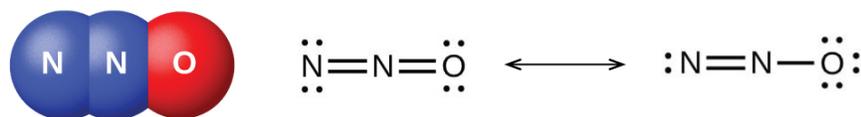
Figure 11.8.2: Nitrous oxide, N_2O, is an anesthetic that has these molecular (left) and resonance (right) structures.

Low yields of nitric oxide, NO, form when heating nitrogen and oxygen together. NO also forms when lightning passes through air during thunderstorms. Burning ammonia is the commercial method of preparing nitric oxide. In the laboratory, the reduction of nitric acid is the best method for preparing nitric oxide. When copper reacts with dilute nitric acid, nitric oxide is the principal reduction product:

$$3\,Cu(s) + 8\,HNO_3(aq) \longrightarrow 2\,NO(g) + 3\,Cu(NO_3)_2(aq) + 4\,H_2O(l)$$
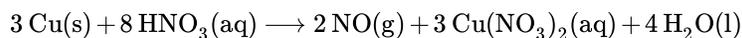
Gaseous nitric oxide is the most thermally stable of the nitrogen oxides and is the simplest known thermally stable molecule with an unpaired electron. It is one of the air pollutants generated by internal combustion engines, resulting from the reaction of atmospheric nitrogen and oxygen during the combustion process.

At room temperature, nitric oxide is a colorless gas consisting of diatomic molecules. As is often the case with molecules that contain an unpaired electron, two molecules combine to form a dimer by pairing their unpaired electrons to form a bond. Liquid and solid NO both contain N_2O_2 dimers, like that shown in Figure 11.8.3. Most substances with unpaired electrons exhibit color by absorbing visible light; however, NO is colorless because the absorption of light is not in the visible region of the spectrum.
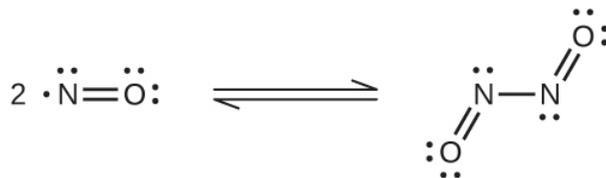
Figure 11.8.3: This shows the equilibrium between NO and N_2O_2. The molecule, N_2O_2, absorbs light.

Cooling a mixture of equal parts nitric oxide and nitrogen dioxide to −21 °C produces dinitrogen trioxide, a blue liquid consisting of N_2O_3 molecules (shown in Figure 11.8.4). Dinitrogen trioxide exists only in the liquid and solid states. When heated, it reverts to a mixture of NO and NO_2.
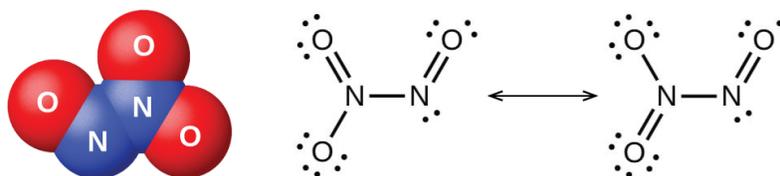
Figure 11.8.4: Dinitrogen trioxide, N_2O_3, only exists in liquid or solid states and has these molecular (left) and resonance (right) structures.

It is possible to prepare nitrogen dioxide in the laboratory by heating the nitrate of a heavy metal, or by the reduction of concentrated nitric acid with copper metal, as shown in Figure 11.8.5. Commercially, it is possible to prepare nitrogen dioxide by oxidizing nitric oxide with air.
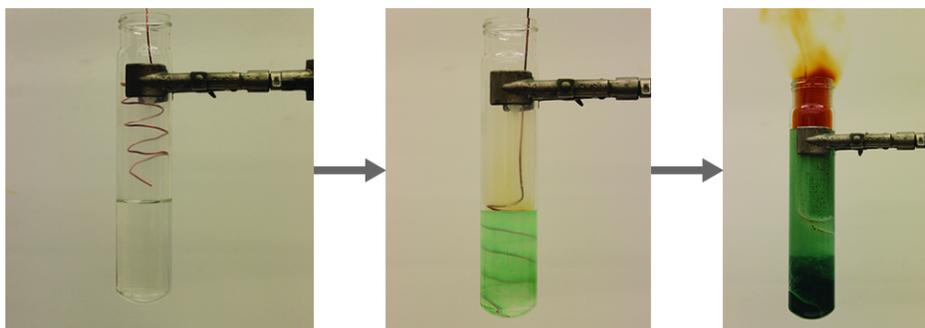
Figure 11.8.5: The reaction of copper metal with concentrated HNO_3 produces a solution of $Cu(NO_3)_2$ and brown fumes of NO_2. (credit: modification of work by Mark Ott)

The nitrogen dioxide molecule (illustrated in Figure 11.8.6) contains an unpaired electron, which is responsible for its color and paramagnetism. It is also responsible for the dimerization of NO_2. At low pressures or at high temperatures, nitrogen dioxide has a deep brown color that is due to the presence of the NO_2 molecule. At low temperatures, the color almost entirely disappears as dinitrogen tetraoxide, N_2O_4, forms. At room temperature, an equilibrium exists:

$$2\,NO_2(g) \rightleftharpoons N_2O_4(g) \qquad K_P = 6.86$$
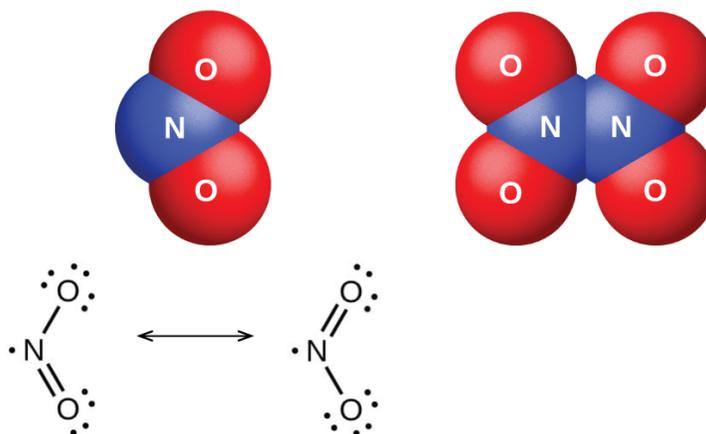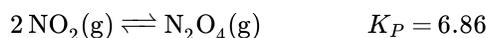
Figure 11.8.6: The molecular and resonance structures for nitrogen dioxide (NO_2, left) and dinitrogen tetraoxide (N_2O_4, right) are shown.

Dinitrogen pentaoxide, N_2O_5 (illustrated in Figure 11.8.7), is a white solid that is formed by the dehydration of nitric acid by phosphorus(V) oxide (tetraphosphorus decoxide):

$$P_4O_{10}(s) + 4\,HNO_3(l) \longrightarrow 4\,HPO_3(s) + 2\,N_2O_5(s)$$
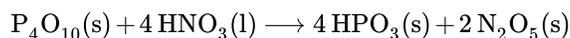
It is unstable above room temperature, decomposing to N_2O_4 and O_2.
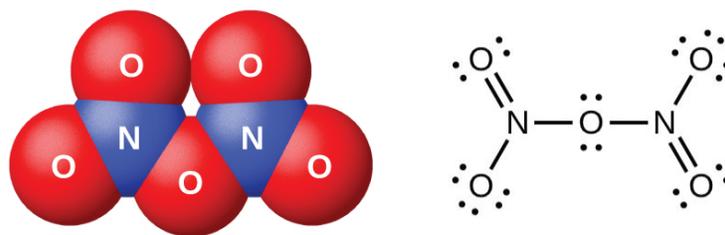
Figure 11.8.7: This image shows the molecular structure and one resonance structure of a molecule of dinitrogen pentaoxide, N$_2$O$_5$.

The oxides of nitrogen(III), nitrogen(IV), and nitrogen(V) react with water and form nitrogen-containing oxyacids. Nitrogen(III) oxide, N$_2$O$_3$, is the anhydride of nitrous acid; HNO$_2$ forms when N$_2$O$_3$ reacts with water. There are no stable oxyacids containing nitrogen with an oxidation state of 4+; therefore, nitrogen(IV) oxide, NO$_2$, disproportionates in one of two ways when it reacts with water. In cold water, a mixture of HNO$_2$ and HNO$_3$ forms. At higher temperatures, HNO$_3$ and NO will form. Nitrogen(V) oxide, N$_2$O$_5$, is the anhydride of nitric acid; HNO$_3$ is produced when N$_2$O$_5$ reacts with water:

$$N_2O_5(s) + H_2O(l) \longrightarrow 2\,HNO_3(aq)$$
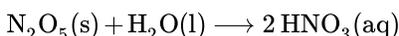
The nitrogen oxides exhibit extensive oxidation-reduction behavior. Nitrous oxide resembles oxygen in its behavior when heated with combustible substances. N$_2$O is a strong oxidizing agent that decomposes when heated to form nitrogen and oxygen. Because one-third of the gas liberated is oxygen, nitrous oxide supports combustion better than air (one-fifth oxygen). A glowing splinter bursts into flame when thrust into a bottle of this gas. Nitric oxide acts both as an oxidizing agent and as a reducing agent. For example:

$$\text{oxidizing agent:} \qquad P_4(s) + 6\,NO(g) \longrightarrow P_4O_6(s) + 3\,N_2(g)$$

$$[4pt]\,\text{reducing agent:} \qquad Cl_2(g) + 2\,NO(g) \longrightarrow 2\,ClNO(g)$$
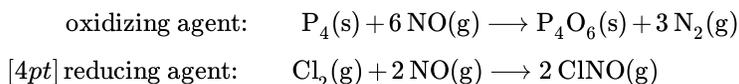
Nitrogen dioxide (or dinitrogen tetraoxide) is a good oxidizing agent. For example:

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

$$[4pt]NO_2(g) + 2\,HCl(aq) \longrightarrow NO(g) + Cl_2(g) + H_2O(l)$$
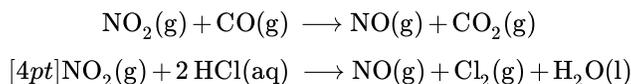
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11.9: Occurrence, Preparation, and Properties of Phosphorus

> **◀▶ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Describe the properties, preparation, and uses of phosphorus

The industrial preparation of phosphorus is by heating calcium phosphate, obtained from phosphate rock, with sand and coke:

$$2\,Ca_3(PO_4)_2(s) + 6\,SiO_2(s) + 10\,C(s) \xrightarrow{\Delta} 6\,CaSiO_3(l) + 10\,CO(g) + P_4(g)$$
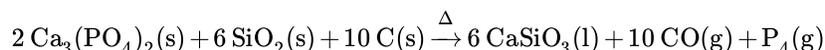
The phosphorus distills out of the furnace and is condensed into a solid or burned to form P_4O_{10}. The preparation of many other phosphorus compounds begins with P_4O_{10}. The acids and phosphates are useful as fertilizers and in the chemical industry. Other uses are in the manufacture of special alloys such as ferrophosphorus and phosphor bronze. Phosphorus is important in making pesticides, matches, and some plastics. Phosphorus is an active nonmetal. In compounds, phosphorus usually occurs in oxidation states of 3−, 3+, and 5+. Phosphorus exhibits oxidation numbers that are unusual for a group 15 element in compounds that contain phosphorus-phosphorus bonds; examples include diphosphorus tetrahydride, H_2P-PH_2, and tetraphosphorus trisulfide, P_4S_3, illustrated in Figure 11.9.1.
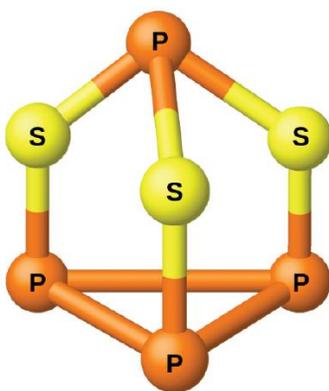
Figure 11.9.1: P_4S_3 is a component of the heads of strike-anywhere matches.

Phosphorus Oxygen Compounds

Phosphorus forms two common oxides, phosphorus(III) oxide (or tetraphosphorus hexaoxide), P_4O_6, and phosphorus(V) oxide (or tetraphosphorus decaoxide), P_4O_{10}, both shown in Figure 11.9.2. Phosphorus(III) oxide is a white crystalline solid with a garlic-like odor. Its vapor is very poisonous. It oxidizes slowly in air and inflames when heated to 70 °C, forming P_4O_{10}. Phosphorus(III) oxide dissolves slowly in cold water to form phosphorous acid, H_3PO_3.
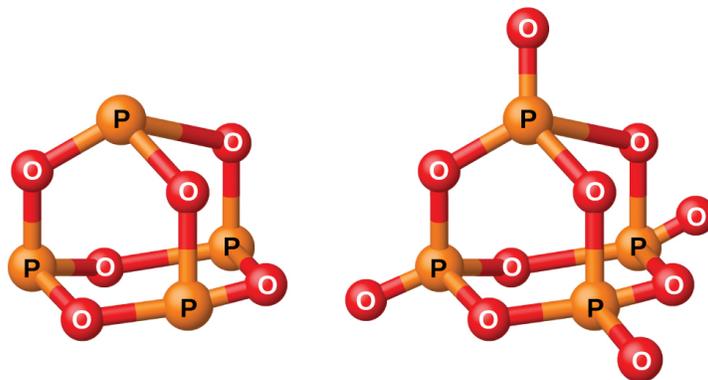
Figure 11.9.2: This image shows the molecular structures of P_4O_6 (left) and P_4O_{10} (right).

Phosphorus(V) oxide, P_4O_{10}, is a white powder that is prepared by burning phosphorus in excess oxygen. Its enthalpy of formation is very high (−2984 kJ), and it is quite stable and a very poor oxidizing agent. Dropping P_4O_{10} into water produces a hissing sound,

heat, and orthophosphoric acid:

$$P_4O_{10}(s) + 6\,H_2O(l) \longrightarrow 4\,H_3PO_4(aq)$$
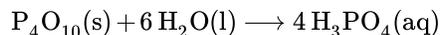
Because of its great affinity for water, phosphorus(V) oxide is an excellent drying agent for gases and solvents, and for removing water from many compounds.

Phosphorus Halogen Compounds

Phosphorus will react directly with the halogens, forming trihalides, PX_3, and pentahalides, PX_5. The trihalides are much more stable than the corresponding nitrogen trihalides; nitrogen pentahalides do not form because of nitrogen's inability to form more than four bonds.

The chlorides PCl_3 and PCl_5, both shown in Figure 11.9.3 , are the most important halides of phosphorus. Phosphorus trichloride is a colorless liquid that is prepared by passing chlorine over molten phosphorus. Phosphorus pentachloride is an off-white solid that is prepared by oxidizing the trichloride with excess chlorine. The pentachloride sublimes when warmed and forms an equilibrium with the trichloride and chlorine when heated.
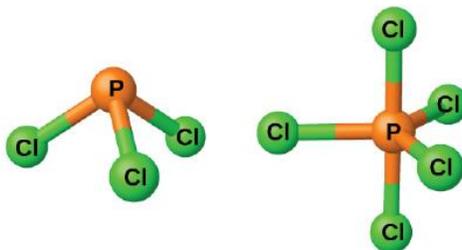
Figure 11.9.3: This image shows the molecular structure of PCl_3 (left) and PCl_5 (right) in the gas phase.

Like most other nonmetal halides, both phosphorus chlorides react with an excess of water and yield hydrogen chloride and an oxyacid: PCl_3 yields phosphorous acid H_3PO_3 and PCl_5 yields phosphoric acid, H_3PO_4.

The pentahalides of phosphorus are Lewis acids because of the empty valence d orbitals of phosphorus. These compounds readily react with halide ions (Lewis bases) to give the anion PX_6^-. Whereas phosphorus pentafluoride is a molecular compound in all states, X-ray studies show that solid phosphorus pentachloride is an ionic compound, $[PCl_4^+][PCl_6^-]$ as are phosphorus pentabromide, $[PBr_4^+][Br^-]$, and phosphorus pentaiodide, $[[PI_6^+][I^-]$.

11.10: Occurrence, Preparation, and Compounds of Oxygen

> **◑ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Describe the properties, preparation, and compounds of oxygen
> - Describe the preparation, properties, and uses of some representative metal oxides, peroxides, and hydroxides

Oxygen is the most abundant element on the earth's crust. The earth's surface is composed of the crust, atmosphere, and hydrosphere. About 50% of the mass of the earth's crust consists of oxygen (combined with other elements, principally silicon). Oxygen occurs as O_2 molecules and, to a limited extent, as O_3 (ozone) molecules in air. It forms about 20% of the mass of the air. About 89% of water by mass consists of combined oxygen. In combination with carbon, hydrogen, and nitrogen, oxygen is a large part of plants and animals.

Oxygen is a colorless, odorless, and tasteless gas at ordinary temperatures. It is slightly denser than air. Although it is only slightly soluble in water (49 mL of gas dissolves in 1 L at STP), oxygen's solubility is very important to aquatic life.

Most of the oxygen isolated commercially comes from air and the remainder from the electrolysis of water. The separation of oxygen from air begins with cooling and compressing the air until it liquefies. As liquid air warms, oxygen with its higher boiling point (90 K) separates from nitrogen, which has a lower boiling point (77 K). It is possible to separate the other components of air at the same time based on differences in their boiling points.

Oxygen is essential in combustion processes such as the burning of fuels. Plants and animals use the oxygen from the air in respiration. The administration of oxygen-enriched air is an important medical practice when a patient is receiving an inadequate supply of oxygen because of shock, pneumonia, or some other illness.

The chemical industry employs oxygen for oxidizing many substances. A significant amount of oxygen produced commercially is important in the removal of carbon from iron during steel production. Large quantities of pure oxygen are also necessary in metal fabrication and in the cutting and welding of metals with oxyhydrogen and oxyacetylene torches.

Liquid oxygen is important to the space industry. It is an oxidizing agent in rocket engines. It is also the source of gaseous oxygen for life support in space.

As we know, oxygen is very important to life. The energy required for the maintenance of normal body functions in human beings and in other organisms comes from the slow oxidation of chemical compounds. Oxygen is the final oxidizing agent in these reactions. In humans, oxygen passes from the lungs into the blood, where it combines with hemoglobin, producing oxyhemoglobin. In this form, blood transports the oxygen to tissues, where it is transferred to the tissues. The ultimate products are carbon dioxide and water. The blood carries the carbon dioxide through the veins to the lungs, where the blood releases the carbon dioxide and collects another supply of oxygen. Digestion and assimilation of food regenerate the materials consumed by oxidation in the body; the energy liberated is the same as if the food burned outside the body.

Green plants continually replenish the oxygen in the atmosphere by a process called **photosynthesis**. The products of photosynthesis may vary, but, in general, the process converts carbon dioxide and water into glucose (a sugar) and oxygen using the energy of light:

$$\underset{\substack{\text{carbon}\\[4pt]\text{dioxide}}}{6\,CO_2(g)} + \underset{\text{water}}{6\,H_2O(l)} \xrightarrow[\text{light}]{\text{chlorophyll}} \underset{\text{glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{oxygen}}{6\,O_2(g)}$$
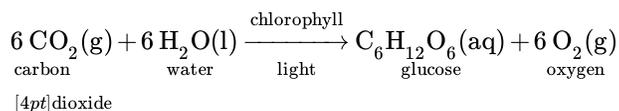
Thus, the oxygen that became carbon dioxide and water by the metabolic processes in plants and animals returns to the atmosphere by photosynthesis.

When dry oxygen is passed between two electrically charged plates, **ozone** (O_3, illustrated in Figure 11.10.1), an allotrope of oxygen possessing a distinctive odor, forms. The formation of ozone from oxygen is an endothermic reaction, in which the energy comes from an electrical discharge, heat, or ultraviolet light:

$$3\,O_2(g) \xrightarrow{\text{electric discharge}} O_3(g) \qquad \Delta H^\circ = 287\text{ kJ}$$
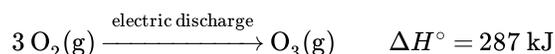
The sharp odor associated with sparking electrical equipment is due, in part, to ozone.
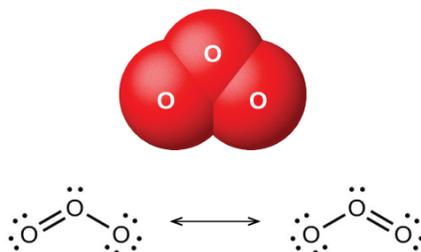
Figure 11.10.1: The image shows the bent ozone (O_3) molecule and the resonance structures necessary to describe its bonding.

Ozone forms naturally in the upper atmosphere by the action of ultraviolet light from the sun on the oxygen there. Most atmospheric ozone occurs in the stratosphere, a layer of the atmosphere extending from about 10 to 50 kilometers above the earth's surface. This ozone acts as a barrier to harmful ultraviolet light from the sun by absorbing it via a chemical decomposition reaction:

$$O_3(g) \xrightarrow{\text{ultraviolet light}} O(g) + O_2(g)$$
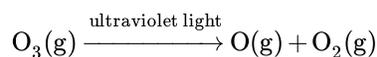
The reactive oxygen atoms recombine with molecular oxygen to complete the ozone cycle. The presence of stratospheric ozone decreases the frequency of skin cancer and other damaging effects of ultraviolet radiation. It has been clearly demonstrated that chlorofluorocarbons, CFCs (known commercially as Freons), which were present as aerosol propellants in spray cans and as refrigerants, caused depletion of ozone in the stratosphere. This occurred because ultraviolet light also causes CFCs to decompose, producing atomic chlorine. The chlorine atoms react with ozone molecules, resulting in a net removal of O_3 molecules from stratosphere. This process is explored in detail in our coverage of chemical kinetics. There is a worldwide effort to reduce the amount of CFCs used commercially, and the ozone hole is already beginning to decrease in size as atmospheric concentrations of atomic chlorine decrease. While ozone in the stratosphere helps protect us, ozone in the troposphere is a problem. This ozone is a toxic component of photochemical smog.

The uses of ozone depend on its reactivity with other substances. It can be used as a bleaching agent for oils, waxes, fabrics, and starch: It oxidizes the colored compounds in these substances to colorless compounds. It is an alternative to chlorine as a disinfectant for water.

Reactions

Elemental oxygen is a strong oxidizing agent. It reacts with most other elements and many compounds.

Reaction with Elements

Oxygen reacts directly at room temperature or at elevated temperatures with all other elements except the noble gases, the halogens, and few second- and third-row transition metals of low reactivity (those with higher reduction potentials than copper). Rust is an example of the reaction of oxygen with iron. The more active metals form peroxides or superoxides. Less active metals and the nonmetals give oxides. Two examples of these reactions are:

$$2\,Mg(s) + O_2(g) \longrightarrow 2\,MgO(s)$$

$$[4pt]P_4(s) + 5\,O_2(g) \longrightarrow P_4O_{10}(s)$$
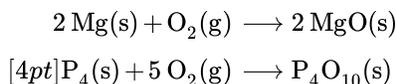
The oxides of halogens, at least one of the noble gases, and metals with higher reduction potentials than copper do not form by the direct action of the elements with oxygen.

Reaction with Compounds

Elemental oxygen also reacts with some compounds. If it is possible to oxidize any of the elements in a given compound, further oxidation by oxygen can occur. For example, hydrogen sulfide, H_2S, contains sulfur with an oxidation state of 2−. Because the sulfur does not exhibit its maximum oxidation state, we would expect H_2S to react with oxygen. It does, yielding water and sulfur dioxide. The reaction is:

$$2\,H_2S(g) + 3\,O_2(g) \longrightarrow 2\,H_2O(l) + 2\,SO_2(g)$$
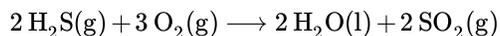
It is also possible to oxidize oxides such as CO and P_4O_6 that contain an element with a lower oxidation state. The ease with which elemental oxygen picks up electrons is mirrored by the difficulty of removing electrons from oxygen in most oxides. Of the

elements, only the very reactive fluorine can oxidize oxides to form oxygen gas.

Oxides, Peroxides, and Hydroxides

Compounds of the representative metals with oxygen fall into three categories:

1. **oxides** containing oxide ions, O^{2-},
2. **peroxides** containing peroxides ions, O_2^{2-} with oxygen-oxygen covalent single bonds and a very limited number of superoxides, containing superoxide ions, O_2^- with oxygen-oxygen covalent bonds that have a bond order of $\frac{3}{2}$,
3. **hydroxides** containing hydroxide ions, OH^-. All representative metals form oxides. Some of the metals of group 2 also form peroxides, MO_2, and the metals of group 1 also form peroxides, M_2O_2, and superoxides, MO_2.

Oxides

It is possible to produce the oxides of most representative metals by heating the corresponding hydroxides (forming the oxide and gaseous water) or carbonates (forming the oxide and gaseous CO_2). Equations for example reactions are:

$$2\,Al(OH)_3(s) \xrightarrow{\Delta} Al_2O_3(s) + 3\,H_2O(g)$$

$$[4pt]\,CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$$
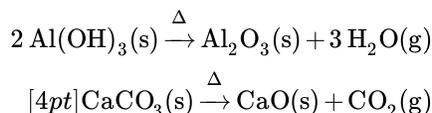
However, alkali metal salts generally are very stable and do not decompose easily when heated. Alkali metal oxides result from the oxidation-reduction reactions created by heating nitrates or hydroxides with the metals. Equations for sample reactions are:

$$2\,KNO_3(s) + 10\,K(s) \xrightarrow{\Delta} 6\,K_2O(s) + N_2(g)$$

$$[4pt]\,2\,LiOH(s) + 2\,Li(s) \xrightarrow{\Delta} 2\,Li_2O(s) + H_2(g)$$
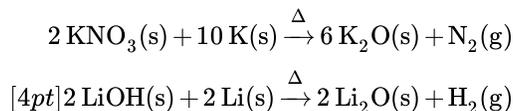
With the exception of mercury(II) oxide, it is possible to produce the oxides of the metals of groups 2–15 by burning the corresponding metal in air. The heaviest member of each group, the member for which the inert pair effect is most pronounced, forms an oxide in which the oxidation state of the metal ion is two less than the group oxidation state (inert pair effect). Thus, Tl_2O, PbO, and Bi_2O_3 form when burning thallium, lead, and bismuth, respectively. The oxides of the lighter members of each group exhibit the group oxidation state. For example, SnO_2 forms from burning tin. Mercury(II) oxide, HgO, forms slowly when mercury is warmed below 500 °C; it decomposes at higher temperatures.

Burning the members of groups 1 and 2 in air is not a suitable way to form the oxides of these elements. These metals are reactive enough to combine with nitrogen in the air, so they form mixtures of oxides and ionic nitrides. Several also form peroxides or superoxides when heated in air.

Ionic oxides all contain the oxide ion, a very powerful hydrogen ion acceptor. With the exception of the very insoluble aluminum oxide, Al_2O_3, tin(IV), SnO_2, and lead(IV), PbO_2, the oxides of the representative metals react with acids to form salts. Some equations for these reactions are:

$$Na_2O + 2\,HNO_3(aq) \longrightarrow 2\,NaNO_3(aq) + H_2O(l)$$

$$[4pt]\,CaO(s) + 2\,HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l)$$

$$[4pt]\,SnO(s) + 2\,HClO_4(aq) \longrightarrow Sn(ClO_4)_2(aq) + H_2O(l)$$
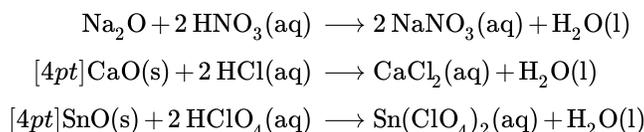
The oxides of the metals of groups 1 and 2 and of thallium(I) oxide react with water and form hydroxides. Examples of such reactions are:

$$Na_2O(s) + H_2O(l) \longrightarrow NaOH(aq)$$

$$[4pt]\,CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(aq)$$

$$[4pt]\,Tl_2O(s) + H_2O(aq) \longrightarrow 2\,TlOH(aq)$$
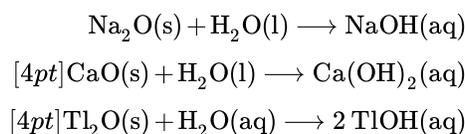
The oxides of the alkali metals have little industrial utility, unlike magnesium oxide, calcium oxide, and aluminum oxide. Magnesium oxide is important in making firebrick, crucibles, furnace linings, and thermal insulation—applications that require chemical and thermal stability. Calcium oxide, sometimes called *quicklime* or lime in the industrial market, is very reactive, and its principal uses reflect its reactivity. Pure calcium oxide emits an intense white light when heated to a high temperature (as illustrated

in Figure 11.10.2. Blocks of calcium oxide heated by gas flames were the stage lights in theaters before electricity was available. This is the source of the phrase "in the limelight."
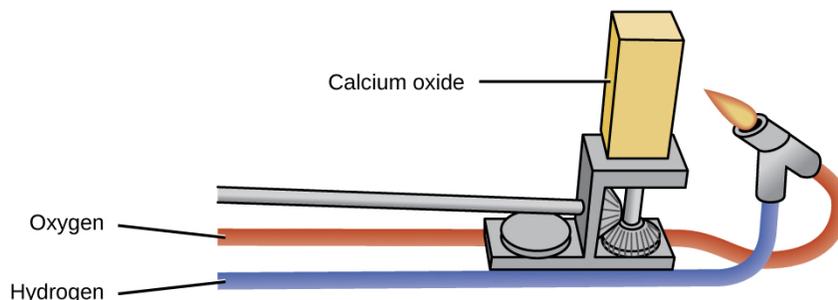
Figure 11.10.2: Calcium oxide has many industrial uses. When it is heated at high temperatures, it emits an intense white light.

Calcium oxide and calcium hydroxide are inexpensive bases used extensively in chemical processing, although most of the useful products prepared from them do not contain calcium. Calcium oxide, CaO, is made by heating calcium carbonate, $CaCO_3$, which is widely and inexpensively available as limestone or oyster shells:

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

Although this decomposition reaction is reversible, it is possible to obtain a 100% yield of CaO by allowing the CO_2 to escape. It is possible to prepare calcium hydroxide by the familiar acid-base reaction of a soluble metal oxide with water:

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s)$$
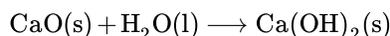
Both CaO and $Ca(OH)_2$ are useful as bases; they accept protons and neutralize acids.

Alumina (Al_2O_3) occurs in nature as the mineral corundum, a very hard substance used as an abrasive for grinding and polishing. Corundum is important to the jewelry trade as ruby and sapphire. The color of ruby is due to the presence of a small amount of chromium; other impurities produce the wide variety of colors possible for sapphires. Artificial rubies and sapphires are now manufactured by melting aluminum oxide (melting point = 2050 °C) with small amounts of oxides to produce the desired colors and cooling the melt in such a way as to produce large crystals. Ruby lasers use synthetic ruby crystals.

Zinc oxide, ZnO, was a useful white paint pigment; however, pollutants tend to discolor the compound. The compound is also important in the manufacture of automobile tires and other rubber goods, and in the preparation of medicinal ointments. For example, zinc-oxide-based sunscreens, as shown in Figure 11.10.3 help prevent sunburn. The zinc oxide in these sunscreens is present in the form of very small grains known as nanoparticles. Lead dioxide is a constituent of charged lead storage batteries. Lead(IV) tends to revert to the more stable lead(II) ion by gaining two electrons, so lead dioxide is a powerful oxidizing agent.

Figure 11.10.3: Zinc oxide protects exposed skin from sunburn. (credit: modification of work by "osseous"/Flickr)

Peroxides and Superoxides

Peroxides and superoxides are strong oxidizers and are important in chemical processes. Hydrogen peroxide, H_2O_2, prepared from metal peroxides, is an important bleach and disinfectant. Peroxides and superoxides form when the metal or metal oxides of groups 1 and 2 react with pure oxygen at elevated temperatures. Sodium peroxide and the peroxides of calcium, strontium, and barium form by heating the corresponding metal or metal oxide in pure oxygen:

$$2\,\mathrm{Na(s)} + \mathrm{O_2(g)} \xrightarrow{\Delta} \mathrm{Na_2O_2(s)}$$

$$[4pt]\,2\,\mathrm{Na_2O(s)} + \mathrm{O_2(g)} \xrightarrow{\Delta} 2\,\mathrm{Na_2O_2(s)}$$

$$[4pt]\,2\,\mathrm{SrO(s)} + \mathrm{O_2(g)} \xrightarrow{\Delta} 2\,\mathrm{SrO_2(s)}$$
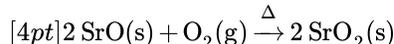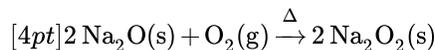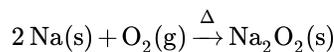
The peroxides of potassium, rubidium, and cesium can be prepared by heating the metal or its oxide in a carefully controlled amount of oxygen:

$$2\,\mathrm{K(s)} + \mathrm{O_2(g)} \longrightarrow \mathrm{K_2O_2(s)} \qquad (2\ \mathrm{mol\ K\ per\ mol\ O_2})$$
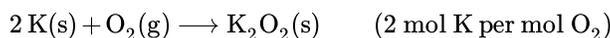
With an excess of oxygen, the superoxides KO_2, RbO_2, and CsO_2 form. For example:

$$\mathrm{K(s)} + \mathrm{O_2(g)} \longrightarrow \mathrm{KO_2(s)} \qquad (1\ \mathrm{mol\ K\ per\ mol\ O_2})$$
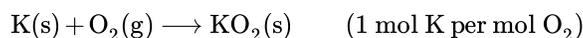
The stability of the peroxides and superoxides of the alkali metals increases as the size of the cation increases.

Hydroxides

Hydroxides are compounds that contain the OH^- ion. It is possible to prepare these compounds by two general types of reactions. Soluble metal hydroxides can be produced by the reaction of the metal or metal oxide with water. Insoluble metal hydroxides form when a solution of a soluble salt of the metal combines with a solution containing hydroxide ions.

With the exception of beryllium and magnesium, the metals of groups 1 and 2 react with water to form hydroxides and hydrogen gas. Examples of such reactions include:

$$2\,\mathrm{Li(s)} + 2\,\mathrm{H_2O(l)} \longrightarrow 2\,\mathrm{LiOH(aq)} + \mathrm{H_2(g)}$$

$$[4pt]\,\mathrm{Ca(s)} + 2\,\mathrm{H_2O(l)} \longrightarrow \mathrm{Ca(OH)_2(aq)} + \mathrm{H_2(g)}$$
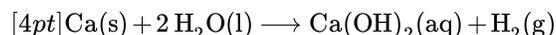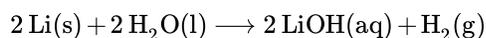
However, these reactions can be violent and dangerous; therefore, it is preferable to produce soluble metal hydroxides by the reaction of the respective oxide with water:

$$\mathrm{Li_2O(s)} + \mathrm{H_2O(l)} \longrightarrow 2\,\mathrm{LiOH(aq)}$$

$$[4pt]\,\mathrm{CaO(s)} + \mathrm{H_2O(l)} \longrightarrow \mathrm{Ca(OH)_2(aq)}$$
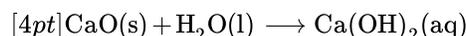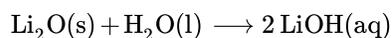
Most metal oxides are **base anhydrides**. This is obvious for the soluble oxides because they form metal hydroxides. Most other metal oxides are insoluble and do not form hydroxides in water; however, they are still base anhydrides because they will react with acids.

It is possible to prepare the insoluble hydroxides of beryllium, magnesium, and other representative metals by the addition of sodium hydroxide to a solution of a salt of the respective metal. The net ionic equations for the reactions involving a magnesium salt, an aluminum salt, and a zinc salt are:

$$\mathrm{Mg^{2+}(aq)} + 2\,\mathrm{OH^-(aq)} \longrightarrow \mathrm{Mg(OH)_2(s)}$$

$$[4pt]\,\mathrm{Al^{3+}(aq)} + 3\,\mathrm{OH^-(aq)} \longrightarrow \mathrm{Al(OH)_3(s)}$$

$$[4pt]\,\mathrm{Zn^{2+}(aq)} + 2\,\mathrm{OH^-(aq)} \longrightarrow \mathrm{Zn(OH)_2(s)}$$
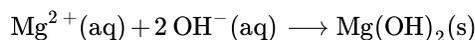
An excess of hydroxide must be avoided when preparing aluminum, gallium, zinc, and tin(II) hydroxides, or the hydroxides will dissolve with the formation of the corresponding complex ions: $Al(OH)_4^-$, $Ga(OH)_4^-$, $Zn(OH)_4^{2-}$, and $Sn(OH)_3^-$ (Figure 11.10.4). The important aspect of complex ions for this chapter is that they form by a Lewis acid-base reaction with the metal being the Lewis acid.
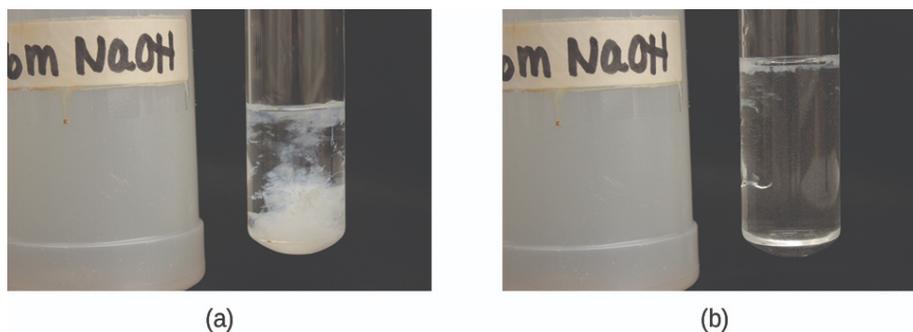
Figure 11.10.4: (a) Mixing solutions of NaOH and Zn(NO₃)₂ produces a white precipitate of $Zn(OH)_2$. (b) Addition of an excess of NaOH results in dissolution of the precipitate. (credit: modification of work by Mark Ott)

Industry uses large quantities of sodium hydroxide as a cheap, strong base. Sodium chloride is the starting material for the production of NaOH because NaCl is a less expensive starting material than the oxide. Sodium hydroxide is among the top 10 chemicals in production in the United States, and this production was almost entirely by electrolysis of solutions of sodium chloride. This process is the chlor-alkali process, and it is the primary method for producing chlorine.

Sodium hydroxide is an ionic compound and melts without decomposition. It is very soluble in water, giving off a great deal of heat and forming very basic solutions: 40 grams of sodium hydroxide dissolves in only 60 grams of water at 25 °C. Sodium hydroxide is employed in the production of other sodium compounds and is used to neutralize acidic solutions during the production of other chemicals such as petrochemicals and polymers.

Many of the applications of hydroxides are for the neutralization of acids (such as the antacid shown in Figure 11.10.5) and for the preparation of oxides by thermal decomposition. An aqueous suspension of magnesium hydroxide constitutes the antacid milk of magnesia. Because of its ready availability (from the reaction of water with calcium oxide prepared by the decomposition of limestone, $CaCO_3$), low cost, and activity, calcium hydroxide is used extensively in commercial applications needing a cheap, strong base. The reaction of hydroxides with appropriate acids is also used to prepare salts.

Figure 11.10.5: Calcium carbonate, $CaCO_3$, can be consumed in the form of an antacid to neutralize the effects of acid in your stomach. (credit: "Midnightcomm"/Wikimedia Commons)

📌 Chemistry in Everyday Life: The Chlor-Alkali Process

Although they are very different chemically, there is a link between chlorine and sodium hydroxide because there is an important electrochemical process that produces the two chemicals simultaneously. The process known as the chlor-alkali process, utilizes sodium chloride, which occurs in large deposits in many parts of the world. This is an electrochemical process to oxidize chloride ion to chlorine and generate sodium hydroxide.

Passing a direct current of electricity through a solution of NaCl causes the chloride ions to migrate to the positive electrode where oxidation to gaseous chlorine occurs when the ion gives up an electron to the electrode:

$$2\,Cl^-(aq) \longrightarrow Cl_2(g) + 2\,e^- \qquad (\text{at the positive electrode})$$
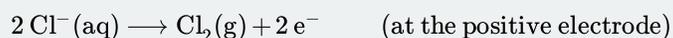
The electrons produced travel through the outside electrical circuit to the negative electrode. Although the positive sodium ions migrate toward this negative electrode, metallic sodium does not form because sodium ions are too difficult to reduce under the

conditions used. (Recall that metallic sodium is active enough to react with water and hence, even if produced, would immediately react with water to produce sodium ions again.) Instead, water molecules pick up electrons from the electrode and undergo reduction to form hydrogen gas and hydroxide ions:

$$2\,\text{H}_2\text{O(l)} + 2\,\text{e}^-\,(\text{from the negative electrode}) \longrightarrow \text{H}_2\text{(g)} + 2\,\text{OH}^-\text{(aq)}$$

The overall result is the conversion of the aqueous solution of NaCl to an aqueous solution of NaOH, gaseous Cl$_2$, and gaseous H$_2$:

$$2\,\text{Na}^+\text{(aq)} + 2\,\text{Cl}^-\text{(aq)} + 2\,\text{H}_2\text{O(l)} \xrightarrow{\text{electrolysis}} 2\,\text{Na}^+\text{(aq)} + 2\,\text{OH}^-\text{(aq)} + \text{Cl}_2\text{(g)} + \text{H}_2\text{(g)}$$
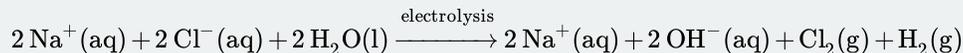
Nonmetal Oxygen Compounds

Most nonmetals react with oxygen to form nonmetal oxides. Depending on the available oxidation states for the element, a variety of oxides might form. Fluorine will combine with oxygen to form fluorides such as OF$_2$, where the oxygen has a 2+-oxidation state.

Sulfur Oxygen Compounds

The two common oxides of sulfur are sulfur dioxide, SO$_2$, and sulfur trioxide, SO$_3$. The odor of burning sulfur comes from sulfur dioxide. Sulfur dioxide, shown in Figure 11.10.6, occurs in volcanic gases and in the atmosphere near industrial plants that burn fuel containing sulfur compounds.
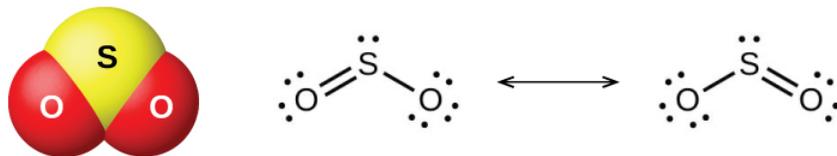
Figure 11.10.6: This image shows the molecular structure (left) and resonance forms (right) of sulfur dioxide.

Commercial production of sulfur dioxide is from either burning sulfur or roasting sulfide ores such as ZnS, FeS$_2$, and Cu$_2$S in air. (Roasting, which forms the metal oxide, is the first step in the separation of many metals from their ores.) A convenient method for preparing sulfur dioxide in the laboratory is by the action of a strong acid on either sulfite salts containing the SO$_3^{2-}$ ion or hydrogen sulfite salts containing HSO$_3^-$. Sulfurous acid, H$_2$SO$_3$, forms first, but quickly decomposes into sulfur dioxide and water. Sulfur dioxide also forms when many reducing agents react with hot, concentrated sulfuric acid. Sulfur trioxide forms slowly when heating sulfur dioxide and oxygen together, and the reaction is exothermic:

$$2\,\text{SO}_2\text{(g)} + \text{O}_2\text{(g)} \longrightarrow 2\,\text{SO}_3\text{(g)} \qquad \Delta H^\circ = -197.8 kJ$$
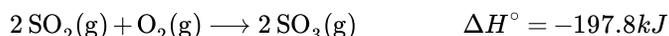
Sulfur dioxide is a gas at room temperature, and the SO$_2$ molecule is bent. Sulfur trioxide melts at 17 °C and boils at 43 °C. In the vapor state, its molecules are single SO$_3$ units (shown in Figure 11.10.7), but in the solid state, SO$_3$ exists in several polymeric forms.
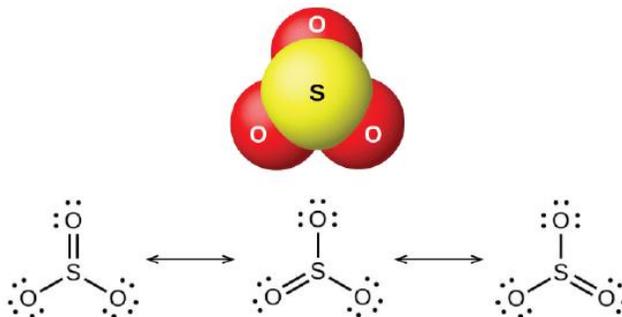
Figure 11.10.7: This image shows the structure (top) of sulfur trioxide in the gas phase and its resonance forms (bottom).

The sulfur oxides react as Lewis acids with many oxides and hydroxides in Lewis acid-base reactions, with the formation of **sulfites** or **hydrogen sulfites**, and **sulfates** or **hydrogen sulfates**, respectively.

Halogen Oxygen Compounds

The halogens do not react directly with oxygen, but it is possible to prepare binary oxygen-halogen compounds by the reactions of the halogens with oxygen-containing compounds. Oxygen compounds with chlorine, bromine, and iodine are oxides because oxygen is the more electronegative element in these compounds. On the other hand, fluorine compounds with oxygen are fluorides because fluorine is the more electronegative element.

As a class, the oxides are extremely reactive and unstable, and their chemistry has little practical importance. Dichlorine oxide, formally called dichlorine monoxide, and chlorine dioxide, both shown in Figure 11.10.8, are the only commercially important compounds. They are important as bleaching agents (for use with pulp and flour) and for water treatment.

(a)   (b)
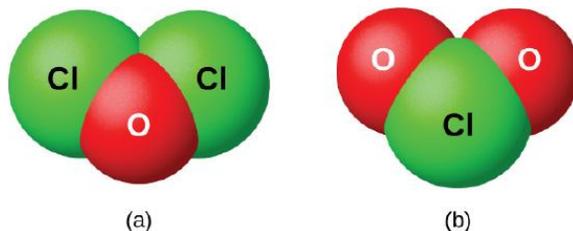
Figure 11.10.8: This image shows the structures of the (a) Cl$_2$O and (b) ClO$_2$ molecules.

Nonmetal Oxyacids and Their Salts

Nonmetal oxides form acids when allowed to react with water; these are acid anhydrides. The resulting oxyanions can form salts with various metal ions.

Nitrogen Oxyacids and Salts

Nitrogen pentaoxide, N$_2$O$_5$, and NO$_2$ react with water to form nitric acid, HNO$_3$. Alchemists, as early as the eighth century, knew nitric acid (shown in Figure 11.10.9) as *aqua fortis* (meaning "strong water"). The acid was useful in the separation of gold from silver because it dissolves silver but not gold. Traces of nitric acid occur in the atmosphere after thunderstorms, and its salts are widely distributed in nature. There are tremendous deposits of Chile saltpeter, NaNO$_3$, in the desert region near the boundary of Chile and Peru. Bengal saltpeter, KNO$_3$, occurs in India and in other countries of the Far East.
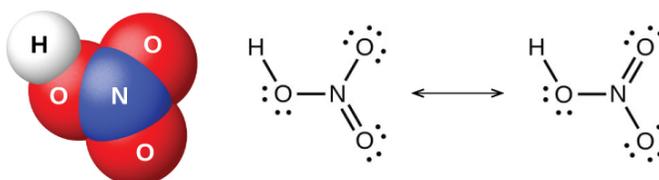
Figure 11.10.9: This image shows the molecular structure (left) of nitric acid, HNO$_3$ and its resonance forms (right).

In the laboratory, it is possible to produce nitric acid by heating a nitrate salt (such as sodium or potassium nitrate) with concentrated sulfuric acid:

$$\mathrm{NaNO_3(s) + H_2SO_4(l) \xrightarrow{\Delta} NaHSO_4(s) + HNO_3(g)}$$
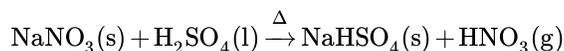
The **Ostwald process** is the commercial method for producing nitric acid. This process involves the oxidation of ammonia to nitric oxide, NO; oxidation of nitric oxide to nitrogen dioxide, NO$_2$; and further oxidation and hydration of nitrogen dioxide to form nitric acid:

$$\mathrm{4\,NH_3(g) + 5\,O_2(g) \longrightarrow 4\,NO(g) + 6\,H_2O(g)}$$
$$\mathrm{2\,NO(g) + O_2(g) \longrightarrow 2\,NO_2(g)}$$
$$\mathrm{3\,NO_2(g) + H_2O(l) \longrightarrow 2\,HNO_3(aq) + NO(g)}$$

Or

$$\mathrm{4\,NO_2(g) + O_2(g) + 2\,H_2O(g) \longrightarrow 4\,HNO_3(l)}$$
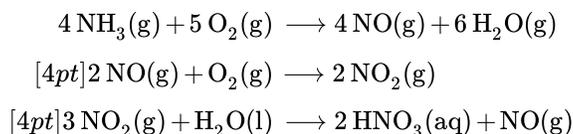
Pure nitric acid is a colorless liquid. However, it is often yellow or brown in color because NO$_2$ forms as the acid decomposes. Nitric acid is stable in aqueous solution; solutions containing 68% of the acid are commercially available concentrated nitric acid. It

is both a strong oxidizing agent and a strong acid.

The action of nitric acid on a metal rarely produces H_2 (by reduction of H^+) in more than small amounts. Instead, the reduction of nitrogen occurs. The products formed depend on the concentration of the acid, the activity of the metal, and the temperature. Normally, a mixture of nitrates, nitrogen oxides, and various reduction products form. Less active metals such as copper, silver, and lead reduce concentrated nitric acid primarily to nitrogen dioxide. The reaction of dilute nitric acid with copper produces NO. In each case, the nitrate salts of the metals crystallize upon evaporation of the resultant solutions.

Nonmetallic elements, such as sulfur, carbon, iodine, and phosphorus, undergo oxidation by concentrated nitric acid to their oxides or oxyacids, with the formation of NO_2:

$$S(s) + 6\,HNO_3(aq) \longrightarrow H_2SO_4(aq) + 6\,NO_2(g) + 2\,H_2O(l)$$

$$[4pt]\,C(s) + 4\,HNO_3(aq) \longrightarrow CO_2(g) + 4\,NO_2(g) + 2\,H_2O(l)$$
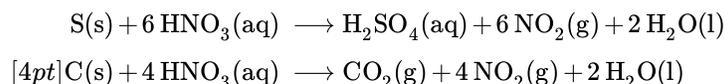
Nitric acid oxidizes many compounds; for example, concentrated nitric acid readily oxidizes hydrochloric acid to chlorine and chlorine dioxide. A mixture of one part concentrated nitric acid and three parts concentrated hydrochloric acid (called *aqua regia*, which means royal water) reacts vigorously with metals. This mixture is particularly useful in dissolving gold, platinum, and other metals that are more difficult to oxidize than hydrogen. A simplified equation to represent the action of *aqua regia* on gold is:

$$Au(s) + 4\,HCl(aq) + 3\,HNO_3(aq) \longrightarrow HAuCl_4(aq) + 3\,NO_2(g) + 3\,H_2O(l)$$
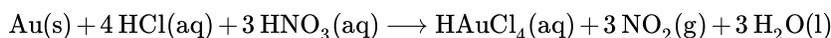
> 📌 Link to Learning
>
> Although gold is generally unreactive, you can watch a video of the complex mixture of compounds present in *aqua regia* dissolving it into solution.

Nitrates, salts of nitric acid, form when metals, oxides, hydroxides, or carbonates react with nitric acid. Most nitrates are soluble in water; indeed, one of the significant uses of nitric acid is to prepare soluble metal nitrates.

Nitric acid finds extensive use in the laboratory and in chemical industries as a strong acid and strong oxidizing agent. It is important in the manufacture of explosives, dyes, plastics, and drugs. Salts of nitric acid (nitrates) are valuable as fertilizers. Gunpowder is a mixture of potassium nitrate, sulfur, and charcoal.

The reaction of N_2O_3 with water gives a pale blue solution of nitrous acid, HNO_2. However, HNO_2 (shown in Figure 11.10.10) is easier to prepare by the addition of an acid to a solution of nitrite; nitrous acid is a weak acid, so the nitrite ion is basic in aqueous solution:

$$NO_2^-(aq) + H_3O^+(aq) \longrightarrow HNO_2(aq) + H_2O(l)$$
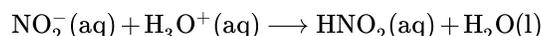
Nitrous acid is very unstable and exists only in solution. It disproportionates slowly at room temperature (rapidly when heated) into nitric acid and nitric oxide. Nitrous acid is an active oxidizing agent with strong reducing agents, and strong oxidizing agents oxidize it to nitric acid.
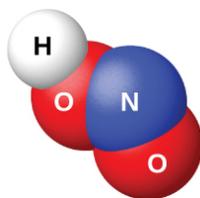
Figure 11.10.10: This image shows the molecular structure of a molecule of nitrous acid, HNO_2.

Sodium nitrite, $NaNO_2$, is an additive to meats such as hot dogs and cold cuts. The nitrite ion has two functions. It limits the growth of bacteria that can cause food poisoning, and it prolongs the meat's retention of its red color. The addition of sodium nitrite to meat products is controversial because nitrous acid reacts with certain organic compounds to form a class of compounds known as nitrosamines. Nitrosamines produce cancer in laboratory animals. This has prompted the FDA to limit the amount of $NaNO_2$ in foods.

The nitrites are much more stable than the acid, but nitrites, like nitrates, can explode. Nitrites, like nitrates, are also soluble in water ($AgNO_2$ is only slightly soluble).

Phosphorus Oxyacids and Salts

Pure orthophosphoric acid, H_3PO_4 (shown in Figure 11.10.11), forms colorless, deliquescent crystals that melt at 42 °C. The common name of this compound is phosphoric acid, and is commercially available as a viscous 82% solution known as syrupy phosphoric acid. One use of phosphoric acid is as an additive to many soft drinks.

One commercial method of preparing orthophosphoric acid is to treat calcium phosphate rock with concentrated sulfuric acid:

$$Ca_3(PO_4)_2(s) + 3\,H_2SO_4(aq) \longrightarrow 2\,H_3PO_4(aq) + 3\,CaSO_4(s)$$
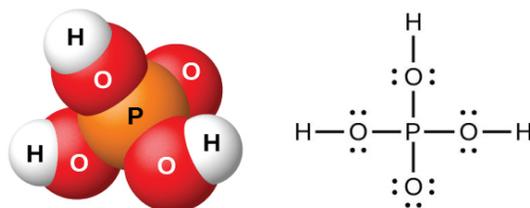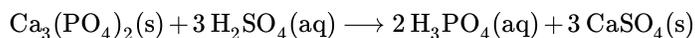
Figure 11.10.11: Orthophosphoric acid, H_3PO_4, is colorless when pure and has this molecular (left) and Lewis structure (right).

Dilution of the products with water, followed by filtration to remove calcium sulfate, gives a dilute acid solution contaminated with calcium dihydrogen phosphate, $Ca(H_2PO_4)_2$, and other compounds associated with calcium phosphate rock. It is possible to prepare pure orthophosphoric acid by dissolving P_4O_{10} in water.

The action of water on P_4O_6, PCl_3, PBr_3, or PI_3 forms phosphorous acid, H_3PO_3 (shown in Figure 11.10.12). The best method for preparing pure phosphorous acid is by hydrolyzing phosphorus trichloride:

$$PCl_3(l) + 3\,H_2O(l) \longrightarrow H_3PO_3(aq) + 3\,HCl(g)$$
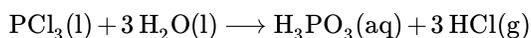
Heating the resulting solution expels the hydrogen chloride and leads to the evaporation of water. When sufficient water evaporates, white crystals of phosphorous acid will appear upon cooling. The crystals are deliquescent, very soluble in water, and have an odor like that of garlic. The solid melts at 70.1 °C and decomposes at about 200 °C by disproportionation into phosphine and orthophosphoric acid:

$$4\,H_3PO_3(l) \longrightarrow PH_3(g) + 3\,H_3PO_4(l)$$
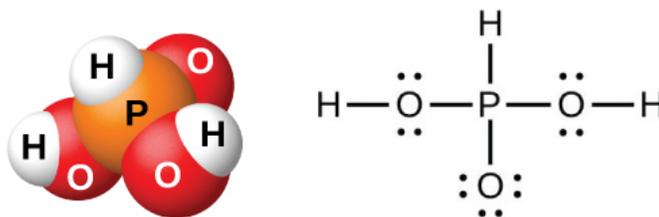
Figure 11.10.12: In a molecule of phosphorous acid, H_3PO_3, only the two hydrogen atoms bonded to an oxygen atom are acidic.

Phosphorous acid forms only two series of salts, which contain the dihydrogen phosphite ion, $H_2PO_3^-$, or the hydrogen phosphate ion, HPO_3^{2-} respectively. It is not possible to replace the third atom of hydrogen because it is not very acidic, as it is not easy to ionize the P-H bond.

Sulfur Oxyacids and Salts

The preparation of sulfuric acid, H_2SO_4 (shown in Figure 11.10.13), begins with the oxidation of sulfur to sulfur trioxide and then converting the trioxide to sulfuric acid. Pure sulfuric acid is a colorless, oily liquid that freezes at 10.5 °C. It fumes when heated because the acid decomposes to water and sulfur trioxide. The heating process causes the loss of more sulfur trioxide than water, until reaching a concentration of 98.33% acid. Acid of this concentration boils at 338 °C without further change in concentration (a constant boiling solution) and is commercially concentrated H_2SO_4. The amount of sulfuric acid used in industry exceeds that of any other manufactured compound.
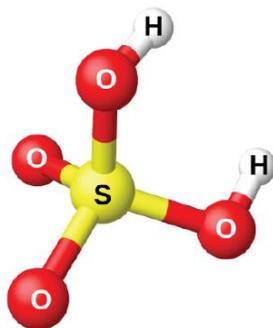
Figure 11.10.13: Sulfuric acid has a tetrahedral molecular structure.

The strong affinity of concentrated sulfuric acid for water makes it a good dehydrating agent. It is possible to dry gases and immiscible liquids that do not react with the acid by passing them through the acid.

Sulfuric acid is a strong diprotic acid that ionizes in two stages. In aqueous solution, the first stage is essentially complete. The secondary ionization is not nearly so complete, and HSO_4^- is a moderately strong acid (about 25% ionized in solution of a HSO_4^- salt ($K_a = 1.2 \times 10^{-2}$)).

Being a diprotic acid, sulfuric acid forms both sulfates, such as Na_2SO_4, and hydrogen sulfates, such as $NaHSO_4$. Most sulfates are soluble in water; however, the sulfates of barium, strontium, calcium, and lead are only slightly soluble in water.

Among the important sulfates are $Na_2SO_4 \cdot 10H_2O$ and Epsom salts, $MgSO_4 \cdot 7H_2O$. Because the HSO_4^- ion is an acid, hydrogen sulfates, such as $NaHSO_4$, exhibit acidic behavior, and this compound is the primary ingredient in some household cleansers.

Hot, concentrated sulfuric acid is an oxidizing agent. Depending on its concentration, the temperature, and the strength of the reducing agent, sulfuric acid oxidizes many compounds and, in the process, undergoes reduction to SO_2, HSO_3^-, SO_3^{2-}, S, H_2S, or S^{2-}.

Sulfur dioxide dissolves in water to form a solution of sulfurous acid, as expected for the oxide of a nonmetal. Sulfurous acid is unstable, and it is not possible to isolate anhydrous H_2SO_3. Heating a solution of sulfurous acid expels the sulfur dioxide. Like other diprotic acids, sulfurous acid ionizes in two steps: The hydrogen sulfite ion, HSO_3^- and the sulfite ion, SO_3^{2-}, form. Sulfurous acid is a moderately strong acid. Ionization is about 25% in the first stage, but it is much less in the second ($K_{a1} = 1.2 \times 10^{-2}$ and $K_{a2} = 6.2 \times 10^{-8}$).

In order to prepare solid sulfite and hydrogen sulfite salts, it is necessary to add a stoichiometric amount of a base to a sulfurous acid solution and then evaporate the water. These salts also form from the reaction of SO_2 with oxides and hydroxides. Heating solid sodium hydrogen sulfite forms sodium sulfite, sulfur dioxide, and water:

$$2\,NaHSO_3\,(s) \overset{\Delta}{\longrightarrow} Na_2SO_3\,(s) + SO_2\,(g) + H_2O(l)$$
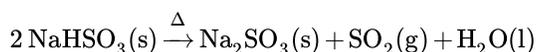
Strong oxidizing agents can oxidize sulfurous acid. Oxygen in the air oxidizes it slowly to the more stable sulfuric acid:

$$2\,H_2SO_3\,(aq) + O_2\,(g) + 2\,H_2O(l) \overset{\Delta}{\longrightarrow} 2\,H_3O^+\,(aq) + 2\,HSO_4^-\,(aq)$$
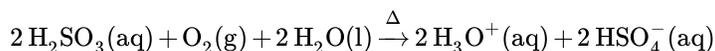
Solutions of sulfites are also very susceptible to air oxidation to produce sulfates. Thus, solutions of sulfites always contain sulfates after exposure to air.

Halogen Oxyacids and Their Salts

The compounds HXO, HXO_2, HXO_3, and HXO_4, where X represents Cl, Br, or I, are the hypohalous, halous, halic, and perhalic acids, respectively. The strengths of these acids increase from the hypohalous acids, which are very weak acids, to the perhalic acids, which are very strong. Table 11.10.1 lists the known acids, and, where known, their pK_a values are given in parentheses.

Table 11.10.1: Oxyacids of the Halogens

Name	Fluorine	Chlorine	Bromine	Iodine
hypohalous	HOF	HOCl (7.5)	HOBr (8.7)	HOI (11)
halous		$HClO_2$ (2.0)		

Name	Fluorine	Chlorine	Bromine	Iodine
halic		$HClO_3$	$HBrO_3$	HIO_3 (0.8)
perhalic		$HClO_4$	$HBrO_4$	HIO_4 (1.6)
paraperhalic				H_5IO_6 (1.6)

The only known oxyacid of fluorine is the very unstable hypofluorous acid, HOF, which is prepared by the reaction of gaseous fluorine with ice:

$$F_2(g) + H_2O(s) \longrightarrow HOF(g) + HF(g)$$
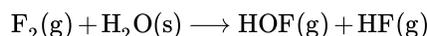
The compound is very unstable and decomposes above −40 °C. This compound does not ionize in water, and there are no known salts. It is uncertain whether the name hypofluorous acid is even appropriate for HOF; a more appropriate name might be hydrogen hypofluorite.

The reactions of chlorine and bromine with water are analogous to that of fluorine with ice, but these reactions do not go to completion, and mixtures of the halogen and the respective hypohalous and hydrohalic acids result. Other than HOF, the hypohalous acids only exist in solution. The hypohalous acids are all very weak acids; however, HOCl is a stronger acid than HOBr, which, in turn, is stronger than HOI.

The addition of base to solutions of the hypohalous acids produces solutions of salts containing the basic hypohalite ions, OX^-. It is possible to isolate these salts as solids. All of the hypohalites are unstable with respect to disproportionation in solution, but the reaction is slow for hypochlorite. Hypobromite and hypoiodite disproportionate rapidly, even in the cold:

$$3\,XO^-(aq) \longrightarrow 2\,X^-(aq) + XO_3^-(aq)$$

Sodium hypochlorite is an inexpensive bleach (Clorox) and germicide. The commercial preparation involves the electrolysis of cold, dilute, aqueous sodium chloride solutions under conditions where the resulting chlorine and hydroxide ion can react. The net reaction is:

$$Cl^-(aq) + H_2O(l) \xrightarrow{\text{electrical}\,\text{energy}} ClO^-(aq) + H_2(g)$$
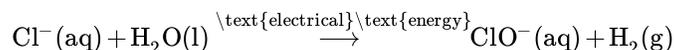
The only definitely known halous acid is chlorous acid, $HClO_2$, obtained by the reaction of barium chlorite with dilute sulfuric acid:

$$\ce{Ba(ClO_2)_2(aq) + H_2SO_4(aq) \longrightarrow BaSO_4(s) + 2 HClO_2(aq)} \nonumber$$
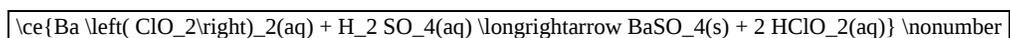
Filtering the insoluble barium sulfate leaves a solution of $HClO_2$. Chlorous acid is not stable; it slowly decomposes in solution to yield chlorine dioxide, hydrochloric acid, and water. Chlorous acid reacts with bases to give salts containing the chlorite ion (shown in Figure 11.10.14). Sodium chlorite finds an extensive application in the bleaching of paper because it is a strong oxidizing agent and does not damage the paper.
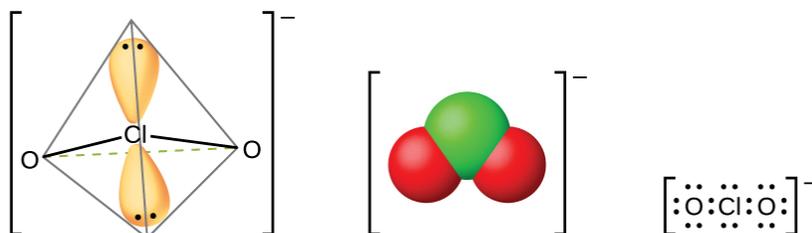
Figure 11.10.14: Chlorite ions, are produced when chlorous acid reacts with bases.

Chloric acid, $HClO_3$, and bromic acid, $HBrO_3$, are stable only in solution. The reaction of iodine with concentrated nitric acid produces stable white iodic acid, HIO_3:

$$I_2(s) + 10\,HNO_3(aq) \longrightarrow 2\,HIO_3(s) + 10\,NO_2(g) + 4\,H_2O(l)$$

It is possible to obtain the lighter halic acids from their barium salts by reaction with dilute sulfuric acid. The reaction is analogous to that used to prepare chlorous acid. All of the halic acids are strong acids and very active oxidizing agents. The acids react with

bases to form salts containing chlorate ions (shown in Figure 11.10.15). Another preparative method is the electrochemical oxidation of a hot solution of a metal halide to form the appropriate metal chlorates. Sodium chlorate is a weed killer; potassium chlorate is used as an oxidizing agent.
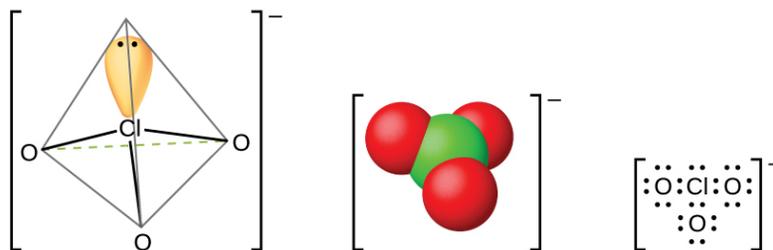
Figure 11.10.15: Chlorate ions, are produced when halic acids react with bases.

Perchloric acid, $HClO_4$, forms when treating a perchlorate, such as potassium perchlorate, with sulfuric acid under reduced pressure. The $HClO_4$ can be distilled from the mixture:

$$KClO_4(s) + H_2SO_4(aq) \longrightarrow HClO_4(g) + KHSO_4(s)$$

Dilute aqueous solutions of perchloric acid are quite stable thermally, but concentrations above 60% are unstable and dangerous. Perchloric acid and its salts are powerful oxidizing agents, as the very electronegative chlorine is more stable in a lower oxidation state than 7+. Serious explosions have occurred when heating concentrated solutions with easily oxidized substances. However, its reactions as an oxidizing agent are slow when perchloric acid is cold and dilute. The acid is among the strongest of all acids. Most salts containing the perchlorate ion (shown in Figure 11.10.16) are soluble. It is possible to prepare them from reactions of bases with perchloric acid and, commercially, by the electrolysis of hot solutions of their chlorides.
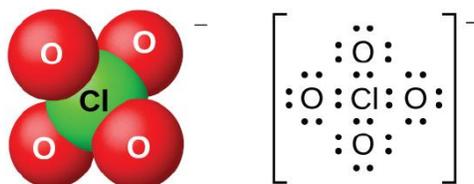
Figure 11.10.16: Perchlorate ions, can be produced when perchloric acid reacts with a base or by electrolysis of hot solutions of their chlorides.

Perbromate salts are difficult to prepare, and the best syntheses currently involve the oxidation of bromates in basic solution with fluorine gas followed by acidification. There are few, if any, commercial uses of this acid or its salts.

There are several different acids containing iodine in the 7+-oxidation state; they include metaperiodic acid, HIO_4, and paraperiodic acid, H_5IO_6. These acids are strong oxidizing agents and react with bases to form the appropriate salts.

11.11: Occurrence, Preparation, and Properties of Sulfur

> **◑ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Describe the properties, preparation, and uses of sulfur

Sulfur exists in nature as elemental deposits as well as sulfides of iron, zinc, lead, and copper, and sulfates of sodium, calcium, barium, and magnesium. Hydrogen sulfide is often a component of natural gas and occurs in many volcanic gases, like those shown in Figure 11.11.1 Sulfur is a constituent of many proteins and is essential for life.

Figure 11.11.1: Volcanic gases contain hydrogen sulfide. (credit: Daniel Julie/Wikimedia Commons)

The Frasch process, illustrated in Figure 11.11.2 , is important in the mining of free sulfur from enormous underground deposits in Texas and Louisiana. Superheated water (170 °C and 10 atm pressure) is forced down the outermost of three concentric pipes to the underground deposit. The hot water melts the sulfur. The innermost pipe conducts compressed air into the liquid sulfur. The air forces the liquid sulfur, mixed with air, to flow up through the outlet pipe. Transferring the mixture to large settling vats allows the solid sulfur to separate upon cooling. This sulfur is 99.5% to 99.9% pure and requires no purification for most uses.
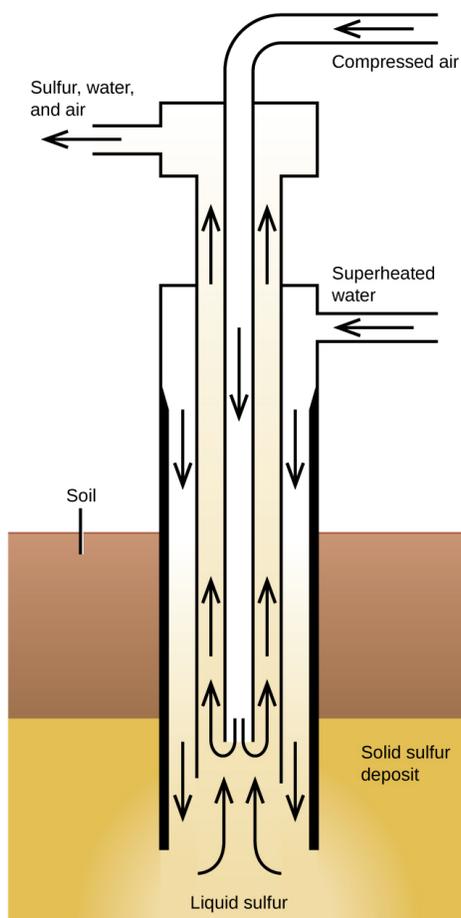
Figure 11.11.2: The Frasch process is used to mine sulfur from underground deposits.

Larger amounts of sulfur also come from hydrogen sulfide recovered during the purification of natural gas.

Sulfur exists in several allotropic forms. The stable form at room temperature contains eight-membered rings, and so the true formula is S_8. However, chemists commonly use S to simplify the coefficients in chemical equations; we will follow this practice in this book.

Like oxygen, which is also a member of group 16, sulfur exhibits a distinctly nonmetallic behavior. It oxidizes metals, giving a variety of binary sulfides in which sulfur exhibits a negative oxidation state (2−). Elemental sulfur oxidizes less electronegative nonmetals, and more electronegative nonmetals, such as oxygen and the halogens, will oxidize it. Other strong oxidizing agents also oxidize sulfur. For example, concentrated nitric acid oxidizes sulfur to the sulfate ion, with the concurrent formation of nitrogen(IV) oxide:

$$\mathrm{S(s) + 6\,HNO_3(aq) \longrightarrow 2\,H_3O^+(aq) + SO_4^{2-}(aq) + 6\,NO_2(g)}$$
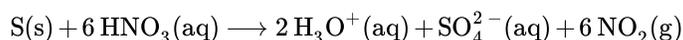
The chemistry of sulfur with an oxidation state of 2− is similar to that of oxygen. Unlike oxygen, however, sulfur forms many compounds in which it exhibits positive oxidation states.

11.12: Occurrence, Preparation, and Properties of Halogens

> **◖◗ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Describe the preparation, properties, and uses of halogens
> - Describe the properties, preparation, and uses of halogen compounds

The elements in group 17 are the halogens. These are the elements fluorine, chlorine, bromine, iodine, and astatine. These elements are too reactive to occur freely in nature, but their compounds are widely distributed. Chlorides are the most abundant; although fluorides, bromides, and iodides are less common, they are reasonably available. In this section, we will examine the occurrence, preparation, and properties of halogens. Next, we will examine halogen compounds with the representative metals followed by an examination of the interhalogens. This section will conclude with some applications of halogens.

Occurrence and Preparation

All of the halogens occur in seawater as halide ions. The concentration of the chloride ion is 0.54 M; that of the other halides is less than 10^{-4} M. Fluoride also occurs in minerals such as CaF_2, $Ca(PO_4)_3F$, and Na_3AlF_6. Chloride also occurs in the Great Salt Lake and the Dead Sea, and in extensive salt beds that contain NaCl, KCl, or $MgCl_2$. Part of the chlorine in your body is present as hydrochloric acid, which is a component of stomach acid. Bromine compounds occur in the Dead Sea and underground brines. Iodine compounds are found in small quantities in Chile saltpeter, underground brines, and sea kelp. Iodine is essential to the function of the thyroid gland.

The best sources of halogens (except iodine) are halide salts. It is possible to oxidize the halide ions to free diatomic halogen molecules by various methods, depending on the ease of oxidation of the halide ion. Fluoride is the most difficult to oxidize, whereas iodide is the easiest.

The major method for preparing fluorine is electrolytic oxidation. The most common electrolysis procedure is to use a molten mixture of potassium hydrogen fluoride, KHF_2, and anhydrous hydrogen fluoride. Electrolysis causes HF to decompose, forming fluorine gas at the anode and hydrogen at the cathode. It is necessary to keep the two gases separated to prevent their explosive recombination to reform hydrogen fluoride.

Most commercial chlorine comes from the electrolysis of the chloride ion in aqueous solutions of sodium chloride; this is the chlor-alkali process discussed previously. Chlorine is also a product of the electrolytic production of metals such as sodium, calcium, and magnesium from their fused chlorides. It is also possible to prepare chlorine by the chemical oxidation of the chloride ion in acid solution with strong oxidizing agents such as manganese dioxide (MnO_2) or sodium dichromate ($Na_2Cr_2O_7$). The reaction with manganese dioxide is:

$$MnO_2(s) + 2\,Cl^-(aq) + 4\,H_3O^+(aq) \longrightarrow Mn^{2+}(aq) + Cl_2(g) + 6\,H_2O(l)$$
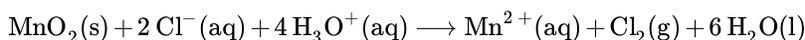
The commercial preparation of bromine involves the oxidation of bromide ion by chlorine:

$$2\,Br^-(aq) + Cl_2(g) \longrightarrow Br_2(l) + 2\,Cl^-(aq)$$

Chlorine is a stronger oxidizing agent than bromine. This method is important for the production of essentially all domestic bromine.

Some iodine comes from the oxidation of iodine chloride, ICl, or iodic acid, HlO_3. The commercial preparation of iodine utilizes the reduction of sodium iodate, $NaIO_3$, an impurity in deposits of Chile saltpeter, with sodium hydrogen sulfite:

$$2\,IO_3^-(aq) + 5\,HSO_3^-(aq) \longrightarrow 3\,HSO_4^-(aq) + 2\,SO_4^{2-}(aq) + H_2O(l) + I_2(s)$$

Properties of the Halogens

Fluorine is a pale yellow gas, chlorine is a greenish-yellow gas, bromine is a deep reddish-brown liquid, and iodine is a grayish-black crystalline solid. Liquid bromine has a high vapor pressure, and the reddish vapor is readily visible in Figure 11.12.1 Iodine crystals have a noticeable vapor pressure. When gently heated, these crystals sublime and form a beautiful deep violet vapor.

Figure 11.12.1: Chlorine is a pale yellow-green gas (left), gaseous bromine is deep orange (center), and gaseous iodine is purple (right). (Fluorine is so reactive that it is too dangerous to handle.) (credit: Sahar Atwa)

Bromine is only slightly soluble in water, but it is miscible in all proportions in less polar (or nonpolar) solvents such as chloroform, carbon tetrachloride, and carbon disulfide, forming solutions that vary from yellow to reddish-brown, depending on the concentration.

Iodine is soluble in chloroform, carbon tetrachloride, carbon disulfide, and many hydrocarbons, giving violet solutions of I_2 molecules. Iodine dissolves only slightly in water, giving brown solutions. It is quite soluble in aqueous solutions of iodides, with which it forms brown solutions. These brown solutions result because iodine molecules have empty valence d orbitals and can act as weak Lewis acids towards the iodide ion. The equation for the reversible reaction of iodine (Lewis acid) with the iodide ion (Lewis base) to form triiodide ion, is:

$$I_2(s) + I^-(aq) \longrightarrow I_3^-(aq)$$
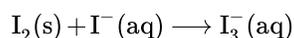
The easier it is to oxidize the halide ion, the more difficult it is for the halogen to act as an oxidizing agent. Fluorine generally oxidizes an element to its highest oxidation state, whereas the heavier halogens may not. For example, when excess fluorine reacts with sulfur, SF_6 forms. Chlorine gives SCl_2 and bromine, S_2Br_2. Iodine does not react with sulfur.

Fluorine is the most powerful oxidizing agent of the known elements. It spontaneously oxidizes most other elements; therefore, the reverse reaction, the oxidation of fluorides, is very difficult to accomplish. Fluorine reacts directly and forms binary fluorides with all of the elements except the lighter noble gases (He, Ne, and Ar). Fluorine is such a strong oxidizing agent that many substances ignite on contact with it. Drops of water inflame in fluorine and form O_2, OF_2, H_2O_2, O_3, and HF. Wood and asbestos ignite and burn in fluorine gas. Most hot metals burn vigorously in fluorine. However, it is possible to handle fluorine in copper, iron, or nickel containers because an adherent film of the fluoride salt passivates their surfaces. Fluorine is the only element that reacts directly with the noble gas xenon.

Although it is a strong oxidizing agent, chlorine is less active than fluorine. Mixing chlorine and hydrogen in the dark makes the reaction between them to be imperceptibly slow. Exposure of the mixture to light causes the two to react explosively. Chlorine is also less active towards metals than fluorine, and oxidation reactions usually require higher temperatures. Molten sodium ignites in chlorine. Chlorine attacks most nonmetals (C, N_2, and O_2 are notable exceptions), forming covalent molecular compounds. Chlorine generally reacts with compounds that contain only carbon and hydrogen (hydrocarbons) by adding to multiple bonds or by substitution.

In cold water, chlorine undergoes a disproportionation reaction:

$$Cl_2(aq) + 2\,H_2O(l) \longrightarrow HOCl(aq) + H_3O^+(aq) + Cl^-(aq)$$

Half the chlorine atoms oxidize to the 1+ oxidation state (hypochlorous acid), and the other half reduce to the 1− oxidation state (chloride ion). This disproportionation is incomplete, so chlorine water is an equilibrium mixture of chlorine molecules, hypochlorous acid molecules, hydronium ions, and chloride ions. When exposed to light, this solution undergoes a photochemical decomposition:

$$2\,HOCl(aq) + 2\,H_2O(l) \xrightarrow{\text{sunlight}} 2\,H_3O^+(aq) + 2\,Cl^-(aq) + O_2(g)$$
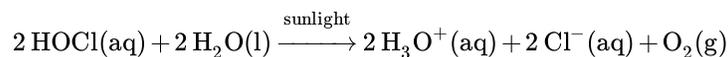
The nonmetal chlorine is more electronegative than any other element except fluorine, oxygen, and nitrogen. In general, very electronegative elements are good oxidizing agents; therefore, we would expect elemental chlorine to oxidize all of the other elements except for these three (and the nonreactive noble gases). Its oxidizing property, in fact, is responsible for its principal use. For example, phosphorus(V) chloride, an important intermediate in the preparation of insecticides and chemical weapons, is manufactured by oxidizing the phosphorus with chlorine:

$$P_4(s) + 10\,Cl_2(g) \longrightarrow 4\,PCl_5(l)$$
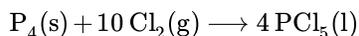
A great deal of chlorine is also used to oxidize, and thus to destroy, organic or biological materials in water purification and in bleaching.

The chemical properties of bromine are similar to those of chlorine, although bromine is the weaker oxidizing agent and its reactivity is less than that of chlorine.

Iodine is the least reactive of the halogens. It is the weakest oxidizing agent, and the iodide ion is the most easily oxidized halide ion. Iodine reacts with metals, but heating is often required. It does not oxidize other halide ions.

Compared with the other halogens, iodine reacts only slightly with water. Traces of iodine in water react with a mixture of starch and iodide ion, forming a deep blue color. This reaction is a very sensitive test for the presence of iodine in water.

Halides of the Representative Metals

Thousands of salts of the representative metals have been prepared. The binary halides are an important subclass of salts. A salt is an ionic compound composed of cations and anions, other than hydroxide or oxide ions. In general, it is possible to prepare these salts from the metals or from oxides, hydroxides, or carbonates. We will illustrate the general types of reactions for preparing salts through reactions used to prepare binary halides.

The binary compounds of a metal with the halogens are the **halides**. Most binary halides are ionic. However, mercury, the elements of group 13 with oxidation states of 3+, tin(IV), and lead(IV) form covalent binary halides.

The direct reaction of a metal and a halogen produce the halide of the metal. Examples of these oxidation-reduction reactions include:

$$Cd(s) + Cl_2(g) \longrightarrow CdCl_2(s)$$
$$[4pt]\,2\,Ga(l) + 3\,Br_2(l) \longrightarrow 2\,GaBr_3(s)$$
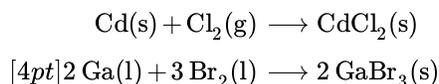
> 📌 **Link to Learning**
>
> Reactions of the alkali metals with elemental halogens are very exothermic and often quite violent. Under controlled conditions, they provide exciting demonstrations for budding students of chemistry. You can view the initial heating of the sodium that removes the coating of sodium hydroxide, sodium peroxide, and residual mineral oil to expose the reactive surface. The reaction with chlorine gas then proceeds very nicely.

If a metal can exhibit two oxidation states, it may be necessary to control the stoichiometry in order to obtain the halide with the lower oxidation state. For example, preparation of tin(II) chloride requires a 1:1 ratio of Sn to Cl_2, whereas preparation of tin(IV) chloride requires a 1:2 ratio:

$$Sn(s) + Cl_2(g) \longrightarrow SnCl_2(s)$$
$$[4pt]\,Sn(s) + 2\,Cl_2(g) \longrightarrow SnCl_4(l)$$
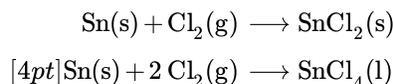
The active representative metals—those that are easier to oxidize than hydrogen—react with gaseous hydrogen halides to produce metal halides and hydrogen. The reaction of zinc with hydrogen fluoride is:

$$Zn(s) + 2\,HF(g) \longrightarrow ZnF_2(s) + H_2(g)$$
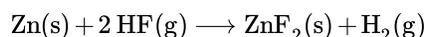
The active representative metals also react with solutions of hydrogen halides to form hydrogen and solutions of the corresponding halides. Examples of such reactions include:

$$Cd(s) + 2\,HBr(aq) \longrightarrow CdBr_2(aq) + H_2(g)$$

$$[4pt]Sn(s) + 2\,HI(aq) \longrightarrow SnI_2(aq) + H_2(g)$$
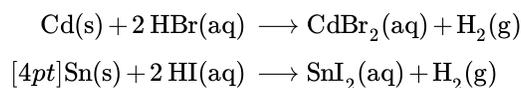
Hydroxides, carbonates, and some oxides react with solutions of the hydrogen halides to form solutions of halide salts. It is possible to prepare additional salts by the reaction of these hydroxides, carbonates, and oxides with aqueous solution of other acids:

$$CaCo_3(s) + 2\,HCl(aq) \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

$$[4pt]TlOH(aq) + HF(aq) \longrightarrow TlF(aq) + H_2O(l)$$
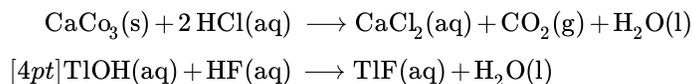
A few halides and many of the other salts of the representative metals are insoluble. It is possible to prepare these soluble salts by metathesis reactions that occur when solutions of soluble salts are mixed (see Figure 11.12.2). Metathesis reactions are examined in the chapter on the stoichiometry of chemical reactions.

Figure 11.12.2: Solid HgI_2 forms when solutions of KI and $Hg(NO_3)_2$ are mixed. (credit: Sahar Atwa)

Several halides occur in large quantities in nature. The ocean and underground brines contain many halides. For example, magnesium chloride in the ocean is the source of magnesium ions used in the production of magnesium. Large underground deposits of sodium chloride, like the salt mine shown in Figure 11.12.3, occur in many parts of the world. These deposits serve as the source of sodium and chlorine in almost all other compounds containing these elements. The chlor-alkali process is one example.

Figure 11.12.3: Underground deposits of sodium chloride are found throughout the world and are often mined. This is a tunnel in the Kłodawa salt mine in Poland. (credit: Jarek Zok)

Interhalogens

Compounds formed from two or more different halogens are interhalogens. Interhalogen molecules consist of one atom of the heavier halogen bonded by single bonds to an odd number of atoms of the lighter halogen. The structures of IF_3, IF_5, and IF_7 are

illustrated in Figure 11.12.4 Formulas for other interhalogens, each of which comes from the reaction of the respective halogens, are in Table 11.12.1
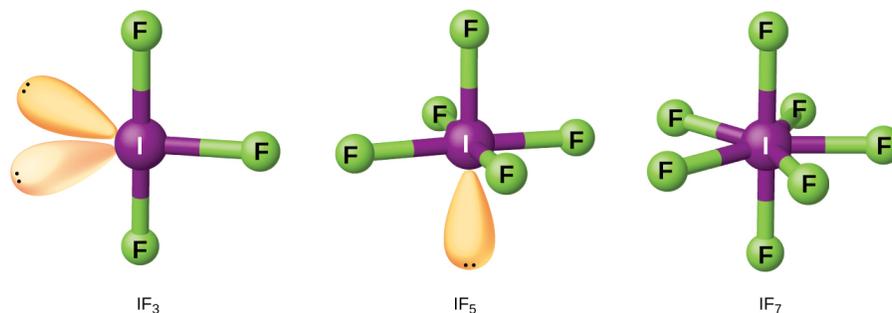
Figure 11.12.4: The structure of IF$_3$ is T-shaped (left), IF$_5$ is square pyramidal (center), and IF$_7$ is pentagonal bipyramidal (right).

Note from Table 11.12.1 that fluorine is able to oxidize iodine to its maximum oxidation state, 7+, whereas bromine and chlorine, which are more difficult to oxidize, achieve only the 5+-oxidation state. A 7+-oxidation state is the limit for the halogens. Because smaller halogens are grouped about a larger one, the maximum number of smaller atoms possible increases as the radius of the larger atom increases. Many of these compounds are unstable, and most are extremely reactive. The interhalogens react like their component halides; halogen fluorides, for example, are stronger oxidizing agents than are halogen chlorides.

The ionic polyhalides of the alkali metals, such as KI_3, $KICl_2$, $KICl_4$, $CsIBr_2$, and $CsBrCl_2$, which contain an anion composed of at least three halogen atoms, are closely related to the interhalogens. As seen previously, the formation of the polyhalide I_3^- anion is responsible for the solubility of iodine in aqueous solutions containing an iodide ion.

Table 11.12.1: Interhalogens

YX	YX$_3$	YX$_5$	YX$_7$
ClF(g)	ClF$_3$(g)	ClF$_5$(g)	
BrF(g)	BrF$_3$(l)	BrF$_5$(l)	
BrCl(g)			
IF(s)	IF$_3$(s)	IF$_5$(l)	IF$_7$(g)
ICl(l)	ICl$_3$(s)		
IBr(s)			

Applications

The fluoride ion and fluorine compounds have many important uses. Compounds of carbon, hydrogen, and fluorine are replacing Freons (compounds of carbon, chlorine, and fluorine) as refrigerants. Teflon is a polymer composed of –CF$_2$CF$_2$– units. Fluoride ion is added to water supplies and to some toothpastes as SnF_2 or NaF to fight tooth decay. Fluoride partially converts teeth from $Ca_5(PO_4)_3(OH)$ into $Ca_5(PO_4)_3F$.

Chlorine is important to bleach wood pulp and cotton cloth. The chlorine reacts with water to form hypochlorous acid, which oxidizes colored substances to colorless ones. Large quantities of chlorine are important in chlorinating hydrocarbons (replacing hydrogen with chlorine) to produce compounds such as tetrachloride (CCl_4), chloroform ($CHCl_3$), and ethyl chloride (C_2H_5Cl), and in the production of polyvinyl chloride (PVC) and other polymers. Chlorine is also important to kill the bacteria in community water supplies.

Bromine is important in the production of certain dyes, and sodium and potassium bromides are used as sedatives. At one time, light-sensitive silver bromide was a component of photographic film.

Iodine in alcohol solution with potassium iodide is an antiseptic (tincture of iodine). Iodide salts are essential for the proper functioning of the thyroid gland; an iodine deficiency may lead to the development of a goiter. Iodized table salt contains 0.023% potassium iodide. Silver iodide is useful in the seeding of clouds to induce rain; it was important in the production of photographic film and iodoform, CHI_3, is an antiseptic.

11.13: Occurrence, Preparation, and Properties of the Noble Gases

> **◑ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Describe the properties, preparation, and uses of the noble gases

The elements in group 18 are the noble gases (helium, neon, argon, krypton, xenon, and radon). They earned the name "noble" because they were assumed to be nonreactive since they have filled valence shells. In 1962, Dr. Neil Bartlett at the University of British Columbia proved this assumption to be false.

These elements are present in the atmosphere in small amounts. Some natural gas contains 1–2% helium by mass. Helium is isolated from natural gas by liquefying the condensable components, leaving only helium as a gas. The United States possesses most of the world's commercial supply of this element in its helium-bearing gas fields. Argon, neon, krypton, and xenon come from the fractional distillation of liquid air. Radon comes from other radioactive elements. More recently, it was observed that this radioactive gas is present in very small amounts in soils and minerals. Its accumulation in well-insulated, tightly sealed buildings, however, constitutes a health hazard, primarily lung cancer.

The boiling points and melting points of the noble gases are extremely low relative to those of other substances of comparable atomic or molecular masses. This is because only weak London dispersion forces are present, and these forces can hold the atoms together only when molecular motion is very slight, as it is at very low temperatures. Helium is the only substance known that does not solidify on cooling at normal pressure. It remains liquid close to absolute zero (0.001 K) at ordinary pressures, but it solidifies under elevated pressure.

Helium is used for filling balloons and lighter-than-air craft because it does not burn, making it safer to use than hydrogen. Helium at high pressures is not a narcotic like nitrogen. Thus, mixtures of oxygen and helium are important for divers working under high pressures. Using a helium-oxygen mixture avoids the disoriented mental state known as nitrogen narcosis, the so-called rapture of the deep. Helium is important as an inert atmosphere for the melting and welding of easily oxidizable metals and for many chemical processes that are sensitive to air.

Liquid helium (boiling point, 4.2 K) is an important coolant to reach the low temperatures necessary for cryogenic research, and it is essential for achieving the low temperatures necessary to produce superconduction in traditional superconducting materials used in powerful magnets and other devices. This cooling ability is necessary for the magnets used for magnetic resonance imaging, a common medical diagnostic procedure. The other common coolant is liquid nitrogen (boiling point, 77 K), which is significantly cheaper.

Neon is a component of neon lamps and signs. Passing an electric spark through a tube containing neon at low pressure generates the familiar red glow of neon. It is possible to change the color of the light by mixing argon or mercury vapor with the neon or by utilizing glass tubes of a special color.

Argon was useful in the manufacture of gas-filled electric light bulbs, where its lower heat conductivity and chemical inertness made it preferable to nitrogen for inhibiting the vaporization of the tungsten filament and prolonging the life of the bulb. Fluorescent tubes commonly contain a mixture of argon and mercury vapor. Argon is the third most abundant gas in dry air.

Krypton-xenon flash tubes are used to take high-speed photographs. An electric discharge through such a tube gives a very intense light that lasts only of a second. Krypton forms a difluoride, KrF_2, which is thermally unstable at room temperature.

Stable compounds of xenon form when xenon reacts with fluorine. Xenon difluoride, XeF_2, forms after heating an excess of xenon gas with fluorine gas and then cooling. The material forms colorless crystals, which are stable at room temperature in a dry atmosphere. Xenon tetrafluoride, XeF_4, and xenon hexafluoride, XeF_6, are prepared in an analogous manner, with a stoichiometric amount of fluorine and an excess of fluorine, respectively. Compounds with oxygen are prepared by replacing fluorine atoms in the xenon fluorides with oxygen.

When XeF_6 reacts with water, a solution of XeO_3 results and the xenon remains in the 6+-oxidation state:

$$XeF_6(s) + 3\,H_2O(l) \longrightarrow XeO_3(aq) + 6\,HF(aq)$$
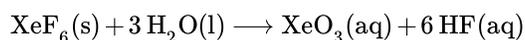
Dry, solid xenon trioxide, XeO_3, is extremely explosive—it will spontaneously detonate. Both XeF_6 and XeO_3 disproportionate in basic solution, producing xenon, oxygen, and salts of the perxenate ion, in which xenon reaches its maximum oxidation sate of 8+.

Radon apparently forms RnF_2—evidence of this compound comes from radiochemical tracer techniques.

Unstable compounds of argon form at low temperatures, but stable compounds of helium and neon are not known.

11.14: Key Terms

start

acid anhydride
compound that reacts with water to form an acid or acidic solution

alkaline earth metal
any of the metals (beryllium, magnesium, calcium, strontium, barium, and radium) occupying group 2 of the periodic table; they are reactive, divalent metals that form basic oxides

allotropes
two or more forms of the same element, in the same physical state, with different chemical structures

amorphous
solid material such as a glass that does not have a regular repeating component to its three-dimensional structure; a solid but not a crystal

base anhydride
metal oxide that behaves as a base towards acids

bicarbonate anion
salt of the hydrogen carbonate ion,

bismuth
heaviest member of group 15; a less reactive metal than other representative metals

borate
compound containing boron-oxygen bonds, typically with clusters or chains as a part of the chemical structure

carbonate
salt of the anion often formed by the reaction of carbon dioxide with bases

chemical reduction
method of preparing a representative metal using a reducing agent

chlor-alkali process
electrolysis process for the synthesis of chlorine and sodium hydroxide

disproportionation reaction
chemical reaction where a single reactant is simultaneously reduced and oxidized; it is both the reducing agent and the oxidizing agent

Downs cell
electrochemical cell used for the commercial preparation of metallic sodium (and chlorine) from molten sodium chloride

Frasch process
important in the mining of free sulfur from enormous underground deposits

Haber process
main industrial process used to produce ammonia from nitrogen and hydrogen; involves the use of an iron catalyst and elevated temperatures and pressures

halide

compound containing an anion of a group 17 element in the 1− oxidation state (fluoride, F^-; chloride, Cl^-; bromide, Br^-; and iodide, I^-)

Hall–Héroult cell

electrolysis apparatus used to isolate pure aluminum metal from a solution of alumina in molten cryolite

hydrogen carbonate

salt of carbonic acid, H_2CO_3 (containing the anion in which one hydrogen atom has been replaced; an acid carbonate; also known as *bicarbonate ion*

hydrogen halide

binary compound formed between hydrogen and the halogens: HF, HCl, HBr, and HI

hydrogen sulfate

ion

hydrogen sulfite

ion

hydrogenation

addition of hydrogen (H_2) to reduce a compound

hydroxide

compound of a metal with the hydroxide ion OH^- or the group −OH

interhalogen

compound formed from two or more different halogens

metal (representative)

atoms of the metallic elements of groups 1, 2, 12, 13, 14, 15, and 16, which form ionic compounds by losing electrons from their outer *s* or *p* orbitals

metalloid

element that has properties that are between those of metals and nonmetals; these elements are typically semiconductors

nitrate

ion; salt of nitric acid

nitrogen fixation

formation of nitrogen compounds from molecular nitrogen

Ostwald process

industrial process used to convert ammonia into nitric acid

oxide

binary compound of oxygen with another element or group, typically containing O^{2-} ions or the group –O– or =O

ozone

allotrope of oxygen; O_3

passivation

metals with a protective nonreactive film of oxide or other compound that creates a barrier for chemical reactions; physical or chemical removal of the passivating film allows the metals to demonstrate their expected chemical reactivity

peroxide

molecule containing two oxygen atoms bonded together or as the anion,

photosynthesis

process whereby light energy promotes the reaction of water and carbon dioxide to form carbohydrates and oxygen; this allows photosynthetic organisms to store energy

Pidgeon process

chemical reduction process used to produce magnesium through the thermal reaction of magnesium oxide with silicon

polymorph

variation in crystalline structure that results in different physical properties for the resulting compound

representative element

element where the *s* and *p* orbitals are filling

representative metal

metal among the representative elements

silicate

compound containing silicon-oxygen bonds, with silicate tetrahedra connected in rings, sheets, or three-dimensional networks, depending on the other elements involved in the formation of the compounds

sulfate

ion

sulfite

ion

superoxide

oxide containing the anion

end

11.15: Summary

This section focuses on the periodicity of the representative elements. These are the elements where the electrons are entering the *s* and *p* orbitals. The representative elements occur in groups 1, 2, and 12–18. These elements are representative metals, metalloids, and nonmetals. The alkali metals (group 1) are very reactive, readily form ions with a charge of 1+ to form ionic compounds that are usually soluble in water, and react vigorously with water to form hydrogen gas and a basic solution of the metal hydroxide. The outermost electrons of the alkaline earth metals (group 2) are more difficult to remove than the outer electron of the alkali metals, leading to the group 2 metals being less reactive than those in group 1. These elements easily form compounds in which the metals exhibit an oxidation state of 2+. Zinc, cadmium, and mercury (group 12) commonly exhibit the group oxidation state of 2+ (although mercury also exhibits an oxidation state of 1+ in compounds that contain Aluminum, gallium, indium, and thallium (group 13) are easier to oxidize than is hydrogen. Aluminum, gallium, and indium occur with an oxidation state 3+ (however, thallium also commonly occurs as the Tl^+ ion). Tin and lead form stable divalent cations and covalent compounds in which the metals exhibit the 4+-oxidation state.

Because of their chemical reactivity, it is necessary to produce the representative metals in their pure forms by reduction from naturally occurring compounds. Electrolysis is important in the production of sodium, potassium, and aluminum. Chemical reduction is the primary method for the isolation of magnesium, zinc, and tin. Similar procedures are important for the other representative metals.

The elements boron, silicon, germanium, arsenic, antimony, and tellurium separate the metals from the nonmetals in the periodic table. These elements, called metalloids or sometimes semimetals, exhibit properties characteristic of both metals and nonmetals. The structures of these elements are similar in many ways to those of nonmetals, but the elements are electrical semiconductors.

Nonmetals have structures that are very different from those of the metals, primarily because they have greater electronegativity and electrons that are more tightly bound to individual atoms. Most nonmetal oxides are acid anhydrides, meaning that they react with water to form acidic solutions. Molecular structures are common for most of the nonmetals, and several have multiple allotropes with varying physical properties.

Hydrogen is the most abundant element in the universe and its chemistry is truly unique. Although it has some chemical reactivity that is similar to that of the alkali metals, hydrogen has many of the same chemical properties of a nonmetal with a relatively low electronegativity. It forms ionic hydrides with active metals, covalent compounds in which it has an oxidation state of 1− with less electronegative elements, and covalent compounds in which it has an oxidation state of 1+ with more electronegative nonmetals. It reacts explosively with oxygen, fluorine, and chlorine, less readily with bromine, and much less readily with iodine, sulfur, and nitrogen. Hydrogen reduces the oxides of metals with lower reduction potentials than chromium to form the metal and water. The hydrogen halides are all acidic when dissolved in water.

The usual method for the preparation of the carbonates of the alkali and alkaline earth metals is by reaction of an oxide or hydroxide with carbon dioxide. Other carbonates form by precipitation. Metal carbonates or hydrogen carbonates such as limestone ($CaCO_3$), the antacid Tums ($CaCO_3$), and baking soda ($NaHCO_3$) are common examples. Carbonates and hydrogen carbonates decompose in the presence of acids and most decompose on heating.

Nitrogen exhibits oxidation states ranging from 3− to 5+. Because of the stability of the N≡N triple bond, it requires a great deal of energy to make compounds from molecular nitrogen. Active metals such as the alkali metals and alkaline earth metals can reduce nitrogen to form metal nitrides. Nitrogen oxides and nitrogen hydrides are also important substances.

Phosphorus (group 15) commonly exhibits oxidation states of 3− with active metals and of 3+ and 5+ with more electronegative nonmetals. The halogens and oxygen will oxidize phosphorus. The oxides are phosphorus(V) oxide, P_4O_{10}, and phosphorus(III) oxide, P_4O_6. The two common methods for preparing orthophosphoric acid, H_3PO_4, are either the reaction of a phosphate with sulfuric acid or the reaction of water with phosphorus(V) oxide. Orthophosphoric acid is a triprotic acid that forms three types of salts.

Oxygen is one of the most reactive elements. This reactivity, coupled with its abundance, makes the chemistry of oxygen very rich and well understood.

Compounds of the representative metals with oxygen exist in three categories (1) oxides, (2) peroxides and superoxides, and (3) hydroxides. Heating the corresponding hydroxides, nitrates, or carbonates is the most common method for producing oxides. Heating the metal or metal oxide in oxygen may lead to the formation of peroxides and superoxides. The soluble oxides dissolve in

water to form solutions of hydroxides. Most metals oxides are base anhydrides and react with acids. The hydroxides of the representative metals react with acids in acid-base reactions to form salts and water. The hydroxides have many commercial uses.

All nonmetals except fluorine form multiple oxides. Nearly all of the nonmetal oxides are acid anhydrides. The acidity of oxyacids requires that the hydrogen atoms bond to the oxygen atoms in the molecule rather than to the other nonmetal atom. Generally, the strength of the oxyacid increases with the number of oxygen atoms bonded to the nonmetal atom and not to a hydrogen.

Sulfur (group 16) reacts with almost all metals and readily forms the sulfide ion, S^{2-}, in which it has as oxidation state of 2−. Sulfur reacts with most nonmetals.

The halogens form halides with less electronegative elements. Halides of the metals vary from ionic to covalent; halides of nonmetals are covalent. Interhalogens form by the combination of two or more different halogens.

All of the representative metals react directly with elemental halogens or with solutions of the hydrohalic acids (HF, HCl, HBr, and HI) to produce representative metal halides. Other laboratory preparations involve the addition of aqueous hydrohalic acids to compounds that contain such basic anions, such as hydroxides, oxides, or carbonates.

The most significant property of the noble gases (group 18) is their inactivity. They occur in low concentrations in the atmosphere. They find uses as inert atmospheres, neon signs, and as coolants. The three heaviest noble gases react with fluorine to form fluorides. The xenon fluorides are the best characterized as the starting materials for a few other noble gas compounds.

11.16: Exercises

1.

How do alkali metals differ from alkaline earth metals in atomic structure and general properties?

2.

Why does the reactivity of the alkali metals decrease from cesium to lithium?

3.

Predict the formulas for the nine compounds that may form when each species in column 1 of the table reacts with each species in column 2.

1	2
Na	I
Sr	Se
Al	O

4.

Predict the best choice in each of the following. You may wish to review the chapter on electronic structure for relevant examples.

  a. the most metallic of the elements Al, Be, and Ba
  b. the most covalent of the compounds NaCl, $CaCl_2$, and $BeCl_2$
  c. the lowest first ionization energy among the elements Rb, K, and Li
  d. the smallest among Al, Al^+, and Al^{3+}
  e. the largest among Cs^+, Ba^{2+}, and Xe

5.

Sodium chloride and strontium chloride are both white solids. How could you distinguish one from the other?

6.

The reaction of quicklime, CaO, with water produces slaked lime, $Ca(OH)_2$, which is widely used in the construction industry to make mortar and plaster. The reaction of quicklime and water is highly exothermic:

  a. What is the enthalpy of reaction per gram of quicklime that reacts?
  b. How much heat, in kilojoules, is associated with the production of 1 ton of slaked lime?

7.

Write a balanced equation for the reaction of elemental strontium with each of the following:

  a. oxygen
  b. hydrogen bromide
  c. hydrogen
  d. phosphorus
  e. water

8.

How many moles of ionic species are present in 1.0 L of a solution marked 1.0 M mercury(I) nitrate?

9.

What is the mass of fish, in kilograms, that one would have to consume to obtain a fatal dose of mercury, if the fish contains 30 parts per million of mercury by weight? (Assume that all the mercury from the fish ends up as mercury(II) chloride in the body and that a fatal dose is 0.20 g of $HgCl_2$.) How many pounds of fish is this?

10.

The elements sodium, aluminum, and chlorine are in the same period.

a. Which has the greatest electronegativity?
b. Which of the atoms is smallest?
c. Write the Lewis structure for the simplest covalent compound that can form between aluminum and chlorine.
d. Will the oxide of each element be acidic, basic, or amphoteric?

11.

Does metallic tin react with HCl?

12.

What is tin pest, also known as tin disease?

13.

Compare the nature of the bonds in $PbCl_2$ to that of the bonds in $PbCl_4$.

14.

Is the reaction of rubidium with water more or less vigorous than that of sodium? How does the rate of reaction of magnesium compare?

15.

Write an equation for the reduction of cesium chloride by elemental calcium at high temperature.

16.

Why is it necessary to keep the chlorine and sodium, resulting from the electrolysis of sodium chloride, separate during the production of sodium metal?

17.

Give balanced equations for the overall reaction in the electrolysis of molten lithium chloride and for the reactions occurring at the electrodes. You may wish to review the chapter on electrochemistry for relevant examples.

18.

The electrolysis of molten sodium chloride or of aqueous sodium chloride produces chlorine.

Calculate the mass of chlorine produced from 3.00 kg sodium chloride in each case. You may wish to review the chapter on electrochemistry for relevant examples.

19.

What mass, in grams, of hydrogen gas forms during the complete reaction of 10.01 g of calcium with water?

20.

How many grams of oxygen gas are necessary to react completely with $3.01 \ 10^{21}$ atoms of magnesium to yield magnesium oxide?

21.

Magnesium is an active metal; it burns in the form of powder, ribbons, and filaments to provide flashes of brilliant light. Why is it possible to use magnesium in construction?

22.

Why is it possible for an active metal like aluminum to be useful as a structural metal?

23.

Describe the production of metallic aluminum by electrolytic reduction.

24.

What is the common ore of tin and how is tin separated from it?

25.

A chemist dissolves a 1.497-g sample of a type of metal (an alloy of Sn, Pb, Sb, and Cu) in nitric acid, and metastannic acid, H_2SnO_3, is precipitated. She heats the precipitate to drive off the water, which leaves 0.4909 g of tin(IV) oxide. What was the percentage of tin in the original sample?

26.

Consider the production of 100 kg of sodium metal using a current of 50,000 A, assuming a 100% yield.

  a. How long will it take to produce the 100 kg of sodium metal?
  b. What volume of chlorine at 25 °C and 1.00 atm forms?

27.

What mass of magnesium forms when 100,000 A is passed through a $MgCl_2$ melt for 1.00 h if the yield of magnesium is 85% of the theoretical yield?

28.

Give the hybridization of the metalloid and the molecular geometry for each of the following compounds or ions. You may wish to review the chapters on chemical bonding and advanced covalent bonding for relevant examples.

  a. (i) TeF_6

29.

Write a Lewis structure for each of the following molecules or ions. You may wish to review the chapter on chemical bonding.

  a. H_3BPH_3
  b.
  c. BBr_3
  d. $B(CH_3)_3$
  e. $B(OH)_3$

30.

Describe the hybridization of boron and the molecular structure about the boron in each of the following:

  a. H_3BPH_3
  b.
  c. BBr_3
  d. $B(CH_3)_3$
  e. $B(OH)_3$

31.

Using only the periodic table, write the complete electron configuration for silicon, including any empty orbitals in the valence shell. You may wish to review the chapter on electronic structure.

32.

Write a Lewis structure for each of the following molecules and ions:

  a. $(CH_3)_3SiH$
  b.
  c. Si_2H_6
  d. $Si(OH)_4$
  e.

33.

Describe the hybridization of silicon and the molecular structure of the following molecules and ions:

  a. $(CH_3)_3SiH$
  b.
  c. Si_2H_6
  d. $Si(OH)_4$
  e.

34.

Describe the hybridization and the bonding of a silicon atom in elemental silicon.

35.

Classify each of the following molecules as polar or nonpolar. You may wish to review the chapter on chemical bonding.

  a. SiH_4
  b. Si_2H_6
  c. $SiCl_3H$
  d. SiF_4
  e. $SiCl_2F_2$

36.

Silicon reacts with sulfur at elevated temperatures. If 0.0923 g of silicon reacts with sulfur to give 0.3030 g of silicon sulfide, determine the empirical formula of silicon sulfide.

37.

Name each of the following compounds:

  a. TeO_2
  b. Sb_2S_3
  c. GeF_4
  d. SiH_4
  e. GeH_4

38.

Write a balanced equation for the reaction of elemental boron with each of the following (most of these reactions require high temperature):

  a. F_2
  b. O_2
  c. S
  d. Se
  e. Br_2

39.

Why is boron limited to a maximum coordination number of four in its compounds?

40.

Write a formula for each of the following compounds:

  a. silicon dioxide
  b. silicon tetraiodide
  c. silane
  d. silicon carbide
  e. magnesium silicide

41.

From the data given in Appendix G, determine the standard enthalpy change and the standard free energy change for each of the following reactions:

  a.
  b.
  c.

42.

A hydride of silicon prepared by the reaction of Mg_2Si with acid exerted a pressure of 306 torr at 26 °C in a bulb with a volume of 57.0 mL. If the mass of the hydride was 0.0861 g, what is its molecular mass? What is the molecular formula for the hydride?

43.

Suppose you discovered a diamond completely encased in a silicate rock. How would you chemically free the diamond without harming it?

44.

Carbon forms a number of allotropes, two of which are graphite and diamond. Silicon has a diamond structure. Why is there no allotrope of silicon with a graphite structure?

45.

Nitrogen in the atmosphere exists as very stable diatomic molecules. Why does phosphorus form less stable P_4 molecules instead of P_2 molecules?

46.

Write balanced chemical equations for the reaction of the following acid anhydrides with water:

  a. SO_3
  b. N_2O_3
  c. Cl_2O_7
  d. P_4O_{10}
  e. NO_2

47.

Determine the oxidation number of each element in each of the following compounds:

  a. HCN
  b. OF_2
  c. $AsCl_3$

48.

Determine the oxidation state of sulfur in each of the following:

  a. SO_3
  b. SO_2
  c.

49.

Arrange the following in order of increasing electronegativity: F; Cl; O; and S.

50.

Why does white phosphorus consist of tetrahedral P_4 molecules while nitrogen consists of diatomic N_2 molecules?

51.

Why does hydrogen not exhibit an oxidation state of 1− when bonded to nonmetals?

52.

The reaction of calcium hydride, CaH_2, with water can be characterized as a Lewis acid-base reaction:

Identify the Lewis acid and the Lewis base among the reactants. The reaction is also an oxidation-reduction reaction. Identify the oxidizing agent, the reducing agent, and the changes in oxidation number that occur in the reaction.

53.

In drawing Lewis structures, we learn that a hydrogen atom forms only one bond in a covalent compound. Why?

54.

What mass of CaH_2 is necessary to react with water to provide enough hydrogen gas to fill a balloon at 20 °C and 0.8 atm pressure with a volume of 4.5 L? The balanced equation is:

55.

What mass of hydrogen gas results from the reaction of 8.5 g of KH with water?

56.

Carbon forms the ion, yet silicon does not form an analogous ion. Why?

57.

Complete and balance the following chemical equations:

(a) hardening of plaster containing slaked lime

(b) removal of sulfur dioxide from the flue gas of power plants

(c) the reaction of baking powder that produces carbon dioxide gas and causes bread to rise

58.

Heating a sample of $Na_2CO_3 \cdot xH_2O$ weighing 4.640 g until the removal of the water of hydration leaves 1.720 g of anhydrous Na_2CO_3. What is the formula of the hydrated compound?

59.

Write the Lewis structures for each of the following:

  a. NH^{2-}
  b. N_2F_4
  c.
  d. NF_3
  e.

60.

For each of the following, indicate the hybridization of the nitrogen atom (for the central nitrogen).

  a. N_2F_4
  b.
  c. NF_3
  d.

61.

Explain how ammonia can function both as a Brønsted base and as a Lewis base.

62.

Determine the oxidation state of nitrogen in each of the following. You may wish to review the chapter on chemical bonding for relevant examples.

  a. (i) HNO_2

63.

For each of the following, draw the Lewis structure, predict the ONO bond angle, and give the hybridization of the nitrogen. You may wish to review the chapters on chemical bonding and advanced theories of covalent bonding for relevant examples.

  a. NO_2
  b.
  c.

64.

How many grams of gaseous ammonia will the reaction of 3.0 g hydrogen gas and 3.0 g of nitrogen gas produce?

65.

Although PF_5 and AsF_5 are stable, nitrogen does not form NF_5 molecules. Explain this difference among members of the same group.

66.

The equivalence point for the titration of a 25.00-mL sample of CsOH solution with 0.1062 M HNO_3 is at 35.27 mL. What is the concentration of the CsOH solution?

67.

Write the Lewis structure for each of the following. You may wish to review the chapter on chemical bonding and molecular geometry.

  a. PH_3

  b.

  c. P_2H_4

  d.

  e. PF_5

68.

Describe the molecular structure of each of the following molecules or ions listed. You may wish to review the chapter on chemical bonding and molecular geometry.

  a. PH_3

  b.

  c. P_2H_4

  d.

69.

Complete and balance each of the following chemical equations. (In some cases, there may be more than one correct answer.)

  a. (f)

70.

Describe the hybridization of phosphorus in each of the following compounds: P_4O_{10}, P_4O_6, PH_4I (an ionic compound), PBr_3, H_3PO_4, H_3PO_3, PH_3, and P_2H_4. You may wish to review the chapter on advanced theories of covalent bonding.

71.

What volume of 0.200 M NaOH is necessary to neutralize the solution produced by dissolving 2.00 g of PCl_3 is an excess of water? Note that when H_3PO_3 is titrated under these conditions, only one proton of the acid molecule reacts.

72.

How much $POCl_3$ can form from 25.0 g of PCl_5 and the appropriate amount of H_2O?

73.

How many tons of $Ca_3(PO_4)_2$ are necessary to prepare 5.0 tons of phosphorus if the yield is 90%?

74.

Write equations showing the stepwise ionization of phosphorous acid.

75.

Draw the Lewis structures and describe the geometry for the following:

  a.

  b. PF_5

  c.

  d. POF_3

76.

Why does phosphorous acid form only two series of salts, even though the molecule contains three hydrogen atoms?

77.

Assign an oxidation state to phosphorus in each of the following:

  a. (f) $Na_4P_2O_7$

78.

Phosphoric acid, one of the acids used in some cola drinks, is produced by the reaction of phosphorus(V) oxide, an acidic oxide, with water. Phosphorus(V) oxide is prepared by the combustion of phosphorus.

a. Write the empirical formula of phosphorus(V) oxide.
b. What is the molecular formula of phosphorus(V) oxide if the molar mass is about 280.
c. Write balanced equations for the production of phosphorus(V) oxide and phosphoric acid.
d. Determine the mass of phosphorus required to make 1.00×10^4 kg of phosphoric acid, assuming a yield of 98.85%.

79.

Predict the product of burning francium in air.

80.

Using equations, describe the reaction of water with potassium and with potassium oxide.

81.

Write balanced chemical equations for the following reactions:

a. zinc metal heated in a stream of oxygen gas
b. zinc carbonate heated until loss of mass stops
c. zinc carbonate added to a solution of acetic acid, CH_3CO_2H
d. zinc added to a solution of hydrobromic acid

82.

Write balanced chemical equations for the following reactions:

a. cadmium burned in air
b. elemental cadmium added to a solution of hydrochloric acid
c. cadmium hydroxide added to a solution of acetic acid, CH_3CO_2H

83.

Illustrate the amphoteric nature of aluminum hydroxide by citing suitable equations.

84.

Write balanced chemical equations for the following reactions:

a. metallic aluminum burned in air
b. elemental aluminum heated in an atmosphere of chlorine
c. aluminum heated in hydrogen bromide gas
d. aluminum hydroxide added to a solution of nitric acid

85.

Write balanced chemical equations for the following reactions:

a. sodium oxide added to water
b. cesium carbonate added to an excess of an aqueous solution of HF
c. aluminum oxide added to an aqueous solution of $HClO_4$
d. a solution of sodium carbonate added to solution of barium nitrate
e. titanium metal produced from the reaction of titanium tetrachloride with elemental sodium

86.

What volume of 0.250 M H_2SO_4 solution is required to neutralize a solution that contains 5.00 g of $CaCO_3$?

87.

Which is the stronger acid, $HClO_4$ or $HBrO_4$? Why?

88.

Write a balanced chemical equation for the reaction of an excess of oxygen with each of the following. Remember that oxygen is a strong oxidizing agent and tends to oxidize an element to its maximum oxidation state.

a. Mg
b. Rb
c. Ga

    d. C_2H_2

    e. CO

89.

Which is the stronger acid, H_2SO_4 or H_2SeO_4? Why? You may wish to review the chapter on acid-base equilibria.

90.

Explain why hydrogen sulfide is a gas at room temperature, whereas water, which has a lower molecular mass, is a liquid.

91.

Give the hybridization and oxidation state for sulfur in SO_2, in SO_3, and in H_2SO_4.

92.

Which is the stronger acid, $NaHSO_3$ or $NaHSO_4$?

93.

Determine the oxidation state of sulfur in SF_6, SO_2F_2, and KHS.

94.

Which is a stronger acid, sulfurous acid or sulfuric acid? Why?

95.

Oxygen forms double bonds in O_2, but sulfur forms single bonds in S_8. Why?

96.

Give the Lewis structure of each of the following:

    a. SF_4

    b. K_2SO_4

    c. SO_2Cl_2

    d. H_2SO_3

    e. SO_3

97.

Write two balanced chemical equations in which sulfuric acid acts as an oxidizing agent.

98.

Explain why sulfuric acid, H_2SO_4, which is a covalent molecule, dissolves in water and produces a solution that contains ions.

99.

How many grams of Epsom salts ($MgSO_4 \cdot 7H_2O$) will form from 5.0 kg of magnesium?

100.

What does it mean to say that mercury(II) halides are weak electrolytes?

101.

Why is $SnCl_4$ not classified as a salt?

102.

The following reactions are all similar to those of the industrial chemicals. Complete and balance the equations for these reactions:

(a) reaction of a weak base and a strong acid

(b) preparation of a soluble silver salt for silver plating

(c) preparation of strontium hydroxide by electrolysis of a solution of strontium chloride

103.

Which is the stronger acid, $HClO_3$ or $HBrO_3$? Why?

104.

What is the hybridization of iodine in IF_3 and IF_5?

105.

Predict the molecular geometries and draw Lewis structures for each of the following. You may wish to review the chapter on chemical bonding and molecular geometry.

  a. IF_5
  b.
  c. PCl_5
  d. SeF_4
  e. ClF_3

106.

Which halogen has the highest ionization energy? Is this what you would predict based on what you have learned about periodic properties?

107.

Name each of the following compounds:

  a. BrF_3
  b. $NaBrO_3$
  c. PBr_5
  d. $NaClO_4$
  e. $KClO$

108.

Explain why, at room temperature, fluorine and chlorine are gases, bromine is a liquid, and iodine is a solid.

109.

What is the oxidation state of the halogen in each of the following?

  a. H_5IO_6
  b.
  c. ClO_2
  d. ICl_3
  e. F_2

110.

Physiological saline concentration—that is, the sodium chloride concentration in our bodies—is approximately 0.16 M. A saline solution for contact lenses is prepared to match the physiological concentration. If you purchase 25 mL of contact lens saline solution, how many grams of sodium chloride have you bought?

111.

Give the hybridization of xenon in each of the following. You may wish to review the chapter on the advanced theories of covalent bonding.

  a. XeF_2
  b. XeF_4
  c. XeO_3
  d. XeO_4
  e. $XeOF_4$

112.

What is the molecular structure of each of the following molecules? You may wish to review the chapter on chemical bonding and molecular geometry.

  a. XeF_2
  b. XeF_4

c. XeO_3
d. XeO_4
e. $XeOF_4$

113.

Indicate whether each of the following molecules is polar or nonpolar. You may wish to review the chapter on chemical bonding and molecular geometry.

a. XeF_2
b. XeF_4
c. XeO_3
d. XeO_4
e. $XeOF_4$

114.

What is the oxidation state of the noble gas in each of the following? You may wish to review the chapter on chemical bonding and molecular geometry.

a. XeO_2F_2
b. KrF_2
c.
d.
e. XeO_3

115.

A mixture of xenon and fluorine was heated. A sample of the white solid that formed reacted with hydrogen to yield 81 mL of xenon (at STP) and hydrogen fluoride, which was collected in water, giving a solution of hydrofluoric acid. The hydrofluoric acid solution was titrated, and 68.43 mL of 0.3172 M sodium hydroxide was required to reach the equivalence point. Determine the empirical formula for the white solid and write balanced chemical equations for the reactions involving xenon.

116.

Basic solutions of Na_4XeO_6 are powerful oxidants. What mass of $Mn(NO_3)_2$•$6H_2O$ reacts with 125.0 mL of a 0.1717 M basic solution of Na_4XeO_6 that contains an excess of sodium hydroxide if the products include Xe and solution of sodium permanganate?

12: Nuclear Chemistry

The chemical reactions that we have considered in previous chapters involve changes in the *electronic* structure of the species involved, that is, the arrangement of the **electrons** around atoms, ions, or molecules. *Nuclear* structure, the numbers of protons and neutrons within the nuclei of the atoms involved, remains unchanged during chemical reactions. This chapter will introduce the topic of nuclear chemistry, which began with the discovery of radioactivity in 1896 by French physicist Antoine Becquerel and has become increasingly important during the twentieth and twenty-first centuries, providing the basis for various technologies related to energy, medicine, geology, and many other areas.

12.1: Introduction

The chemical reactions that we have considered in previous chapters involve changes in the *electronic* structure of the species involved, that is, the arrangement of the electrons around atoms, ions, or molecules. *Nuclear* structure, the numbers of protons and neutrons within the nuclei of the atoms involved, remains unchanged during chemical reactions.
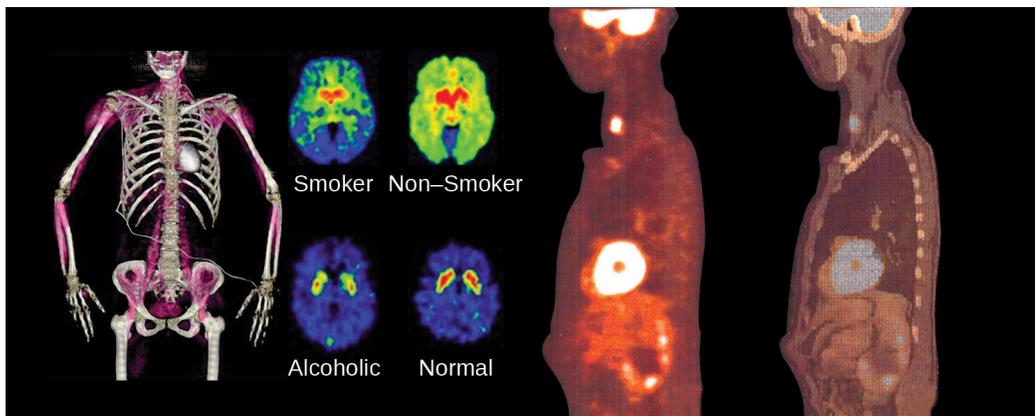
Figure 12.1.1: Nuclear chemistry provides the basis for many useful diagnostic and therapeutic methods in medicine, such as these positron emission tomography (PET) scans. The PET/computed tomography scan on the left shows muscle activity. The brain scans in the center show chemical differences in dopamine signaling in the brains of addicts and nonaddicts. The images on the right show an oncological application of PET scans to identify lymph node metastasis.

This chapter will introduce the topic of nuclear chemistry, which began with the discovery of radioactivity in 1896 by French physicist Antoine Becquerel and has become increasingly important during the twentieth and twenty-first centuries, providing the basis for various technologies related to energy, medicine, geology, and many other areas.

12.2: Nuclear Structure and Stability

◗ Learning Objectives

By the end of this section, you will be able to:

- Describe nuclear structure in terms of protons, neutrons, and electrons
- Calculate mass defect and binding energy for nuclei
- Explain trends in the relative stability of nuclei

Nuclear chemistry is the study of reactions that involve changes in nuclear structure. The chapter on atoms, molecules, and ions introduced the basic idea of nuclear structure, that the nucleus of an atom is composed of protons and, with the exception of ^1_1H.

Recall that the number of protons in the nucleus is called the atomic number (Z) of the element, and the sum of the number of protons and the number of neutrons is the mass number (A). Atoms with the same atomic number but different mass numbers are isotopes of the same element. When referring to a single type of nucleus, we often use the term **nuclide** and identify it by the notation ^A_ZX, where X is the symbol for the element, A is the mass number, and Z is the atomic number (for example, $^{14}_6\text{C}$). Often a nuclide is referenced by the name of the element followed by a hyphen and the mass number. For example, $^{14}_6\text{C}$ is called "carbon-14."

Protons and neutrons, collectively called **nucleons**, are packed together tightly in a nucleus. With a radius of about 10^{-15} meters, a nucleus is quite small compared to the radius of the entire atom, which is about 10^{-10} meters. Nuclei are extremely dense compared to bulk matter, averaging 1.8×10^{14} grams per cubic centimeter. For example, water has a density of 1 gram per cubic centimeter, and iridium, one of the densest elements known, has a density of 22.6 g/cm3. If the earth's density were equal to the average nuclear density, the earth's radius would be only about 200 meters (earth's actual radius is approximately 6.4×10^6 meters, 30,000 times larger). Example 12.2.1demonstrates just how great nuclear densities can be in the natural world.

✔ Example 12.2.1: Density of a Neutron Star

Neutron stars form when the core of a very massive star undergoes gravitational collapse, causing the star's outer layers to explode in a supernova. Composed almost completely of neutrons, they are the densest-known stars in the universe, with densities comparable to the average density of an atomic nucleus. A neutron star in a faraway galaxy has a mass equal to 2.4 solar masses (1 solar mass = $M_\odot$ = mass of the sun = $1.99 \times 10^{30}\ kg$) and a diameter of 26 km.

a. What is the density of this neutron star?
b. How does this neutron star's density compare to the density of a uranium nucleus, which has a diameter of about 15 fm (1 fm = 10^{-15} m)?

Solution
We can treat both the neutron star and the U-235 nucleus as spheres. Then the density for both is given by:

$$d = \frac{m}{V} \quad \text{with} \quad V = \frac{4}{3}\pi r^3$$

a. The radius of the neutron star is so the density of the neutron star is:

$$d = \frac{m}{V} = \frac{m}{\frac{4}{3}\pi r^3} = \frac{2.4\left(1.99 \times 10^{30}\,\text{kg}\right)}{\frac{4}{3}\pi\left(1.3 \times 10^4 m\right)^3} = 5.2 \times 10^{17}\,\text{kg/m}^3$$

b. The radius of the U-235 nucleus is so the density of the U-235 nucleus is:

$$d = \frac{m}{V} = \frac{m}{\frac{4}{3}\pi r^3} = \frac{235\,\text{amu}\left(\dfrac{1.66 \times 10^{-27}\,\text{kg}}{1\,\text{amu}}\right)}{\frac{4}{3}\pi\left(7.5 \times 10^{-15}\,\text{m}\right)^3} = 2.2 \times 10^{17}\,\text{kg/m}^3$$

These values are fairly similar (same order of magnitude), but the neutron star is more than twice as dense as the U-235 nucleus.

> **? Exercise 12.2.1**
>
> Find the density of a neutron star with a mass of 1.97 solar masses and a diameter of 13 km, and compare it to the density of a hydrogen nucleus, which has a diameter of $1.75\,\text{fm}\,(1\,\text{fm} = 1 \times 10^{-15}\,\text{m}\,)$.
>
> **Answer**
>
> The density of the neutron star is $3.4 \times 10^{18}\,\text{kg}/\text{m}^3$. The density of a hydrogen nucleus is $6.0 \times 10^{17}\, \text{kg}/\text{m}^3$. The neutron star is 5.7 times denser than the hydrogen nucleus.

To hold positively charged protons together in the very small volume of a nucleus requires very strong attractive forces because the positively charged protons repel one another strongly at such short distances. The force of attraction that holds the nucleus together is the strong nuclear force. (The strong force is one of the four fundamental forces that are known to exist. The others are the electromagnetic force, the gravitational force, and the nuclear weak force.) This force acts between protons, between neutrons, and between protons and neutrons. It is very different from the electrostatic force that holds negatively charged electrons around a positively charged nucleus (the attraction between opposite charges). Over distances less than 10^{-15} meters and within the nucleus, the strong nuclear force is much stronger than electrostatic repulsions between protons; over larger distances and outside the nucleus, it is essentially nonexistent.

> **📌 Link to Learning**
>
> Visit this website for more information about the four fundamental forces.

Nuclear Binding Energy

As a simple example of the energy associated with the strong nuclear force, consider the helium atom composed of two protons, two neutrons, and two electrons. The total mass of these six subatomic particles may be calculated as:

$$\underbrace{(2 \times 1.0073\,\text{amu})}_{\text{protons}} + \underbrace{(2 \times 1.0087\,\text{amu})}_{\text{neutrons}} + \underbrace{(2 \times 0.00055\,\text{amu})}_{\text{electrons}} = 4.0331\,\text{amu}$$

However, mass spectrometric measurements reveal that the mass of an atom is 4.0026 amu, less than the combined masses of its six constituent subatomic particles. This difference between the calculated and experimentally measured masses is known as the mass defect of the atom. In the case of helium, the **mass defect** indicates a "loss" in mass of 4.0331 amu – 4.0026 amu = 0.0305 amu. The loss in mass accompanying the formation of an atom from protons, neutrons, and electrons is due to the conversion of that mass into energy that is evolved as the atom forms. The **nuclear binding energy** is the energy produced when the atoms' nucleons are bound together; this is also the energy needed to break a nucleus into its constituent protons and neutrons. In comparison to chemical bond energies, nuclear binding energies are *vastly* greater, as we will learn in this section. Consequently, the energy changes associated with nuclear reactions are vastly greater than are those for chemical reactions.

The conversion between mass and energy is most identifiably represented by the **mass-energy equivalence equation** as stated by Albert Einstein:

$$E = mc^2 \tag{12.2.1}$$

where E is energy, m is mass of the matter being converted, and c is the speed of light in a vacuum. This equation can be used to find the amount of energy that results when matter is converted into energy. Using this mass-energy equivalence equation, the nuclear binding energy of a nucleus may be calculated from its mass defect, as demonstrated in Example 12.2.2 A variety of units are commonly used for nuclear binding energies, including electron volts (eV), with 1 eV equaling the amount of energy necessary to the move the charge of an electron across an electric potential difference of 1 volt, making 1 eV = 1.602 10^{-19} J.

> **✔ Example 12.2.2: Calculation of Nuclear Binding Energy**
>
> Determine the binding energy for the nuclide in:
>
> a. joules per mole of nuclei
> b. joules per nucleus

c. MeV per nucleus

Solution

The mass defect for a $^4_2$He nucleus is 0.0305 amu, as shown previously. Determine the binding energy in joules per nuclide using the mass-energy equivalence equation. To accommodate the requested energy units, the mass defect must be expressed in kilograms (recall that 1 J = 1 kg m^2/s^2).

a. First, express the mass defect in g/mol. This is easily done considering the *numerical equivalence* of atomic mass (amu) and molar mass (g/mol) that results from the definitions of the amu and mole units (refer to the previous discussion in the chapter on atoms, molecules, and ions if needed). The mass defect is therefore 0.0305 g/mol. To accommodate the units of the other terms in the mass-energy equation, the mass must be expressed in kg, since 1 J = 1 kg m^2/s^2. Converting grams into kilograms yields a mass defect of 3.05×10^{-5} kg/mol. Substituting this quantity into the mass-energy equivalence equation yields:

$$E = mc^2 = \frac{3.05 \times 10^{-5}\,kg}{mol} \times \left(\frac{2.998 \times 10^8\,m}{s} \right)^2 = 2.74 \times 10^{12}\, \text{kg m}^2\text{s}^{-2}\text{mol}^{-1}$$

$$= 2.74 \times 10^{12}\text{J mol}^{-1} = 2.74\,\text{TJ mol}^{-1}$$

Note that this tremendous amount of energy is associated with the conversion of a very small amount of matter (about 30 mg, roughly the mass of typical drop of water).

b. The binding energy for a single nucleus is computed from the molar binding energy using Avogadro's number:

$$E = 2.74 \times 10^{12}\,\text{J mol}^{-1} \times \frac{1\,\text{mol}}{6.022 \times 10^{23}\,\text{nuclei}}$$

$$= 4.55 \times 10^{-12}\,\text{J} = 4.55\,\text{pJ}$$

c. Recall that $1\,\text{eV} = 1.602 \times 10^{-19}$ J. Using the binding energy computed in part (b):

$$E = 4.55 \times 10^{-12}\,\text{J} \times \frac{1\,\text{eV}}{1.602 \times 10^{-19}\,\text{J}} = 2.84 \times 10^7\,\text{eV} = 28.4\,\text{MeV}$$

? Exercise 12.2.1

What is the binding energy for the $^{19}_9$F nuclide (atomic mass: 18.9984 amu) in MeV per nucleus?

Answer

148.4 MeV

Because the energy changes for breaking and forming bonds are so small compared to the energy changes for breaking or forming nuclei, the changes in mass during all ordinary chemical reactions are virtually undetectable. As described in the chapter on thermochemistry, the most energetic chemical reactions exhibit enthalpies on the order of *thousands* of kJ/mol, which is equivalent to mass differences in the nanogram range (10^{-9} g). On the other hand, nuclear binding energies are typically on the order of *billions* of kJ/mol, corresponding to mass differences in the milligram range (10^{-3} g).

Nuclear Stability

A nucleus is stable if it cannot be transformed into another configuration without adding energy from the outside. Of the thousands of nuclides that exist, about 250 are stable. A plot of the number of neutrons versus the number of protons for stable nuclei reveals that the stable isotopes fall into a narrow band. This region is known as the **band of stability** (also called the belt, zone, or valley of stability). The straight line in Figure 12.2.1 represents nuclei that have a 1:1 ratio of protons to neutrons (n:p ratio). Note that the lighter stable nuclei, in general, have equal numbers of protons and neutrons. For example, nitrogen-14 has seven protons and seven neutrons. Heavier stable nuclei, however, have increasingly more neutrons than protons. For example: iron-56 has 30 neutrons and 26 protons, an n:p ratio of 1.15, whereas the stable nuclide lead-207 has 125 neutrons and 82 protons, an n:p ratio equal to 1.52. This is because larger nuclei have more proton-proton repulsions, and require larger numbers of neutrons to provide compensating strong forces to overcome these electrostatic repulsions and hold the nucleus together.

Figure 12.2.1: This plot shows the nuclides that are known to exist and those that are stable. The stable nuclides are indicated in blue, and the unstable nuclides are indicated in green. Note that all isotopes of elements with atomic numbers greater than 83 are unstable. The solid line is the line where n = Z.

The nuclei that are to the left or to the right of the band of stability are unstable and exhibit **radioactivity**. They change spontaneously (decay) into other nuclei that are either in, or closer to, the band of stability. These nuclear decay reactions convert one unstable isotope (or **radioisotope**) into another, more stable, isotope. We will discuss the nature and products of this radioactive decay in subsequent sections of this chapter.

Several observations may be made regarding the relationship between the stability of a nucleus and its structure. Nuclei with even numbers of protons, neutrons, or both are more likely to be stable (see Table 12.2.1). Nuclei with certain numbers of nucleons, known as **magic numbers**, are stable against nuclear decay. These numbers of protons or neutrons (2, 8, 20, 28, 50, 82, and 126) make complete shells in the nucleus. These are similar in concept to the stable electron shells observed for the noble gases. Nuclei that have magic numbers of both protons and neutrons, such as and are called "double magic" and are particularly stable. These trends in nuclear stability may be rationalized by considering a quantum mechanical model of nuclear energy states analogous to that used to describe electronic states earlier in this textbook. The details of this model are beyond the scope of this chapter.

Table 12.2.1: Stable Nuclear Isotopes

Number of Stable Isotopes	Proton Number	Neutron Number
157	even	even
53	even	odd
50	odd	even
5	odd	odd

The relative stability of a nucleus is correlated with its **binding energy per nucleon**, the total binding energy for the nucleus divided by the number or nucleons in the nucleus. For instance, we saw in Example 12.2.2 that the binding energy for a $_2^4\text{He}$

nucleus is 28.4 MeV. The *binding energy per nucleon* for a $^4_2$He nucleus is therefore:

In Example 12.2.3, we learn how to calculate the binding energy per nucleon of a nuclide on the curve shown in Figure 12.2.2
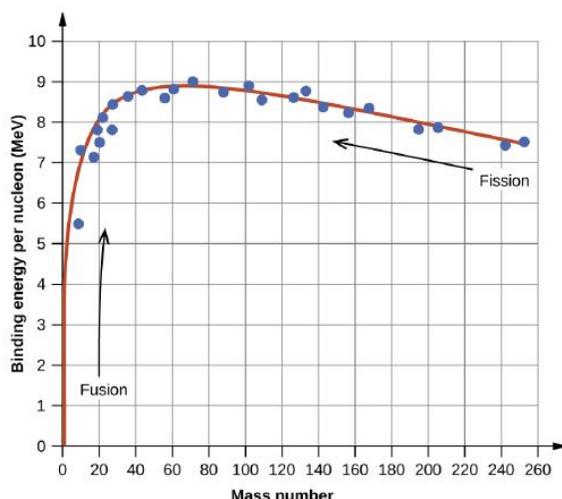
Figure 12.2.2: The binding energy per nucleon is largest for nuclides with mass number of approximately 56.

✔ Example 12.2.3: Calculation of Binding Energy per Nucleon

The iron nuclide atom $^{56}_{26}$Fe lies near the top of the binding energy curve (Figure 12.2.2) and is one of the most stable nuclides. What is the binding energy per nucleon (in MeV) for the nuclide $^{56}_{26}$Fe (atomic mass of 55.9349 amu)?

Solution

As in Example 12.2.2, we first determine the mass defect of the nuclide, which is the difference between the mass of 26 protons, 30 neutrons, and 26 electrons, and the observed mass of an $^{56}_{26}$Fe atom:

$$\begin{aligned} \text{Mass defect} \quad &= [(26 \times 1.0073\,\text{amu}) + (30 \times 1.0087\,\text{amu}) + (26 \times 0.00055\,\text{amu})] - 55.9349\,amu \\ &= 56.4651\,\text{amu} - 55.9349\,\text{amu} \\ &= 0.5302\,\text{amu} \end{aligned}$$

We next calculate the binding energy for one nucleus from the mass defect using the mass-energy equivalence equation:

$$\begin{aligned} E = mc^2 &= 0.5302\,\text{amu} \times \left(\frac{1.6605 \times 10^{-27}\,\text{kg}}{1\,\text{amu}} \right) \times \left(2.998 \times 10^8\,\text{m/s}\right)^2 \\ &= 7.913 \times 10^{-11}\,\text{kg} \cdot \text{m/s}^2 \\ &= 7.913 \times 10^{-11}\,\text{J} \end{aligned}$$

We then convert the binding energy in joules per nucleus into units of MeV per nuclide:

$$7.913 \times 10^{-11}\,\text{J} \times \frac{1\,\text{MeV}}{1.602 \times 10^{-13}\,\text{J}} = 493.9\,\text{MeV}$$

Finally, we determine the binding energy per nucleon by dividing the total nuclear binding energy by the number of nucleons in the atom:

Note that this is almost 25% larger than the binding energy per nucleon for $^4_2$He.

$$\text{Binding energy per nucleon} = \frac{493.9\,\text{MeV}}{56} = 8.820\,\text{MeV/ nucleon}$$

(Note also that this is the same process as in Example 12.2.1, but with the additional step of dividing the total nuclear binding energy by the number of nucleons.)

> **?** Exercise 12.2.1
>
> What is the binding energy per nucleon in $^{19}_{9}\text{F}$ (atomic mass, 18.9984 amu)?
>
> **Answer**
>
> $7.810\,\text{MeV/nucleon}$

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12.3: Nuclear Equations

> 🧠 **Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Identify common particles and energies involved in nuclear reactions
> - Write and balance nuclear equations

Changes of nuclei that result in changes in their atomic numbers, mass numbers, or energy states are nuclear reactions. To describe a nuclear reaction, we use an equation that identifies the nuclides involved in the reaction, their mass numbers and atomic numbers, and the other particles involved in the reaction.

Types of Particles in Nuclear Reactions

Many entities can be involved in nuclear reactions. The most common are protons, neutrons, alpha particles, beta particles, positrons, and gamma rays, as shown in Figure $12.3.1$. Protons ($_1^1p$, also represented by the symbol $_1^1H$) and neutrons ($_0^1n$) are the constituents of atomic nuclei, and have been described previously. **Alpha particles** ($_2^4He$, also represented by the symbol $_2^4\alpha$) are high-energy helium nuclei. **Beta particles** ($_{-1}^0\beta$, also represented by the symbol $_{-1}^0e$) are high-energy electrons, and gamma rays are photons of very high-energy electromagnetic radiation. **Positrons** ($_{+1}^0e$, also represented by the symbol $_{+1}^0\beta$) are positively charged electrons ("anti-electrons"). The subscripts and superscripts are necessary for balancing nuclear equations, but are usually optional in other circumstances. For example, an alpha particle is a helium nucleus (He) with a charge of +2 and a mass number of 4, so it is symbolized $_2^4He$. This works because, in general, the ion charge is not important in the balancing of nuclear equations.

Name	Symbol(s)	Representation	Description
Alpha particle	$_2^4He$ or $_2^4\alpha$		(High-energy) helium nuclei consisting of two protons and two neutrons
Beta particle	$_{-1}^0e$ or $_{-1}^0\beta$		(High-energy) electrons
Positron	$_{+1}^0e$ or $_{+1}^0\beta$		Particles with the same mass as an electron but with 1 unit of positive charge
Proton	$_1^1H$ or $_1^1p$		Nuclei of hydrogen atoms
Neutron	$_0^1n$		Particles with a mass approximately equal to that of a proton but with no charge
Gamma ray	γ		Very high-energy electromagnetic radiation

Figure 12.3.1: Although many species are encountered in nuclear reactions, this table summarizes the names, symbols, representations, and descriptions of the most common of these.

Note that positrons are exactly like electrons, except they have the opposite charge. They are the most common example of **antimatter**, particles with the same mass but the opposite state of another property (for example, charge) than ordinary matter. When antimatter encounters ordinary matter, both are annihilated and their mass is converted into energy in the form of **gamma rays** (γ)—and other much smaller subnuclear particles, which are beyond the scope of this chapter—according to the mass-energy equivalence equation $E = mc^2$, seen in the preceding section. For example, when a positron and an electron collide, both are annihilated and two gamma ray photons are created:

$$_{-1}^0e + _{+1}^0e \longrightarrow \gamma + \gamma$$
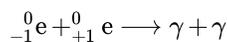
As seen in the chapter discussing light and electromagnetic radiation, gamma rays compose short wavelength, high-energy electromagnetic radiation and are (much) more energetic than better-known X-rays that can behave as particles in the wave-particle duality sense. Gamma rays are a type of high energy electromagnetic radiation produced when a nucleus undergoes a transition from a higher to a lower energy state, similar to how a photon is produced by an electronic transition from a higher to a lower

energy level. Due to the much larger energy differences between nuclear energy shells, gamma rays emanating from a nucleus have energies that are typically millions of times larger than electromagnetic radiation emanating from electronic transitions.

Balancing Nuclear Reactions

A balanced chemical reaction equation reflects the fact that during a chemical reaction, bonds break and form, and atoms are rearranged, but the total numbers of atoms of each element are conserved and do not change. A balanced nuclear reaction equation indicates that there is a rearrangement during a nuclear reaction, but of nucleons (subatomic particles within the atoms' nuclei) rather than atoms. Nuclear reactions also follow conservation laws, and they are balanced in two ways:

1. The sum of the mass numbers of the reactants equals the sum of the mass numbers of the products.
2. The sum of the charges of the reactants equals the sum of the charges of the products.

If the atomic number and the mass number of all but one of the particles in a nuclear reaction are known, we can identify the particle by balancing the reaction. For instance, we could determine that $^{17}_{8}O$ is a product of the nuclear reaction of $^{14}_{7}N$ and $^{4}_{2}He$ if we knew that a proton, $^{1}_{1}H$, were one of the two products. Example 12.3.1 shows how we can identify a nuclide by balancing the nuclear reaction.

✔ Example 12.3.1: Balancing Equations for Nuclear Reactions

The reaction of an α particle with magnesium-25 ($^{25}_{12}Mg$) produces a proton and a nuclide of another element. Identify the new nuclide produced.

Solution

The nuclear reaction can be written as:

$$^{25}_{12}Mg + ^{4}_{2}He \longrightarrow ^{1}_{1}H + ^{A}_{Z}X$$
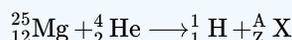
where A is the mass number and Z is the atomic number of the new nuclide, X. Because the sum of the mass numbers of the reactants must equal the sum of the mass numbers of the products:

$$25 + 4 = A + 1$$

or $A = 28$.

Similarly, the charges must balance, so:

$$12 + 2 = Z + 1$$

and $Z = 13$.

Check the periodic table: The element with nuclear charge = +13 is aluminum. Thus, the product is $^{28}_{13}Al$

? Exercise 12.3.1

The nuclide $^{125}_{53}I$ combines with an electron and produces a new nucleus and no other massive particles. What is the equation for this reaction?

Answer

$$^{125}_{53}I + ^{0}_{-1}e \longrightarrow ^{125}_{52}Te$$
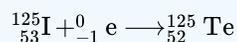
Following are the equations of several nuclear reactions that have important roles in the history of nuclear chemistry:

- The first naturally occurring unstable element that was isolated, polonium, was discovered by the Polish scientist Marie Curie and her husband Pierre in 1898. It decays, emitting α particles:

$$^{212}_{84}Po \longrightarrow ^{208}_{82}Pb + ^{4}_{2}He$$
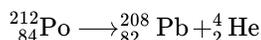
- The first nuclide to be prepared by artificial means was an isotope of oxygen, ^{17}O. It was made by Ernest Rutherford in 1919 by bombarding nitrogen atoms with α particles:

$$\ce{^{14}_{7}N + ^{4}_{2}He \longrightarrow ^{17}_{8}O + ^{1}_{1}H}$$
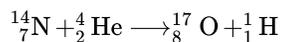
- James Chadwick discovered the neutron in 1932, as a previously unknown neutral particle produced along with ^{12}C by the nuclear reaction between ^{9}Be and ^{4}He:

$$\ce{^{9}_{4}Be + ^{4}_{2}He \longrightarrow ^{12}_{6}C + ^{1}_{0}n}$$
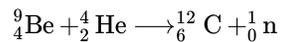
- The first element to be prepared that does not occur naturally on the earth, technetium, was created by bombardment of molybdenum by deuterons (heavy hydrogen, $^{2}_{1}$H), by Emilio Segre and Carlo Perrier in 1937:

$$\ce{^{2}_{1}H + ^{97}_{42}Mo \longrightarrow 2\,^{1}_{0}n + ^{97}_{43}Tc}$$
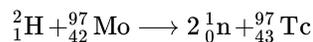
- The first controlled nuclear chain reaction was carried out in a reactor at the University of Chicago in 1942. One of the many reactions involved was:
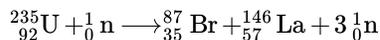
$$\ce{^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{87}_{35}Br + ^{146}_{57}La + 3\,^{1}_{0}n}$$

12.4: Radioactive Decay

> **◀▶ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Recognize common modes of radioactive decay
> - Identify common particles and energies involved in nuclear decay reactions
> - Write and balance nuclear decay equations
> - Calculate kinetic parameters for decay processes, including half-life
> - Describe common radiometric dating techniques

Following the somewhat serendipitous discovery of radioactivity by Becquerel, many prominent scientists began to investigate this new, intriguing phenomenon. Among them were Marie Curie (the first woman to win a Nobel Prize, and the only person to win two Nobel Prizes in different sciences—chemistry and physics), who was the first to coin the term "radioactivity," and Ernest Rutherford (of gold foil experiment fame), who investigated and named three of the most common types of radiation. During the beginning of the twentieth century, many radioactive substances were discovered, the properties of radiation were investigated and quantified, and a solid understanding of radiation and nuclear decay was developed.

The spontaneous change of an unstable nuclide into another is **radioactive decay**. The unstable nuclide is called the **parent nuclide**; the nuclide that results from the decay is known as the **daughter nuclide**. The daughter nuclide may be stable, or it may decay itself. The radiation produced during radioactive decay is such that the daughter nuclide lies closer to the band of stability than the parent nuclide, so the location of a nuclide relative to the band of stability can serve as a guide to the kind of decay it will undergo (Figure 12.4.1).

| Parent nucleus | α particle | Daughter nucleus |
| uranium-238 | | thorium-234 |
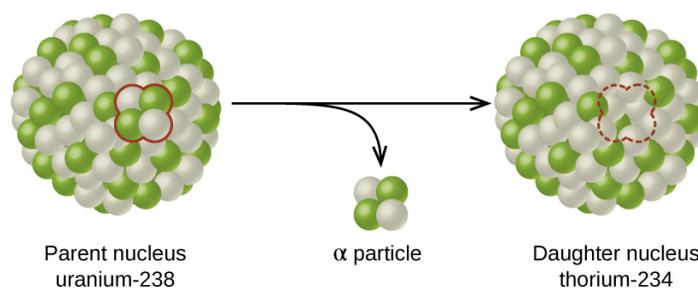
Figure 12.4.1: A nucleus of uranium-238 (the parent nuclide) undergoes α decay to form thorium-234 (the daughter nuclide). The alpha particle removes two protons (green) and two neutrons (gray) from the uranium-238 nucleus.

> **⚑ Link to Learning**
>
> Although the radioactive decay of a nucleus is too small to see with the naked eye, we can indirectly view radioactive decay in an environment called a cloud chamber. Click here to learn about cloud chambers and to view an interesting Cloud Chamber Demonstration from the Jefferson Lab.

Types of Radioactive Decay

Ernest Rutherford's experiments involving the interaction of radiation with a magnetic or electric field (Figure 12.4.2) helped him determine that one type of radiation consisted of positively charged and relatively massive α particles; a second type was made up of negatively charged and much less massive β particles; and a third was uncharged electromagnetic waves, γ rays. We now know that α particles are high-energy helium nuclei, β particles are high-energy electrons, and γ radiation compose high-energy electromagnetic radiation. We classify different types of radioactive decay by the radiation produced.
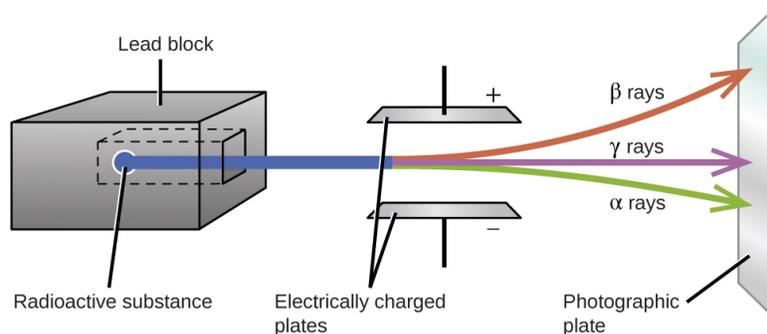
Figure 12.4.2: Alpha particles, which are attracted to the negative plate and deflected by a relatively small amount, must be positively charged and relatively massive. Beta particles, which are attracted to the positive plate and deflected a relatively large amount, must be negatively charged and relatively light. Gamma rays, which are unaffected by the electric field, must be uncharged.

Alpha (α) decay is the emission of an α particle from the nucleus. For example, polonium-210 undergoes α decay:

$$^{210}_{84}\text{Po} \longrightarrow ^4_2\text{He} + ^{206}_{82}\text{Pb}$$

or

$$^{210}_{84}\text{Po} \longrightarrow ^4_2\alpha + ^{206}_{82}\text{Pb}$$
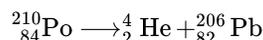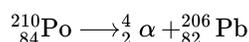
Alpha decay occurs primarily in heavy nuclei ($A > 200$, $Z > 83$). Because the loss of an α particle gives a daughter nuclide with a mass number four units smaller and an atomic number two units smaller than those of the parent nuclide, the daughter nuclide has a larger n:p ratio than the parent nuclide. If the parent nuclide undergoing α decay lies below the band of stability (refer to Figure 21.2), the daughter nuclide will lie closer to the band.

Beta (β) decay is the emission of an electron (i.e., a β particle) from a nucleus. Iodine-131 is an example of a nuclide that undergoes β decay:

$$^{131}_{53}\text{I} \longrightarrow ^0_{-1}\text{e} + ^{131}_{54}\text{Xe}$$

or

$$^{131}_{53}\text{I} \longrightarrow ^0_{-1}\beta + ^{131}_{54}\text{Xe}$$
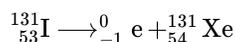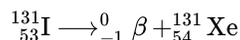
Beta decay, which can be thought of as the conversion of a neutron into a proton and a β particle, is observed in nuclides with a large n:p ratio. The beta particle (electron) emitted is from the atomic nucleus and is not one of the electrons surrounding the nucleus. Such nuclei lie above the band of stability. Emission of an electron does not change the mass number of the nuclide but does increase the number of its protons and decrease the number of its neutrons. Consequently, the n:p ratio is decreased, and the daughter nuclide lies closer to the band of stability than did the parent nuclide.

Gamma emission (γ emission) is observed when a nuclide is formed in an excited state and then decays to its ground state with the emission of a γ ray, a quantum of high-energy electromagnetic radiation. The presence of a nucleus in an excited state is often indicated by an asterisk (*). Cobalt-60 emits γ radiation and is used in many applications including cancer treatment:

$$^{60}_{27}\text{Co}^. \longrightarrow ^0_0\gamma + ^{60}_{27}\text{Co}$$
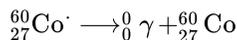
There is no change in mass number or atomic number during the emission of a γ ray unless the γ emission accompanies one of the other modes of decay.

Positron emission (β^+ decay) is the emission of a positron from the nucleus. Oxygen-15 is an example of a nuclide that undergoes positron emission:

$$^{15}_8\text{O} \longrightarrow ^0_{+1}\text{e} + ^{15}_7\text{N}$$

or

$$^{15}_8\text{O} \longrightarrow ^0_{+1}\beta + ^{15}_7\text{N}$$
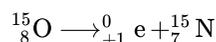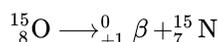
Positron emission is observed for nuclides in which the n:p ratio is low. These nuclides lie below the band of stability. Positron decay is the conversion of a proton into a neutron with the emission of a positron. The n:p ratio increases, and the daughter nuclide lies closer to the band of stability than did the parent nuclide.

Electron capture occurs when one of the inner electrons in an atom is captured by the atom's nucleus. For example, potassium-40 undergoes electron capture:

$$^{40}_{19}\text{K} + ^{0}_{-1}\text{e} \longrightarrow ^{40}_{18}\text{Ar}$$
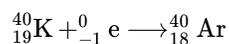
Electron capture occurs when an inner shell electron combines with a proton and is converted into a neutron. The loss of an inner shell electron leaves a vacancy that will be filled by one of the outer electrons. As the outer electron drops into the vacancy, it will emit energy. In most cases, the energy emitted will be in the form of an X-ray. Like positron emission, electron capture occurs for "proton-rich" nuclei that lie below the band of stability. Electron capture has the same effect on the nucleus as does positron emission: The atomic number is decreased by one and the mass number does not change. This increases the n:p ratio, and the daughter nuclide lies closer to the band of stability than did the parent nuclide. Whether electron capture or positron emission occurs is difficult to predict. The choice is primarily due to kinetic factors, with the one requiring the smaller activation energy being the one more likely to occur.

Figure 12.4.3 summarizes these types of decay, along with their equations and changes in atomic and mass numbers.

Type	Nuclear equation	Representation	Change in mass/atomic numbers
Alpha decay	$^{A}_{Z}\text{X} \rightarrow ^{4}_{2}\text{He} + ^{A-4}_{Z-2}\text{Y}$		A: decrease by 4 / Z: decrease by 2
Beta decay	$^{A}_{Z}\text{X} \rightarrow ^{0}_{-1}\text{e} + ^{A}_{Z+1}\text{Y}$		A: unchanged / Z: increase by 1
Gamma decay	$^{A}_{Z}\text{X} \rightarrow ^{0}_{0}\gamma + ^{A}_{Z}\text{Y}$ Excited nuclear state		A: unchanged / Z: unchanged
Positron emission	$^{A}_{Z}\text{X} \rightarrow ^{0}_{+1}\text{e} + ^{A}_{Y-1}\text{Y}$		A: unchanged / Z: decrease by 1
Electron capture	$^{A}_{Z}\text{X} + ^{0}_{-1}\text{e} \rightarrow ^{A}_{Y-1}\text{Y}$ X-ray		A: unchanged / Z: decrease by 1
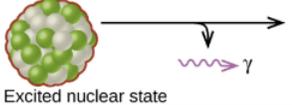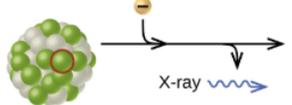
Figure 12.4.3: This table summarizes the type, nuclear equation, representation, and any changes in the mass or atomic numbers for various types of decay.

⚑ Chemistry in Everyday Life: PET Scan

Positron emission tomography (PET) scans use radiation to diagnose and track health conditions and monitor medical treatments by revealing how parts of a patient's body function (Figure 12.4.4). To perform a PET scan, a positron-emitting radioisotope is produced in a cyclotron and then attached to a substance that is used by the part of the body being investigated. This "tagged" compound, or radiotracer, is then put into the patient (injected via IV or breathed in as a gas), and how it is used by the tissue reveals how that organ or other area of the body functions.
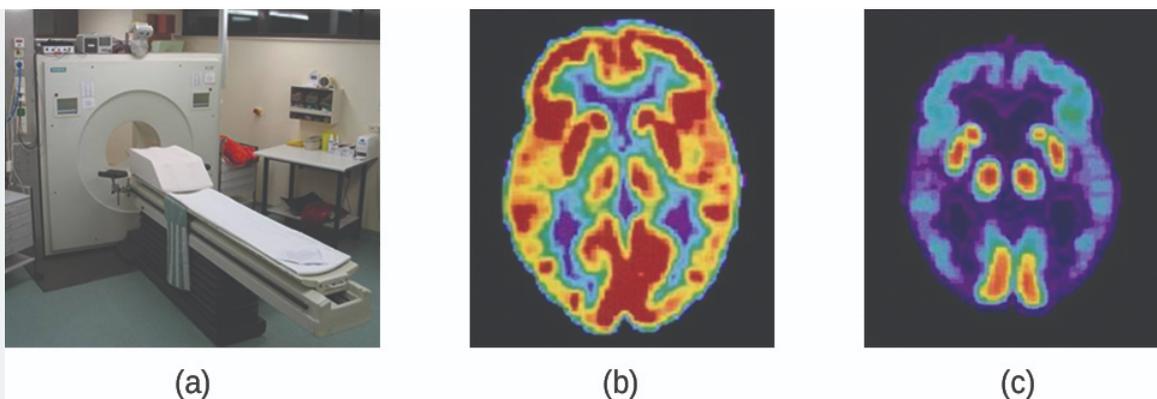
Figure 12.4.4: A PET scanner (a) uses radiation to provide an image of how part of a patient's body functions. The scans it produces can be used to image a healthy brain (b) or can be used for diagnosing medical conditions such as Alzheimer's disease (c). (credit a: modification of work by Jens Maus)

For example, F-18 is produced by proton bombardment of $\ce{^{18}O}$

$$\ce{^{18}_{8}O + ^{1}_{1}p -> ^{18}_{9}F + ^{1}_{0}n}$$
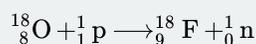
and incorporated into a glucose analog called fludeoxyglucose (FDG). How FDG is used by the body provides critical diagnostic information; for example, since cancers use glucose differently than normal tissues, FDG can reveal cancers. The ^{18}F emits positrons that interact with nearby electrons, producing a burst of gamma radiation. This energy is detected by the scanner and converted into a detailed, three-dimensional, color image that shows how that part of the patient's body functions. Different levels of gamma radiation produce different amounts of brightness and colors in the image, which can then be interpreted by a radiologist to reveal what is going on. PET scans can detect heart damage and heart disease, help diagnose Alzheimer's disease, indicate the part of a brain that is affected by epilepsy, reveal cancer, show what stage it is, and how much it has spread, and whether treatments are effective. Unlike magnetic resonance imaging and X-rays, which only show how something looks, the big advantage of PET scans is that they show how something functions. PET scans are now usually performed in conjunction with a computed tomography scan.

Radioactive Decay Series

The naturally occurring radioactive isotopes of the heaviest elements fall into chains of successive disintegrations, or decays, and all the species in one chain constitute a radioactive family, or **radioactive decay series**. Three of these series include most of the naturally radioactive elements of the periodic table. They are the uranium series, the actinide series, and the thorium series. The neptunium series is a fourth series, which is no longer significant on the earth because of the short half-lives of the species involved. Each series is characterized by a parent (first member) that has a long half-life and a series of daughter nuclides that ultimately lead to a stable end-product—that is, a nuclide on the band of stability (Figure 12.4.5). In all three series, the end-product is a stable isotope of lead. The neptunium series, previously thought to terminate with bismuth-209, terminates with thallium-205.
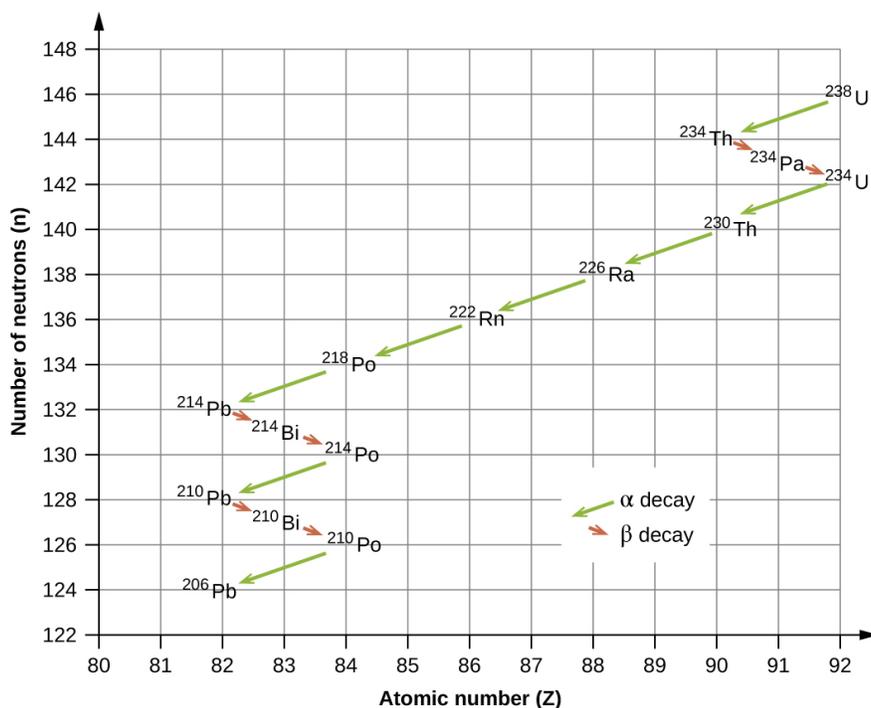
Figure 12.4.5: Uranium-238 undergoes a radioactive decay series consisting of 14 separate steps before producing stable lead-206. This series consists of eight α decays and six β decays.

Radioactive Half-Lives

Radioactive decay follows first-order kinetics. Since first-order reactions have already been covered in detail in the kinetics chapter, we will now apply those concepts to nuclear decay reactions. Each radioactive nuclide has a characteristic, constant **half-life** ($t_{1/2}$), the time required for half of the atoms in a sample to decay. An isotope's half-life allows us to determine how long a sample of a useful isotope will be available, and how long a sample of an undesirable or dangerous isotope must be stored before it decays to a low-enough radiation level that is no longer a problem.

For example, coba source, since half of the nuclei decay every 5.27 years, both the amount of material and the intensity of the radiation emitted is cut in half every 5.27 years. (Note that for a given substance, the intensity of radiation that it produces is directly proportional to the rate of decay of the substance and the amount of the substance.) This is as expected for a process following first-order kinetics. Thus, a cobalt-60 source that is used for cancer treatment must be replaced regularly to continue to be effective.
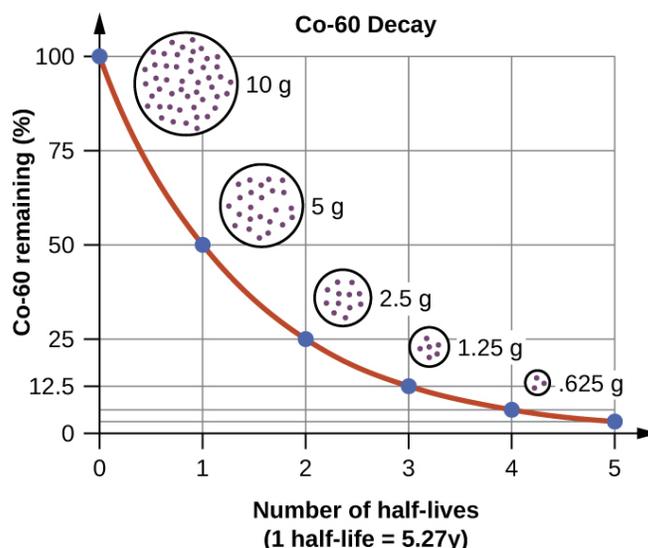
Figure 12.4.6: For cobalt-60, which has a half-life of 5.27 years, 50% remains after 5.27 years (one half-life), 25% remains after 10.54 years (two half-lives), 12.5% remains after 15.81 years (three half-lives), and so on.

Since nuclear decay follows first-order kinetics, we can adapt the mathematical relationships used for first-order chemical reactions. We generally substitute the number of nuclei, N, for the concentration. If the rate is stated in nuclear decays per second, we refer to it as the **activity** of the radioactive sample. The rate for radioactive decay is:

$$\text{decay rate} = \lambda N$$

with λ = the decay constant for the particular radioisotope.

The decay constant, λ, which is the same as a rate constant discussed in the kinetics chapter. It is possible to express the decay constant in terms of the half-life, $t_{1/2}$:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{t_{1/2}}$$

or

$$t_{1/2} = \frac{\ln 2}{\lambda} = \frac{0.693}{\lambda}$$

The first-order equations relating amount, N, and time are:

$$N_t = N_0 e^{-\lambda t} \tag{12.4.1}$$

or

$$t = -\frac{1}{\lambda} \ln\left(\frac{N_t}{N_0}\right)$$

✔ Example 12.4.1: Rates of Radioactive Decay

$^{60}_{27}\text{Co}$ decays with a half-life of 5.27 years to produce $^{60}_{28}\text{Co}$

   a. What is the decay constant for the radioactive disintegration of cobalt-60?

   b. Calculate the fraction of a sample of the $^{60}_{27}\text{Co}$ isotope that will remain after 15 years.

   c. How long does it take for a sample of $^{60}_{27}\text{Co}$ to disintegrate to the extent that only 2.0% of the original amount remains?

Solution

(a) The value of the rate constant is given by:

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5.27y} = 0.132y^{-1}$$

(b) The fraction of $^{60}_{27}$Co that is left after time t is given by $\frac{N_t}{N_0}$. Rearranging the first-order relationship in Equation 12.4.1 ($N_t = N_0 e^{-\lambda t}$ to solve for this ratio yields:

$$\frac{N_t}{N_0} = e^{-\lambda t} = e^{-(0.132/\text{y})(15\,\text{y})} = 0.138$$

The fraction of $^{60}_{27}$Co that will remain after 15.0 years is 0.138. Or put another way, 13.8% of the original $^{60}_{27}$Co present will remain after 15 years.

(c) 2.00% of the original amount of $^{60}_{27}$Co is equal to 0.0200 N_0. Substituting this into the equation for time for first-order kinetics, we have:

$$t = -\frac{1}{\lambda}\ln\left(\frac{N_t}{N_0}\right) = -\frac{1}{0.132\,\text{y}^{-1}}\ln\left(\frac{0.0200 \times N_0}{N_0}\right) = 29.6y$$

> **? Exercise 12.4.1**
>
> Radon-222, $^{222}_{86}$Rn has a half-life of 3.823 days. How long will it take a sample of radon-222 with a mass of 0.750 g to decay into other elements, leaving only 0.100 g of radon-222?
>
> **Answer**
>
> 11.1 days

Because each nuclide has a specific number of nucleons, a particular balance of repulsion and attraction, and its own degree of stability, the half-lives of radioactive nuclides vary widely. For example: the half-life of $^{209}_{83}$Bi is 1.9×10^{19} years; $^{239}_{94}$Ra is 24,000 years; $^{222}_{86}$Rn is 3.82 days; and element-111 (Rg for roentgenium) is 1.5×10^{-3} seconds. The half-lives of a number of radioactive isotopes important to medicine are shown in Table 12.4.1, and others are listed in Appendix M.

Table 12.4.1: Half-lives of Radioactive Isotopes Important to Medicine

Type[1]	Decay Mode	Half-Life	Uses
F-18	β^+ decay	110. minutes	PET scans
Co-60	β decay, γ decay	5.27 years	cancer treatment
Tc-99m	γ decay	8.01 hours	scans of brain, lung, heart, bone
I-131	β decay	8.02 days	thyroid scans and treatment
Tl-201	electron capture	73 hours	heart and arteries scans; cardiac stress tests

Radiometric Dating

Several radioisotopes have half-lives and other properties that make them useful for purposes of "dating" the origin of objects such as archaeological artifacts, formerly living organisms, or geological formations. This process is **radiometric dating** and has been responsible for many breakthrough scientific discoveries about the geological history of the earth, the evolution of life, and the history of human civilization. We will explore some of the most common types of radioactive dating and how the particular isotopes work for each type.

Radioactive Dating Using Carbon-14

The radioactivity of carbon-14 provides a method for dating objects that were a part of a living organism. This method of radiometric dating, which is also called **radiocarbon dating** or carbon-14 dating, is accurate for dating carbon-containing substances that are up to about 30,000 years old, and can provide reasonably accurate dates up to a maximum of about 50,000 years old.

Naturally occurring carbon consists of three isotopes: $^{12}_{6}\text{C}$ which constitutes about 99% of the carbon on earth; $^{13}_{6}\text{C}$, about 1% of the total; and trace amounts of $^{14}_{6}\text{C}$. Carbon-14 forms in the upper atmosphere by the reaction of nitrogen atoms with neutrons from cosmic rays in space:

$$^{14}_{7}\text{N} + ^{1}_{0}\text{n} \longrightarrow ^{14}_{6}\text{C} + ^{1}_{1}\text{H}$$
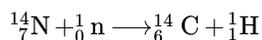
All isotopes of carbon react with oxygen to produce CO_2 molecules. The ratio of $^{14}_{6}CO_2$ to $^{12}_{6}CO_2$ depends on the ratio of $^{14}_{6}CO$ to $^{12}_{6}CO$ in the atmosphere. The natural abundance of $^{14}_{6}CO$ in the atmosphere is approximately 1 part per trillion; until recently, this has generally been constant over time, as seen is gas samples found trapped in ice. The incorporation of $^{14}_{6}CO_2$ and $^{14}_{6}CO_2$ into plants is a regular part of the photosynthesis process, which means that the $^{14}_{6}\text{C} : ^{12}_{6}\text{C}$ ratio found in a living plant is the **same** as the $^{14}_{6}\text{C} : ^{12}_{6}\text{C}$ ratio in the atmosphere. But when the plant dies, it no longer traps carbon through photosynthesis. Because $^{12}_{6}\text{C}$ is a stable isotope and does not undergo radioactive decay, its concentration in the plant does not change. However, carbon-14 decays by β emission with a half-life of 5730 years:

$$^{14}_{6}\text{C} \longrightarrow ^{14}_{7}\text{N} + ^{0}_{-1}\text{e}$$
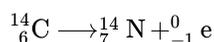
Thus, the ratio gradually decreases after the plant dies. The decrease in the ratio with time provides a measure of the time that has elapsed since the death of the plant (or other organism that ate the plant). Figure $12.4.7$: visually depicts this process.
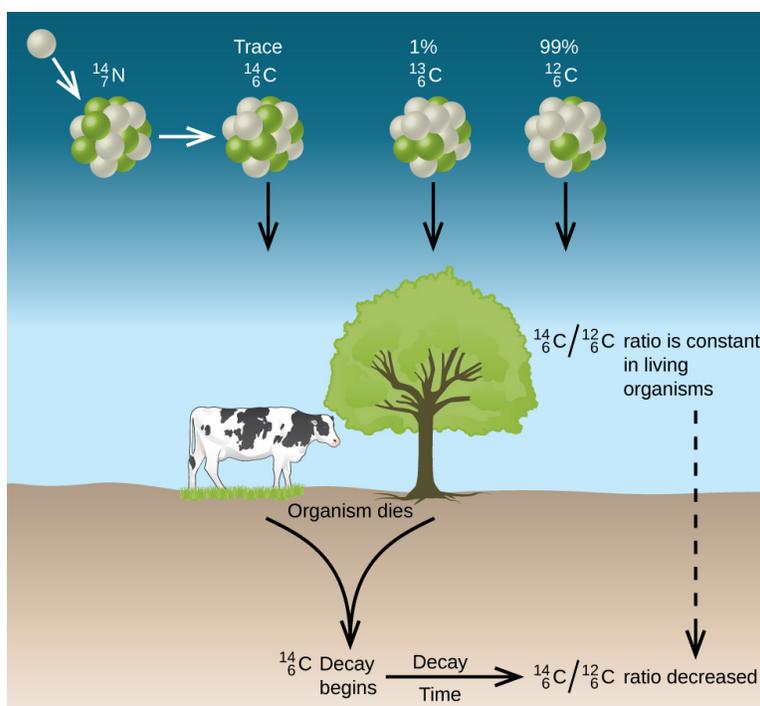
Figure 12.4.7: Along with stable carbon-12, radioactive carbon-14 is taken in by plants and animals, and remains at a constant level within them while they are alive. After death, the C-14 decays and the C-14:C-12 ratio in the remains decreases. Comparing this ratio to the C-14:C-12 ratio in living organisms allows us to determine how long ago the organism lived (and died).

For example, with the half-life of being 5730 years, if the ratio in a wooden object found in an archaeological dig is half what it is in a living tree, this indicates that the wooden object is 5730 years old. Highly accurate determinations of ratios can be obtained from very small samples (as little as a milligram) by the use of a mass spectrometer.

📌 Link to Learning

Visit this website to perform simulations of radiometric dating.

> ✔ Example 12.4.2: Radiocarbon Dating
>
> A tiny piece of paper (produced from formerly living plant matter) taken from the Dead Sea Scrolls has an activity of 10.8 disintegrations per minute per gram of carbon. If the initial C-14 activity was 13.6 disintegrations/min/g of C, estimate the age of the Dead Sea Scrolls.
>
> **Solution**
>
> The rate of decay (number of disintegrations/minute/gram of carbon) is proportional to the amount of radioactive C-14 left in the paper, so we can substitute the rates for the amounts, N, in the relationship:
>
> $$t = -\frac{1}{\lambda} \ln\left(\frac{N_t}{N_0} \right) \longrightarrow t = -\frac{1}{\lambda} \ln\left(\frac{\text{Rate}_t}{\text{Rate}_0} \right)$$
>
> where the subscript 0 represents the time when the plants were cut to make the paper, and the subscript t represents the current time.
>
> The decay constant can be determined from the half-life of C-14, 5730 years:
>
> $$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{5730 \text{ y}} = 1.21 \times 10^{-4} \text{ y}^{-1}$$
>
> Substituting and solving, we have:
>
> $$t = -\frac{1}{\lambda} \ln\left(\frac{\text{Rate}_t}{\text{Rate}_0} \right) = -\frac{1}{1.21 \times 10^{-4} \text{ y}^{-1}} \ln\left(\frac{10.8 \text{ dis/min/g C}}{13.6 \text{ dis/min/g C}} \right) = 1910 \text{ y}$$
>
> Therefore, the Dead Sea Scrolls are approximately 1900 years old (Figure 12.4.8).
>
>
>
> Figure 12.4.8: Carbon-14 dating has shown that these pages from the Dead Sea Scrolls were written or copied on paper made from plants that died between 100 BC and AD 50.

> ? Exercise 12.4.1
>
> More accurate dates of the reigns of ancient Egyptian pharaohs have been determined recently using plants that were preserved in their tombs. Samples of seeds and plant matter from King Tutankhamun's tomb have a C-14 decay rate of 9.07 disintegrations/min/g of C. How long ago did King Tut's reign come to an end?
>
> **Answer**
>
> about 3350 years ago, or approximately 1340 BC

There have been some significant, well-documented changes to the $_6^{14}\text{C} : _6^{12}\text{C}$ ratio. The accuracy of a straightforward application of this technique depends on the $_6^{14}\text{C} : _6^{12}\text{C}$ ratio in a living plant being the same now as it was in an earlier era, but this is not always valid. Due to the increasing accumulation of CO_2 molecules (largely $_6^{12}\text{C}$) in the atmosphere caused by combustion of fossil fuels (in which essentially all of the $_6^{14}\text{C}$ has decayed), the ratio of $_6^{14}\text{C} : _6^{12}\text{C}$ in the atmosphere may be changing. This manmade increase in $_6^{12}\text{C}$ in the atmosphere causes the $_6^{14}\text{C} : _6^{12}\text{C}$ ratio to decrease, and this in turn affects the ratio in currently living organisms on the earth. Fortunately, however, we can use other data, such as tree dating via examination of annual growth rings, to calculate correction factors. With these correction factors, accurate dates can be determined. In general, radioactive dating only works for about 10 half-lives; therefore, the limit for carbon-14 dating is about 57,000 years.

Radioactive Dating Using Nuclides Other than Carbon-14

Radioactive dating can also use other radioactive nuclides with longer half-lives to date older events. For example, uranium-238 (which decays in a series of steps into lead-206) can be used for establishing the age of rocks (and the approximate age of the oldest rocks on earth). Since U-238 has a half-life of 4.5 billion years, it takes that amount of time for half of the original U-238 to decay into Pb-206. In a sample of rock that does not contain appreciable amounts of Pb-208, the most abundant isotope of lead, we can assume that lead was not present when the rock was formed. Therefore, by measuring and analyzing the ratio of U-238:Pb-206, we can determine the age of the rock. This assumes that all of the lead-206 present came from the decay of uranium-238. If there is additional lead-206 present, which is indicated by the presence of other lead isotopes in the sample, it is necessary to make an adjustment. Potassium-argon dating uses a similar method. K-40 decays by positron emission and electron capture to form Ar-40 with a half-life of 1.25 billion years. If a rock sample is crushed and the amount of Ar-40 gas that escapes is measured, determination of the Ar-40:K-40 ratio yields the age of the rock. Other methods, such as rubidium-strontium dating (Rb-87 decays into Sr-87 with a half-life of 48.8 billion years), operate on the same principle. To estimate the lower limit for the earth's age, scientists determine the age of various rocks and minerals, making the assumption that the earth is older than the oldest rocks and minerals in its crust. As of 2014, the oldest known rocks on earth are the Jack Hills zircons from Australia, found by uranium-lead dating to be almost 4.4 billion years old.

> ### ✔ Example 12.4.3: Radioactive Dating of Rocks
>
> An igneous rock contains 9.58×10^{-5} g of U-238 and 2.51×10^{-5} g of Pb-206, and much, much smaller amounts of Pb-208. Determine the approximate time at which the rock formed.
>
> **Solution**
>
> The sample of rock contains very little Pb-208, the most common isotope of lead, so we can safely assume that all the Pb-206 in the rock was produced by the radioactive decay of U-238. When the rock formed, it contained all of the U-238 currently in it, plus some U-238 that has since undergone radioactive decay.
>
> The amount of U-238 currently in the rock is:
>
> $$9.58 \times 10^{-5} \ \text{g U} \times \left(\frac{1 \, \text{mol U}}{238 \ \text{g U}} \right) = 4.03 \times 10^{-7} \, \text{mol U}$$
>
> Because when one mole of U-238 decays, it produces one mole of Pb-206, the amount of U-238 that has undergone radioactive decay since the rock was formed is:
>
> $$2.51 \times 10^{-5} \ \text{g Pb} \times \left(\frac{1 \ \text{mol Pb}}{206 \ \text{g Pb}} \right) \times \left(\frac{1 \, \text{mol U}}{1 \ \text{mol Pb}} \right) = 1.22 \times 10^{-7} \, \text{mol U}$$
>
> The total amount of U-238 originally present in the rock is therefore:
>
> $$4.03 \times 10^{-7} \, \text{mol U} + 1.22 \times 10^{-7} \, \text{mol U} = 5.25 \times 10^{-7} \, \text{mol U}$$
>
> The amount of time that has passed since the formation of the rock is given by:
>
> $$t = -\frac{1}{\lambda} \ln \left(\frac{N_t}{N_0} \right)$$
>
> with N_0 representing the original amount of U-238 and N_t representing the present amount of U-238.
>
> U-238 decays into Pb-206 with a half-life of 4.5×10^9 y, so the decay constant λ is:
>
> $$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{4.5 \times 10^9 \, \text{y}} = 1.54 \times 10^{-10} \, \text{y}^{-1}$$
>
> Substituting and solving, we have:
>
> $$t = -\frac{1}{1.54 \times 10^{-10} \, \text{y}^{-1}} \ln \left(\frac{4.03 \times 10^{-7} \ \text{mol U}}{5.25 \times 10^{-7} \ \text{mol U}} \right) = 1.7 \times 10^9 \, \text{y}$$

> Therefore, the rock is approximately 1.7 billion years old.

? Exercise 12.4.1

A sample of rock contains 6.14×10^{-4} g of Rb-87 and $3.51 \times 10^{-5} g$ of Sr-87. Calculate the age of the rock. (The half-life of the β decay of Rb-87 is 4.7×10^{10} y.)

Answer

3.7 10^9 y

Footnotes

- 1The "m" in Tc-99m stands for "metastable," indicating that this is an unstable, high-energy state of Tc-99. Metastable isotopes emit γ radiation to rid themselves of excess energy and become (more) stable.

12.5: Transmutation and Nuclear Energy

> **◑ Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Describe the synthesis of transuranium nuclides
> - Explain nuclear fission and fusion processes
> - Relate the concepts of critical mass and nuclear chain reactions
> - Summarize basic requirements for nuclear fission and fusion reactors

After the discovery of radioactivity, the field of nuclear chemistry was created and developed rapidly during the early twentieth century. A slew of new discoveries in the 1930s and 1940s, along with World War II, combined to usher in the Nuclear Age in the mid-twentieth century. Scientists learned how to create new substances, and certain isotopes of certain elements were found to possess the capacity to produce unprecedented amounts of energy, with the potential to cause tremendous damage during war, as well as produce enormous amounts of power for society's needs during peace.

Synthesis of Nuclides

Nuclear transmutation is the conversion of one nuclide into another. It can occur by the radioactive decay of a nucleus, or the reaction of a nucleus with another particle. The first manmade nucleus was produced in Ernest Rutherford's laboratory in 1919 by a transmutation reaction, the bombardment of one type of nuclei with other nuclei or with neutrons. Rutherford bombarded nitrogen atoms with high-speed α particles from a natural radioactive isotope of radium and observed protons resulting from the reaction:

$$^{14}_{7}\text{N} + ^{4}_{2}\text{He} \longrightarrow ^{17}_{8}\text{O} + ^{1}_{1}\text{H}$$
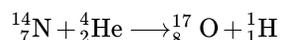
The $^{17}_{8}$O and $^{14}_{7}$N nuclei that are produced are stable, so no further (nuclear) changes occur.

To reach the kinetic energies necessary to produce transmutation reactions, devices called **particle accelerators** are used. These devices use magnetic and electric fields to increase the speeds of nuclear particles. In all accelerators, the particles move in a vacuum to avoid collisions with gas molecules.

When neutrons are required for transmutation reactions, they are usually obtained from radioactive decay reactions or from various nuclear reactions occurring in nuclear reactors. The Chemistry in Everyday Life feature that follows discusses a famous particle accelerator that made worldwide news.

> **📌 Chemistry in Everyday Life: CERN Particle Accelerator**
>
> Located near Geneva, the CERN ("Conseil Européen pour la Recherche Nucléaire," or European Council for Nuclear Research) Laboratory is the world's premier center for the investigations of the fundamental particles that make up matter. It contains the 27-kilometer (17 mile) long, circular Large Hadron Collider (LHC), the largest particle accelerator in the world (Figure 12.5.1). In the LHC, particles are boosted to high energies and are then made to collide with each other or with stationary targets at nearly the speed of light. Superconducting electromagnets are used to produce a strong magnetic field that guides the particles around the ring. Specialized, purpose-built detectors observe and record the results of these collisions, which are then analyzed by CERN scientists using powerful computers.

Figure 12.5.1: A small section of the LHC is shown with workers traveling along it. (credit: Christophe Delaere)

In 2012, CERN announced that experiments at the LHC showed the first observations of the Higgs boson, an elementary particle that helps explain the origin of mass in fundamental particles. This long-anticipated discovery made worldwide news and resulted in the awarding of the 2013 Nobel Prize in Physics to François Englert and Peter Higgs, who had predicted the existence of this particle almost 50 years previously.

📌 Link to Learning

Famous physicist Brian Cox talks about his work on the Large Hadron Collider at CERN, providing an entertaining and engaging tour of this massive project and the physics behind it.

View a short video from CERN, describing the basics of how its particle accelerators work.

Prior to 1940, the heaviest-known element was uranium, whose atomic number is 92. Now, many artificial elements have been synthesized and isolated, including several on such a large scale that they have had a profound effect on society. One of these—element 93, neptunium (Np)—was first made in 1940 by McMillan and Abelson by bombarding uranium-238 with neutrons. The reaction creates unstable uranium-239, with a half-life of 23.5 minutes, which then decays into neptunium-239. Neptunium-239 is also radioactive, with a half-life of 2.36 days, and it decays into plutonium-239. The nuclear reactions are:

$$^{238}_{92}\text{U} + ^{1}_{0}\text{n} \longrightarrow ^{239}_{92}\text{U}$$

$$^{239}_{92}\text{U} \longrightarrow ^{239}_{93}\text{Np} + ^{0}_{-1}\text{e} \quad \text{half-life} = 23.5 \text{ min}$$
$$^{239}_{93}\text{Np} \longrightarrow ^{239}_{94}\text{Pu} + ^{0}_{-1}\text{e} \quad \text{half-life} = 2.36 \text{ days}$$
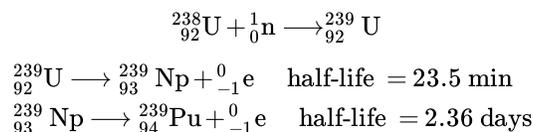
Plutonium is now mostly formed in nuclear reactors as a byproduct during the fission of U-235. Additional neutrons are released during this fission process (see the next section), some of which combine with U-238 nuclei to form uranium-239; this undergoes β decay to form neptunium-239, which in turn undergoes β decay to form plutonium-239 as illustrated in the preceding three equations. These processes are summarized in the equation:

$$^{238}_{92}\text{U} + ^{1}_{0}\text{n} \longrightarrow ^{239}_{92}\text{U} \xrightarrow{\beta^-} ^{239}_{93}\text{Np} \xrightarrow{\beta^-} ^{239}_{94}\text{Pu} \tag{12.5.1}$$
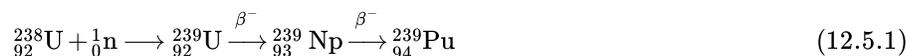
Heavier isotopes of plutonium—Pu-240, Pu-241, and Pu-242—are also produced when lighter plutonium nuclei capture neutrons. Some of this highly radioactive plutonium is used to produce military weapons, and the rest presents a serious storage problem because they have half-lives from thousands to hundreds of thousands of years.

Although they have not been prepared in the same quantity as plutonium, many other synthetic nuclei have been produced. Nuclear medicine has developed from the ability to convert atoms of one type into other types of atoms. Radioactive isotopes of several dozen elements are currently used for medical applications. The radiation produced by their decay is used to image or treat various organs or portions of the body, among other uses.

The elements beyond element 92 (uranium) are called **transuranium elements**. As of this writing, 22 transuranium elements have been produced and officially recognized by IUPAC; several other elements have formation claims that are waiting for approval. Some of these elements are shown in Table 21.3.

Table 21.3: Preparation of Some of the Transuranium Elements

Name	Symbol	Atomic Number	Reaction
americium	Am	95	$_{94}^{239}\text{Pu} + _{0}^{1}\text{n} \longrightarrow _{95}^{240}\text{Am} + _{-1}^{0}\text{e}$
curium	Cm	96	$_{94}^{239}\text{Pu} + _{2}^{4}\text{He} \longrightarrow _{96}^{242}\text{Cm} + _{0}^{1}\text{n}$
californium	Cf	98	$_{96}^{242}\text{Cm} + _{2}^{4}\text{He} \longrightarrow _{98}^{245}\text{Cf} + _{0}^{1}\text{n}$
einsteinium	Es	99	$_{96}^{242}\text{Cm} + _{2}^{4}\text{He} \longrightarrow _{98}^{245}\text{Cf} + _{0}^{1}\text{n}$
mendelevium	Md	101	$_{99}^{253}\text{Es} + _{2}^{4}\text{He} \longrightarrow _{101}^{256}\text{Md} + _{0}^{1}\text{n}$
nobelium	No	102	$_{96}^{246}\text{Cm} + _{6}^{12}\text{C} \longrightarrow _{102}^{254}\text{No} + 4_{0}^{1}\text{n}$
rutherfordium	Rf	104	$_{98}^{249}\text{Cf} + _{6}^{12}\text{C} \longrightarrow _{104}^{257}\text{Rf} + 4_{0}^{1}\text{n}$ $_{98}^{249}\text{Cf} + _{8}^{18}\text{O} \longrightarrow _{106}^{263}\text{Sg} + 4_{0}^{1}\text{n}$
seaborgium	Sg	106	$_{82}^{206}\text{Pb} + _{24}^{54}\text{Cr} \longrightarrow _{106}^{257}\text{Sg} + 3_{0}^{1}\text{n}$
meitnerium	Mt	107	$_{83}^{209}\text{Bi} + _{26}^{58}\text{Fe} \longrightarrow _{109}^{266}\text{Mt} + _{0}^{1}\text{n}$

Nuclear Fission

Many heavier elements with smaller binding energies per nucleon can decompose into more stable elements that have intermediate mass numbers and larger binding energies per nucleon—that is, mass numbers and binding energies per nucleon that are closer to the "peak" of the binding energy graph near 56 (see Figure 21.3). Sometimes neutrons are also produced. This decomposition is called fission, the breaking of a large nucleus into smaller pieces. The breaking is rather random with the formation of a large number of different products. Fission usually does not occur naturally, but is induced by bombardment with neutrons. The first reported nuclear fission occurred in 1939 when three German scientists, Lise Meitner, Otto Hahn, and Fritz Strassman, bombarded uranium-235 atoms with slow-moving neutrons that split the U-238 nuclei into smaller fragments that consisted of several neutrons and elements near the middle of the periodic table. Since then, fission has been observed in many other isotopes, including most actinide isotopes that have an odd number of neutrons. A typical nuclear fission reaction is shown in Figure 12.5.2.

$$_{92}^{235}\text{U} + _{0}^{1}\text{n} \longrightarrow _{92}^{236}\text{U} \longrightarrow _{36}^{141}\text{Ba} + _{36}^{92}\text{Kr} + 3\ _{0}^{1}\text{n}$$
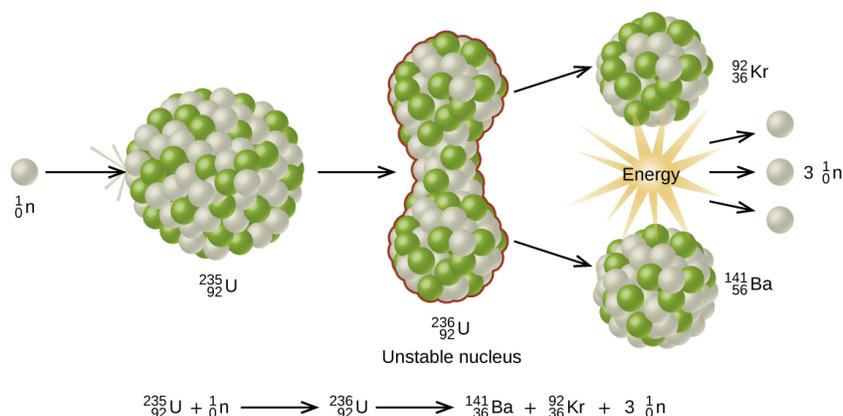
Figure 12.5.2: When a slow neutron hits a fissionable U-235 nucleus, it is absorbed and forms an unstable U-236 nucleus. The U-236 nucleus then rapidly breaks apart into two smaller nuclei (in this case, Ba-141 and Kr-92) along with several neutrons (usually two or three), and releases a very large amount of energy.

Among the products of Meitner, Hahn, and Strassman's fission reaction were barium, krypton, lanthanum, and cerium, all of which have nuclei that are more stable than uranium-235. Since then, hundreds of different isotopes have been observed among the products of fissionable substances. A few of the many reactions that occur for U-235, and a graph showing the distribution of its fission products and their yields, are shown in Figure 12.5.3. Similar fission reactions have been observed with other uranium isotopes, as well as with a variety of other isotopes such as those of plutonium.

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{90}_{38}Sr + {}^{144}_{54}Xe + 2\,{}^{1}_{0}n$$

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{87}_{35}Br + {}^{146}_{57}La + 3\,{}^{1}_{0}n$$

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{96}_{37}Rb + {}^{137}_{55}Cs + 3\,{}^{1}_{0}n$$

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{137}_{52}Te + {}^{97}_{40}Zr + 2\,{}^{1}_{0}n$$

$$^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{236}_{92}U \longrightarrow {}^{141}_{56}Ba + {}^{92}_{36}Kr + 3\,{}^{1}_{0}n$$
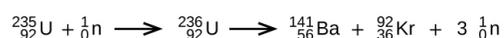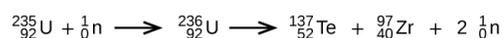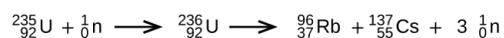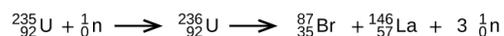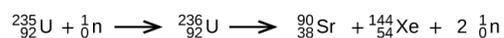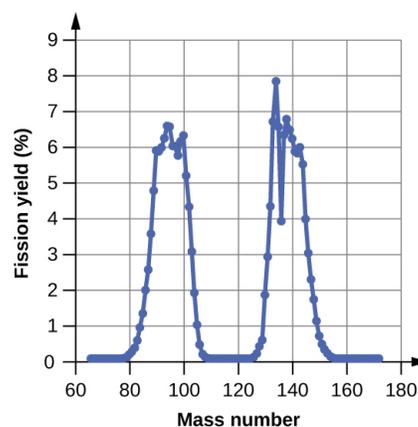
(a)   (b)

Figure 12.5.3: (a) Nuclear fission of U-235 produces a range of fission products. (b) The larger fission products of U-235 are typically one isotope with a mass number around 85–105, and another isotope with a mass number that is about 50% larger, that is, about 130–150.

📌 Link to Learning

View this link to see a simulation of nuclear fission.

A tremendous amount of energy is produced by the fission of heavy elements. For instance, when one mole of U-235 undergoes fission, the products weigh about 0.2 grams less than the reactants; this "lost" mass is converted into a very large amount of energy, about 1.8×10^{10} kJ per mole of U-235. Nuclear fission reactions produce incredibly large amounts of energy compared to chemical reactions. The fission of 1 kilogram of uranium-235, for example, produces about 2.5 million times as much energy as is produced by burning 1 kilogram of coal.

As described earlier, when undergoing fission U-235 produces two "medium-sized" nuclei, and two or three neutrons. These neutrons may then cause the fission of other uranium-235 atoms, which in turn provide more neutrons that can cause fission of even more nuclei, and so on. If this occurs, we have a nuclear **chain reaction** (see Figure 12.5.4). On the other hand, if too many neutrons escape the bulk material without interacting with a nucleus, then no chain reaction will occur.

Figure 12.5.4: The fission of a large nucleus, such as U-235, produces two or three neutrons, each of which is capable of causing fission of another nucleus by the reactions shown. If this process continues, a nuclear chain reaction occurs.

Material that can sustain a nuclear fission chain reaction is said to be **fissile** or **fissionable**. (Technically, fissile material can undergo fission with neutrons of any energy, whereas fissionable material requires high-energy neutrons.) Nuclear fission becomes self-sustaining when the number of neutrons produced by fission equals or exceeds the number of neutrons absorbed by splitting nuclei plus the number that escape into the surroundings. The amount of a fissionable material that will support a self-sustaining chain reaction is a **critical mass**. An amount of fissionable material that cannot sustain a chain reaction is a **subcritical mass**. An amount of material in which there is an increasing rate of fission is known as a **supercritical mass**. The critical mass depends on the type of material: its purity, the temperature, the shape of the sample, and how the neutron reactions are controlled (Figure 12.5.5).
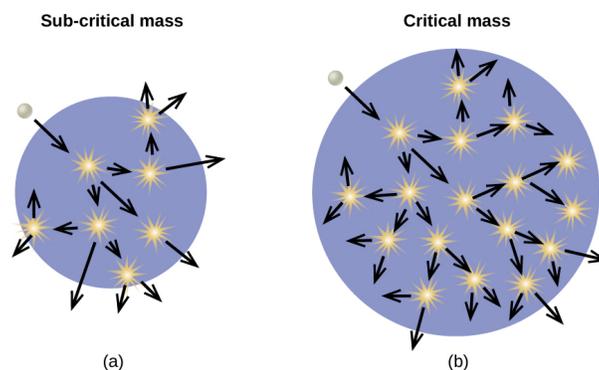
Figure 12.5.5: (a) In a subcritical mass, the fissile material is too small and allows too many neutrons to escape the material, so a chain reaction does not occur. (b) In a critical mass, a large enough number of neutrons in the fissile material induce fission to create a chain reaction.

An atomic bomb (Figure 12.5.6) contains several pounds of fissionable material, $^{235}_{92}$U or $^{239}_{94}$Pu a source of neutrons, and an explosive device for compressing it quickly into a small volume. When fissionable material is in small pieces, the proportion of neutrons that escape through the relatively large surface area is great, and a chain reaction does not take place. When the small pieces of fissionable material are brought together quickly to form a body with a mass larger than the critical mass, the relative number of escaping neutrons decreases, and a chain reaction and explosion result.
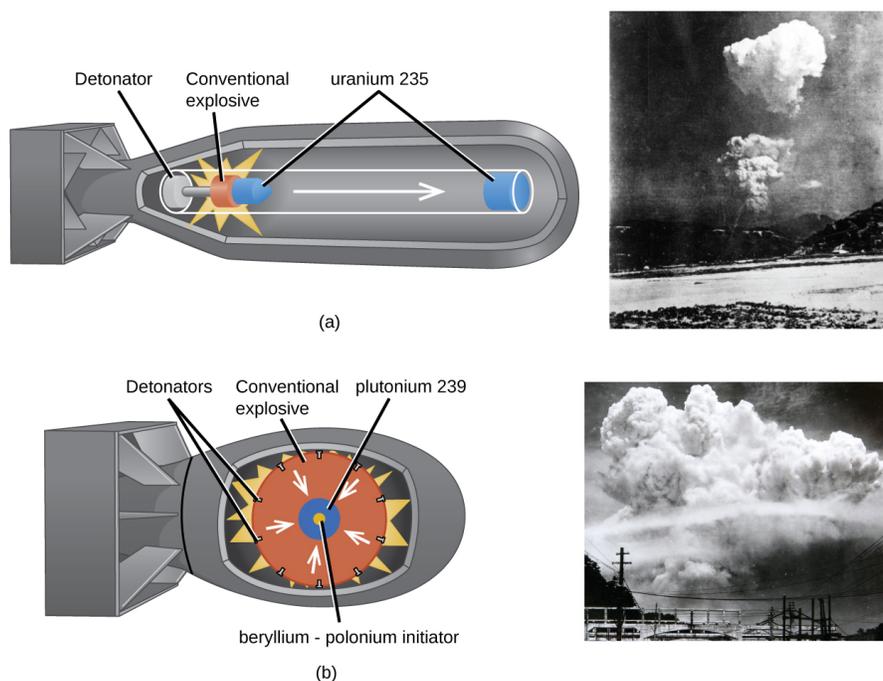
Figure 12.5.6: (a) The nuclear fission bomb that destroyed Hiroshima on August 6, 1945, consisted of two subcritical masses of U-235, where conventional explosives were used to fire one of the subcritical masses into the other, creating the critical mass for the nuclear explosion. (b) The plutonium bomb that destroyed Nagasaki on August 9, 1945, consisted of a hollow sphere of plutonium that was rapidly compressed by conventional explosives. This led to a concentration of plutonium in the center that was greater than the critical mass necessary for the nuclear explosion.

Fission Reactors

Chain reactions of fissionable materials can be controlled and sustained without an explosion in a **nuclear reactor** (Figure 12.5.7). Any nuclear reactor that produces power via the fission of uranium or plutonium by bombardment with neutrons must have at least five components: nuclear fuel consisting of fissionable material, a nuclear moderator, reactor coolant, control rods, and a shield and containment system. We will discuss these components in greater detail later in the section. The reactor works by separating the fissionable nuclear material such that a critical mass cannot be formed, controlling both the flux and absorption of neutrons to allow shutting down the fission reactions. In a nuclear reactor used for the production of electricity, the energy released by fission

reactions is trapped as thermal energy and used to boil water and produce steam. The steam is used to turn a turbine, which powers a generator for the production of electricity.
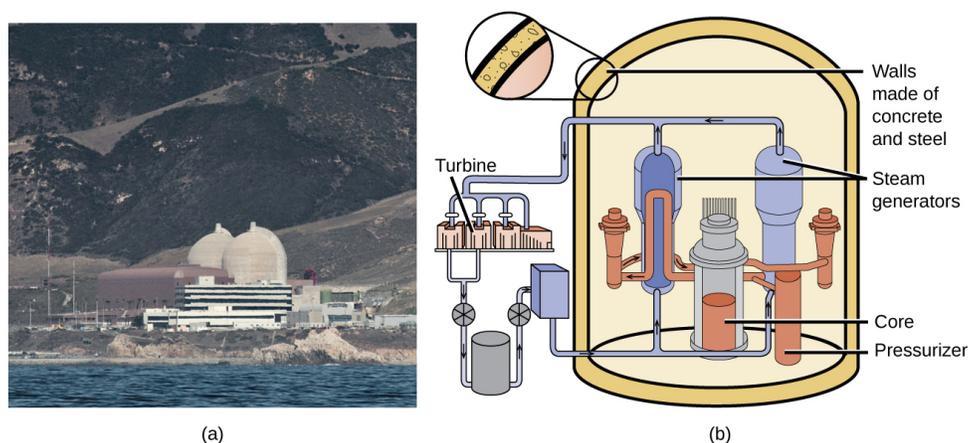
Figure 12.5.7: (a) The Diablo Canyon Nuclear Power Plant near San Luis Obispo is the only nuclear power plant currently in operation in California. The domes are the containment structures for the nuclear reactors, and the brown building houses the turbine where electricity is generated. Ocean water is used for cooling. (b) The Diablo Canyon uses a pressurized water reactor, one of a few different fission reactor designs in use around the world, to produce electricity. Energy from the nuclear fission reactions in the core heats water in a closed, pressurized system. Heat from this system produces steam that drives a turbine, which in turn produces electricity. (credit a: modification of work by "Mike" Michael L. Baird; credit b: modification of work by the Nuclear Regulatory Commission)

Nuclear Fuels

Nuclear fuel consists of a fissionable isotope, such as uranium-235, which must be present in sufficient quantity to provide a self-sustaining chain reaction. In the United States, uranium ores contain from 0.05–0.3% of the uranium oxide U_3O_8; the uranium in the ore is about 99.3% nonfissionable U-238 with only 0.7% fissionable U-235. Nuclear reactors require a fuel with a higher concentration of U-235 than is found in nature; it is normally enriched to have about 5% of uranium mass as U-235. At this concentration, it is not possible to achieve the supercritical mass necessary for a nuclear explosion. Uranium can be enriched by gaseous diffusion (the only method currently used in the US), using a gas centrifuge, or by laser separation.

In the gaseous diffusion enrichment plant where U-235 fuel is prepared, UF_6 (uranium hexafluoride) gas at low pressure moves through barriers that have holes just barely large enough for UF_6 to pass through. The slightly lighter $^{235}UF_6$ molecules diffuse through the barrier slightly faster than the heavier $^{238}UF_6$ molecules. This process is repeated through hundreds of barriers, gradually increasing the concentration of $^{235}UF_6$ to the level needed by the nuclear reactor. The basis for this process, Graham's law, is described in the chapter on gases. The enriched UF_6 gas is collected, cooled until it solidifies, and then taken to a fabrication facility where it is made into fuel assemblies. Each fuel assembly consists of fuel rods that contain many thimble-sized, ceramic-encased, enriched uranium (usually UO_2) fuel pellets. Modern nuclear reactors may contain as many as 10 million fuel pellets. The amount of energy in each of these pellets is equal to that in almost a ton of coal or 150 gallons of oil.

Nuclear Moderators

Neutrons produced by nuclear reactions move too fast to cause fission (refer back to Figure 12.5.5). They must first be slowed to be absorbed by the fuel and produce additional nuclear reactions. A **nuclear moderator** is a substance that slows the neutrons to a speed that is low enough to cause fission. Early reactors used high-purity graphite as a moderator. Modern reactors in the US exclusively use heavy water or light water (ordinary H_2O), whereas some reactors in other countries use other materials, such as carbon dioxide, beryllium, or graphite.

Reactor Coolants

A nuclear reactor coolant is used to carry the heat produced by the fission reaction to an external boiler and turbine, where it is transformed into electricity. Two overlapping coolant loops are often used; this counteracts the transfer of radioactivity from the reactor to the primary coolant loop. All nuclear power plants in the US use water as a coolant. Other coolants include molten sodium, lead, a lead-bismuth mixture, or molten salts.

Control Rods

Nuclear reactors use control rods (Figure 12.5.8) to control the fission rate of the nuclear fuel by adjusting the number of slow neutrons present to keep the rate of the chain reaction at a safe level. Control rods are made of boron, cadmium, hafnium, or other elements that are able to absorb neutrons. Boron-10, for example, absorbs neutrons by a reaction that produces lithium-7 and alpha particles:

$$^{10}_{5}\text{B} + ^{1}_{0}\text{n} \longrightarrow ^{7}_{3}\text{Li} + ^{4}_{2}\text{He} \tag{12.5.2}$$

When control rod assemblies are inserted into the fuel element in the reactor core, they absorb a larger fraction of the slow neutrons, thereby slowing the rate of the fission reaction and decreasing the power produced. Conversely, if the control rods are removed, fewer neutrons are absorbed, and the fission rate and energy production increase. In an emergency, the chain reaction can be shut down by fully inserting all of the control rods into the nuclear core between the fuel rods.
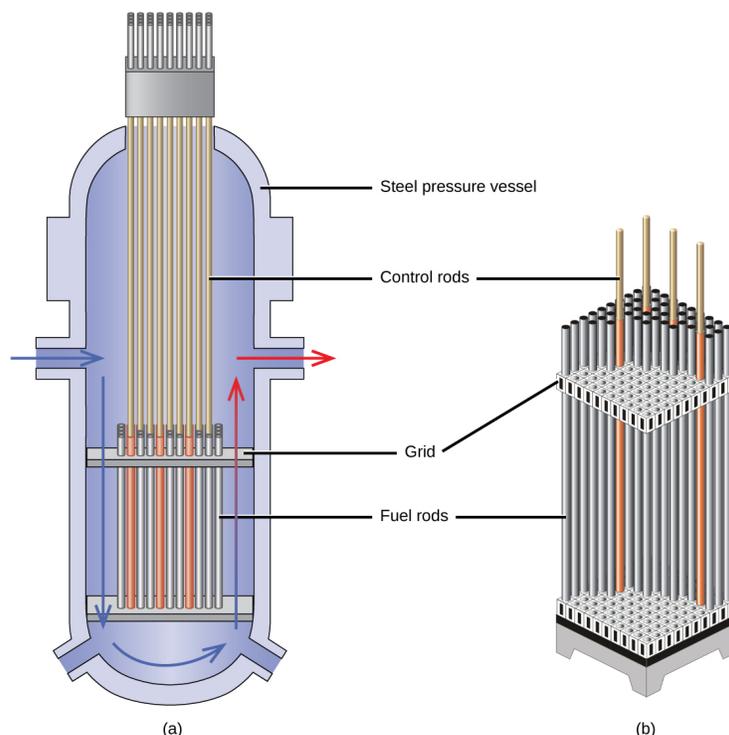
Figure 12.5.8: The nuclear reactor core shown in (a) contains the fuel and control rod assembly shown in (b). (credit: modification of work by E. Generalic, http://glossary.periodni.com/glossar...en=control+rod)

Shield and Containment System

During its operation, a nuclear reactor produces neutrons and other radiation. Even when shut down, the decay products are radioactive. In addition, an operating reactor is thermally very hot, and high pressures result from the circulation of water or another coolant through it. Thus, a reactor must withstand high temperatures and pressures, and must protect operating personnel from the radiation. Reactors are equipped with a **containment system** (or shield) that consists of three parts:

1. The reactor vessel, a steel shell that is 3–20-centimeters thick and, with the moderator, absorbs much of the radiation produced by the reactor
2. A main shield of 1–3 meters of high-density concrete
3. A personnel shield of lighter materials that protects operators from γ rays and X-rays

In addition, reactors are often covered with a steel or concrete dome that is designed to contain any radioactive materials might be released by a reactor accident.

Nuclear power plants are designed in such a way that they cannot form a supercritical mass of fissionable material and therefore cannot create a nuclear explosion. But as history has shown, failures of systems and safeguards can cause catastrophic accidents, including chemical explosions and nuclear meltdowns (damage to the reactor core from overheating). The following Chemistry in Everyday Life feature explores three infamous meltdown incidents.

📌 Chemistry in Everyday Life: Nuclear Accidents

The importance of cooling and containment are amply illustrated by three major accidents that occurred with the nuclear reactors at nuclear power generating stations in the United States (Three Mile Island), the former Soviet Union (Chernobyl), and Japan (Fukushima).

In March 1979, the cooling system of the Unit 2 reactor at Three Mile Island Nuclear Generating Station in Pennsylvania failed, and the cooling water spilled from the reactor onto the floor of the containment building. After the pumps stopped, the reactors overheated due to the high radioactive decay heat produced in the first few days after the nuclear reactor shut down. The temperature of the core climbed to at least 2200 °C, and the upper portion of the core began to melt. In addition, the zirconium alloy cladding of the fuel rods began to react with steam and produced hydrogen:

$$\mathrm{Zr(s) + 2\,H_2O(g) \longrightarrow ZrO_2(s) + 2\,H_2(g)}$$
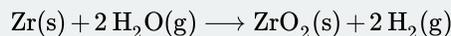
The hydrogen accumulated in the confinement building, and it was feared that there was danger of an explosion of the mixture of hydrogen and air in the building. Consequently, hydrogen gas and radioactive gases (primarily krypton and xenon) were vented from the building. Within a week, cooling water circulation was restored and the core began to cool. The plant was closed for nearly 10 years during the cleanup process.

Although zero discharge of radioactive material is desirable, the discharge of radioactive krypton and xenon, such as occurred at the Three Mile Island plant, is among the most tolerable. These gases readily disperse in the atmosphere and thus do not produce highly radioactive areas. Moreover, they are noble gases and are not incorporated into plant and animal matter in the food chain. Effectively none of the heavy elements of the core of the reactor were released into the environment, and no cleanup of the area outside of the containment building was necessary (Figure 12.5.9).

(a) (b)
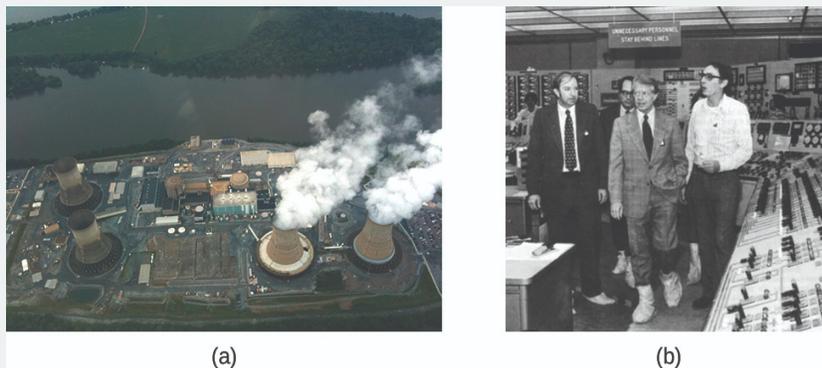
Figure 12.5.9: (a) In this 2010 photo of Three Mile Island, the remaining structures from the damaged Unit 2 reactor are seen on the left, whereas the separate Unit 1 reactor, unaffected by the accident, continues generating power to this day (right). (b) President Jimmy Carter visited the Unit 2 control room a few days after the accident in 1979.

Another major nuclear accident involving a reactor occurred in April 1986, at the Chernobyl Nuclear Power Plant in Ukraine, which was still a part of the former Soviet Union. While operating at low power during an unauthorized experiment with some of its safety devices shut off, one of the reactors at the plant became unstable. Its chain reaction became uncontrollable and increased to a level far beyond what the reactor was designed for. The steam pressure in the reactor rose to between 100 and 500 times the full power pressure and ruptured the reactor. Because the reactor was not enclosed in a containment building, a large amount of radioactive material spewed out, and additional fission products were released, as the graphite (carbon) moderator of the core ignited and burned. The fire was controlled, but over 200 plant workers and firefighters developed acute radiation sickness and at least 32 soon died from the effects of the radiation. It is predicted that about 4000 more deaths will

occur among emergency workers and former Chernobyl residents from radiation-induced cancer and leukemia. The reactor has since been encapsulated in steel and concrete, a now-decaying structure known as the sarcophagus. Almost 30 years later, significant radiation problems still persist in the area, and Chernobyl largely remains a wasteland.

In 2011, the Fukushima Daiichi Nuclear Power Plant in Japan was badly damaged by a 9.0-magnitude earthquake and resulting tsunami. Three reactors up and running at the time were shut down automatically, and emergency generators came online to power electronics and coolant systems. However, the tsunami quickly flooded the emergency generators and cut power to the pumps that circulated coolant water through the reactors. High-temperature steam in the reactors reacted with zirconium alloy to produce hydrogen gas. The gas escaped into the containment building, and the mixture of hydrogen and air exploded. Radioactive material was released from the containment vessels as the result of deliberate venting to reduce the hydrogen pressure, deliberate discharge of coolant water into the sea, and accidental or uncontrolled events.

An evacuation zone around the damaged plant extended over 12.4 miles away, and an estimated 200,000 people were evacuated from the area. All 48 of Japan's nuclear power plants were subsequently shut down, remaining shuttered as of December 2014. Since the disaster, public opinion has shifted from largely favoring to largely opposing increasing the use of nuclear power plants, and a restart of Japan's atomic energy program is still stalled (Figure 12.5.10).

Figure 12.5.10: (a) After the accident, contaminated waste had to be removed, and (b) an evacuation zone was set up around the plant in areas that received heavy doses of radioactive fallout. (credit a: modification of work by "Live Action Hero"/Flickr)

The energy produced by a reactor fueled with enriched uranium results from the fission of uranium as well as from the fission of plutonium produced as the reactor operates. As discussed previously, the plutonium forms from the combination of neutrons and the uranium in the fuel. In any nuclear reactor, only about 0.1% of the mass of the fuel is converted into energy. The other 99.9% remains in the fuel rods as fission products and unused fuel. All of the fission products absorb neutrons, and after a period of several months to a few years, depending on the reactor, the fission products must be removed by changing the fuel rods. Otherwise, the concentration of these fission products would increase and absorb more neutrons until the reactor could no longer operate.

Spent fuel rods contain a variety of products, consisting of unstable nuclei ranging in atomic number from 25 to 60, some transuranium elements, including plutonium and americium, and unreacted uranium isotopes. The unstable nuclei and the transuranium isotopes give the spent fuel a dangerously high level of radioactivity. The long-lived isotopes require thousands of years to decay to a safe level. The ultimate fate of the nuclear reactor as a significant source of energy in the United States probably rests on whether or not a politically and scientifically satisfactory technique for processing and storing the components of spent fuel rods can be developed.

📌 Link to Learning

Explore the information in this link to learn about the approaches to nuclear waste management.

Nuclear Fusion and Fusion Reactors

The process of converting very light nuclei into heavier nuclei is also accompanied by the conversion of mass into large amounts of energy, a process called fusion. The principal source of energy in the sun is a net fusion reaction in which four hydrogen nuclei fuse

and produce one helium nucleus and two positrons. This is a net reaction of a more complicated series of events:

$$4\,^1_1\mathrm{H} \longrightarrow \,^4_2\mathrm{He} + 2\,^0_{+1}\mathrm{e}^+$$
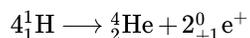
A helium nucleus has a mass that is 0.7% less than that of four hydrogen nuclei; this lost mass is converted into energy during the fusion. This reaction produces about $3.6\ 10^{11}$ kJ of energy per mole of $\,^4_2\mathrm{He}$ produced. This is somewhat larger than the energy produced by the nuclear fission of one mole of U-235 ($1.8\ 10^{10}$ kJ), and over 3 million times larger than the energy produced by the (chemical) combustion of one mole of octane (5471 kJ).

It has been determined that the nuclei of the heavy isotopes of hydrogen, a deuteron, $\,^2_1\mathrm{H}$, and a triton, $\,^3_1\mathrm{H}$, undergo fusion at extremely high temperatures (thermonuclear fusion). They form a helium nucleus and a neutron:

$$\,^2_1\mathrm{H} + \,^3_1\mathrm{H} \longrightarrow \,^4_2\mathrm{He} + \,^1_0\mathrm{n} \tag{12.5.3}$$

This change proceeds with a mass loss of 0.0188 amu, corresponding to the release of $1.69\ 10^9$ kilojoules per mole of $\,^4_2\mathrm{He}$ formed. The very high temperature is necessary to give the nuclei enough kinetic energy to overcome the very strong repulsive forces resulting from the positive charges on their nuclei so they can collide.

Useful fusion reactions require very high temperatures for their initiation—about 15,000,000 K or more. At these temperatures, all molecules dissociate into atoms, and the atoms ionize, forming plasma. These conditions occur in an extremely large number of locations throughout the universe—stars are powered by fusion. Humans have already figured out how to create temperatures high enough to achieve fusion on a large scale in thermonuclear weapons. A thermonuclear weapon such as a hydrogen bomb contains a nuclear fission bomb that, when exploded, gives off enough energy to produce the extremely high temperatures necessary for fusion to occur.

Another much more beneficial way to create fusion reactions is in a **fusion reactor**, a nuclear reactor in which fusion reactions of light nuclei are controlled. Because no solid materials are stable at such high temperatures, mechanical devices cannot contain the plasma in which fusion reactions occur. Two techniques to contain plasma at the density and temperature necessary for a fusion reaction are currently the focus of intensive research efforts: containment by a magnetic field and by the use of focused laser beams (Figure 12.5.11). A number of large projects are working to attain one of the biggest goals in science: getting hydrogen fuel to ignite and produce more energy than the amount supplied to achieve the extremely high temperatures and pressures that are required for fusion. At the time of this writing, there are no self-sustaining fusion reactors operating in the world, although small-scale controlled fusion reactions have been run for very brief periods.

(a) (b)
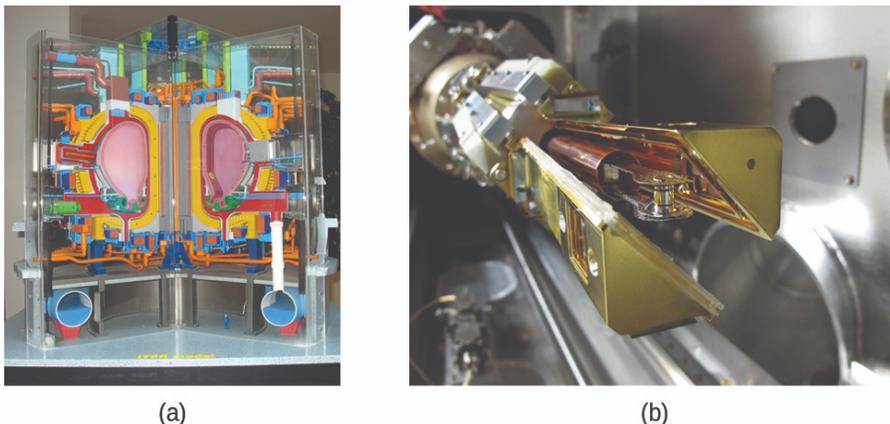
Figure 12.5.11: (a) This model is of the International Thermonuclear Experimental Reactor (ITER) reactor. Currently under construction in the south of France with an expected completion date of 2027, the ITER will be the world's largest experimental Tokamak nuclear fusion reactor with a goal of achieving large-scale sustained energy production. (b) In 2012, the National Ignition Facility at Lawrence Livermore National Laboratory briefly produced over 500,000,000,000 watts (500 terawatts, or 500 TW) of peak power and delivered 1,850,000 joules (1.85 MJ) of energy, the largest laser energy ever produced and 1000 times the power usage of the entire United States in any given moment. Although lasting only a few billionths of a second, the 192 lasers attained the conditions needed for nuclear fusion ignition. This image shows the target prior to the laser shot. (credit a: modification of work by Stephan Mosel)

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12.6: Uses of Radioisotopes

> ◗ **Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - List common applications of radioactive isotopes

Radioactive isotopes have the same chemical properties as stable isotopes of the same element, but they emit radiation, which can be detected. If we replace one (or more) atom(s) with radioisotope(s) in a compound, we can track them by monitoring their radioactive emissions. This type of compound is called a radioactive tracer (or radioactive label). Radioisotopes are used to follow the paths of biochemical reactions or to determine how a substance is distributed within an organism. Radioactive tracers are also used in many medical applications, including both diagnosis and treatment. They are used to measure engine wear, analyze the geological formation around oil wells, and much more.

Radioimmunossays (RIA), for example, rely on radioisotopes to detect the presence and/or concentration of certain antigens. Developed by Rosalyn Sussman Yalow and Solomon Berson in the 1950s, the technique is known for extreme sensitivity, meaning that it can detect and measure very small quantities of a substance. Prior to its discovery, most similar detection relied on large enough quantities to produce visible outcomes. RIA revolutionized and expanded entire fields of study, most notably endocrinology, and is commonly used in narcotics detection, blood bank screening, early cancer screening, hormone measurement, and allergy diagnosis. Based on her significant contribution to medicine, Yalow received a Nobel Prize, making her the second woman to be awarded the prize for medicine.

Radioisotopes have revolutionized medical practice (see Appendix M), where they are used extensively. Over 10 million nuclear medicine procedures and more than 100 million nuclear medicine tests are performed annually in the United States. Four typical examples of radioactive tracers used in medicine are technetium-99 ($^{99}_{43}$Tc), thallium-201 ($^{201}_{81}$Tl), iodine-131 ($^{131}_{53}$I), and sodium-24 ($^{24}_{11}$Na). Damaged tissues in the heart, liver, and lungs absorb certain compounds of technetium-99 preferentially. After it is injected, the location of the technetium compound, and hence the damaged tissue, can be determined by detecting the γ rays emitted by the Tc-99 isotope. Thallium-201 (Figure 12.6.1) becomes concentrated in healthy heart tissue, so the two isotopes, Tc-99 and Tl-201, are used together to study heart tissue. Iodine-131 concentrates in the thyroid gland, the liver, and some parts of the brain. It can therefore be used to monitor goiter and treat thyroid conditions, such as Grave's disease, as well as liver and brain tumors. Salt solutions containing compounds of sodium-24 are injected into the bloodstream to help locate obstructions to the flow of blood.

Figure 12.6.1: Administering thallium-201 to a patient and subsequently performing a stress test offer medical professionals an opportunity to visually analyze heart function and blood flow. (credit: modification of work by "Blue0ctane"/Wikimedia Commons)

Radioisotopes used in medicine typically have short half-lives—for example, the ubiquitous Tc-99m has a half-life of 6.01 hours. This makes Tc-99m essentially impossible to store and prohibitively expensive to transport, so it is made on-site instead. Hospitals and other medical facilities use Mo-99 (which is primarily extracted from U-235 fission products) to generate Tc-99. Mo-99 undergoes β decay with a half-life of 66 hours, and the Tc-99 is then chemically extracted (Figure 12.6.2). The parent nuclide Mo-99 is part of a molybdate ion, MoO_4^{2-}; when it decays, it forms the pertechnetate ion, TcO_4^-. These two water-soluble ions are separated by column chromatography, with the higher charge molybdate ion adsorbing onto the alumina in the column, and the lower charge pertechnetate ion passing through the column in the solution. A few micrograms of Mo-99 can produce enough Tc-99 to perform as many as 10,000 tests.
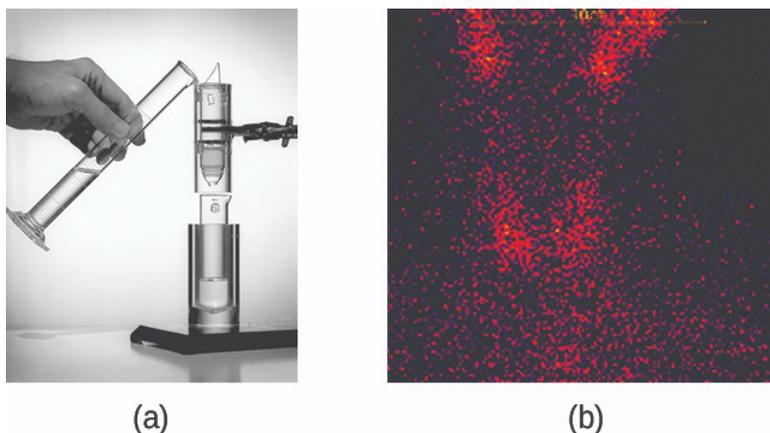
Figure 12.6.2: (a) The first Tc-99m generator (circa 1958) is used to separate Tc-99 from Mo-99. The is retained by the matrix in the column, whereas the passes through and is collected. (b) Tc-99 was used in this scan of the neck of a patient with Grave's disease. The scan shows the location of high concentrations of Tc-99. (credit a: modification of work by the Department of Energy; credit b: modification of work by "MBq"/Wikimedia Commons)

Radioisotopes can also be used, typically in higher doses than as a tracer, as treatment. Radiation therapy is the use of high-energy radiation to damage the DNA of cancer cells, which kills them or keeps them from dividing (Figure 12.6.3). A cancer patient may receive external beam radiation therapy delivered by a machine outside the body, or internal radiation therapy (brachytherapy) from a radioactive substance that has been introduced into the body. Note that chemotherapy is similar to internal radiation therapy in that the cancer treatment is injected into the body, but differs in that chemotherapy uses chemical rather than radioactive substances to kill the cancer cells.
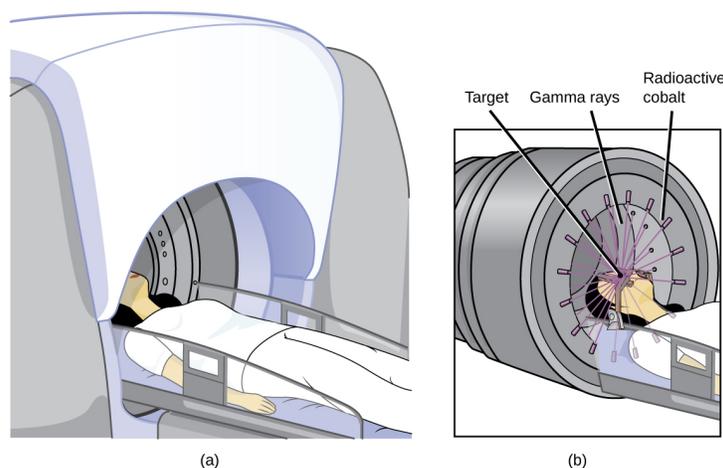
Figure 12.6.3: The cartoon in (a) shows a coba machine swings through an arc, focusing radiation on the targeted region (tumor) and minimizing the amount of radiation that passes through nearby regions.

Cobalt-60 is a synthetic radioisotope produced by the neutron activation of Co-59, which then undergoes β decay to form Ni-60, along with the emission of γ radiation. The overall process is:

$$\,^{59}_{27}Co + \,^{1}_{0}n \rightarrow \,^{60}_{27}Co \rightarrow \,^{60}_{28}Ni + \,^{0}_{-1}\beta + 2\,^{0}_{0}\gamma \tag{12.6.1}$$

The overall decay scheme for this is shown graphically in Figure 12.6.4.
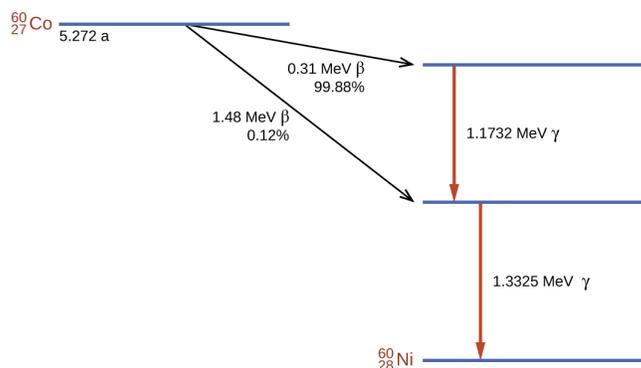
Figure 12.6.4: Co-60 undergoes a series of radioactive decays. The γ emissions are used for radiation therapy.

Radioisotopes are used in diverse ways to study the mechanisms of chemical reactions in plants and animals. These include labeling fertilizers in studies of nutrient uptake by plants and crop growth, investigations of digestive and milk-producing processes in cows, and studies on the growth and metabolism of animals and plants.

For example, the radioisotope C-14 was used to elucidate the details of how photosynthesis occurs. The overall reaction is:

$$6CO_2\,(g) + 6H_2O\,(l) \rightarrow C_6H_{12}O_6\,(s) + 6O_2\,(g), \tag{12.6.2}$$
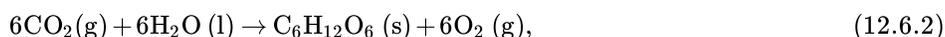
but the process is much more complex, proceeding through a series of steps in which various organic compounds are produced. In studies of the pathway of this reaction, plants were exposed to CO_2 containing a high concentration of $\binom{14}{6}C$. At regular intervals, the plants were analyzed to determine which organic compounds contained carbon-14 and how much of each compound was present. From the time sequence in which the compounds appeared and the amount of each present at given time intervals, scientists learned more about the pathway of the reaction.

Commercial applications of radioactive materials are equally diverse (Figure 12.6.5). They include determining the thickness of films and thin metal sheets by exploiting the penetration power of various types of radiation. Flaws in metals used for structural purposes can be detected using high-energy gamma rays from cobalt-60 in a fashion similar to the way X-rays are used to examine the human body. In one form of pest control, flies are controlled by sterilizing male flies with γ radiation so that females breeding with them do not produce offspring. Many foods are preserved by radiation that kills microorganisms that cause the foods to spoil.

(a)   (b)
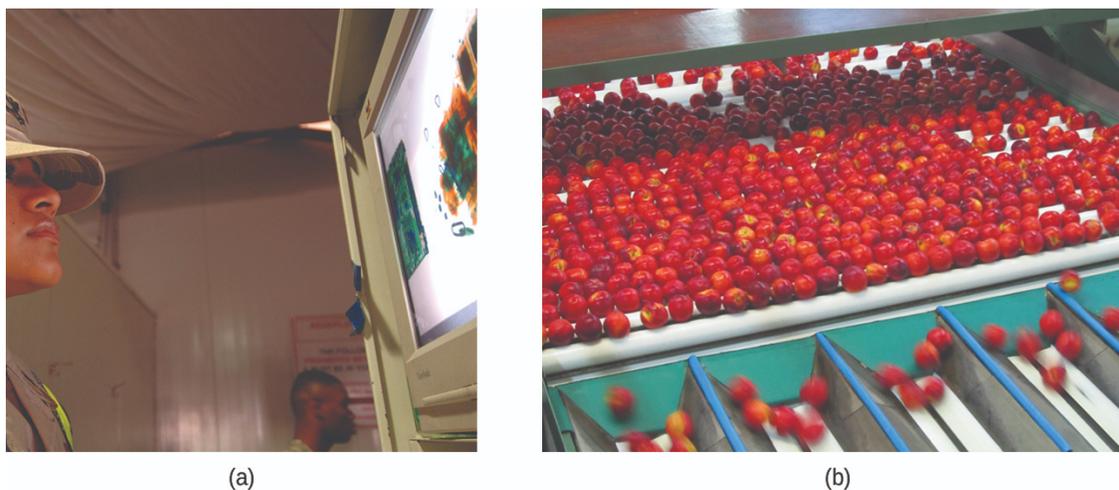
Figure 12.6.5: Common commercial uses of radiation include (a) X-ray examination of luggage at an airport and (b) preservation of food. (credit a: modification of work by the Department of the Navy; credit b: modification of work by the US Department of Agriculture)

Americium-241, an α emitter with a half-life of 458 years, is used in tiny amounts in ionization-type smoke detectors (Figure 12.6.6). The α emissions from Am-241 ionize the air between two electrode plates in the ionizing chamber. A battery supplies a potential that causes movement of the ions, thus creating a small electric current. When smoke enters the chamber, the movement of the ions is impeded, reducing the conductivity of the air. This causes a marked drop in the current, triggering an alarm.
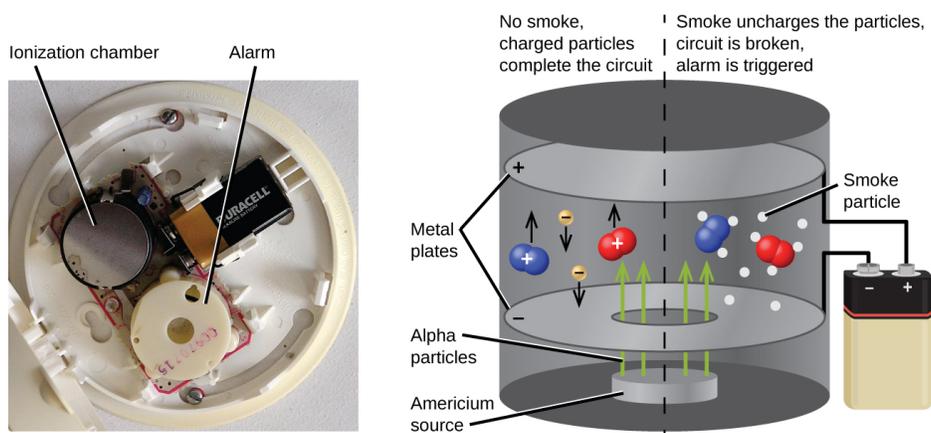
Figure 12.6.6: Inside a smoke detector, Am-241 emits α particles that ionize the air, creating a small electric current. During a fire, smoke particles impede the flow of ions, reducing the current and triggering an alarm. (credit a: modification of work by "Muffet"/Wikimedia Commons)

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12.7: Biological Effects of Radiation

> **Learning Objectives**
>
> By the end of this section, you will be able to:
>
> - Describe the biological impact of ionizing radiation
> - Define units for measuring radiation exposure
> - Explain the operation of common tools for detecting radioactivity
> - List common sources of radiation exposure in the US

The increased use of radioisotopes has led to increased concerns over the effects of these materials on biological systems (such as humans). All radioactive nuclides emit high-energy particles or electromagnetic waves. When this radiation encounters living cells, it can cause heating, break chemical bonds, or ionize molecules. The most serious biological damage results when these radioactive emissions fragment or ionize molecules. For example, alpha and beta particles emitted from nuclear decay reactions possess much higher energies than ordinary chemical bond energies. When these particles strike and penetrate matter, they produce ions and molecular fragments that are extremely reactive. The damage this does to biomolecules in living organisms can cause serious malfunctions in normal cell processes, taxing the organism's repair mechanisms and possibly causing illness or even death (Figure 12.7.1).
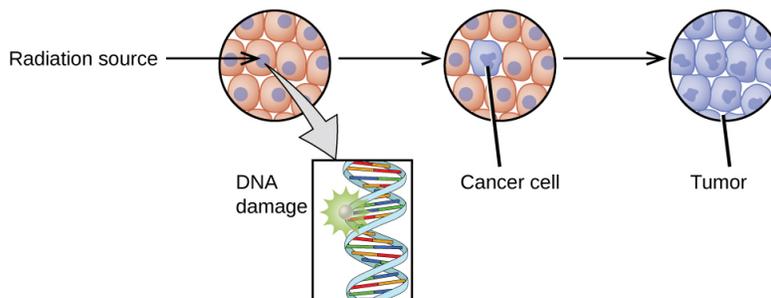
Figure 12.7.1: Radiation can harm biological systems by damaging the DNA of cells. If this damage is not properly repaired, the cells may divide in an uncontrolled manner and cause cancer.

Ionizing and Nonionizing Radiation

There is a large difference in the magnitude of the biological effects of nonionizing radiation (for example, light and microwaves) and ionizing radiation, emissions energetic enough to knock electrons out of molecules (for example, α and β particles, γ rays, X-rays, and high-energy ultraviolet radiation) (Figure 12.7.2).
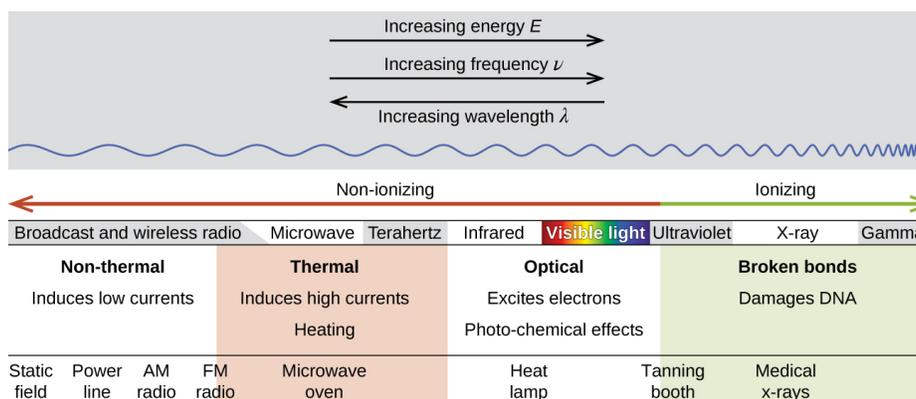
Figure 12.7.2: Lower frequency, lower-energy electromagnetic radiation is nonionizing, and higher frequency, higher-energy electromagnetic radiation is ionizing.

Energy absorbed from nonionizing radiation speeds up the movement of atoms and molecules, which is equivalent to heating the sample. Although biological systems are sensitive to heat (as we might know from touching a hot stove or spending a day at the beach in the sun), a large amount of nonionizing radiation is necessary before dangerous levels are reached. Ionizing radiation,

however, may cause much more severe damage by breaking bonds or removing electrons in biological molecules, disrupting their structure and function. The damage can also be done indirectly, by first ionizing H_2O (the most abundant molecule in living organisms), which forms a H_2O^+ ion that reacts with water, forming a hydronium ion and a hydroxyl radical:

$$H_2O + \text{radiation} \longrightarrow H_2O^+ + H_2O \longrightarrow H_3O^+ + OH^•$$
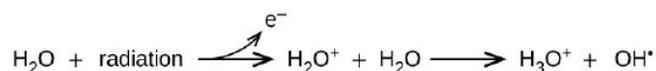
Because the hydroxyl radical has an unpaired electron, it is highly reactive. (This is true of any substance with unpaired electrons, known as a free radical.) This hydroxyl radical can react with all kinds of biological molecules (DNA, proteins, enzymes, and so on), causing damage to the molecules and disrupting physiological processes. Examples of direct and indirect damage are shown in Figure 21.32.

Direct effect
(a)

Indirect effect
(b)
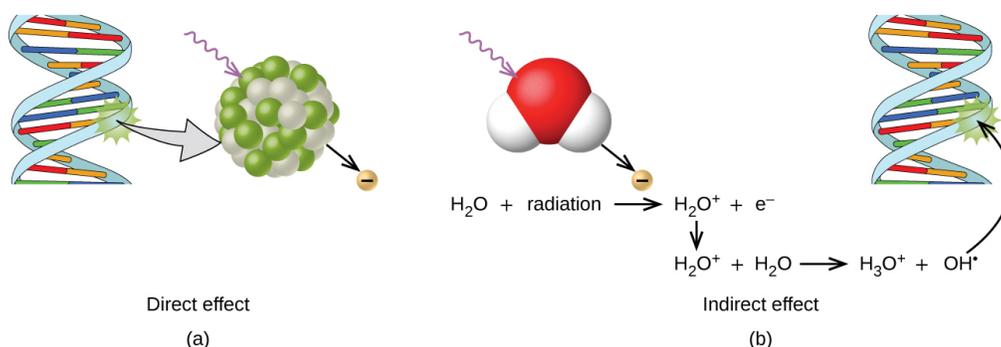
Figure 21.32 Ionizing radiation can (a) directly damage a biomolecule by ionizing it or breaking its bonds, or (b) create an H_2O^+ ion, which reacts with H_2O to form a hydroxyl radical, which in turn reacts with the biomolecule, causing damage indirectly.

Biological Effects of Exposure to Radiation

Radiation can harm either the whole body (somatic damage) or eggs and sperm (genetic damage). Its effects are more pronounced in cells that reproduce rapidly, such as the stomach lining, hair follicles, bone marrow, and embryos. This is why patients undergoing radiation therapy often feel nauseous or sick to their stomach, lose hair, have bone aches, and so on, and why particular care must be taken when undergoing radiation therapy during pregnancy.

Different types of radiation have differing abilities to pass through material (Figure 12.7.3). A very thin barrier, such as a sheet or two of paper, or the top layer of skin cells, usually stops alpha particles. Because of this, alpha particle sources are usually not dangerous if outside the body, but are quite hazardous if ingested or inhaled (see the Chemistry in Everyday Life feature on Radon Exposure). Beta particles will pass through a hand, or a thin layer of material like paper or wood, but are stopped by a thin layer of metal. Gamma radiation is very penetrating and can pass through a thick layer of most materials. Some high-energy gamma radiation is able to pass through a few feet of concrete. Certain dense, high atomic number elements (such as lead) can effectively attenuate gamma radiation with thinner material and are used for shielding. The ability of various kinds of emissions to cause ionization varies greatly, and some particles have almost no tendency to produce ionization. Alpha particles have about twice the ionizing power of fast-moving neutrons, about 10 times that of β particles, and about 20 times that of γ rays and X-rays.
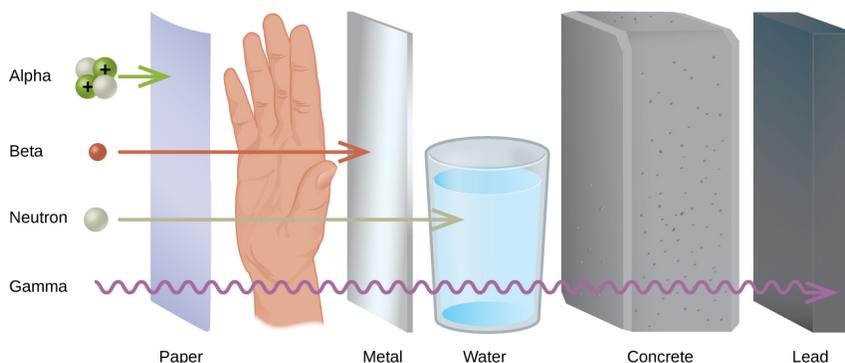
Figure 12.7.3: The ability of different types of radiation to pass through material is shown. From least to most penetrating, they are alpha < beta < neutron < gamma.

> **⊤ Chemistry in Everyday Life: Radon Exposure**
>
> For many people, one of the largest sources of exposure to radiation is from radon gas (Rn-222). Radon-222 is an α emitter with a half–life of 3.82 days. It is one of the products of the radioactive decay series of U-238 (Figure 21.9), which is found in trace amounts in soil and rocks. The radon gas that is produced slowly escapes from the ground and gradually seeps into homes and other structures above. Since it is about eight times more dense than air, radon gas accumulates in basements and lower floors, and slowly diffuses throughout buildings (Figure 12.7.4).
>
>
>
> Figure 12.7.4: Radon-222 seeps into houses and other buildings from rocks that contain uranium-238, a radon emitter. The radon enters through cracks in concrete foundations and basement floors, stone or porous cinderblock foundations, and openings for water and gas pipes.
>
> Radon is found in buildings across the country, with amounts depending on where you live. The average concentration of radon inside houses in the US (1.25 pCi/L) is about three times the levels found in outside air, and about one in six houses have radon levels high enough that remediation efforts to reduce the radon concentration are recommended. Exposure to radon increases one's risk of getting cancer (especially lung cancer), and high radon levels can be as bad for health as smoking a carton of cigarettes a day. Radon is the number one cause of lung cancer in nonsmokers and the second leading cause of lung cancer overall. Radon exposure is believed to cause over 20,000 deaths in the US per year.
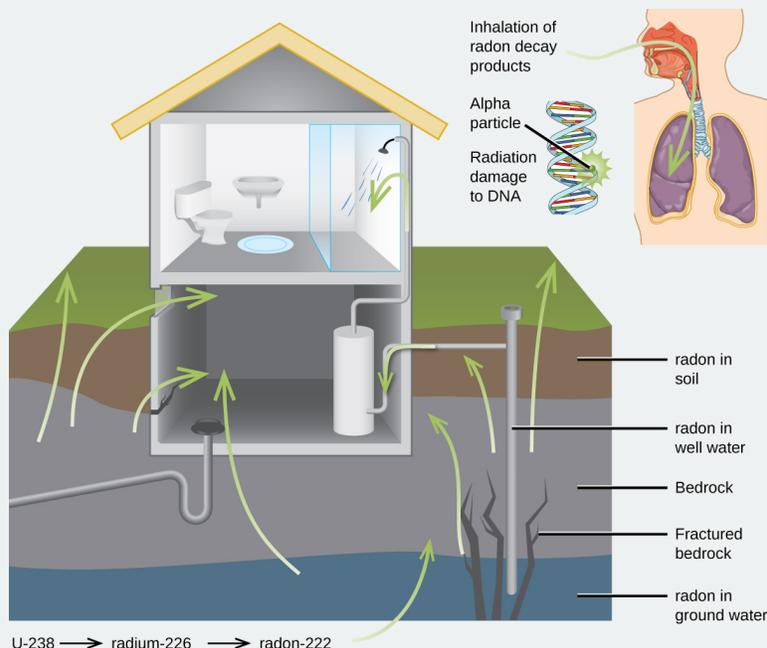
Measuring Radiation Exposure

Several different devices are used to detect and measure radiation, including Geiger counters, scintillation counters (scintillators), and radiation dosimeters (Figure 12.7.5). Probably the best-known radiation instrument, the Geiger counter (also called the Geiger-Müller counter) detects and measures radiation. Radiation causes the ionization of the gas in a Geiger-Müller tube. The rate of ionization is proportional to the amount of radiation. A scintillation counter contains a scintillator—a material that emits light (luminesces) when excited by ionizing radiation—and a sensor that converts the light into an electric signal. Radiation dosimeters also measure ionizing radiation and are often used to determine personal radiation exposure. Commonly used types are electronic, film badge, thermoluminescent, and quartz fiber dosimeters.

Figure 12.7.5: Devices such as (a) Geiger counters, (b) scintillators, and (c) dosimeters can be used to measure radiation. (credit c: modification of work by "osaMu"/Wikimedia commons)

A variety of units are used to measure various aspects of radiation (Figure 12.7.6). The SI unit for rate of radioactive decay is the becquerel (Bq), with 1 Bq = 1 disintegration per second. The curie (Ci) and millicurie (mCi) are much larger units and are frequently used in medicine (1 curie = 1 Ci = 3.7 10^{10} disintegrations per second). The SI unit for measuring radiation dose is the gray (Gy), with 1 Gy = 1 J of energy absorbed per kilogram of tissue. In medical applications, the radiation absorbed dose (rad) is more often used (1 rad = 0.01 Gy; 1 rad results in the absorption of 0.01 J/kg of tissue). The SI unit measuring tissue damage caused by radiation is the sievert (Sv). This takes into account both the energy and the biological effects of the type of radiation involved in the radiation dose. The roentgen equivalent for man (rem) is the unit for radiation damage that is used most frequently in medicine (100 rem = 1 Sv). Note that the tissue damage units (rem or Sv) includes the energy of the radiation dose (rad or Gy) along with a biological factor referred to as the RBE (for relative biological effectiveness) that is an approximate measure of the relative damage done by the radiation. These are related by:

$$\text{number of rems } = \text{RBE} \times \text{ number of rads} \tag{12.7.1}$$

with RBE approximately 10 for α radiation, 2(+) for protons and neutrons, and 1 for β and γ radiation.

Film badge or dosimeter measures tissue damage exposure in rems or sieverts

Rate of radioactive decay measured in bequerels or curies

Absorbed dose measured in grays or rads
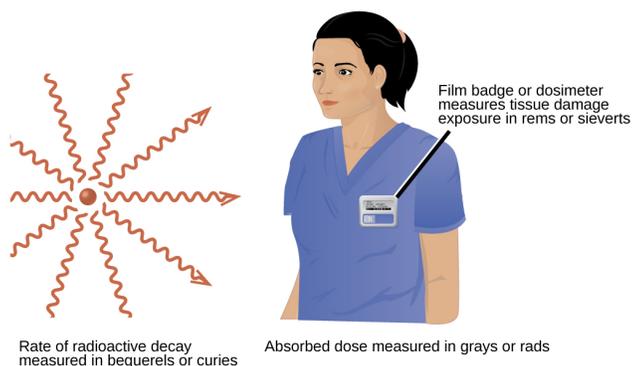
Figure 12.7.6: Different units are used to measure the rate of emission from a radioactive source, the energy that is absorbed from the source, and the amount of damage the absorbed radiation does.

Units of Radiation Measurement

Table 12.7.1 summarizes the units used for measuring radiation.

Table 12.7.1: Units Used for Measuring Radiation

Measurement Purpose	Unit	Quantity Measured	Description
activity of source	becquerel (Bq)	radioactive decays or emissions	amount of sample that undergoes 1 decay/second
	curie (Ci)		amount of sample that undergoes 3.7 10^{10} decays/second
absorbed dose	gray (Gy)	energy absorbed per kg of tissue	1 Gy = 1 J/kg tissue
	radiation absorbed dose (rad)		1 rad = 0.01 J/kg tissue

Measurement Purpose	Unit	Quantity Measured	Description
biologically effective dose	sievert (Sv)	tissue damage	Sv = RBE Gy
	roentgen equivalent for man (rem)		Rem = RBE rad

✔ Example 12.7.1: Amount of Radiation

Cobalt-60 ($t_{1/2} = 5.26\ y$) is used in cancer therapy since the γ rays it emits can be focused in small areas where the cancer is located. A 5.00-g sample of Co-60 is available for cancer treatment.

  a. What is its activity in Bq?
  b. What is its activity in Ci?

Solution

The activity is given by:

$$\text{Activity } = \lambda N = \left(\frac{\ln 2}{t_{1/2}}\right) N = \left(\frac{\ln 2}{5.26\text{y}}\right) \times 5.00\text{ g} = 0.659\frac{\text{g}}{\text{y}}\text{ of Co} -60 \text{ that decay}$$

And to convert this to decays per second:

$$0.659\frac{\text{g}}{\text{y}} \times \frac{1\text{y}}{365\text{ d}} \times \frac{1\text{ d}}{24\text{ h}} \times \frac{1\text{ h}}{3600\text{ s}} \times \frac{1\text{ mol}}{59.9\text{ g}} \times \frac{6.02 \times 10^{23}\text{ atoms}}{1\text{ mol}} \times \frac{1\text{ decay}}{1\text{ atom}}$$

$$= 2.10 \times 10^{14}\frac{\text{decay}}{\text{s}}$$

  a. Since $1\text{ Bq} = \frac{1\text{ decay}}{\text{s}}$ the activity in Becquerel (Bq) is:

$$2.10 \times 10^{14}\frac{\text{decay}}{\text{s}} \times \left(\frac{1\text{ Bq}}{1\frac{\text{decay}}{\text{s}}}\right) = 2.10 \times 10^{14}\text{ Bq}$$

  b. Since $1\text{Ci} = \frac{3.7 \times 10^{11}\text{ decay}}{\text{s}}$ the activity in curie (Ci) is:

$$2.10 \times 10^{14}\frac{\text{decay}}{\text{s}} \times \left(\frac{1\text{Ci}}{\frac{3.7 \times 10^{11}\text{ decay}}{\text{s}}}\right) = 5.7 \times 10^{2}\text{Ci}$$

? Exercise 12.7.1

Tritium is a radioactive isotope of hydrogen ($t_{1/2}$ = 12.32 y) that has several uses, including self-powered lighting, in which electrons emitted in tritium radioactive decay cause phosphorus to glow. Its nucleus contains one proton and two neutrons, and the atomic mass of tritium is 3.016 amu. What is the activity of a sample containing 1.00mg of tritium (a) in Bq and (b) in Ci?

Answer

    a. 3.56 10^{11} Bq;
    b. 0.962 Ci

Effects of Long-term Radiation Exposure on the Human Body

The effects of radiation depend on the type, energy, and location of the radiation source, and the length of exposure. As shown in Figure 12.7.7: , the average person is exposed to background radiation, including cosmic rays from the sun and radon from uranium in the ground (see the Chemistry in Everyday Life feature on Radon Exposure); radiation from medical exposure, including CAT scans, radioisotope tests, X-rays, and so on; and small amounts of radiation from other human activities, such as airplane flights (which are bombarded by increased numbers of cosmic rays in the upper atmosphere), radioactivity from consumer

products, and a variety of radionuclides that enter our bodies when we breathe (for example, carbon-14) or through the food chain (for example, potassium-40, strontium-90, and iodine-131).

Radiation Doses and Regulatory Limits (in Millirems)
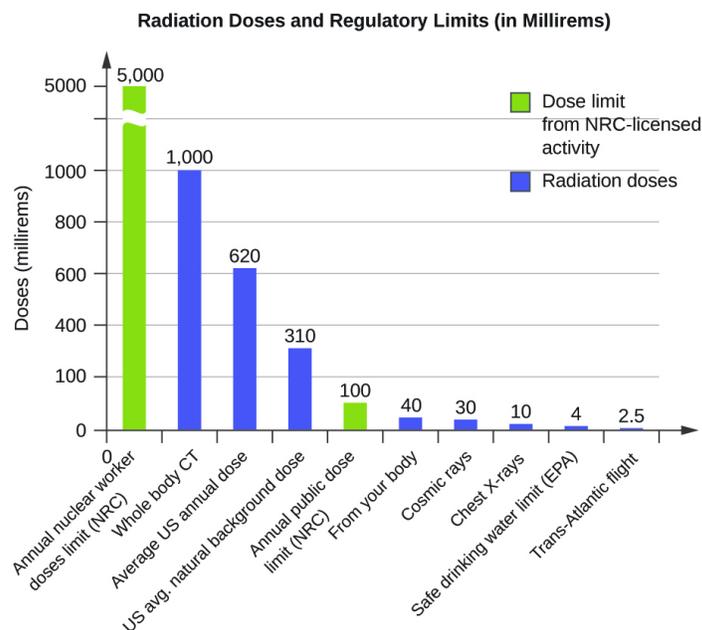
Figure 12.7.7: The total annual radiation exposure for a person in the US is about 620 mrem. The various sources and their relative amounts are shown in this bar graph. (source: U.S. Nuclear Regulatory Commission)

A short-term, sudden dose of a large amount of radiation can cause a wide range of health effects, from changes in blood chemistry to death. Short-term exposure to tens of rems of radiation will likely cause very noticeable symptoms or illness; a dose of about 500 rems is estimated to have a 50% probability of causing the death of the victim within 30 days of exposure. Exposure to radioactive emissions has a cumulative effect on the body during a person's lifetime, which is another reason why it is important to avoid any unnecessary exposure to radiation. Health effects of short-term exposure to radiation are shown in Table 12.7.2

Table 12.7.2: Health Effects of Radiation[2]

Exposure (rem)	Health Effect	Time to Onset (without treatment)
5–10	changes in blood chemistry	—
50	nausea	hours
55	fatigue	—
70	vomiting	—
75	hair loss	2–3 weeks
90	diarrhea	—
100	hemorrhage	—
400	possible death	within 2 months
1000	destruction of intestinal lining	—
	internal bleeding	—
	death	1–2 weeks
2000	damage to central nervous system	—
	loss of consciousness;	minutes
	death	hours to days

It is impossible to avoid some exposure to ionizing radiation. We are constantly exposed to background radiation from a variety of natural sources, including cosmic radiation, rocks, medical procedures, consumer products, and even our own atoms. We can minimize our exposure by blocking or shielding the radiation, moving farther from the source, and limiting the time of exposure.

Footnotes

- 2 Source: US Environmental Protection Agency

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12.8: Key Terms

alpha (α) decay | loss of an alpha particle during radioactive decay

alpha particle | (α or or high-energy helium nucleus; a helium atom that has lost two electrons and contains two protons and two neutrons

antimatter | particles with the same mass but opposite properties (such as charge) of ordinary particles

band of stability | (also, belt of stability, zone of stability, or valley of stability) region of graph of number of protons versus number of neutrons containing stable (nonradioactive) nuclides

becquerel (Bq) | SI unit for rate of radioactive decay; 1 Bq = 1 disintegration/s

beta (β) decay | breakdown of a neutron into a proton, which remains in the nucleus, and an electron, which is emitted as a beta particle

beta particle | or or high-energy electron

binding energy per nucleon | total binding energy for the nucleus divided by the number of nucleons in the nucleus

chain reaction | repeated fission caused when the neutrons released in fission bombard other atoms

chemotherapy | similar to internal radiation therapy, but chemical rather than radioactive substances are introduced into the body to kill cancer cells

containment system | (also, shield) a three-part structure of materials that protects the exterior of a nuclear fission reactor and operating personnel from the high temperatures, pressures, and radiation levels inside the reactor

control rod | material inserted into the fuel assembly that absorbs neutrons and can be raised or lowered to adjust the rate of a fission reaction

critical mass | amount of fissionable material that will support a self-sustaining (nuclear fission) chain reaction

curie (Ci) | larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7 10^{10} disintegrations/s

daughter nuclide | nuclide produced by the radioactive decay of another nuclide; may be stable or may decay further

electron capture | combination of a core electron with a proton to yield a neutron within the nucleus

electron volt (eV) | measurement unit of nuclear binding energies, with 1 eV equaling the amount energy due to the moving an electron across an electric potential difference of 1 volt

external beam radiation therapy | radiation delivered by a machine outside the body

fissile (or fissionable) | when a material is capable of sustaining a nuclear fission reaction

fission | splitting of a heavier nucleus into two or more lighter nuclei, usually accompanied by the conversion of mass into large amounts of energy

fusion | combination of very light nuclei into heavier nuclei, accompanied by the conversion of mass into large amounts of energy

fusion reactor | nuclear reactor in which fusion reactions of light nuclei are controlled

gamma (γ) emission | decay of an excited-state nuclide accompanied by emission of a gamma ray

gamma ray | (γ or short wavelength, high-energy electromagnetic radiation that exhibits wave-particle duality

Geiger counter | instrument that detects and measures radiation via the ionization produced in a Geiger-Müller tube

gray (Gy) | SI unit for measuring radiation dose; 1 Gy = 1 J absorbed/kg tissue

half-life ($t_{1/2}$) | time required for half of the atoms in a radioactive sample to decay

internal radiation therapy | (also, brachytherapy) radiation from a radioactive substance introduced into the body to kill cancer cells

ionizing radiation | radiation that can cause a molecule to lose an electron and form an ion

magic number | nuclei with specific numbers of nucleons that are within the band of stability

mass defect | difference between the mass of an atom and the summed mass of its constituent subatomic particles (or the mass "lost" when nucleons are brought together to form a nucleus)

mass-energy equivalence equation | Albert Einstein's relationship showing that mass and energy are equivalent

millicurie (mCi) | larger unit for rate of radioactive decay frequently used in medicine; 1 Ci = 3.7 10^{10} disintegrations/s

nonionizing radiation | radiation that speeds up the movement of atoms and molecules; it is equivalent to heating a sample, but is not energetic enough to cause the ionization of molecules

nuclear binding energy | energy lost when an atom's nucleons are bound together (or the energy needed to break a nucleus into its constituent protons and neutrons)

nuclear chemistry | study of the structure of atomic nuclei and processes that change nuclear structure

nuclear fuel | fissionable isotope present in sufficient quantities to provide a self-sustaining chain reaction in a nuclear reactor

nuclear moderator | substance that slows neutrons to a speed low enough to cause fission

nuclear reaction | change to a nucleus resulting in changes in the atomic number, mass number, or energy state

nuclear reactor | environment that produces energy via nuclear fission in which the chain reaction is controlled and sustained without explosion

nuclear transmutation | conversion of one nuclide into another nuclide

nucleon | collective term for protons and neutrons in a nucleus

nuclide | nucleus of a particular isotope

parent nuclide | unstable nuclide that changes spontaneously into another (daughter) nuclide

particle accelerator | device that uses electric and magnetic fields to increase the kinetic energy of nuclei used in transmutation reactions

positron or | antiparticle to the electron; it has identical properties to an electron, except for having the opposite (positive) charge

positron emission | (also, β⁺ decay) conversion of a proton into a neutron, which remains in the nucleus, and a positron, which is emitted

radiation absorbed dose (rad) | SI unit for measuring radiation dose, frequently used in medical applications; 1 rad = 0.01 Gy

radiation dosimeter | device that measures ionizing radiation and is used to determine personal radiation exposure

radiation therapy | use of high-energy radiation to damage the DNA of cancer cells, which kills them or keeps them from dividing

radioactive decay | spontaneous decay of an unstable nuclide into another nuclide

radioactive decay series | chains of successive disintegrations (radioactive decays) that ultimately lead to a stable end-product

radioactive tracer | (also, radioactive label) radioisotope used to track or follow a substance by monitoring its radioactive emissions

radioactivity | phenomenon exhibited by an unstable nucleon that spontaneously undergoes change into a nucleon that is more stable; an unstable nucleon is said to be radioactive

radiocarbon dating | highly accurate means of dating objects 30,000–50,000 years old that were derived from once-living matter; achieved by calculating the ratio of in the object vs. the ratio of in the present-day atmosphere

radioisotope | isotope that is unstable and undergoes conversion into a different, more stable isotope

radiometric dating | use of radioisotopes and their properties to date the formation of objects such as archeological artifacts, formerly living organisms, or geological formations

reactor coolant | assembly used to carry the heat produced by fission in a reactor to an external boiler and turbine where it is transformed into electricity

relative biological effectiveness (RBE) | measure of the relative damage done by radiation

roentgen equivalent man (rem) | unit for radiation damage, frequently used in medicine; 100 rem = 1 Sv

scintillation counter | instrument that uses a scintillator—a material that emits light when excited by ionizing radiation—to detect and measure radiation

sievert (Sv) | SI unit measuring tissue damage caused by radiation; takes into account energy and biological effects of radiation

strong nuclear force | force of attraction between nucleons that holds a nucleus together

subcritical mass | amount of fissionable material that cannot sustain a chain reaction; less than a critical mass

supercritical mass | amount of material in which there is an increasing rate of fission

transmutation reaction | bombardment of one type of nuclei with other nuclei or neutrons

transuranium element | element with an atomic number greater than 92; these elements do not occur in nature

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12.9: Key Equations

$E = mc^2$

decay rate $= \lambda N$

rem = RBE rad

Sv = RBE Gy

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12.10: Summary

An atomic nucleus consists of protons and neutrons, collectively called nucleons. Although protons repel each other, the nucleus is held tightly together by a short-range, but very strong, force called the strong nuclear force. A nucleus has less mass than the total mass of its constituent nucleons. This "missing" mass is the mass defect, which has been converted into the binding energy that holds the nucleus together according to Einstein's mass-energy equivalence equation, $E = mc^2$. Of the many nuclides that exist, only a small number are stable. Nuclides with even numbers of protons or neutrons, or those with magic numbers of nucleons, are especially likely to be stable. These stable nuclides occupy a narrow band of stability on a graph of number of protons versus number of neutrons. The binding energy per nucleon is largest for the elements with mass numbers near 56; these are the most stable nuclei.

Nuclei can undergo reactions that change their number of protons, number of neutrons, or energy state. Many different particles can be involved in nuclear reactions. The most common are protons, neutrons, positrons (which are positively charged electrons), alpha (α) particles (which are high-energy helium nuclei), beta (β) particles (which are high-energy electrons), and gamma (γ) rays (which compose high-energy electromagnetic radiation). As with chemical reactions, nuclear reactions are always balanced. When a nuclear reaction occurs, the total mass (number) and the total charge remain unchanged.

Nuclei that have unstable n:p ratios undergo spontaneous radioactive decay. The most common types of radioactivity are α decay, β decay, γ emission, positron emission, and electron capture. Nuclear reactions also often involve γ rays, and some nuclei decay by electron capture. Each of these modes of decay leads to the formation of a new nucleus with a more stable n:p ratio. Some substances undergo radioactive decay series, proceeding through multiple decays before ending in a stable isotope. All nuclear decay processes follow first-order kinetics, and each radioisotope has its own characteristic half-life, the time that is required for half of its atoms to decay. Because of the large differences in stability among nuclides, there is a very wide range of half-lives of radioactive substances. Many of these substances have found useful applications in medical diagnosis and treatment, determining the age of archaeological and geological objects, and more.

It is possible to produce new atoms by bombarding other atoms with nuclei or high-speed particles. The products of these transmutation reactions can be stable or radioactive. A number of artificial elements, including technetium, astatine, and the transuranium elements, have been produced in this way.

Nuclear power as well as nuclear weapon detonations can be generated through fission (reactions in which a heavy nucleus is split into two or more lighter nuclei and several neutrons). Because the neutrons may induce additional fission reactions when they combine with other heavy nuclei, a chain reaction can result. Useful power is obtained if the fission process is carried out in a nuclear reactor. The conversion of light nuclei into heavier nuclei (fusion) also produces energy. At present, this energy has not been contained adequately and is too expensive to be feasible for commercial energy production.

Compounds known as radioactive tracers can be used to follow reactions, track the distribution of a substance, diagnose and treat medical conditions, and much more. Other radioactive substances are helpful for controlling pests, visualizing structures, providing fire warnings, and for many other applications. Hundreds of millions of nuclear medicine tests and procedures, using a wide variety of radioisotopes with relatively short half-lives, are performed every year in the US. Most of these radioisotopes have relatively short half-lives; some are short enough that the radioisotope must be made on-site at medical facilities. Radiation therapy uses high-energy radiation to kill cancer cells by damaging their DNA. The radiation used for this treatment may be delivered externally or internally.

We are constantly exposed to radiation from a variety of naturally occurring and human-produced sources. This radiation can affect living organisms. Ionizing radiation is the most harmful because it can ionize molecules or break chemical bonds, which damages the molecule and causes malfunctions in cell processes. It can also create reactive hydroxyl radicals that damage biological molecules and disrupt physiological processes. Radiation can cause somatic or genetic damage, and is most harmful to rapidly reproducing cells. Types of radiation differ in their ability to penetrate material and damage tissue, with alpha particles the least penetrating but potentially most damaging and gamma rays the most penetrating.

Various devices, including Geiger counters, scintillators, and dosimeters, are used to detect and measure radiation, and monitor radiation exposure. We use several units to measure radiation: becquerels or curies for rates of radioactive decay; gray or rads for energy absorbed; and rems or sieverts for biological effects of radiation. Exposure to radiation can cause a wide range of health effects, from minor to severe, and including death. We can minimize the effects of radiation by shielding with dense materials such as lead, moving away from the source, and limiting time of exposure.

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12.11: Exercises

1. Write the following isotopes in hyphenated form (e.g., "carbon-14")

   (a) $^{24}_{11}\text{Na}$
   (b) $^{29}_{13}\text{Al}$
   (c) $^{73}_{36}\text{Kr}$
   (d) $^{194}_{77}\text{Ir}$

2. Write the following isotopes in nuclide notation (e.g.,

   a. oxygen-14
   b. copper-70
   c. tantalum-175
   d. francium-217

3. For the following isotopes that have missing information, fill in the missing information to complete the notation

   (a) $^{34}_{14}\text{X}$
   (b) $^{36}_{\text{X}}\text{P}$
   (c) $^{57}_{\text{X}}\text{Mn}$
   (d) $^{121}_{56}\text{X}$

4. For each of the isotopes in Exercise 21.1, determine the numbers of protons, neutrons, and electrons in a neutral atom of the isotope.

5. Write the nuclide notation, including charge if applicable, for atoms with the following characteristics:

   a. 25 protons, 20 neutrons, 24 electrons
   b. 45 protons, 24 neutrons, 43 electrons
   c. 53 protons, 89 neutrons, 54 electrons
   d. 97 protons, 146 neutrons, 97 electrons

6. Calculate the density of the nucleus in g/mL, assuming that it has the typical nuclear diameter of $1\ 10^{-13}$ cm and is spherical in shape.   7. What are the two principal differences between nuclear reactions and ordinary chemical changes?

8. The mass of the atom is 22.9898 amu.

   a. Calculate its binding energy per atom in millions of electron volts.
   b. Calculate its binding energy per nucleon.

9. Which of the following nuclei lie within the band of stability shown in Figure 21.2?

   a. chlorine-37
   b. calcium-40
   c. ^{204}Bi
   d. ^{56}Fe
   e. ^{206}Pb
   f. ^{211}Pb
   g. ^{222}Rn
   h. carbon-14

10. Which of the following nuclei lie within the band of stability shown in Figure 21.2?

   a. argon-40
   b. oxygen-16
   c. ^{122}Ba
   d. ^{58}Ni
   e. ^{205}Tl
   f. ^{210}Tl
   g. ^{226}Ra

h. magnesium-24

11. Write a brief description or definition of each of the following:

    a. nucleon

    b. α particle

    c. β particle

    d. positron

    e. γ ray

    f. nuclide

    g. mass number

    h. atomic number

12. Which of the various particles (α particles, β particles, and so on) that may be produced in a nuclear reaction are actually nuclei?

13. Complete each of the following equations by adding the missing species:

    (a) $^{27}_{13}\text{Al} + {}^{4}_{2}\text{He} \rightarrow ? + {}^{1}_{0}\text{n}$
    (b) $^{239}_{94}\text{Pu} + ? \rightarrow {}^{242}_{96}\text{Cm} + {}^{1}_{0}\text{n}$
    (c) $^{14}_{7}\text{N} + {}^{4}_{2}\text{He} \rightarrow ? + {}^{1}_{1}\text{H}$
    (d) $^{235}_{92}\text{U} \rightarrow ? + {}^{135}_{55}\text{Cs} + 4{}^{1}_{0}\text{n}$

14. Complete each of the following equations:

    (a) $^{7}_{3}\text{Li} + ? \rightarrow 2{}^{4}_{2}\text{He}$
    (b) $^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + ?$
    (c) $^{27}_{13}\text{Al} + {}^{4}_{2}\text{He} \rightarrow ? + {}^{1}_{0}\text{n}$
    (d) $^{250}_{96}\text{Cm} \rightarrow ? + {}^{98}_{38}\text{Sr} + 4{}^{1}_{0}\text{n}$

15. Write a balanced equation for each of the following nuclear reactions:

    a. the production of ^{17}O from ^{14}N by α particle bombardment

    b. the production of ^{14}C from ^{14}N by neutron bombardment

    c. the production of ^{233}Th from ^{232}Th by neutron bombardment

    d. the production of ^{239}U from ^{238}U by bombardment

16. Technetium-99 is prepared from ^{98}Mo. Molybdenum-98 combines with a neutron to give molybdenum-99, an unstable isotope that emits a β particle to yield an excited form of technetium-99, represented as $^{99}\text{Tc}^{*}$. This excited nucleus relaxes to the ground state, represented as ^{99}Tc, by emitting a γ ray. The ground state of ^{99}Tc then emits a β particle. Write the equations for each of these nuclear reactions.

17. The mass of the atom is 18.99840 amu.

    a. Calculate its binding energy per atom in millions of electron volts.

    b. Calculate its binding energy per nucleon.

18. For the reaction if 100.0 g of carbon reacts, what volume of nitrogen gas (N_2) is produced at 273K and 1 atm?

19. What are the types of radiation emitted by the nuclei of radioactive elements?

20. What changes occur to the atomic number and mass of a nucleus during each of the following decay scenarios?

    a. an α particle is emitted

    b. a β particle is emitted

    c. γ radiation is emitted

    d. a positron is emitted

    e. an electron is captured

21. What is the change in the nucleus that results from the following decay scenarios?

    a. emission of a β particle

    b. emission of a $β^{+}$ particle

    c. capture of an electron

22. Many nuclides with atomic numbers greater than 83 decay by processes such as electron emission. Explain the observation that the emissions from these unstable nuclides also normally include α particles.

23. Why is electron capture accompanied by the emission of an X-ray?

24. Explain, in terms of Figure 21.2, how unstable heavy nuclides (atomic number > 83) may decompose to form nuclides of greater stability (a) if they are below the band of stability and (b) if they are above the band of stability.

25. Which of the following nuclei is most likely to decay by positron emission? Explain your choice.

    a. chromium-53
    b. manganese-51
    c. iron-59

26. The following nuclei do not lie in the band of stability. How would they be expected to decay? Explain your answer.

    (a) $^{34}_{15}P$
    (b) $^{239}_{92}U$
    (c) $^{38}_{20}Ca$
    (d) $^{3}_{1}H$
    (e) $^{245}_{94}Pu$

27. The following nuclei do not lie in the band of stability. How would they be expected to decay?

    (a) $^{28}_{15}P$
    (b) $^{235}_{92}U$
    (c) $^{37}_{20}Ca$
    (d) $^{9}_{3}Li$
    (e) $^{245}_{96}Cm$

28. Predict by what mode(s) of spontaneous radioactive decay each of the following unstable isotopes might proceed:

    (a) $^{6}_{2}He$
    (b) $^{60}_{30}Zn$
    (c) $^{235}_{91}Pa$
    (d) $^{241}_{94}Np$
    (e) ^{18}F
    (f) ^{129}Ba
    (g) ^{237}Pu

29. Write a nuclear reaction for each step in the formation of from which proceeds by a series of decay reactions involving the step-wise emission of α, β, β, α, α, α particles, in that order.

30. Write a nuclear reaction for each step in the formation of from which proceeds by a series of decay reactions involving the step-wise emission of α, α, α, α, β, β, α particles, in that order.

31. Define the term half-life and illustrate it with an example.

32. A 1.00 10^{-6}-g sample of nobelium, has a half-life of 55 seconds after it is formed. What is the percentage of remaining at the following times?

    a. 5.0 min after it forms
    b. 1.0 h after it forms

33. ^{239}Pu is a nuclear waste byproduct with a half-life of 24,000 y. What fraction of the ^{239}Pu present today will be present in 1000 y?

34. The isotope ^{208}Tl undergoes β decay with a half-life of 3.1 min.

    a. What isotope is produced by the decay?
    b. How long will it take for 99.0% of a sample of pure ^{208}Tl to decay?
    c. What percentage of a sample of pure ^{208}Tl remains un-decayed after 1.0 h?

35. If 1.000 g of produces 0.0001 mL of the gas at STP (standard temperature and pressure) in 24 h, what is the half-life of ^{226}Ra in years?

36. The isotope is one of the extremely hazardous species in the residues from nuclear power generation. The strontium in a 0.500-g sample diminishes to 0.393 g in 10.0 y. Calculate the half-life.

37. Technetium-99 is often used for assessing heart, liver, and lung damage because certain technetium compounds are absorbed by damaged tissues. It has a half-life of 6.0 h. Calculate the rate constant for the decay of

38. What is the age of mummified primate skin that contains 8.25% of the original quantity of ^{14}C?

39. A sample of rock was found to contain 8.23 mg of rubidium-87 and 0.47 mg of strontium-87.

    a. Calculate the age of the rock if the half-life of the decay of rubidium by β emission is 4.7 10^{10} y.
    b. If some was initially present in the rock, would the rock be younger, older, or the same age as the age calculated in (a)? Explain your answer.

40. A laboratory investigation shows that a sample of uranium ore contains 5.37 mg of and 2.52 mg of Calculate the age of the ore. The half-life of is 4.5 10^9 yr.

41. Plutonium was detected in trace amounts in natural uranium deposits by Glenn Seaborg and his associates in 1941. They proposed that the source of this ^{239}Pu was the capture of neutrons by ^{238}U nuclei. Why is this plutonium not likely to have been trapped at the time the solar system formed 4.7 10^9 years ago?

42. A atom (mass = 7.0169 amu) decays into a atom (mass = 7.0160 amu) by electron capture. How much energy (in millions of electron volts, MeV) is produced by this reaction?

43. A atom (mass = 8.0246 amu) decays into a atom (mass = 8.0053 amu) by loss of a β$^+$ particle (mass = 0.00055 amu) or by electron capture. How much energy (in millions of electron volts) is produced by this reaction?

44. Isotopes such as ^{26}Al (half-life: 7.2 10^5 years) are believed to have been present in our solar system as it formed, but have since decayed and are now called extinct nuclides.

    a. ^{26}Al decays by β$^+$ emission or electron capture. Write the equations for these two nuclear transformations.
    b. The earth was formed about 4.7 10^9 (4.7 billion) years ago. How old was the earth when 99.999999% of the ^{26}Al originally present had decayed?

45. Write a balanced equation for each of the following nuclear reactions:

    a. bismuth-212 decays into polonium-212
    b. beryllium-8 and a positron are produced by the decay of an unstable nucleus
    c. neptunium-239 forms from the reaction of uranium-238 with a neutron and then spontaneously converts into plutonium-239
    d. strontium-90 decays into yttrium-90

46. Write a balanced equation for each of the following nuclear reactions:

    a. mercury-180 decays into platinum-176
    b. zirconium-90 and an electron are produced by the decay of an unstable nucleus
    c. thorium-232 decays and produces an alpha particle and a radium-228 nucleus, which decays into actinium-228 by beta decay
    d. neon-19 decays into fluorine-19

47. Write the balanced nuclear equation for the production of the following transuranium elements:

    a. berkelium-244, made by the reaction of Am-241 and He-4
    b. fermium-254, made by the reaction of Pu-239 with a large number of neutrons
    c. lawrencium-257, made by the reaction of Cf-250 and B-11
    d. dubnium-260, made by the reaction of Cf-249 and N-15

48. How does nuclear fission differ from nuclear fusion? Why are both of these processes exothermic?

49. Both fusion and fission are nuclear reactions. Why is a very high temperature required for fusion, but not for fission?

50. Cite the conditions necessary for a nuclear chain reaction to take place. Explain how it can be controlled to produce energy, but not produce an explosion.

51. Describe the components of a nuclear reactor.

52. In usual practice, both a moderator and control rods are necessary to operate a nuclear chain reaction safely for the purpose of energy production. Cite the function of each and explain why both are necessary.

53. Describe how the potential energy of uranium is converted into electrical energy in a nuclear power plant.

54. The mass of a hydrogen atom is 1.007825 amu; that of a tritium atom is 3.01605 amu; and that of an α particle is 4.00150 amu. How much energy in kilojoules per mole of produced is released by the following fusion reaction:

55. How can a radioactive nuclide be used to show that the equilibrium is a dynamic equilibrium?

56. Technetium-99m has a half-life of 6.01 hours. If a patient injected with technetium-99m is safe to leave the hospital once 75% of the dose has decayed, when is the patient allowed to leave?

57. Iodine that enters the body is stored in the thyroid gland from which it is released to control growth and metabolism. The thyroid can be imaged if iodine-131 is injected into the body. In larger doses, I-133 is also used as a means of treating cancer of the thyroid. I-131 has a half-life of 8.70 days and decays by β⁻ emission.

   a. Write an equation for the decay.
   b. How long will it take for 95.0% of a dose of I-131 to decay?

58. If a hospital were storing radioisotopes, what is the minimum containment needed to protect against:

   a. cobalt-60 (a strong γ emitter used for irradiation)
   b. molybdenum-99 (a beta emitter used to produce technetium-99 for imaging)

59. Based on what is known about Radon-222's primary decay method, why is inhalation so dangerous?

60. Given specimens uranium-232 ($t_{1/2}$ = 68.9 y) and uranium-233 ($t_{1/2}$ = 159,200 y) of equal mass, which one would have greater activity and why?

61. A scientist is studying a 2.234 g sample of thorium-229 ($t_{1/2}$ = 7340 y) in a laboratory.

   a. What is its activity in Bq?
   b. What is its activity in Ci?

62. Given specimens neon-24 ($t_{1/2}$ = 3.38 min) and bismuth-211 ($t_{1/2}$ = 2.14 min) of equal mass, which one would have greater activity and why?

CHAPTER OVERVIEW

13: Bioinorganic Chemistry

Metals play a wide range of important roles in biological systems. This chapter will give an overview of the roles metals can play in biochemical reactions and highlight a few metal containing proteins in greater detail.

> **◑ Learning Objectives**
>
> - Observe the different roles metals can play in biological systems
> - Apply inorganic chemistry principles (MO theory, CFT, HSAB, etc.) to metalloproteins

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13.1: Biological Significance of Metals

Overview

The transition metals are among the least abundant metal ions in the sea water from which contemporary organisms are thought to have evolved (Table 13.1.1).[1-5] For many of the metals, the concentration in human blood plasma greatly exceeds that in sea water. Such data indicate the importance of mechanisms for accumulation, storage, and transport of transition metals in living organisms.

Table 13.1.1: Concentrations of transition metals and zinc in sea water and human plasma.*Data from References 1 - 5 and 12

Element	Sea Water (M) x 10^8	Human Plasma (M) x 10^8
Fe	0.005 - 2	2230
Zn	8.0	1720
Cu	1.0	1650
Mo	10.0	1000
Co	0.7	0.0025
Cr	0.4	5.5
V	4.0	17.7
Mn	0.7	10.9
Ni	0.5	4.4

The metals are generally found either bound directly to proteins or in cofactors such as porphyrins or cobalamins, or in clusters that are in turn bound by the protein; the ligands are usually O, N, S, or C. Proteins with which transition metals and zinc are most commonly associated catalyze the intramolecular or intermolecular rearrangement of electrons. Although the redox properties of the metals are important in many of the reactions, in others the metal appears to contribute to the structure of the active state, e.g., zinc in the Cu-Zn dismutases and some of the iron in the photosynthetic reaction center. Sometimes equivalent reactions are catalyzed by proteins with different metal centers; the metal binding sites and proteins have evolved separately for each type of metal center.

Iron

Iron is the most common transition metal in biology.[6,7] Its use has created a dependence that has survived the appearance of dioxygen in the atmosphere ca. 2.5 billion years ago, and the concomitant conversion of ferrous ion to ferric ion and insoluble rust. All plants, animals, and bacteria use iron, except for a lactobacillus that appears to maintain high concentrations of manganese instead of iron. The processes and reactions in which iron participates are crucial to the survival of terrestrial organisms, and include ribonucleotide reduction (DNA synthesis), energy production (respiration), energy conversion (photosynthesis), nitrogen reduction, oxygen transport (respiration, muscle contraction), and oxygenation (e.g., steroid synthesis, solubilization and detoxification of aromatic compounds). Among the transition metals used in living organisms, iron is the most abundant in the environment. Whether this fact alone explains the biological predominance of iron or whether specific features of iron chemistry contribute is not clear.

Many of the other transition metals participate in reactions equivalent to those involving iron, and can sometimes substitute for iron, albeit less effectively, in natural Fe-proteins. Additional biological reactions are unique to nonferrous transition metals.

Zinc

Zinc is relatively abundant in biological materials.[8,9] The major location of zinc in the body is metallothionein, which also binds copper, chromium, mercury, and other metals. Among the other well-characterized zinc proteins are the Cu-Zn superoxide dismutases (other forms have Fe or Mn), carbonic anhydrase (an abundant protein in red blood cells responsible for maintaining the pH of the blood), alcohol dehydrogenase, and a variety of hydrolases involved in the metabolism of sugars, proteins, and nucleic acids. Zinc is a common element in nucleic-acid polymerases and transcription factors, where its role is considered to be structural rather than catalytic. Interestingly, zinc enhances the stereoselectivity of the polymerization of nucleotides under reaction

conditions designed to simulate the environment for prebiotic reactions. Recently a group of nucleic-acid binding proteins, with a repeated sequence containing the amino acids cysteine and histidine, were shown to bind as many as eleven zinc atoms necessary for protein function (transcribing DNA to RNA).[10] Zinc plays a structural role, forming the peptide into multiple domains or "zinc fingers" by means of coordination to cysteine and histidine. A survey of the sequences of many nucleic-acid binding proteins shows that many of them have the common motif required to form zinc fingers. Other zinc-finger proteins called steroid receptors bind both steroids such as progesterone and the progesterone gene DNA. Much of the zinc in animals and plants has no known function, but it may be maintaining the structures of proteins that activate and deactivate genes.[11]

Copper

Copper and iron proteins participate in many of the same biological reactions:

1. reversible binding of dioxygen, e.g., hemocyanin (Cu), hemerythrin (Fe), and hemoglobin (Fe);
2. activation of dioxygen, e.g., dopamine hydroxylase (Cu) (important in the synthesis of the hormone epinephrine), tyrosinases (Cu), and catechol dioxygenases (Fe);
3. electron transfer, e.g., plastocyanins (Cu), ferredoxins, and c-type cytochromes (Fe);
4. dismutation of superoxide by Cu or Fe as the redox-active metal (superoxide dismutases).

The two metal ions also function in concert in proteins such as cytochrome oxidase, which catalyzes the transfer of four electrons to dioxygen to form water during respiration. Whether any types of biological reactions are unique to copper proteins is not clear. However, use of stored iron is reduced by copper deficiency, which suggests that iron metabolism may depend on copper proteins, such as the serum protein ceruloplasmin, which can function as a ferroxidase, and the cellular protein ascorbic acid oxidase, which also is a ferrireductase.

Cobalt

Cobalt is found in vitamin B_{12} , its only apparent biological site.[12] The vitamin is a cyano complex, but a methyl or methylene group replaces CN in native enzymes. Vitamin-B_{12} deficiency causes the severe disease of pernicious anemia in humans, which indicates the critical role of cobalt. The most common type of reaction in which cobalamin enzymes participate results in the reciprocal exchange of hydrogen atoms if they are on adjacent carbon atoms, yet not with hydrogen in solvent water:

$$
\begin{array}{ccc}
\begin{array}{cc} b & c \\ | & | \\ a-C-C-d \\ | & | \\ X & H \end{array}
& \rightleftharpoons &
\begin{array}{cc} b & c \\ | & | \\ a-C-C-d \\ | & | \\ H & X \end{array}
\end{array}
$$
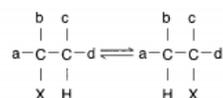
(An important exception is the ribonucleotide reductase from some bacteria and lower plants, which converts ribonucleotides to the DNA precursors, deoxyribonucleotides, a reaction in which a sugar -OH is replaced by -H. Note that ribonucleotide reductases catalyzing the same reaction in higher organisms and viruses are proteins with an oxo-bridged dimeric iron center.) The cobalt in vitamin B_{12} is coordinated to five N atoms, four contributed by a tetrapyrrole (corrin); the sixth ligand is C, provided either by C5 of deoxyadenosine in enzymes such as methylmalonyl-CoA mutase (fatty acid metabolism) or by a methyl group in the enzyme that synthesizes the amino acid methionine in bacteria.

Nickel

Nickel is a component of a hydrolase (urease), of hydrogenase, of CO dehydrogenase, and of S-methyl CoM reductase, which catalyzes the terminal step in methane production by methanogenic bacteria. All the Ni-proteins known to date are from plants or bacteria.[13,14] However, about 50 years elapsed between the crystallization of jack-bean urease in 1925 and the identification of the nickel component in the plant protein. Thus it is premature to exclude the possibility of Ni-proteins in animals. Despite the small number of characterized Ni-proteins, it is clear that many different environments exist, from apparently direct coordination to protein ligands (urease) to the tetrapyrrole F430 in methylreductase and the multiple metal sites of Ni and Fe-S in a hydrogenase from the bacterium *Desulfovibrio gigas*. Specific environments for nickel are also indicated for nucleic acids (or nucleic acid-binding proteins), since nickel activates the gene for hydrogenase.[15]

Manganese

Manganese plays a critical role in oxygen evolution catalyzed by the proteins of the photosynthetic reaction center. The superoxide dismutase of bacteria and mitochondria, as well as pyruvate carboxylase in mammals, are also manganese proteins.[16,17] How the

multiple manganese atoms of the photosynthetic reaction center participate in the removal of four electrons and protons from water is the subject of intense investigation by spectroscopists, synthetic inorganic chemists, and molecular biologists.[17]

Vanadium and Chromium

Vanadium and chromium have several features in common, from a bioinorganic viewpoint.[18a] First, both metals are present in only small amounts in most organisms. Second, the biological roles of each remain largely unknown.[18] Finally, each has served as a probe to characterize the sites of other metals, such as iron and zinc. Vanadium is required for normal health, and could act *in vivo* either as a metal cation or as a phosphate analogue, depending on the oxidation state, V(lV) or V(V), respectively. Vanadium in a sea squirt (tunicate), a primitive vertebrate, is concentrated in blood cells, apparently as the major cellular transition metal, but whether it participates in the transport of dioxygen (as iron and copper do) is not known. In proteins, vanadium is a cofactor in an algal bromoperoxidase and in certain prokaryotic nitrogenases. Chromium imbalance affects sugar metabolism and has been associated with the glucose tolerance factor in animals. But little is known about the structure of the factor or of any other specific chromium complexes from plants, animals, or bacteria.

Molybdenum

Molybdenum proteins catalyze the reduction of nitrogen and nitrate, as well as the oxidation of aldehydes, purines, and sulfite.[19] Few Mo-proteins are known compared to those involving other transition metals. Nitrogenases, which also contain iron, have been the focus of intense investigations by bioinorganic chemists and biologists; the iron is found in a cluster with molybdenum (the iron-molybdenum cofactor, or FeMoCo) and in an iron-sulfur center. Interestingly, certain bacteria (*Azotobacter*) have alternative nitrogenases, which are produced when molybdenum is deficient and which contain vanadium and iron or only iron. All other known Mo-proteins are also Fe-proteins with iron centers, such as tetrapyrroles (heme and chlorins), Fe-sulfur clusters, and, apparently, non-heme/non-sulfur iron. Some Mo-proteins contain additional cofactors such as the flavins, e.g., in xanthine oxidase and aldehyde oxidase. The number of redox centers in some Mo-proteins exceeds the number of electrons transferred; reasons for this are unknown currently.

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13.2: Introduction to Amino Acids and Proteins

Common amino acids

There are 20 common amino acids. They are composed of C, H, O, N and S atoms. They are structurally and chemically different, and also differ in size and volume. Some are branched structures, some are linear, some have ring structures. One of the 20 common amino acids is actually an imino acid. A typical grouping of their chemical nature is as follows:

- Nonpolar (hydrocarbons and one sulfur-containing amino acid). Dispersion forces and hydrophobic effects predominate in their interactions. They cannot H-bond with water and these side chains have a characteristic hydrophobic effect in water.
- Polar uncharged. Contain functional groups that can H-bond with water and other amino acids. Include C, H, O, N and S atoms.
- Acidic. Contain a carboxylic acid functional group with a negative charge at neutral pH. Can H-bond with water, can form ionic interactions, and can also serve as nucleophiles or participate in acid-base chemistry.
- Basic. Nitrogen containing bases (e.g. guanidino, imidazole or amino groups) with a net positive charge at neutral pH. Can serve as proton donors in chemical reactions, and form ionic interactions.

The amino acids have a name, as well as a three letter or single letter mnemonic code:

Type	Name	R-group Structure
Nonpolar	Leucine Leu, L	
	Isoleucine Ile, I	
	Valine Val, V	
	Alanine Ala, A	
	Methionine Met, M	

Type	Name	R-group Structure
	Phenylalanine Phe, F	
	Tryptophan Trp, W	
	Proline Pro, P	
	Glycine Gly, G (note: sometimes included in polar group)	
Polar, uncharged	Serine Ser, S	
	Asparagine Asn, N	
	Glutamine Gln, Q	 glutamine
	Threonine Thr, T	
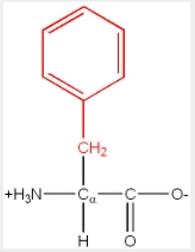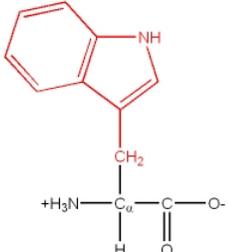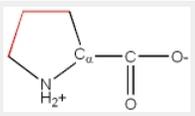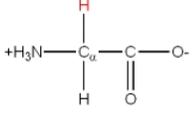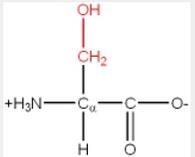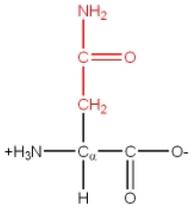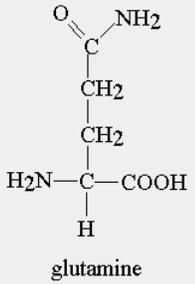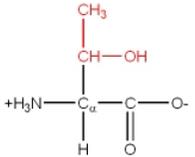
Type	Name	R-group Structure
	Cysteine Cys, C	
	Tyrosine Tyr, Y	
Acidic	Aspartic acid Asp, D	
	Glutamic acid Glu, E	
Basic	Lysine Lys, K	
	Arginine Arg, R	

Type	Name	R-group Structure
	Histidine His, H	
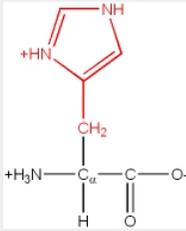
Uncommon amino acids

In addition to the 20 common amino acids, there are several uncommon ones found:

- Hydroxylysine and hydroxyproline. These are found in the protein collagen. Collagen is a fibrous protein made up of three polypeptides that form a stable assembly, but only if the proline and lysine residues are hydroxylated. (requires vitamin C for reduction of these amino acids to hydroxy form)
- Thyroxine, an iodinated derivative of tyrosine, found in thyroglobulin (produced by thyroid gland; requires iodine in diet)
- g-carboxyglutamic acid (i.e. glutamic acid with two carboxyl groups) found in certain blood clotting enzymes (requires vitamin K for production)
- N-methyl arginine and n-acetyl lysine. Found in some DNA binding proteins known as histones

Amino acid derivatives not found in proteins

Some amino acids are made that are not intended for incorporation into proteins, rather they have important functionalities on their own

- Serotonin (derivative of tryptophan) and g-amino butyric acid (a derivative of glutamic acid) are both neurotransmitters
- Histamine (derivative of histidine) involved in allergic response
- Adrenaline (derivative of tyrosine) a hormone
- Various antibiotics are amino acid derivatives (penicillin)

Contributors and Attributions

- Mike Blaber (Florida State University)

Thumbnail: 3D model of L-tryptophan. (Public Domain; Benjah-bmm27).

13.3: Biological Dioxygen Transport and Storage

Oxygen Transport

Most organisms require molecular oxygen in order to survive. The oxygen is used in a host of biochemical transformations, although most is consumed in the reaction that is the terminal (or primary) step of oxidative phosphorylation to form ATP.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (13.3.1)$$
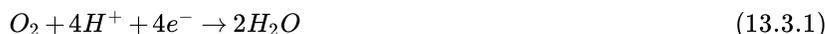
The transportation of oxygen from the air or water to the cells of an organism is vital. In the three chemically distinct dioxygen carrier proteins that have evolved and are found today, the dioxygen binding site in the protein, the active site, is an iron or copper complex. For hemoglobins, the most widely distributed family of dioxygen carriers, the active site has long been known to consist of an iron porphyrin (heme) group embedded in the protein. Almost all hemoglobins share the basic structure illustrated in Figure 4.2. Hemocyanin and hemerythrin, the other two biological dioxygen carriers, feature pairs of copper atoms and iron atoms, respectively, at the active sites.* Some basic properties of these metalloproteins are summarized in Table 13.3.1.
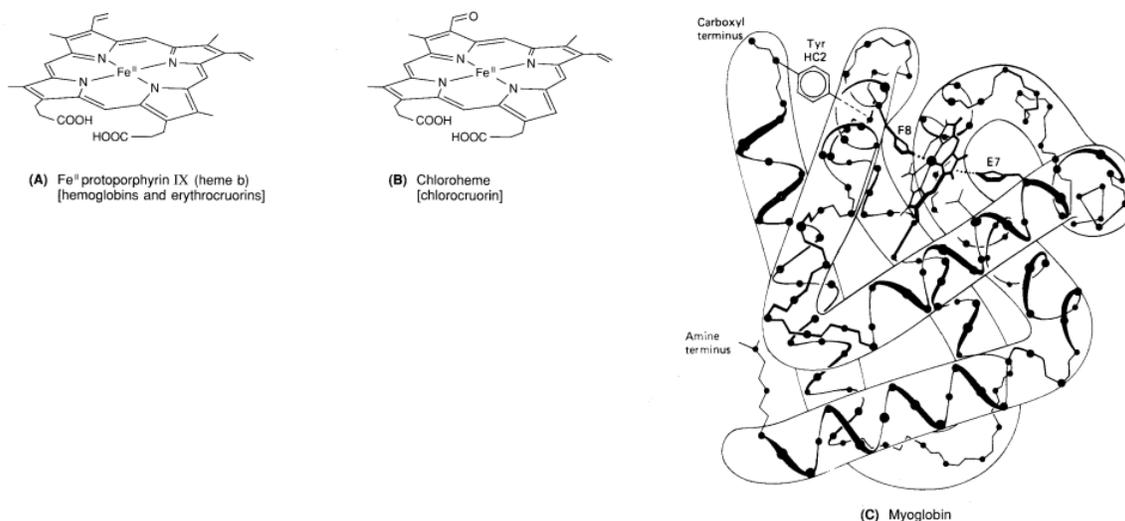
Figure 13.3.1: Heme groups used in hemoglobin: (A) Protoporphyrin IX (heme b), (hemoglobins and erythrocruorins); (B) Chloroheme (chlorocruorin); (C) The encapsulation of the heme molecule in myoglobin.[11a] Reproduced with permission from M. F. Perutz, Nature **228** (1970), 726-737.

Table 13.3.1: General Features of Dioxygen-carrier Proteins

Metalloprotein	Active Site of deoxy	Color Change deoxy → oxy	MW (Dalton)	# Subunits	Average MW Subunit (Dalton)
Hemoglobins					
Vertebrate					
Human A	heme Fe^{II}	purple → red	64,000	4	16,000
Invertebrate					
Erythrocruroin (*Lumbricus terrestris*, earthworm)	heme Fe^{II}	purple → red	up to 3.3×10^6	192	17,000
Chlorocruorn (*Eudistylia vancouveri*, feather duster worm*)	chloroheme Fe^{II}	purple → green	3.1×10^6	192	15,000

Metalloprotein	Active Site of deoxy	Color Change deoxy → oxy	MW (Dalton)	# Subunits	Average MW Subunit (Dalton)
Hemocyanins					
Mollusk (*Helix pomatia-α*, edible snail)	$Cu^1 \ldots Cu1$	colorless → blue	-9 x 10^6	160	52,700
Arthropod *(Cancer magister*, crab)	$Cu^1 \ldots Cu1$	colorless → blue	-9 x 10^5	12	76,600
Hemerythrins *(Phascolopsis* syn. *golfingia gouldii)*	$Fe^{II} \ldots Fe^{II}$	colorless → burgundy	108,000	8	13,500

* The use of the prefix *hem-* is confusing. In this context *hem* connotes blood. Thus, since hemocyanin and hemerythrin lack a heme group [an iron(II) porphyrin], they are nonheme metalloproteins.

In many organisms an additional dioxygen-binding protein, which stores dioxygen, is located in tissues that are subject to sudden and high dioxygen demand, such as muscles. These dioxygen-storage proteins are prefixed *myo-* (from the Greek root *mys* for muscle). Thus for the dioxygen-transport protein hemerythrin there exists a chemically similar dioxygen-storage protein myohemerythrin. For the hemoglobin family the corresponding storage protein is called myoglobin. Interestingly, some organisms that use hemocyanin as the dioxygen-*transport* protein use myoglobin as the dioxygen-*storage* protein.

Introduction to Myoglobin and Hemoglobin

Myoglobin: O$_2$ storage
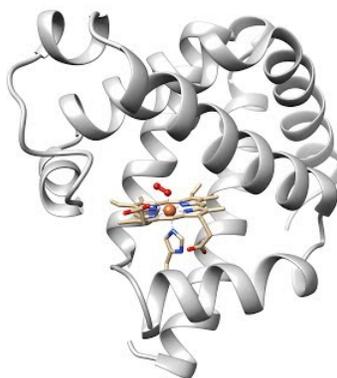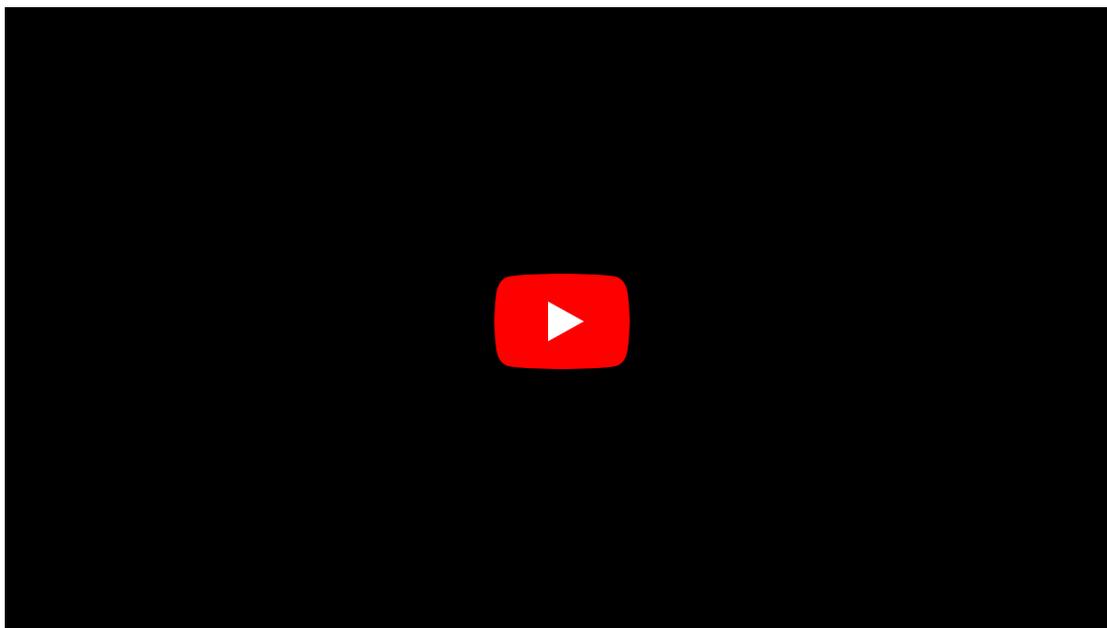
The respiratory system is an organ system in the body that functions in gas exchange with the environment. Exchange of gases like carbon dioxide (CO_2) and dioxygen (O_2) are essential for sustaining life forms. O_2 is necessary in aerobic metabolism for oxidative phosphorylation (synthesis of ATP) at the electron transport chain (ETC).[2] ATP is the energy source needed for muscular contraction in mammals. ATP synthesis requires oxygen as an electron acceptor in the ETC, therefore oxygen must be readily available for use in metabolically active muscles. Since muscles need large quantities of O_2, it is transported by proteins in the blood and stored in muscle tissue. One of these proteins is myoglobin. Myoglobin is a hemoprotein found in the skeletal muscle of mammals that functions in oxygen storage and diffusion. The heme in myoglobin can reversibly bind a O_2 molecule to regulate the transportation of O_2 from red blood cells to mitochondria when skeletal muscles are metabolically active.

Structure of Myoglobin

The structure of myoglobin (Figure $13.3.2$) is similar to the structure of one of the β subunits of hemoglobin. Myoglobin and hemoglobin are both part of the globin family; a family of heme-containing globular polypeptides with eight α-helices in their protein fold. Myoglobin contains only one subunit of globin, while hemoglobin has four subunits.

The iron-containing heme group allows myoglobin to reversibly bind to O_2 (Figure $13.3.2$). Heme is a large, aromatic porphyrin ring with four pyrrole nitrogens bound to an Fe(II) ion at the center (Figure $13.3.2C$).[2,3] The nitrogens from the porphyrin ring and a histidine serve as ligands for the Fe(II) metal center. The heme Fe is bound to the myoglobin polypeptide through the proximal histidine residue. The iron ion has six coordination sites: four equitorial sites are occupied by pyrole nitrogens of heme, and one axial site is occupied by a proximal histidine residue. The remaining axial coordination site is available for binding a O_2 molecule (Figure $13.3.2A-C$).
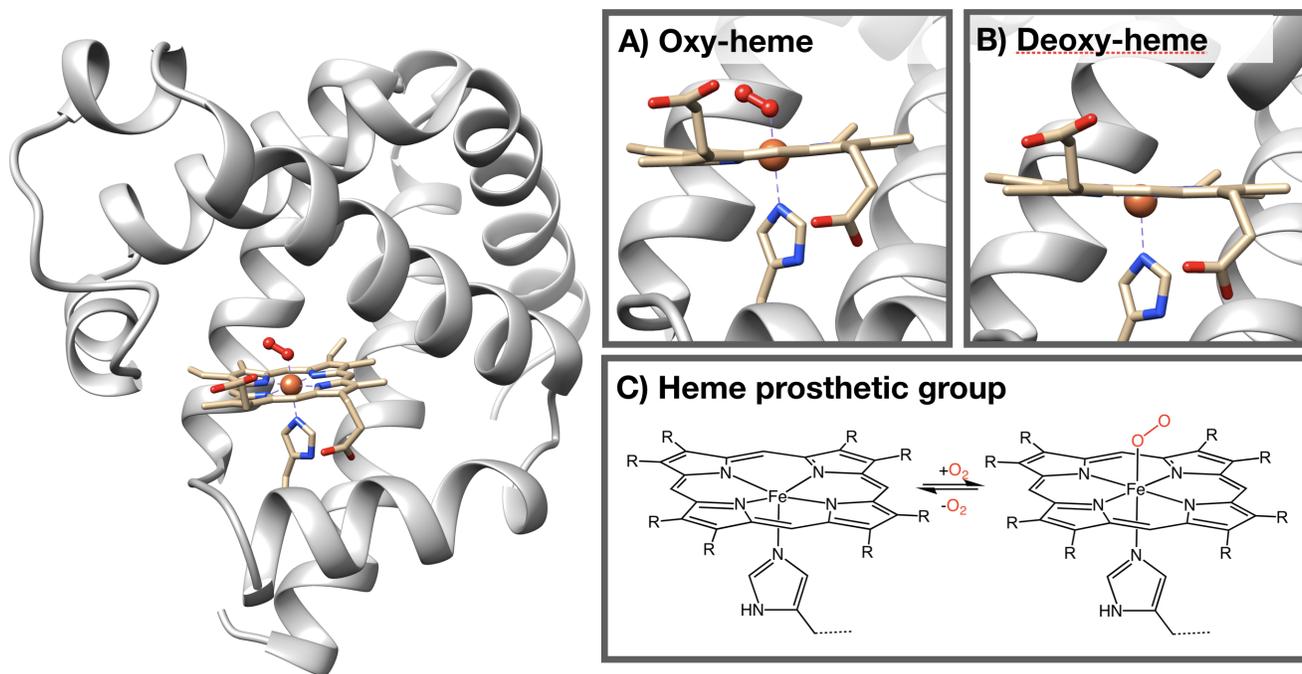
Figure 13.3.2: Structure of myoglobin. This is a ribbon depiction of mammalian myoglobin protein (grey, PDB code 1a6m). The heme group, shown in stick depiction (tan) with Fe shown as an orange sphere, bound to a O_2 molecule (red ball-and-stick). Inset A shows enlarged view of the O_2-bound heme. Inset B illustrates the de-oxygenated heme (PDB code 1a6n). The proximal histidine imidazole bound to Fe is shown toward the bottom of insets A and B. Inset C shows reversible binding of O_2 to the skeletal structure of the heme prosthetic group. This group consists of four central nitrogen donor atoms bound to iron (II) (attribution: Smokefoot, Mboxygenation, CC BY-SA 4.0). The porphyrin ring contains four pyrrole nitrogens bound to a ferrous (Fe(II)) ion center. There are six coordination sites in the Fe(II) ion; four are occupied by the pyrrole nitrogens, one is occupied by a proximal histidine, and the final site has the ability to reversibly bond to an O_2 molecule.

Reversible binding of oxygen

Now let's move on to the function of myoglobin: oxygen storage. Myoglobin can reversibly bind a dioxygen molecule to regulate the transportation of oxygen from red blood cells to mitochondria when skeletal muscles are metabolically active. This binding occurs at the iron center of the heme group. Although the 18-electron rule was a rule developed for organometallic complexes and chemistry, we can apply it here to explain the O_2-binding behavior of myoglobin. In deoxymyoglobin, the total valence electron count around Fe is 16 electrons (See Fig. 13.3.2, 10 electrons from ligands plus 6 electrons from Fe(II)). Under the 18-electron rule, a predictable step for a 16-electron species is ligand addition. The binding of O_2 to Fe(II) is a ligand addition reaction. Once O_2 binds to the Fe(II) in myoglobin, the new valence electron count around Fe is 18 electron. A predictable step for an 18-electron species is a ligand dissociation reaction, as is the reaction of O_2 dissociation from the Fe center. The binding and dissociation of O_2 makes sense based on the 18-electron rule.
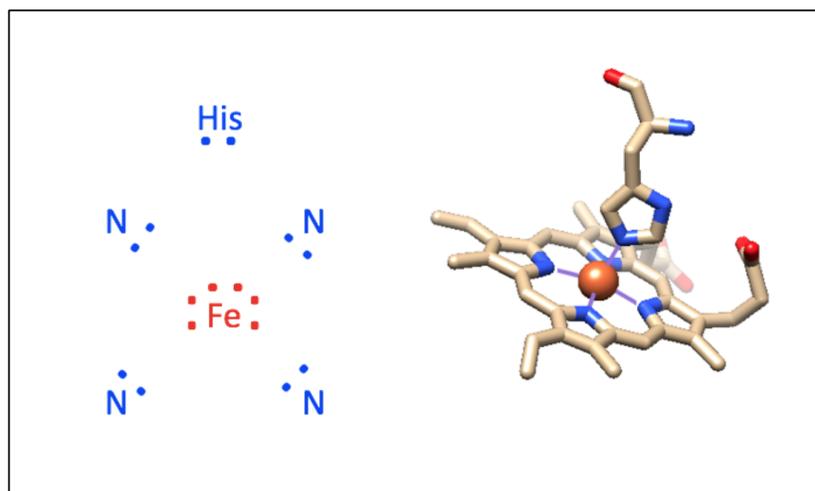
Figure 13.3.3: The electron count of deoxygenated heme Fe is 16 electrons. A total of 10 electrons are donated from the ligands (8 from pyrrole nitrogens of the porphyrin ring and 2 from the imidaziole nitrogen of the proximal histidine); 6 electrons are present from the 6 d electrons of Fe(II). Thus, the deoxy-heme complex is available for another ligand to bind; this case in the form of oxygen. The image was created using PDB code 1a6n and UCSF Chimera.

Iron oxidation state

The oxidation state of Fe in oxy-myoglobin is a highly debated topic because data is inconclusive and seemingly contradictory. Data from infrared (IR) spectroscopy and magnetic measurements have lead scientists to propose two different modes of oxygen binding to the iron ion. In one model (Figure 13.3.4 left), Fe(II) simply binds to O_2. A second model predicts that electrons are transfered from the Fe center to the dioxygen molecule to create Fe(III) bound to superoxide (Figure 13.3.4 right). Although many debate whether the iron, after binding to oxygen, remains iron (II) or becomes iron (III), it is difficult to assign an oxidation state to the bound iron or the oxygen. The actual molecular orbitals that result from the iron-oxygen interaction have both iron and O_2 character. It is therefore not quite correct to focus on the electrons "belong" to Fe or dioxygen. The two extremes, where one is that Fe becomes an iron superoxide by donating an electron from iron to the oxygen, and the other that Fe becomes an iron oxide by sharing the electrons are probably both incorrect. The molecular orbitals contain characteristics of both iron superoxide and iron oxide.

Fe(II)-dioxygen   **Fe(III)-superoxide**
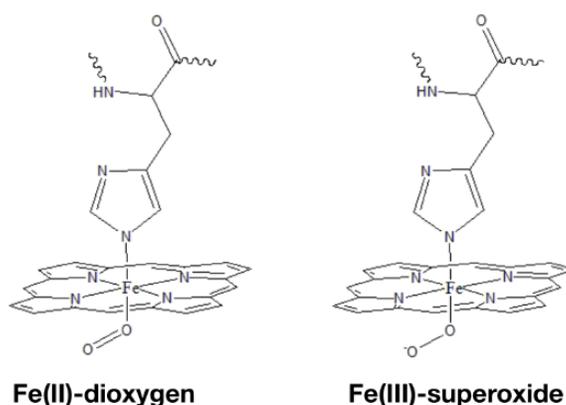
Figure 13.3.4: The binding of oxygen to the metal iron ion center of heme, occupying the 6th binding site of heme. **Left:** illustrates the iron oxide binding of oxygen where there is no transfer of electrons from the oxygen to the iron ion. **Right:** illustrates the formation of the superoxide from the transfer of electrons from oxygen to iron.

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Hemoglobin

Hemoglobin, a polypeptide found in red blood cells, allows dioxygen (O_2) to be transported within blood from the lungs to other tissues within the body. Hemoglobin is a polypeptide found in red blood cells. It allows for the transportation of O_2 from the lungs to other tissues within the body. This molecule also is also responsible for the color of blood.[1] Oxygenated blood is a bright red because hemoglobin absorbs green light of wavelengths 540-542 nm, and thus it results in a bright red colored solution.[2] Deoxygenated blood, however, is darker in color because it absorbs a more yellow/green color of wavelength 554 nm, and thus produces a darker color of red.

Hemoglobin is able to transport oxygen within the body due to its unique structure. Its structure consists of four globin subunits: two α and two β subunits. Each subunit contains a heme prosthetic group with an iron bound (Figure 1). Hemoglobin exists in high concentrations in the cytoplasm of red blood cells, so it needs to be very soluble in aqueous cytoplasm. This requirement is reflected in the protein's globular shape, and the fact that it is folded in such a way that hydrophilic residues are found on the surface of the protein exposed to water, while hydrophobic residues are found on the interior of the protein. This folding enables hemoglobin to have a stable fold in aqueous solution that also allows the protein to interact favorably with water and to be soluble in the water-filled cytoplasm of the cell.
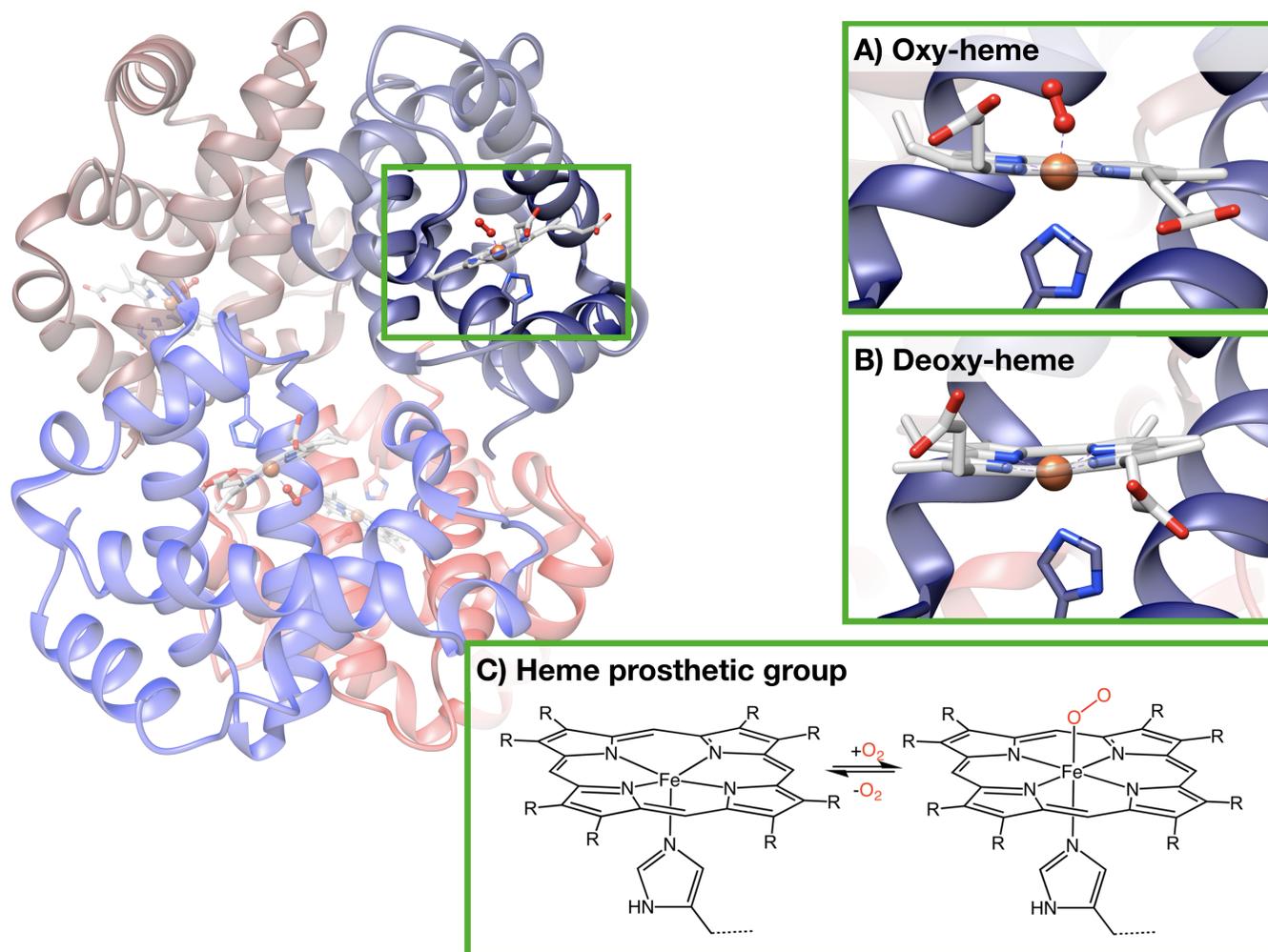
Figure 13.3.5: On the left, the ribbon diagram of hemoglobin is displayed. Hemoglobin consists of four subunits: two α (blue) and two β subunits (red). A heme group (stick depiction) is located within each subunit, and within each heme an inorganic iron ion (orange) is located. **Inset A:** Oxy-hemoglobin has dioxygen (red) bound to the iron core of each heme group. The iron of the oxygenated hemoglobin is pulled into the porphyrin plane. **Inset B:** Deoxy-hemoglobin (no oxygen bound). The iron (II) ion lies 0.4 Å outside of the porphyrin plane. **Inset C:** Reversible binding of O_2 to the skeletal structure of the heme prosthetic group. This group consists of four central nitrogen donor atoms bound to iron (II) (attribution: Smokefoot, Mboxygenation, CC BY-SA 4.0). Iron (II) has two axial binding sites and, in hemoglobin, one is occupied by an imidazole N of the proximal histidine. The second axial coordination site has the ability to reversibly bond to an oxygen atom.

Cooperative binding of O_2

An important feature of hemoglobin is a cooperative binding of oxygen to each subunit due to conformational changes upon oxygen binding to the heme iron. Hemoglobin exists in both the T-state (tense state) and the R-state (relaxed). The T-state has lower affinity for dioxygen due to the tilting of the proximal histidine and steric hindrance of the O_2 coordination site. Steric hindrance makes it difficult for oxygen molecule to enter the site and bind to Fe. When an oxygen binds to one subunit of hemoglobin, the iron shifts into the plane of the porphoryn ring, and tugs on the proximal histidine.[3,9] This causes the proximal histidine ring to be pulled toward the plane of the prosthetic group, decreasing the tilt of the histidine, causing a shift in the tertiary structure of that subunit, and displacing residues that were providing steric hiderance of the oxygen binding site. These conformational changes in one subunit cause similar changes to the tertiary structures of adjacent subunits, in turn decreasing steric and electrostatic constraints in those adjacent units. The result is adoption of the R-state and a subsequent increase in oxygen affinity to the other subunits.

When the iron ion is bound to only five coordination sites the iron (II) lies 0.4 Å outside of the porphyrin ring.[3,9,12] When the oxygen binds to the iron core the iron becomes smaller as it becomes low-spin because electrons are pulled closer to the Fe core or are transfered to the dioxygen molecule due to backbonding. The low spin iron and is able to fit in the plane of the porphyrin ring.[3,9]

The short video below illustrates conformational differences between fully oxygenated hemoglobin and deoxygenated hemoglobin. (Click here if the video does not load).
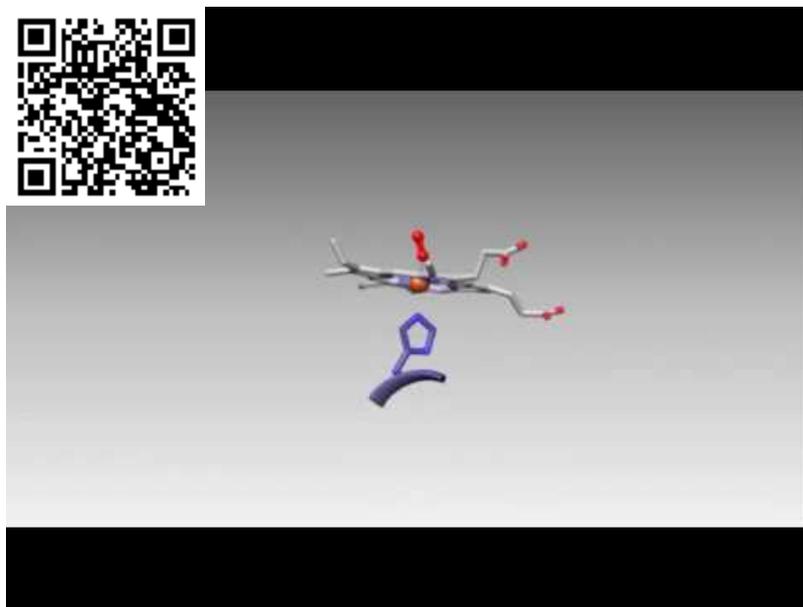
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13. Spin-Pairing Model of Dioxygen Binding and Its Application to Various Transition-Metal Systems as well as Hemoglobin Coopera

Hemocyanin

Hemocyanin is the oxygen transporter protein present in the hemolymph of arthropods and mollusks.[1] Hemolymph is the circulating fluid for these animals that is the invertebrate equivalent to vertebrate blood.[2] In hemocyanin, the active site contains two copper ions. Hemocyanin is a type-3 copper protein, meaning that it contains of two copper centers, each coordinated by three histidine residues, as seen in Figure 13.3.6 and Figure 13.3.7. When deoxygenated (see Figure 13.3.6, left), the copper exists in the colorless, reduced Cu(I) state. Molecular oxygen binds at the copper site and is reduced to peroxide (O_2^{2-}), Cu(I) is oxidized to Cu(II), and a blue complex forms. This change in the oxidation state of copper is responsible for the blue color of oxygenated invertebrate hemolymph. The oxygen bound as peroxide bridges the two copper centers together in μ-η²-η² fashion.[5]
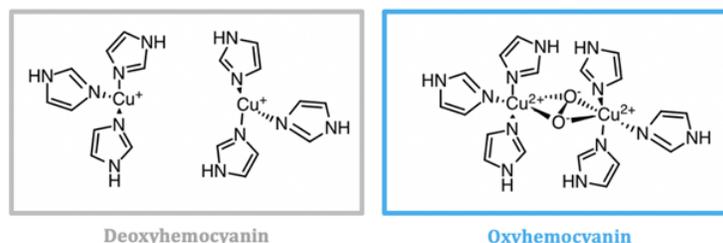
Figure 13.3.6: Chemical Structure of Oxygen Binding Site of Hemocyanin. (Left) The deoxygenated form of the hemocyanin binding site. Each copper ion is bound to three histidine residues, however there is no oxygen bound to copper. In this state, copper is colorless and exists in the form of Cu(I). (Right) The oxygenated form of the hemocyanin binding site. Each copper is coordinated with three histidine residues, and molecular oxygen binds at the center to the copper ion as a peroxide, O_2^{2-}, bridging the two copper centers together in a μ-η^2-η^2 fashion. Because copper is in the Cu(II) oxidation state, the oxygen-bound hemocyanin is a blue color.
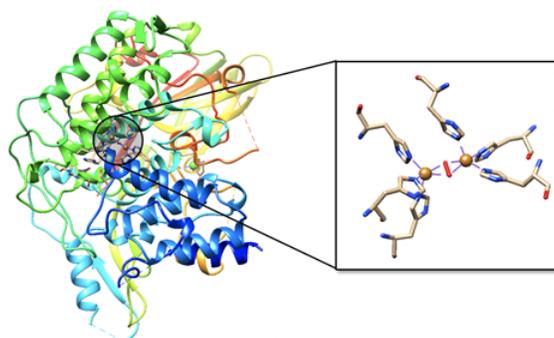
Figure 13.3.7:[8] (Left) *Ribbon Structure of Arthropod Hemocyanin (PDB code 1NOL).* Image depicting the structure of arthropod hemocyanin (specifically from the horseshoe crab). The thin ribbons represent regions of the molecule that are unstructured. (Right) *Binding Site of Oxygen to Copper on Hemocyanin.* In the inset, three histidine residues (blue) can be seen coordinating with a copper (gold). The copper binds a molecular oxygen (red).

Mollusk and arthropod hemocyanins are structurally very different, however the active sites both contain two coppers at the center coordinated to three histidines. Arthropod hemocyanins have kidney-shaped subunits, each with an oxygen binding site, arranged into hexamers. Mollusk hemocyanin, on the other hand, is composed of about 10 subunits forming a hollow cylinder. Recently, there has been research into different therapeutic applications of hemocyanins. Studies suggest these metalloproteins have applications as viral and bacterial antigens, immune-stimulants for treatment of some cancers such as melanoma, and carrier molecules for vaccines.[9]

> Note
>
>

Structure

As seen in Figure $13.3.6$ the active site of hemocyanin contains two copper ions, each bound to three histidine (His) residues. When the Cu(I) ions bind to oxygen they are oxidized to Cu(II). Cu(I) is a soft acid, Cu(II) is a borderline acid, and the imidazole ring of histidine is a borderline base. Because the copper ion alternates between a soft acid (Cu(I)) and a borderline acid (Cu(II)), it makes sense that it is bound to a borderline base. Borderline histidine is a better match for borderline Cu(II) than soft Cu(I), however His is still a better match for Cu(I) than a set of ligands that is harder. It is important to recognize, however, that there are other factors that affect metal ion selectivity, such as ionic size and ligand field stabilization energy, that must also be considered.

Hemocyanin exists in the hemolymph of invertebrates. Hemolymph is simply the invertebrate equivalent of blood that is present in vertebrates and is composed of water and organic and inorganic compounds. The inorganic metals present in hemolymph are sodium, chloride, calcium, magnesium, potassium, and manganese ions.[11,12] Na^+, Ca^{2+}, Mg^{2+}, K^+, and Mn^{2+} can all be seen as potential competitors for the copper at the active site due to the fact that they are all positively charged metal ions. They are all hard acids, indicating that they will likely not bind well with histidine, a borderline base. Based solely on HSAB, the histinines will prefer to bind to Cu(I)/Cu(II) because they are either soft/borderline acids. In addition to HSAB theory, it is also important to consider ionic size when determining if these competitors will bind in the site. These metal ions are larger than the copper ions, which may affect their ability to bind to the histidines in the pre-organized hemocyanin active site; the larger ions will not fit well into the pre-organized site, or if the site could accommodate the larger ion, it may change the protein structure to cause unfavorable steric interactions.

Kinetics and Thermodynamics

The stability of the complex is influenced by the energy of electrons in the d-orbital, as well as the geometry of the metal complexes. Because Cu(I) and Cu(II) have electrons at a higher energy, it makes them less stable and more likely to react. Additionally, Cu(II) is coordinated in a distorted tetrahedral geometry, but based on LFT, the square planar geometry is preferred. If Cu(II) was in the preferred geometry it would be more stable, and therefore reduction to Cu(I) and release of oxygen would be less favorable. Because Cu(II) is not fully stable in this environment, it allows for the cycling between the +1 and +2 oxidation states, and the transport of oxygen.

Lability is a desirable property for oxygen transport and storage proteins. The coordinated oxygen must be able to bind and unbind quickly and reversibly (carbon monoxide and cyanide gas are toxic because they will bind irreversibly with hemoglobin and displace oxygen). Cu(I) is a d^{10} metal and Cu(II) is a d^9 metal, so their higher-energy antibonding t_2 orbitals are occupied by electrons. When electrons occupy this higher-energy set of d-orbitals, the complex has a smaller CFSE and is more kinetically labile (has fast ligand substitutions reactions).

Redox Chemistry

The copper ions at the active site of hemocyanin cycle between Cu(I) and Cu(II) depending on whether or not oxygen is bound. Cu(I) is oxidized by oxygen when O_2 coordinates with the metal. For the copper oxidation half reaction, the reduction potential at pH = 7 is 0.153 V.[19] The one electron reduction of O_2 is difficult because it is spin forbidden.[20] The reduction potential of this reaction at pH = 7 is -0.33 V, which would make E_{rxn} for the one electron redox reaction -0.48 V, a non-spontaneous reaction. The two electron oxidation of O_2 to form H_2O_2 is much more favorable; the reduction potential of this reaction at pH = 7 is 0.281 V. This makes the overall which makes the overall E_{rxn} 0.128 V, which makes the binding of oxygen to hemocyanin spontaneous (Figure $13.3.8$).

$$O_{2\,(g)} + 2H^+ + 2e^- \rightleftharpoons H_2O_{2\,(aq)} \qquad E_{red}^{o\prime} = 0.281\ V$$

$$2Cu^+_{(aq)} \rightleftharpoons 2Cu^{2+}_{(aq)} + 2e^- \qquad E_{ox}^{o\prime} = -0.153\ V$$

$$2Cu^+_{(aq)} + O_{2\,(g)} \rightleftharpoons Cu^{2+}_{(aq)} + H_2O_{2\,(aq)} \qquad E_{rxn}^{o\prime} = 0.128\ V$$

$$E_{rxn}^{o\prime} = E_{red}^{o\prime} + E_{ox}^{o\prime}$$

$$E_{rxn}^{o\prime} = 0.281\ V - 0.153\ V$$

$$E_{rxn}^{o\prime} = 0.128\ V$$
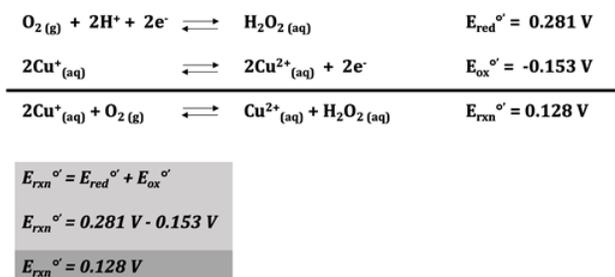
Figure 13.3.8[19] *Oxidation-Reduction Reactions for Hemocyanin.* The reduction half reaction can be seen on the first line. There are two electrons and two hydrogen ions involved in the reduction of oxygen, and the reduction potential of this reaction is 0.281 V at pH 7. On the following line, the oxidation half reaction can be seen where Cu(I) is oxidized to Cu(II) with an oxidation potential of -0.153 V at pH 7. The overall reaction appears on the third line. At pH 7, the redox potential of this reaction is 0.128 V.

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13.4: Biological Metal Storage

Iron

Iron is widely used in a wide number of biological applications. Ferrous (Fe^{2+}) ion appears to have been the environmentally stable form during prebiotic times. The combination of the reactivity of ferrous ion and the relatively large amounts of iron used by cells may have necessitated the storage of ferrous ion; recent results suggest that ferrous ion may be stabilized inside ferritin long enough to be used in some types of cells. The ability of primitive organisms photosynthetically oxidize H_2O into dioxygen, probably produced the worst case of environmental pollution in terrestrial history. As a result, the composition of the atmosphere, the course of biological evolution, and the oxidation state of environmental iron all changed profoundly. Paleontologists and meteorologists estimate that there was a lag of about 200 - 300 million years between the first dioxygen production and the appearance of significant dioxygen concentrations in the atmosphere, because the dioxygen produced at first was consumed by the oxidation of ferrous ions in the oceans. The transition in the atmosphere, which occurred about 2.5 billion years ago, caused the bioavailability of iron to plummet and the need for iron storage to increase. Comparison of the solubility of Fe^{3+} at physiological conditions (about 10^{-18} M) to the iron content of cells (equivalent to 10^{-5} to 10^{-8} M) emphasizes the difficulty of acquiring sufficient iron.

Iron is stored mainly in the ferritins, a family of proteins composed of a protein coat and an iron core of hydrous ferric oxide [$Fe_2O_3(H_2O)_n$] with various amounts of phosphate.[6,7] As many as 4,500 iron atoms can be reversibly stored inside the protein coat in a complex that is soluble; iron concentrations equivalent to 0.25 M [about 10^{16}-fold more concentrated than Fe(III) ions] can be easily achieved *in vitro*. Ferritin is found in animals, plants, and even in bacteria; the role of the stored iron varies, and includes intracellular use for Fe-proteins or mineralization, long-term iron storage for other cells, and detoxification of excess iron. Iron regulates the synthesis of ferritin, with large amounts of ferritin associated with iron excess, small or undetectable amounts associated with iron deficiency.

Ferritin

Despite the importance of iron for life, excess iron can be toxic.[3] Unregulated free iron can catalyze the production of harmful reactive oxygen species (ROS) and free radicals, most commonly via Fenton chemistry. The Fenton reaction (below) is the reaction between iron(II) ions and hydrogen peroxide to produce the extremely reactive and harmful hydroxyl radical (**˙OH).**[1] ROS are generally strong oxidizing agents and can cause permanent cell damage, organ failure, and death

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH$$

Structurally, ferritin is a hollow cage and the sequestered iron is stored as an iron(III) mineral within the protein shell (Figure 13.4.1).[2,3]
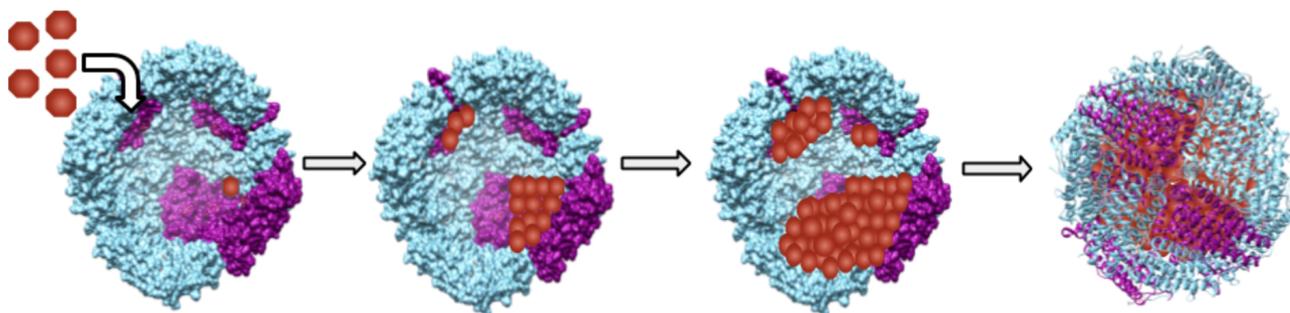
Figure 13.4.1: A cartoon diagram of sequestration of iron, which has been crystallized and is stored as an iron/oxy mineral in the hollow cage of ferritin. From left to right, the diagram depicts the cross section of the ferritin protein cage and the growing nucleation in the hollow center of ferritin. Each red shape represents some crystalline, mineral combination of iron, oxygen, and hydrogen (FeOOH core). Nucleation begins on the purple surfaces of ferritin, which will be discussed in detail later, but is otherwise random. The final image in the diagram on the far right is the spherical ribbon structure of full iron-containing ferritin protein with the cartoon depiction of iron/oxy mineral (red shapes) within the center. While this diagram depicts ferritin being filled to capacity with iron, in reality, ferritin can be filled as much or as little with iron, as needed. Thus, this figure can also be interpreted as different ferritin proteins in environments of different iron concentrations and so storing different amounts of iron.

Ferritin is made of subunits. Each subunit has four polypeptide α-helices or spirals.[2] Structures of ferritin differ based on the organism which produces it. Most ferritin is made of 24 of these subunits.[6] Human ferritin is a 24-subunit, 480 kDa, 12 nm globular protein with a hollow center cavity (cavity diameter of 8 nm).[2] One 24-subunit ferritin protein can store up to 4500 iron ions in its hollow center.[2] Ferritin is a very good space-saving model for the cell because of its high iron to protein ratio (4500 iron ions/8 nm cavity).[2,9] This iron to protein ratio is 200 times that of hemoglobin.[9] Up to 24% of ferritin's weight could be stored iron ions. Meanwhile, bacterial ferritin can be either a 12- or 24-subunit globular protein.[6] However, it is thought that the 12-subunit ferritin's may play an additional role in protecting DNA from oxidative damage, while the 24-subunit bacterial ferritin may control bacterial iron metabolism.[3]

The subunits of human ferritin are classified as the heavy subunit or "H-chain" and the light subunit or "L-chain" (Figure 13.4.2).[6] The two subunits, however, are not extremely different in molecular weight or amino acid sequence. The H-chain is made of 178 amino acids with a molecular weight of 21 kDa and the L-chain is made 171 amino acids and weighs 18 kDa.[4] The two types of subunits have ~53% protein sequence identity.[4] The designations of heavy and light are actually a modern recasting of designations that originally reflected the organs from which the two forms were isolated, "H" for heart and "L" for liver.[8]

The two types of subunits combine in different ratios to form the 24-subunit protein shell in humans (Figure 13.4.2).[6] This ratio is dependent on the tissue where the ferritin is synthesized.[6] The H subunit is responsible for catalyzing the oxidation of iron(II).[8] The L subunit hosts the site of nucleation and storage of iron.[8] The ratio of H:L will be higher in tissues where iron oxidation activity is high and iron detoxification is needed, such as the heart or the brain.[1,4] Tissues, like those in the spleen, are used more for storage and will have a lower H:L ratio. The human liver produces ferritin that is 50% H and 50% L.

L-chain   **H-chain**   **Ferritin model**
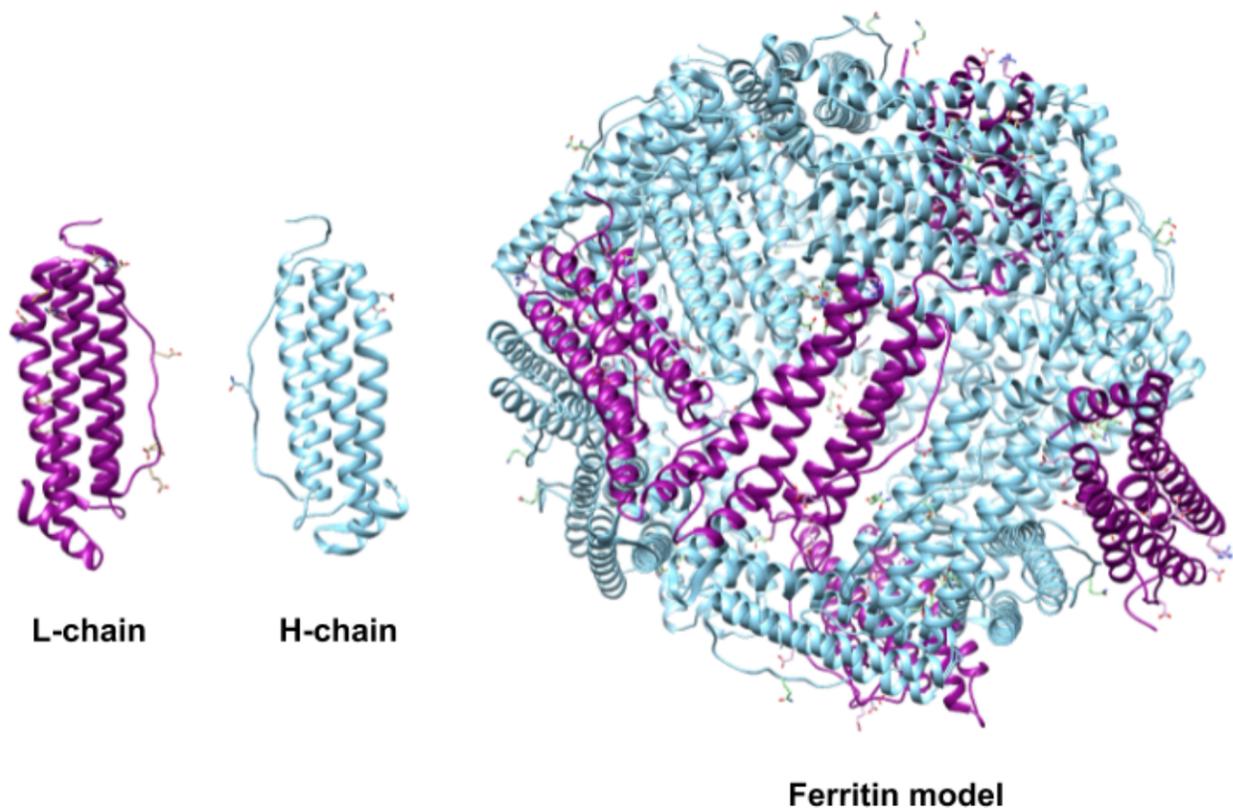
Figure 13.4.2: Light (L) (PDB 2FFX) and heavy (H) (PDB 2FHA) human ferritin subunit chains combine to form the human ferritin shell in specific ratios. The H:L ratio is dependent on the tissue where the protein is synthesized. The model seen here was created from the crystal structures of individual subunits, not a biologically obtained structure. However, it is approximately 30% L-type subunit and 70% H-type subunit and would be of a similar ratio to the ferritin found in the brain.[1]

Selectivity for Iron

Fe^{2+} ions are brought to ferritin for storage by the transport protein transferrin. The ions are believed to enter through one of the eight symmetric 3-fold channels or one of the six symmetric 4-fold channels formed by the subunits in the ferritin structure highlighted in Figure $13.4.3$[6]
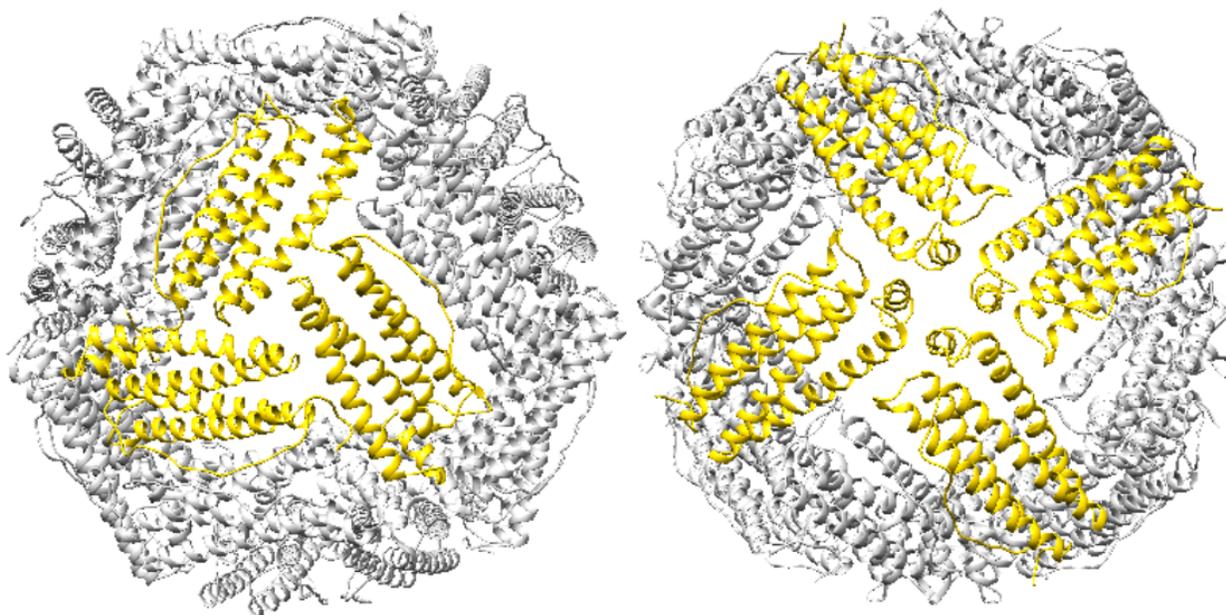
Figure 13.4.3. Symmetric channels of entry and exit in Ferritin (PDB: 1FHA). The 3-fold channel on the left appears eight times in the 24 subunit ferritin protein. The 3-fold channel is formed by three subunits. The 4-fold channel on the right appears six times in the 24 subunit ferritin protein. The 4-fold channel is formed by four subunits.

The 3-fold channels are lined with the polar side chains aspartate and glutamate and make the channel hydrophilic.[2] The hydrophilicity of the channel allows for the transport of water, metal cations, and hydrophilic molecules of an appropriate size into and and out of the ferritin center.[4] Most studies indicate that the 3-fold channel is the main channel for Fe^{2+} ions both into and out of the cell.[1,3] The 4-fold channels are lined with the non-polar side chain leucine and make the channel hydrophobic. It is widely thought that the 4-fold channels are involved with the diffusion of oxygen and hydrogen peroxide into and out of the ferritin center.[1]

Iron(II) ions are oxidized at the "ferroxidase site" on the H-chain subunits (Figure 13.4.4). After conversion to Fe^{3+}, the iron is stored as a crystalline iron/oxy mineral.[2] The mineral accumulates on the L-chain (Figure 13.4.5).[8]
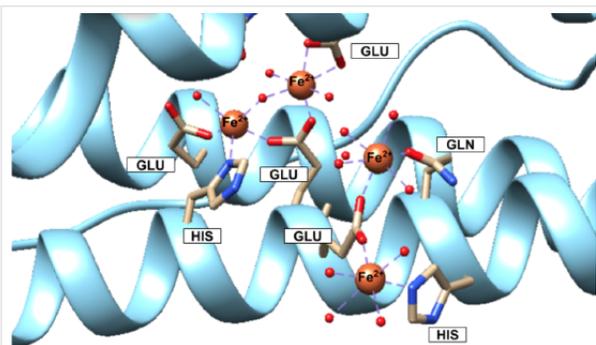
Figure 13.4.4: Human Ferritin H-chain (PDB 4YKH). Fe2+ ions are both shown traveling on their way to the ferroxidase site and at the ferroxidase site, to be covered in detail later. Fe2+ ions can be seen binding to water molecules, oxidizing agents and residues glutamic acid (Glu or GLU), glutamine (Gln or GLN), and histidine (His or HIS). The smaller red balls connecting to the Fe2+ ions via a purple dashed line are the oxidizing agents—oxygen molecules, hydrogen peroxide, or water molecules.
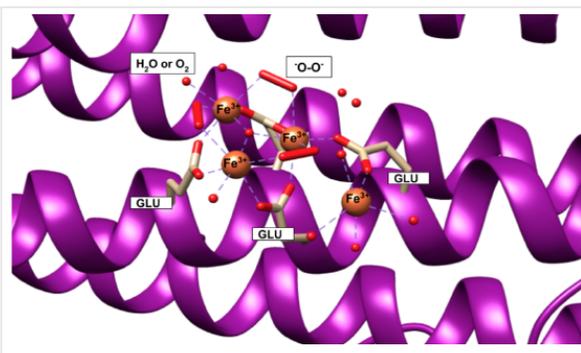
Figure 13.4.5: Human Ferritin L-chain (PDB 5LG8). Fe3+ ions can be seen binding to water and oxygen molecules (small red balls), peroxo groups (long red cylinders), and residues of glutamic acid (Glu or GLU) from the L-chain. Fe3+ is stored as an iron/oxy mineral on the L-chain. This is the beginning of nucleation within the ferritin cavity.

Figures 4 and 5 show iron(II) at the ferroxidase site and iron/oxy mineral at the nucleation site, according to the available crystal structures. The structure of the entire iron mineral core, however, is actually inconsistent throughout the whole mineral and differs even between identical ferritin shells. Traditionally, it was believed that the iron(III)/oxy mineral that makes up the core was similar to ferrihydrite and ideally structured as 20% tetrahedral and 80% octahedral; however, as more evidence has become available this model has been replaced by a "polyphasic" or heterogeneous model of the iron core that is thought to be more accurate.[2,4] According to the polyphasic model, the mineral structure is heterogeneous in its chemical content and geometric structure.[4] X-ray absorption fine structure (EXAFS) studies concluded that the iron core of ferritin was made of iron ions that are surrounded by six or seven oxygen atoms, surrounded by another shell of iron ions.[2] This inconsistency leads to the conclusion that the mineral is a heterogeneous, hydrated iron(III)/oxy.[3] In other words, the iron core itself is not packed regularly or in a pattern within ferritin.[6]

Selectivity of iron(II) by ferritin can be explained through hard-soft acid base (HSAB) theory. Ferritin binds an Fe^{2+} ion for oxidation. Fe^{2+} is categorized as a borderline acid. The binding sites on the H-chain are glutamic acid (Glu), histidine (His), and glutamine (Gln) residues (Figure 13.4.4).[6] Glu and Gln are categorized as hard bases, while His is categorized as borderline base. The oxidizing agents—oxygen molecules, hydrogen peroxide, or water molecules all have hard character. Fe^{2+} as a borderline acid binds well with the binding site of mixed hard and borderline character. The selection of Fe^{2+} in ferritin is further supported by experimental work where metals like zinc (which also exists in the body) were also shown to have binding abilities to ferritin.[5] But, zinc, although it is also borderline, has softer character than Fe^{2+} and so would not be as stable or favorable with the hard Glu and Gln ligands.[10]

Iron Mineralization

Iron(II) is oxidized at the ferroxidase site on the H-chain (sites A and B) by some oxidizing agent, most probably O_2 and H_2O_2.[1] Three reactions/models for Fe^{2+} oxidation and mineralization have been observed. There is a ferroxidation reaction or protein catalysis model (Reactions \PageIndex {1} -\PageIndex {4}), a mineralization reaction or crystal growth model (Reaction

\PageIndex {5}), and a detoxification reaction of Fe^{2+} + H_2O_2 (Reaction \PageIndex {6}).[1] The ferroxidation reaction occurs at the ferroxidase site on the H-chain of ferritin. The ferroxidation reaction for the protein catalysis model of ferritin oxidation can be written as:

$$[2Fe^{2+} + O_2 + 4H_2O \rightarrow [Fe^{3+}-O-O-Fe^{3+}]^{2+} \tag{13.4.1}$$

$$Fe^{3+}-O-O-Fe^{3+}]^{2+}] \rightarrow [Fe_2O-(OH)_2]^{2+} \tag{13.4.2}$$

$$[Fe_2O-(OH)_2]^{2+} \rightarrow 2FeOOH_{core} + H_2O_2 + 4H^+ \tag{13.4.3}$$

$$\text{Net: } 2Fe^{2+} + O_2 + 4H_2O \rightarrow 2FeOOH_{core} + H_2O_2 + 4H^+ \tag{13.4.4}$$
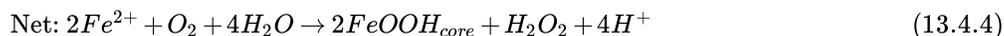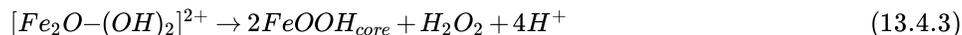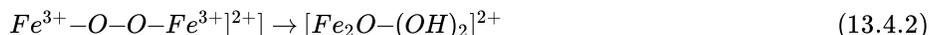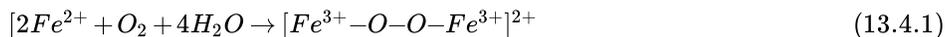
The net mineralization reaction for the crystal growth model of ferritin oxidation is written as:

$$4Fe^{2+} + O_2 + 6H_2O \rightarrow 4FeOOH_{core} + 8H^+ \tag{13.4.5}$$

The most recently identified of the oxidation and mineralization reactions, the Fe^{2+} + H_2O_2 detoxification reaction is written as:

2 Fe^{2+} + H_2O_2 + 2 H_2O → 2 $FeOOH_{core}$ + 4 H^+ (**3.**).[1]
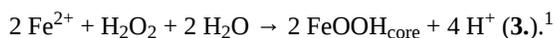
Iron Release

When cells require iron, for enzyme synthesis, after blood loss, or during embryonic development, the iron stored in ferritin must be released rapidly, on demand, and under control.[8] Although, as with many aspects of ferritin function, the mechanism of iron release to the cell from ferritin is unknown. What is known inherently about the process is that over its course it must essentially reverse mineralization: the iron(III)/oxy mineral must be dissolved from its solid state to aqueous ions and the iron(III) ions must be reduced to iron(II).

Proposed models for ferritin iron release include (1) an equilibrium between the iron stored in ferritin and the iron in the cytoplasm of the cell, (2) ferritin protein degradation, (3) spontaneous, direct dissolution of iron(III) from the mineral core from scavenging by iron(III) binding proteins, and (4) the reduction of the iron(III) mineral which is then complexed iron(II) by a chelating agent and transported out of ferritin.[4,12] The last model (4) lacks confirmation, yet is considered by many to be the physiological mechanism. This model is the most efficient method and the presence of reducing agents under physiological conditions.[4]

Except the second model (2), the physiological relevance of all above models is still to be seen.[12] The ferritin degradation model (2) is the only mechanism to have been observed under physiological conditions. However, since this model would require iron release to be dependent of the turnover and synthesis of ferritin, another model is suspected to be necessary.[12]

However iron is released from ferritin, studies indicate that the physical exit of the iron from ferritin takes place via the 3-fold channels. One proposal for exit based on observations in bacterial ferritin is the localized folding/unfolding of ferritin.[4] The ferritin channels can be unfolded without affecting the overall function or structure of the protein. Unfolding the channels and thus, widening the opening, would allow for quick release of demineralized iron. The channels become highly disordered when this occurs to the effect that they do not appear in crystal structures.[8]

Much remains to be determined about human ferritin. Other functions of ferritin in the body, and the mechanisms for how Fe^{2+} enters and binds to ferritin, how Fe^{2+} is oxidized to Fe^{3+} for storage, and how iron is released remain undetermined, among others, are thought to be non-universal—even within the same organism.[3,6]

While much of the chemistry behind ferritin is, as of now, unexplained, ferritin is still an important protein for all life. Wherever iron is noted as an essential nutrient, ferritin must also be present for management and storage. The elucidation of ferritin can lead to advancements in iron metabolism and neurological disorders and new uses of ferritin chemistry in nanochemistry and catalytic industrial applications.[3,4]

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Zinc, Copper, Vanadium, Chromium, Molybdenum, Cobalt, Nickel, and Manganese

Ions of nonferrous transition metals require a much less complex biological storage system, because the solubilities are much higher ($\geq 10^{-8}$ M) than those for Fe^{3+}. As a result, the storage of nonferrous transition metals is less obvious, and information is more limited. In addition, investigations are more difficult than for iron, because the amounts in biological systems are so small. Essentially nothing is known yet about the storage of vanadium, chromium, molybdenum, cobalt, nickel, and manganese, with the possible exception of accumulations of vanadium in the blood cells of tunicates.

Zinc and copper, which are used in the highest concentrations of any of the non-ferrous transition metals, are specifically bound by the protein metallothionein. (see Figure 13.4.8). Like the ferritins, the metallothioneins are a family of proteins, widespread in nature and regulated by the metals they bind. In contrast to ferritin, the amounts of metal stored in metallothioneins are smaller (up to twelve atoms per molecule) and the amount of protein in cells is less. Because the cellular concentrations of the metallothioneins are relatively low and the amount of metal needed is relatively small, it has been difficult to study the biological fate of copper and zinc in living organisms, and to discover the natural role of metallothioneins. However, the regulation of metallothionein synthesis by metals, hormones, and growth factors attests to the biological importance of the proteins. The unusual metal environments of metallothioneins have attracted the attention of bioinorganic chemists.

Metallothioneins, especially in higher animals, are small proteins rich in cysteine (20 per molecule) and devoid of the aromatic amino acids phenylalanine and tyrosine. The cysteine residues are distributed throughout the peptide chain. However, in the native form of the protein, the peptide chains fold to produce two clusters of -SH, which bind either three or four atoms of zinc, cadmium, cobalt, mercury, lead, or nickel. Copper binding is distinct from zinc, with 12 sites per molecule.

In summary, iron is stored in iron cores of a complicated protein. Ferritin, composed of a hollow protein coat, iron-protein interface, and an inorganic core, overcomes the problems of redox and hydrolysis by directing the formation of the quasi-stable mineral hydrous ferric oxide inside the protein coat. The outer surface of the protein is generally hydrophilic, making the complex highly soluble; equivalent concentrations of iron are ≤ 0.25 M. By contrast to iron, storage of zinc, copper, chromium, manganese, vanadium, and molybdenum is relatively simple, because solubility is high and abundance is lower. Little is known about the molecules that store these metals, with the possible exception of metallothionein, which binds small clusters of zinc or copper.
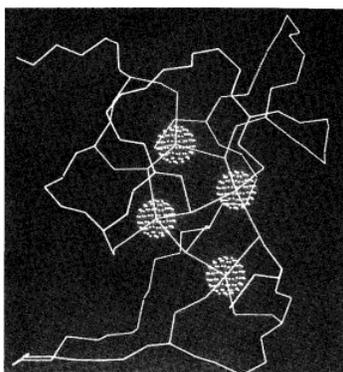
Figure 13.4.8: - The three-dimensional structure of the a domain from rat cd_7 metallothionein-2, determined by NMR in solution, based on data in Reference 36b. The four metal atoms, bonded to the sulfur of cysteine side chains, are indicated as spherical collections of small dots. A recent description of the structure of the cd_5Zn_2 protein, determined from x-ray diffraction of crystals, agrees with the structure determined by NMR.

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13.5: Zinc as Lewis Acid and Template

Introduction

Unlike most other biologically important metals, zinc is not redox active and does not directly participate in catalytic reaction. In biological systems zinc is primarily found as Zn^{2+}, which is a d^{10} ion, making it unfavorable to either oxidize or reduce. Zinc ions do play important biochemical roles. They can act as Lewis acids, to indirectly catalyse reactions such as the hydration of carbon dioxide in carbonic anhydrase. They can also act as templates or scaffolds for protein tertiary structure.

Zinc in Carbonic Anhydrase

Chemical Reaction

Carbon-dioxide (CO_2) hydration and its mechanism in living systems are of fundamental importance for bioinorganic chemistry. In 1932 the existence of an enzyme catalyzing CO_2 hydration in red blood cells, carbonic anhydrase, was established. In 1939 the enzyme was recognized to contain zinc. Because CO_2 is both the starting point for photosynthesis and the endpoint of substrate oxidation, carbonic anhydrases are now known to be ubiquitous, occurring in animals, plants, bacteria, and fungi. Carbonic anhydrase is a classic example of a hydrolytic enzyme, one that catalyzes addition or removal of water to a substrate molecule. More specifically, it catalyzes the reversible conversion of carbon dioxide (CO_2) to bicarbonate (HCO_3^-).

Carbonic Anhydrase Catalysis of Carbon Dioxide Hydration

$$CO_2 \;+\; H_2O \;\xrightleftharpoons{\text{Carbonic Anhydrase}}\; HCO_3^- \;+\; H+$$
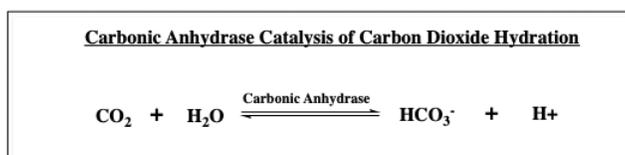
Figure 13.5.1: Reaction catalysed by carbonic anhydrase enzymes.

Although hydration of CO_2 is spontaneous in water at pH 7, the reaction is kinetically slow ($k = 10^{-1}$ s^{-1}), too slow to convert all CO_2 produced in respiration. Only above pH 9 does the uncatalyzed reaction become fast, due to direct attack of OH^-, which is a much better nucleophile than H_2O ($k = 10^4$ M^{-1} s^{-1}, in the presence of OH^-). Figure 13.5.2 compares nucleophilic attack of water versus hydroxide (OH-) on CO_2.
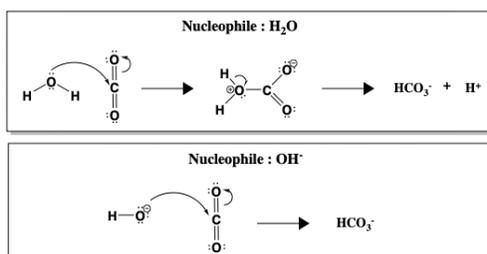
Figure 13.5.2: Nucleophilic attack on carbon in carbon dioxide (CO_2) in the formation of bicarbonate (HCO_3^-). In the top panel, H_2O is the nucleophile. The bottom panel shows the reaction with hydroxide (OH^-) as the nucleophile. Since the OH^- is a stronger nucleophile, HCO_3^- formation is faster when OH^- is the nucleophile.

Between H_2O and OH^-, formation of HCO_3^- occurs faster when OH^- is the nucleophile. A faster reaction at higher pH, when more OH^- ions are present, suggests OH^- is involved in the rate determining step. However, realistically, the pH of human blood cannot be changed to speed up hydration of CO_2. Instead, humans use carbonic anhydrase to catalyse the reaction. When carbonic anhydrase is present, the reaction is sped up to a rate of $k = 10^6$ s^{-1}.

The ubiquity of carbonic anhydrase in different organisms reflects the importance of these enzymes in sustaining life. The speed of catalyzed CO_2 hydration is essential to meet the needs of living cells. Some physiological carbonic anhydrase functions include pH regulation, electrolyte secretion, ion transport, and CO_2 homeostasis. In the digestive tract, carbonic anhydrases plays a role in the secretion of acid and keep saliva neutral by modulating pH. Among these functions, CA most notably plays a role in transport of CO_2 and HCO_3^- related to respiration. With low blood solubility, CO_2 must be converted to a more soluble form, HCO_3^-, for transport throughout the body. Bicarbonate ions eventually reach the lungs, get converted back to CO_2, and exit the body through exhalation.

Medical research revolving around carbonic anhydrase focuses on the Zn-containing active site as a therapeutic target for various disease treatments; both carbonic anhydrase inhibitors and activators are incorporated in drug design. Carbonic anhydrase inhibitors are used as treatment for epilepsy, ulcers, cancer, obesity, and other neurological disorders. In the eye, carbonic anhydrase produces hydrogen ions that maintain optic pressure. However, too much pressure in the eye can damage the optic nerve and cause glaucoma. Carbonic anhydrase activity can create a concentration gradient that drives the transport of water to the optical nerve. When too much water is around the optical nerve, pressure around the nerve increases causing damage. Inhibition of carbonic anhydrase has become a key treatment of glaucoma.

Role of Zinc

The zinc ion is bound to the protein via three links to separate histidine residues in the chain, shown in pink in Figure $13.5.3$ The zinc is also attached to a hydroxide ion shown in the picture using red for the oxygen and white for the hydrogen.
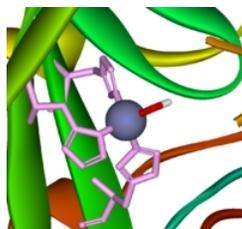
Figure 13.5.3: Zinc active site of carbonic anhydrase showing the coordination of zinc (purple sphere) by three hisiadine residues (pink) and one hydroxide ion.

If you look at the model of the arrangement around the zinc ion in the picture above the arrangement of the four groups around the zinc is approximately tetrahedral.

How does this catalyse the reaction between carbon dioxide and water?

A carbon dioxide molecule is held by a nearby part of the active site so that one of the lone pairs on the oxygen is orientated towards the carbon atom of the carbon dioxide molecule. Binding the carbon dioxide in the enzyme also increases the existing polarity of the carbon-oxygen bonds.
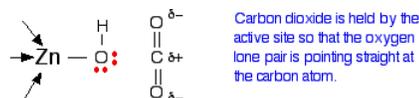
If you have done any work on organic reaction mechanisms at all, then it is pretty obvious what is going to happen. The lone pair forms a bond with the carbon atom and part of one of the carbon-oxygen bonds breaks and leaves the oxygen atom with a negative charge on it. This results in a hydrogen carbonate ion coordinated to the zinc center.
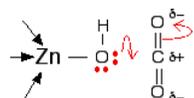
The next step in the reaction is for the hydrogen carbonate to leave and be replaced with a water molecule from the cell solution.
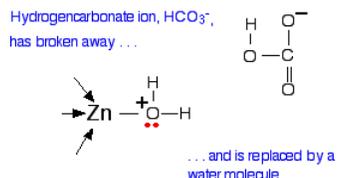
All that now needs to happen to get the catalyst back to where it started is for the water to lose a hydrogen ion. This is transferred away from the zinc center and eventually out of the active site completely through the network of ordered, hydrogen bonded water molecules shown in Figure 13.5.4   The carbonic anhydrase enzyme can do this sequence of reactions about a million times a second.
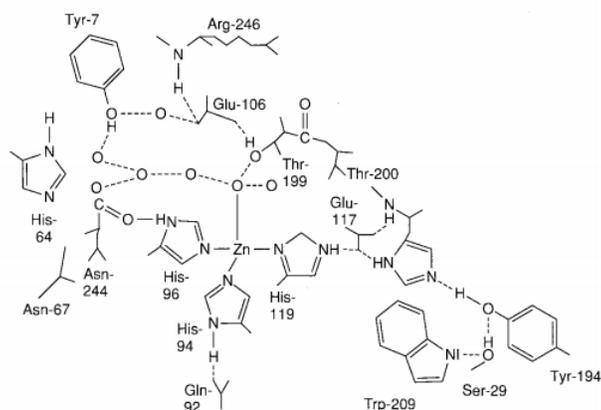
Figure 13.5.4: Schematic representation of the active site of human carbonic anhydrase II. Hydrogen bonds (---) and ordered water molecules (o) are indicated.

Zinc as a Structural Template

Many proteins use Zn^{2+} as a structural scaffold for protein folding. These proteins employ "zinc finger" domains that bind to Zn through combinations of cysteine (Cys) and Histidine (His) side chains. Zinc binding to these domains stabilizes a specific protein fold that is critical to the protein's function. Over half of transcription factors have zinc finger domains that allow the proteins to recognize and bind to DNA. Many other proteins also have zinc-finger domains and these domains are important for a variety of functions including DNA-binding, RNA-binding, protein-protein interactions, and catalysis.

The human glioblastoma protein (GLI) family is a class of transcription factors that demonstrate sequence-specific DNA binding through "classic" Cys2His2 Zn-binding motifs. These proteins are essential during embryonic development. Dysfunction of these proteins are linked closely to glioblastoma and other aggressive cancers. The zinc finger domain of GLI1 is shown in this image (PDB 2gli),[2] where the protein surface is highlighted in yellow. GLI1 possesses five Cys2His2 zinc finger domains. When Zn is not bound to the protein, it does not have the appropriate structure to bind to recognize DNA.

Zn stabilizes a protein fold that is complimentary to DNA surface.

Each Zn(II) ion coordinated by Cys2His2 "Zn-finger" domain

The position that is frequently mutated in Skin Cutaneous Melanomas is highlighted in green.
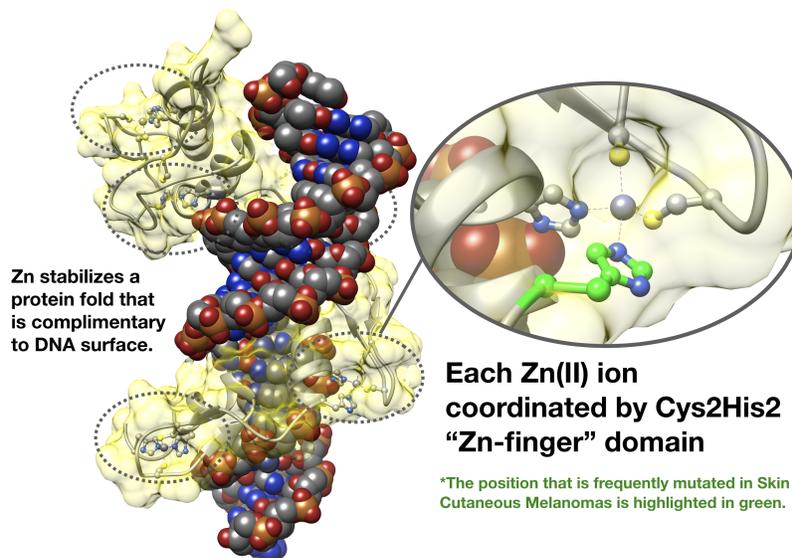
PDB 2gli, human glioblastoma protein in complex with DNA.

Figure 13.5.5: The zinc finger domain of human glioblastoma protein GLI1 complexed with DNA. Inset shows the coordination of Zn^{2+} in the " zinc finger" domain.

The size and structure of the Zn^{2+} ion is critical to provide the correct protein fold for DNA binding. Thus, zinc fingers must bind specifically to Zn (as opposed to other biologically available metal ions). The zinc finger domains use principles of inorganic chemistry to control metal ion selectivity. While other metal ions, like Co^{2+}, Ni^{2+}, Fe^{2+}, and Mn^{2+}, can bind in the zinc finger sites, Zn^{2+} binds 1,000 to 100,000 times more strongly than any of these other metals.

Exercise 13.5.1

Apply HSAB theory to explain why there is such a strong selectivity for Zn^{2+} binding in a zinc finger site as opposed to other biologically available metals, including Co^{2+}, Ni^{2+}, Fe^{2+}, and Mn^{2+}.

Answer

The zinc binding site contains two borderline histadine ligands and two soft cystine ligands. The Zn^{2+} is a softer borderline Lewis acid compared to other biologically available metal ions, especially Fe^{2+}. This is because the size of transition metal cations don't vary much across the period, giving them all similar size to charge ratios and Zn^{2+} has the highest number of valence electrons, making it the most polarizable. Because the active site has two soft base donors and two borderline base donors, softer metals will preferentially bind in the active site.

Exercise 13.5.2

Cadmium (Cd^{2+}) and lead (Pb^{2+}) are toxic metal ions that bind more strongly than Zn^{2+} to zinc binding sites in proteins. Why do these toxic metals compete well with Zn^{2+}, while other metals like Co^{2+}, Ni^{2+}, Fe^{2+}, and Mn^{2+} don't?

Answer

As discussed in Exercise 1, the zinc finger binding site is biased towards coordinating softer metals. Both cadmium and lead ions are much softer than zinc and will have a stronger affinity than zinc for the zinc binding site. Under normal conditions this is not an issue because lead and cadmium are not present in significant concentrations.

Exercise 13.5.1

If a toxic metal, like Cd^{2+} would bind to the Zn^{2+} binding site, how and why might this affect the protein's ability to bind to DNA?.

Answer

The proper folding and structure of these proteins is dependent on zinc coordination in the zinc finger domains. If a larger metal ion, such as Cd^{2+} were to bind in place of Zn^{2+} this would change the size and/or geometry of the zinc finger domain and therefore the entire protein. The correct shape of the protein is essential for recognition and binding of DNA.

References

1. Inspired by Zinc Finger Proteins: A Bioinorganic Example of LFSE and HSAB, a problem set created by Elizabeth R. Jamieson, Smith College (ejamieso@smith.edu) and posted on VIPEr (www.ionicviper.org) on June 24, 2013. Copyright Elizabeth R. Jamieson 2013. This work is licensed under the Creative Commons Attribution-NonCommerical-ShareAlike 3.0 Unported License. To view a copy of this license visit http://creativecommons.org/about/license/.

2. Pavletich, N. P.; Pabo, C. O., Crystal Structure of a Five-Finger Gli-DNA Complex: New Perspectives on Zinc Fingers. *Science* **1993**, *261* (5129), 1701-7.

3. Munro, D.; Ghersi, D.; Singh, M., Two Critical Positions in Zinc Finger Domains Are Heavily Mutated in Three Human Cancer Types. *PLOS Computational Biology* **2018**, *14* (6), e1006290.

13.6: Electron Transfer

Overview

Metalloproteins containing a single type of redox cofactor can be divided into two general classes: electron carriers and proteins involved in the transport or activation of small molecules. Some of the factors that seem to be characteristic of electron-transfer proteins (these proteins are sometimes called "electron transferases") are: (a) possession of a suitable cofactor to act as an electron sink (metal center with multiple stable oxidation states); (b) placement of the cofactor close enough to the protein surface to allow electrons to move in and out; (c) existence of a hydrophobic shell adjacent to, but not always entirely surrounding, the cofactor; (d) small structural changes accompanying electron transfer; and (e) an architecture that permits slight expansion or contraction in preferred directions upon electron transfer.

Metalloproteins that function as electron transferases typically place their metal coordination sites in a hydrophobic environment and may provide hydrogen bonds (in addition to ligands) to assist in stabilizing both the oxidized and the reduced forms of the cofactor. Metal-ligand bonds remain intact upon electron transfer to minimize inner-sphere reorganization energy. Many of the complex multisite metalloenzymes (e.g., cytochrome c oxidase, xanthine oxidase, the nitrogenase FeMo protein) contain redox centers that function as intramolecular electron transferases, shuttling electrons to/from other metal centers that bind exogenous ligands during enzymatic turnover.

There are three classes of metal containing electron transferases, each of which contains many members that exhibit important structural differences: blue copper proteins, iron-sulfur proteins, and cytochromes.

Blue Copper Proteins

Blue copper proteins were first isolated from bacteria in the 1950s and from plant tissues in the early 1960s. The intense blue color of these proteins is due to a strong absorption band at a wavelength of about 600 nm. Although simple Cu^{2+} complexes, such as $[Cu(H_2O)_6]^{2+}$ and $[Cu(NH_3)_4]^{2+}$, are also blue due to an absorption band at 600 nm, the intensity of the absorption band is about 100 times less than that of a blue copper protein. Moreover, the reduction potential for the Cu^{2+}/Cu^+ couple in a blue copper protein is usually +0.3 to +0.5 V, considerably more positive than that of the aqueous Cu^{2+}/Cu^+ couple (+0.15 V).
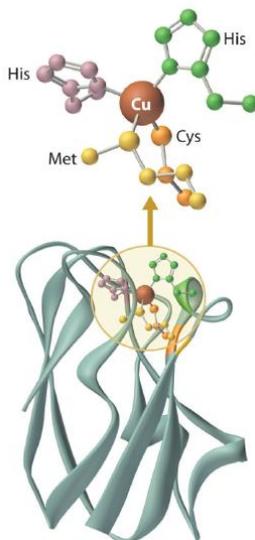
Figure 13.6.1: A Blue Copper Protein. In both the oxidized and reduced forms of a blue copper protein, the copper is coordinated by four ligands (two histidine imidazole nitrogen atoms, a cysteine thiolate sulfur, and a thioether sulfur of a methionine) in a roughly tetrahedral arrangement.

The copper center in blue copper proteins has a distorted tetrahedral structure, in which the copper is bound to four amino acid side chains (Figure 13.6.3). Although the most common structures for four-coordinate Cu^{2+} and Cu^+ complexes are square planar and tetrahedral, respectively, the structures of the oxidized (Cu^{2+}) and reduced (Cu^+) forms of the protein are essentially identical. Thus

the protein forces the Cu^{2+} ion to adopt a higher-energy structure that is more suitable for Cu^+, which makes the Cu^{2+} form easier to reduce and raises its reduction potential.

Moreover, by forcing the oxidized and reduced forms of the metal complex to have essentially the same structure, the protein ensures that electron transfer to and from the copper site is rapid because only minimal structural reorganization of the metal center is required. Kinetics studies on simple metal complexes have shown that electron-transfer reactions tend to be slow when the structures of the oxidized and reduced forms of a metal complex are very different, and fast when they are similar. You will see that other metal centers used for biological electron-transfer reactions are also set up for minimal structural reorganization after electron transfer, which ensures the rapid transfer of electrons.

The blue copper proteins are characterized by intense S(Cys) → Cu chargetransfer absorption near 600 nm, an axial EPR spectrum displaying an unusually small hyperfine coupling constant, and a relatively high reduction potential.[4,8-10] With few exceptions (e.g., photosynthetic organisms), their precise roles in bacterial and plant physiology remain obscure. X-ray structures of several blue copper proteins indicate that the geometry of the copper site is approximately trigonal planar, as illustrated by the *Alcaligenes denitrificans* azurin structure (Figure 6.5).[11,12] In all these proteins, three ligands (one Cys, two His) bind tightly to the copper in a trigonal arrangement. Differences in interactions between the copper center and the axially disposed ligands may significantly contribute to variations in reduction potential that are observed[12] for the blue copper electron transferases. For example, E°' = 276 mV for *A. denitrificans* azurin, whereas that of *P. vulgaris* plastocyanin is 360 mV. In *A. denitrificans* azurin, the Cu-S(Met) bond is 0.2 Å longer than in poplar plastocyanin, and there is a carbonyl oxygen 3.1 Å from the copper center, compared with 3.8 Å in plastocyanin. These differences in bond lengths are expected to stabilize Cu^{II} in azurin to a greater extent than in plastocyanin, and result in a lower E°' value for azurin.
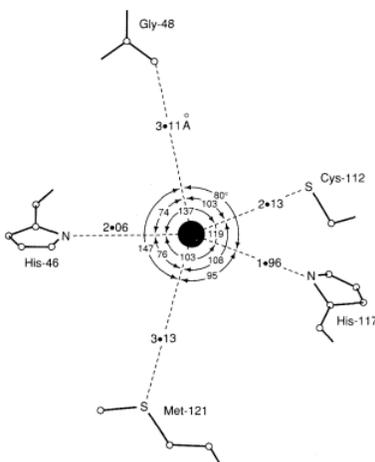
Figure 6.5 - Structure of the blue copper center in azurin.[11]

Iron Sulfur Proteins

Although all known bacteria, plants, and animals use iron–sulfur proteins to transfer electrons, the existence of these proteins was not recognized until the late 1950s. Iron–sulfur proteins transfer electrons over a wide range of reduction potentials, and their iron content can range from 1 to more than 12 Fe atoms per protein molecule. In addition, most iron–sulfur proteins contain stoichiometric amounts of sulfide (S^{2-}).

These properties are due to the presence of four different kinds of iron–sulfur units, which contain one, two, three, or four iron atoms per Fe–S complex (Figure 13.6.5). In all cases, the Fe^{2+} and Fe^{3+} ions are coordinated to four sulfur ligands in a tetrahedral environment. Due to tetrahedral coordination by weak-field sulfur ligands, the iron is high spin in both the Fe^{3+} and Fe^{2+} oxidation states, which results in similar structures for the oxidized and reduced forms of the Fe–S complexes. Consequently, only small structural changes occur after oxidation or reduction of the Fe–S center, which results in rapid electron transfer.
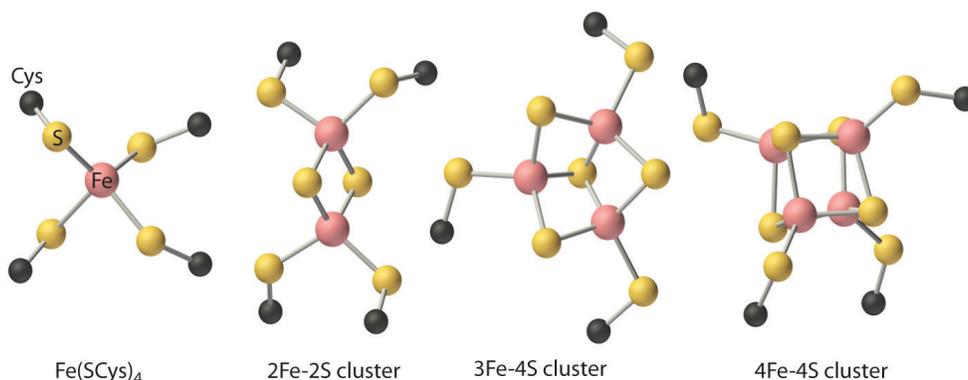
Figure 13.6.5: Fe–S Centers in Proteins: Four kinds of iron–sulfur centers, containing one, two, three, and four iron atoms, respectively, are known in electron-transfer proteins. Although they differ in the number of sulfur atoms provided by cysteine thiolates versus sulfide, in all cases the iron is coordinated to four sulfur ligands in a roughly tetrahedral environment.

The iron-sulfur proteins play important roles[13,14] as electron carriers in virtually all living organisms, and participate in plant photosynthesis, nitrogen fixation, steroid metabolism, and oxidative phosphorylation, as well as many other processes (Chapter 7). The optical spectra of all iron-sulfur proteins are very broad and almost featureless, due to numerous overlapping charge-transfer transitions that impart red-brown-black colors to these proteins. On the other hand, the EPR spectra of iron-sulfur clusters are quite distinctive, and they are of great value in the study of the redox chemistry of these proteins.

The simplest iron-sulfur proteins, known as rubredoxins, are primarily found in anaerobic bacteria, where their function is unknown. Rubredoxins are small proteins (6 kDa) and contain iron ligated to four Cys sulfurs in a distorted tetrahedral arrangement. The E°' value for the $Fe^{III/II}$ couple in water is 770 mV; that of *C. pasteurianum* rubredoxin is -57 mV. The reduction potentials of iron-sulfur proteins are typically quite negative, indicating a stabilization of the oxidized form of the redox couple as a result of negatively charged sulfur ligands.

The [2Fe-2S] ferredoxins (10-20 kDa) are found in plant chloroplasts and mammalian tissue. The structure of *Spirulina platensis* ferredoxin[15] confirmed earlier suggestions, based on EPR and Mössbauer studies, that the iron atoms are present in a spin-coupled [2Fe-2S] cluster structure. One-electron reduction (E°' ~ -420 mV) of the protein results in a mixed-valence dimer (Equation 6.3):

$$[Fe_2S_2(SR)_4]^{2-} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Fe_2S_2(SR)_4]^{3-} \tag{6.3}$$

$$Fd_{ox} \qquad\qquad Fd_{red} \tag{13.6.1}$$

$$2Fe(III) \qquad\qquad Fe(II) + Fe(III) \tag{13.6.2}$$

The additional electron in Fd_{red} is associated with only one of the iron sites, resulting in a so-called trapped-valence structure.[16] The $[Fe_2S_2(SR)_4]^{4-}$ cluster oxidation state, containing two ferrous ions, can be produced *in vitro* when strong reductants are used.

Four-iron clusters [4Fe-4S] are found in many strains of bacteria. In most of these bacterial iron-sulfur proteins, also termed ferredoxins, two such clusters are present in the protein. These proteins have reduction potentials in the -400 mV range and are rather small (6-10 kDa). Each of the clusters contains four iron centers and four sulfides at alternate corners of a distorted cube. Each iron is coordinated to three sulfides and one cysteine thiolate. The irons are strongly exchange-coupled, and the [4Fe-4S] cluster in bacterial ferredoxins is paramagnetic when reduced by one electron. The so-called "high-potential ironsulfur proteins" (HiPIPs) are found in photosynthetic bacteria, and exhibit anomalously high (~350 mV) reduction potentials. The *C. vinosum* HiPIP (10 kDa) structure demonstrates that HiPIPs are distinct from the [4Fe-4S] ferredoxins, and that the reduced HiPIP cluster structure is significantly distorted, as is also observed for the structure of the oxidized *P. aerogenes* ferredoxin. In addition, oxidized HiPIP is paramagnetic, whereas the reduced protein is EPR-silent.

This bewildering set of experimental observations can be rationalized in terms of a "three-state" hypothesis (i.e., $[4Fe-4S(SR)_4]^{n-}$ clusters exist in three physiological oxidation states).[17] This hypothesis nicely explains the differences in magnetic behavior and redox properties observed for these iron-sulfur proteins (Equation 6.4):

$$[4Fe-4S(SR)_4]^{-} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [4Fe-4S(SR)_4]^{2-} \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [4Fe-4S(SR)_4]^{3-} \tag{6.4}$$

$$HiPIP_{ox} \qquad\qquad HiPIP_{red} \qquad\qquad Ferredoxin_{red} \tag{13.6.3}$$
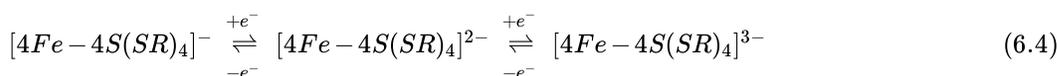
The bacterial ferredoxins and HiPIPs all possess tetracubane clusters containing thiolate ligands, yet the former utilize the -2/-3 cluster redox couple, whereas the latter utilize the -1/-2 cluster redox couple.

The protein environment thus exerts a powerful influence over the cluster reduction potentials. This observation applies to *all* classes of electron transferases—the factors that are critical determinants of cofactor reduction potentials are poorly understood at present but are thought[18] to include the low dielectric constants of protein interiors (~4 for proteins vs. ~78 for H_2O), electrostatic effects due to nearby charged amino-acid residues, hydrogen bonding, and geometric constraints imposed by the protein.

Cytochromes

The cytochromes (from the Greek cytos, meaning "cell", and chroma, meaning "color") were first identified in the 1920s by spectroscopic studies of cell extracts. Based on the wavelength of the maximum absorption in the visible spectrum, they were classified as cytochromes a (with the longest wavelength), cytochromes b (intermediate wavelength), and cytochromes c (shortest wavelength). It quickly became apparent that there was a correlation between their spectroscopic properties and other physical properties. For examples, cytochromes c are generally small, soluble proteins with a reduction potential of about +0.25 V, whereas cytochromes b are larger, less-soluble proteins with reduction potentials of about 0 V.

All cytochromes contain iron, and the iron atom in all cytochromes is coordinated by a planar array of four nitrogen atoms provided by a cyclic tetradentate ligand called a porphyrin. The iron–porphyrin unit is called a heme group. The structures of a typical porphyrin (protoporphyrin IX) and its iron complex (protoheme) are shown here. In addition to the four nitrogen atoms of the porphyrin, the iron in a cytochrome is usually bonded to two additional ligands provided by the protein, as shown in Figure 13.6.4.

Protoporphyrin IX   **Protoheme**
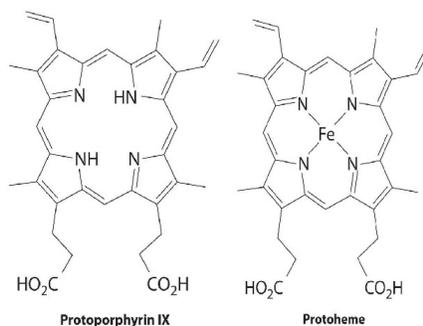
A cytochrome. Shown here is protoporphyrin IX and its iron complex, protoheme.

Side view   Cytochrome with heme   Heme 90° rotation
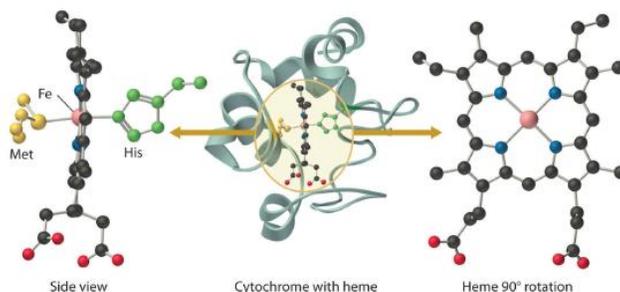
Figure 13.6.4: A Cytochrome c. In a cytochrome c, the heme iron is coordinated to the nitrogen atom of a histidine imidazole and the sulfur atom of a methionine thioether, in addition to the four nitrogen atoms provided by the porphyrin.

In contrast to the blue copper proteins, two electron configurations are possible for both the oxidized and reduced forms of a cytochrome, and this has significant structural consequences. Thus Fe^{2+} is d^6 and can be either high spin (with four unpaired electrons) or low spin (with no unpaired electrons). Similarly, Fe^{3+} is d^5 and can also be high spin (with five unpaired electrons) or low spin (with one unpaired electron). In low-spin heme complexes, both the Fe^{2+} and the Fe^{3+} ions are small enough to fit into the "hole" in the center of the porphyrin; hence the iron atom lies almost exactly in the plane of the four porphyrin nitrogen atoms in both cases. Because cytochromes b and c are low spin in both their oxidized and reduced forms, the structures of the oxidized and

reduced cytochromes are essentially identical. Hence minimal structural changes occur after oxidation or reduction, which makes electron transfer to or from the heme very rapid.

> *Electron transfer reactions occur most rapidly when minimal structural changes occur during oxidation or reduction*

As a class, the cytochromes[19-22] are the most thoroughly characterized of the electron transferases. By definition, a cytochrome contains one or more heme cofactors. These proteins were among the first to be identified in cellular extracts because of their distinctive optical properties, particularly an intense absorption in the 410-430 nm region (called the Soret band). Cytochromes are typically classified on the basis of heme type. Figure 6.6 displays the three most commonly encountered types of heme: heme a possesses a long phytyl "tail" and is found in cytochrome c oxidase; heme b is found in b-type cytochromes and globins; heme c is covalently bound to c-type cytochromes via two thioether linkages. Cytochrome nomenclature presents a real challenge! Some cytochromes are designated according to the historical order of discovery, e.g., cytochrome c_2 in bacterial photosynthesis. Others are designated according to the λ_{max} of the α band in the absorption spectrum of the reduced protein (e.g., cytochrome c_{551}).
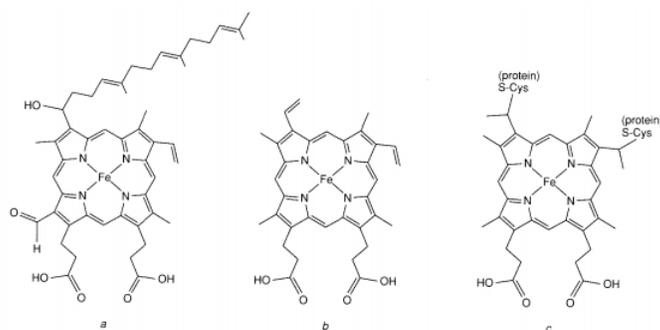
Figure 6.6 - Structures of hemes a, b, and c.

Cytochromes c are widespread in nature. Ambler[23] divided these electron carriers into three classes on structural grounds. The Class I cytochromes c contain axial His and Met ligands, with the heme located near the N-terrninus of the protein. These proteins are globular, as indicated by the ribbon drawing of tuna cytochrome c (Figure 6.7). X-ray structures of Class I cytochromes c from a variety of eukaryotes and prokaryotes clearly show an evolutionarily conserved "cytochrome fold," with the edge of the heme solvent-exposed. The reduction potentials of these cytochromes are quite positive (200 to 320 mV). Mammalian cytochrome c, because of its distinctive role in the mitochondrial electron-transfer chain, will be discussed later.
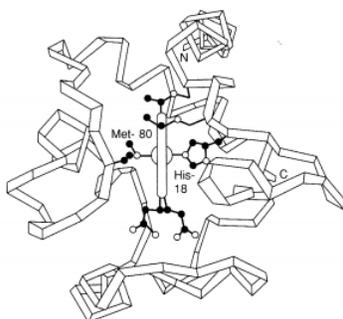
Figure 6. - Structure of tuna cytochrome c.

Class II cytochromes c (E°' ~ -100 mV) are found in photosynthetic bacteria, where they serve an unknown function. Unlike their Class I cousins, these c-type cytochromes are high-spin: the iron is five-coordinate, with an axial His ligand. These proteins, generally referred to as cytochromes c' , are four-α-helix bundles (Figure 6.8). The vacant axial coordination site is buried in the protein interior.

Figure 6.8 - Structure of cytochrome c'.

Finally, Class III cytochromes c, also called cytochromes c_3, contain four hemes, each ligated by two axial histidines. These proteins are found in a restricted class of sulfate-reducing bacteria and may be associated with the cytoplasmic membrane. The low molecular weights of cytochromes c_3 (~14. 7 kDa) require that the four hemes be much more exposed to the solvent than the hemes of other cytochromes (see Figure 6.9), which may be in part responsible for their unusually negative (-200 to -350 mV) reduction potentials. These proteins possess many aromatic residues and short heme-heme distances, two properties that could be responsible for their anomalously large solid-state electrical conductivity.[24]
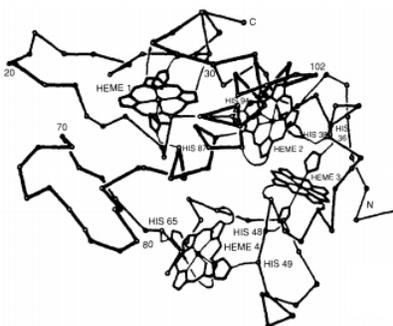
Figure 6.9 - Structure of cytochrome c_3.

13.7: Exercises

General Questions

1. What is bioinorganic chemistry?
2. Why are metals important in biological systems?
3. Which metals are commonly found in biological systems?
4. How do metal ions interact with proteins?
5. What is the role of metalloproteins in cells?

Biological Dioxygen Transport and Storage

6. What is the function of hemoglobin in oxygen transport?
7. How does myoglobin store oxygen?
8. What role does iron play in dioxygen transport proteins?
9. Why is copper important in some dioxygen transport proteins?
10. What is the difference between hemoglobin and myoglobin?

Biological Metal Storage

11. What is ferritin and its function?
12. How is iron stored in the body?
13. What is metallothionein's role in metal storage?
14. How do organisms regulate metal homeostasis?
15. Why is zinc storage important?

Zinc as Lewis Acid and Template

16. How does zinc act as a Lewis acid in enzymes?
17. What is the role of zinc in carbonic anhydrase?
18. Why is zinc not involved in redox reactions?
19. How does zinc function as a structural template?
20. What is the significance of zinc finger motifs?

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