CHEM-3010: SPRING 2026



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Glossary

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Detailed Licensing

Licensing

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CHAPTER OVERVIEW

1: Introduction to Inorganic Chemistry

This chapter introduces some history and context about the field of Inorganic Chemistry.

1.1: What is Inorganic Chemistry?

1.2: Inorganic vs Organic Chemistry

1.3: History of Inorganic Chemistry

1.4: Perspectives

1.5: Practice problems

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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.

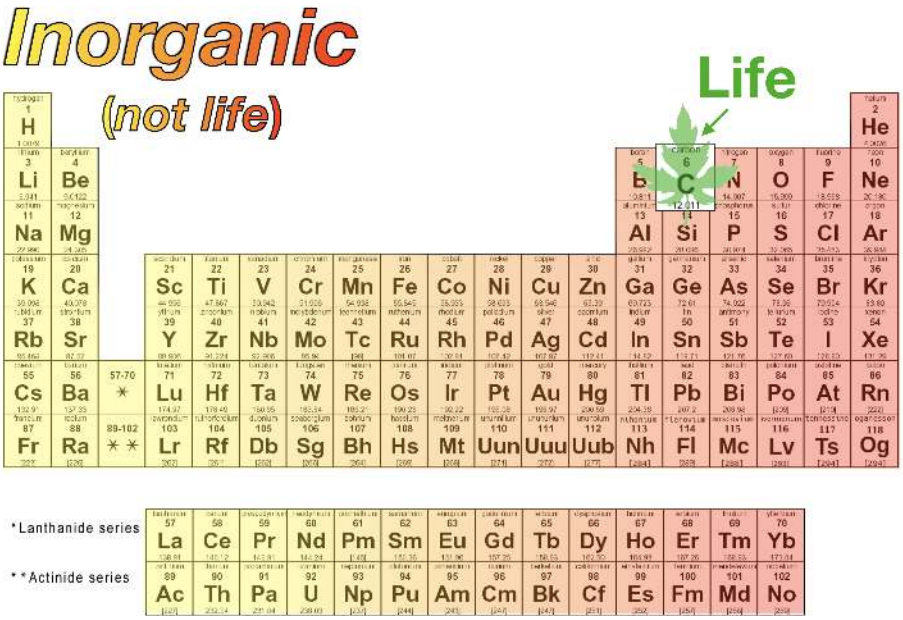


Figure **1.1.1**. An illustration of the historic meaning of "organic" and "inorganic". The modern understanding of organic and inorganic chemistry is not consistent with these historical meanings. (Kathryn Haas; CC-NC-BY-SA)

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.

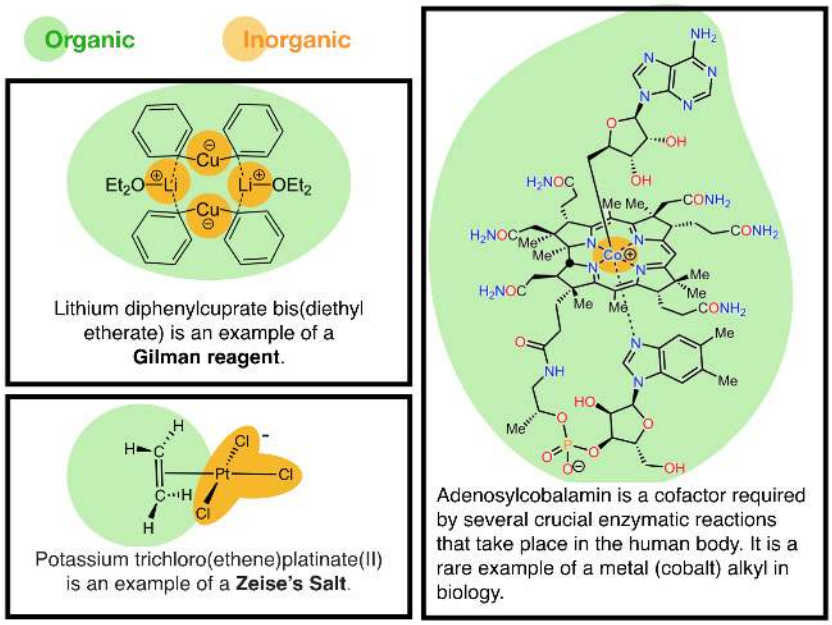


Figure **1.2.1**: Some examples of organometallic catalysts. These compounds catalyze organic reactions or biochemical reactions and they are compounds that contain both carbon and metals. These compounds are examples of molecules that cannot be defined only as organic molecules or only as inorganic 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.

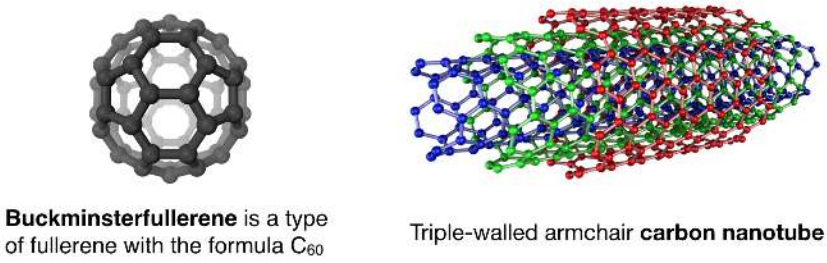


Figure 1.2.2: This figure is created from information found on the Wikipedia articles for Buckmisterfullerene and carbon nanotubes. Attribution Eric Wieser, Multi-walled Carbon Nanotube, CC BY-SA 3.0. (Kathryn Haas; CC-BY-SA)

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.

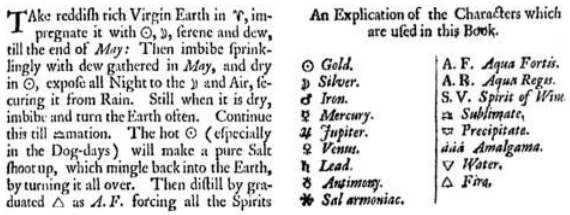
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1.3: History of Inorganic Chemistry

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 the 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 and the Statue of Liberty. 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, 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.


TAke reddiſh rich Virgin Earth in ♈, impregnate it with ☉, ☽, ſerene and dew, till the end of *May*: Then imbibe ſprinklingly with dew gathered in *May*, and dry in ☉, expoſe all Night to the ☽ and Air, ſecuring it from Rain. Still when it is dry, imbibe and turn the Earth often. Continue this till ♎mation. The hot ☉ (eſpecially in the Dog-days) will make a pure Salt ſhoot up, which mingle back into the Earth, by turning it all over. Then diſtill by graduated △ as *A. F.* forcing all the Spirits

An Explication of the Characters which are uſed in this Book.

☉ *Gold.*
☽ *Silver.*
♂ *Iron.*
☿ *Mercury.*
♃ *Jupiter.*
♀ *Venus.*
♄ *Lead.*
♁ *Antimony.*
❋ *Sal armoniac.*

A. F. *Aqua Fortis.*
A. R. *Aqua Regis.*
S. V. *Spirit of Wine.*
♎ *Sublimate.*
♈ *Precipitate.*
ääā Amalgama.
▽ *Water.*
△ *Fire.*

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 rules 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 (*ce*$HNO3$), sulfuric acid (H_2SO_4), and hydrochloric acid (HCl), as well as sodium hydroxide ($NaOH$). Glassware for running chemical reactions was developed, as were methods for distillation, crystallization, and 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 A Brief History of Chemistry.

Inorganic compounds have been known and used since antiquity; probably the oldest is the deep blue pigment called Prussian blue ($Fe_4[Fe(CN)_6]_3$). 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 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 explanations 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 and the Haber-Bosch Process was discovered. 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.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \tag{1.3.1}$$

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 in the roots of plants can carry out this reaction at the mild conditions within the soil. Intense investigations were then aimed at improving 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: Perspectives

The field of inorganic chemistry stands on the shoulders of giants (or in this case, many talented and dedicated scientists). If you are lucky enough to have journal access, peruse the titles and pages of the first issues of Inorganic Chemistry. You will find some lively debate about the puzzles of determining inorganic structure and reactivity. The scientists that made early discoveries in this field practiced elegant science.

The inorganic chemists who built our field are diverse. They are the ones who discovered new elements, developed new materials, characterized the fundamental principles of reactions, and developed the theories that we use to understand and predict metal structure and reactivity. And, there are people who are still working on these things today.

To gain more perspective on Inorganic Chemistry, compare the topics in the very first issue (Feb 1, 1962) to the most recent issue or the current most popular articles using the links below.

- The very first issue of Inorganic Chemistry from 1962: https://pubs.acs.org/toc/inocaj/1/1
- 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

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1.5: Practice problems

These questions are designed to check your understanding of the reading in this chapter.

1. What is the historic definition of *inorganic chemistry*? What are some problems that arise from this definition?
2. Name three sub-fields of inorganic chemistry.
3. What is the class of inorganic compounds that have bonds between metals and carbon?

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CHAPTER OVERVIEW

2: Atomic Structure

2.1: Historical Development of Atomic Theory

2.1.1: The Periodic Table

2.1.2: Discovery of Subatomic Particles and the Bohr Atom

2.2: The Schrödinger equation, particle in a box, and atomic wavefunctions

2.2.1: Particle in a Box

2.2.2: Quantum Numbers and Atomic Wave Functions

2.2.3: Aufbau Principle

2.2.4: Shielding

2.3: Periodic Properties of Atoms

2.3.1: Ionization energy

2.3.2: Electron Affinity

2.3.3: Covalent and Ionic Radii

2.4: Problems

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2.1: Historical Development of Atomic Theory

Notes about this page

The page below is a brief overview on the history of atomic theory. It contains lots of video media.

Alternatives pages on the history of atomic theory are:

- A more detailed overview that includes practice problems is here (click).
- Another brief overview is here (click).

Skills to Develop

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
- Outline milestones in the development of modern atomic theory
- Summarize and interpret the results of the experiments of Thomson, Millikan, and Rutherford

A Video Introduction to Atomic Theory through the Nineteenth Century From Crash Course Chemistry



***Video* 2.1.1*:* Lavoisier's discovery of The Law of Conservation of Matter led to the Laws of Definite and Multiple Proportions and eventually Dalton's Atomic Theory.**

Atomic Theory through the Nineteenth Century

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 **2.1.1**). A macroscopic sample of an element contains an incredibly large number of atoms, all of which have identical chemical properties.
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 **2.1.2**).
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 **2.1.3**).

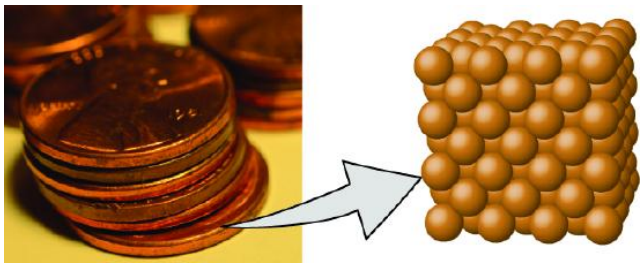


Figure* 2.1.1*: *A pre-1982 copper penny (left) contains approximately 3×10^{22} copper atoms (several dozen are represented as brown spheres at the right), each of which has the same chemical properties. (credit: modification of work by "slgckgc"/Flickr)*

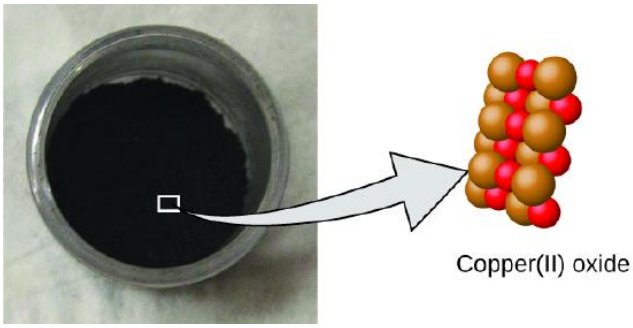


Figure* 2.1.2*: *Copper(II) oxide, a powdery, black compound, results from the combination of two types of atoms—copper (brown spheres) and oxygen (red spheres)—in a 1:1 ratio. (credit: modification of work by "Chemicalinterest"/Wikimedia Commons)*

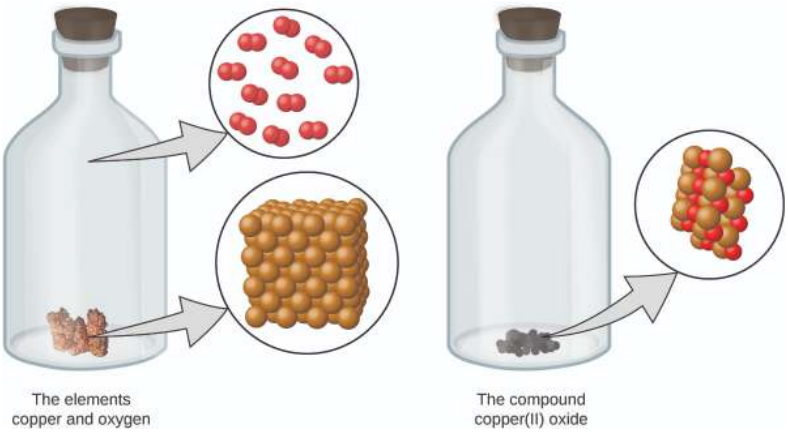


Figure* 2.1.3*: *When the elements copper (a shiny, red-brown solid, shown here as brown spheres) and oxygen (a clear and colorless gas, shown here as red spheres) react, their atoms rearrange to form a compound containing copper and oxygen (a powdery, black solid). (credit copper: modification of work 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 (or mass)).

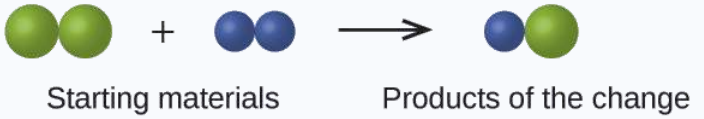
Want to learn more about the Law of Conservation of Mass?



Video 2.1.2: "We are made of star stuff" - Carl Sagan.

Example 2.1.1: 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?



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 2.1.1

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



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 **2.1.1**.

***Table* 2.1.1**: *Constant Composition of Isooctane*

Sample	Carbon	Hydrogen	Mass Ratio
A	14.82 g	2.78 g	$\frac{14.82\text{ g carbon}}{2.78\text{ g hydrogen}} = \frac{5.33\text{ g carbon}}{1.00\text{ g hydrogen}}$
B	22.33 g	4.19 g	$\frac{22.33\text{ g carbon}}{4.19\text{ g hydrogen}} = \frac{5.33\text{ g carbon}}{1.00\text{ g hydrogen}}$
C	19.40 g	3.64 g	$\frac{19.40\text{ g carbon}}{3.63\text{ g hydrogen}} = \frac{5.33\text{ g carbon}}{1.00\text{ g hydrogen}}$

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.

$$\frac{\frac{1.116\text{ g Cl}}{1\text{ g Cu}}}{\frac{0.558\text{ g Cl}}{1\text{ g Cu}}} = \frac{2}{1} \tag{2.1.1}$$

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 **2.1.4**).

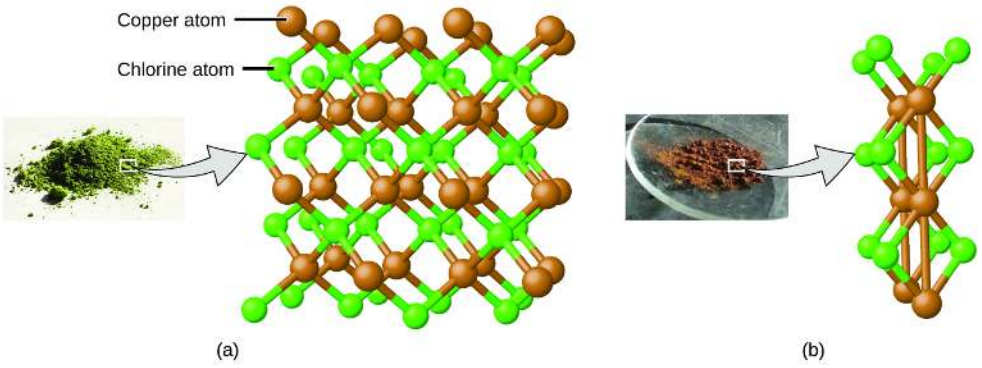


***Figure* 2.1.4**: *Compared to the copper chlorine compound in (a), where copper is represented by brown spheres and chlorine by green spheres, the copper chlorine compound in (b) has twice as many chlorine atoms per copper atom. (credit a: modification of work by "Benjah-bmm27"/Wikimedia Commons; credit b: modification of work by "Walkerma"/Wikimedia Commons)*

Example 2.1.2: 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 carbon to oxygen is:

$$\frac{1.33\text{ g O}}{1\text{ g C}}$$

In compound B, the mass ratio of carbon to oxygen is:

$$\frac{2.67\text{ g O}}{1\text{ g C}}$$

The ratio of these ratios is:

$$\frac{\frac{1.33\text{ g O}}{1\text{ g C}}}{\frac{2.67\text{ g O}}{1\text{ g C}}} = \frac{1}{2}$$

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

Exercise 2.1.2

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 $\frac{14.13\text{ g C}}{2.96\text{ g H}}$.

In compound Y, the mass ratio of carbon to oxygen is $\frac{19.91\text{ g C}}{3.34\text{ g H}}$.

The ratio of these ratios is

$$\frac{\frac{14.13\text{ g C}}{2.96\text{ g H}}}{\frac{19.91\text{ g C}}{3.34\text{ g H}}} = \frac{4.77\text{ g C/g H}}{5.96\text{ g C/g H}} = 0.800 = \frac{4}{5}.$$

This small, whole-number ratio supports the law of multiple proportions. This means that X and Y are different compounds.

In the two centuries since Dalton developed his ideas, scientists have made significant progress in furthering our understanding of atomic theory. Much of this came from the results of several seminal experiments that revealed the details of the internal structure of atoms. Here, we will discuss some of those key developments, with an emphasis on application of the scientific method, as well as understanding how the experimental evidence was analyzed. While the historical persons and dates behind these experiments can be quite interesting, it is most important to understand the concepts resulting from their work.

Atomic Theory after the Nineteenth Century

If matter were composed of atoms, what were atoms composed of? Were they the smallest particles, or was 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 **2.1.1**).

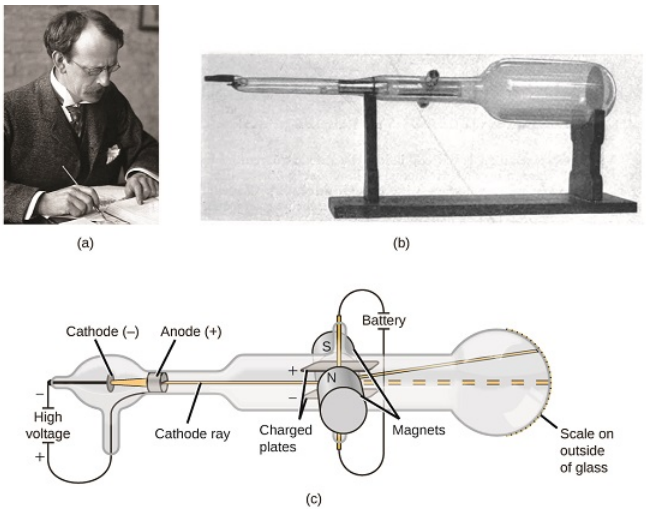
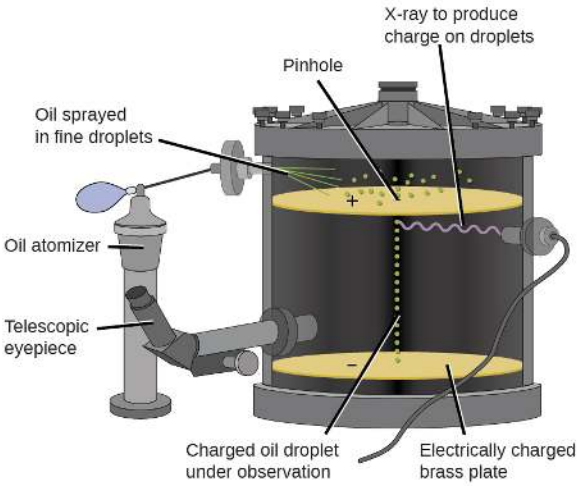


Figure* 2.1.5: (a) J. J. Thomson produced a visible beam in a cathode ray tube. (b) This is an early cathode ray tube, invented in 1897 by Ferdinand Braun. (c) In the cathode ray, the beam (shown in yellow) comes from the cathode and is accelerated past the anode toward a fluorescent scale at the end 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 **2.1.2**).



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 2.1.6: *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.

$$\text{Mass of electron} = 1.602 \times 10^{-19} \cancel{\text{C}} \times \frac{1 \text{ kg}}{1.759 \times 10^{11} \cancel{\text{C}}} = 9.107 \times 10^{-31} \text{ kg} \tag{2.3.1}$$

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 2.1.3).

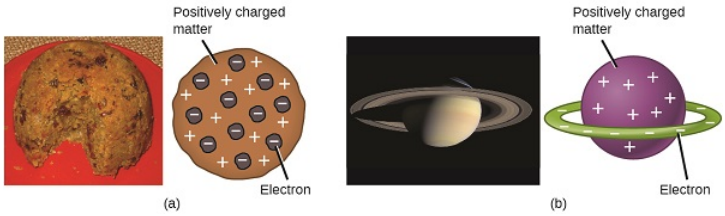


Figure 2.1.7*: (a) Thomson suggested that atoms resembled plum pudding, an English dessert consisting of moist cake with embedded raisins ("plums"). (b) Nagaoka proposed that atoms resembled the planet Saturn, with a ring of electrons surrounding a positive "planet." (credit a: modification of work by "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 **2.1.4**). 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] (p. 68).

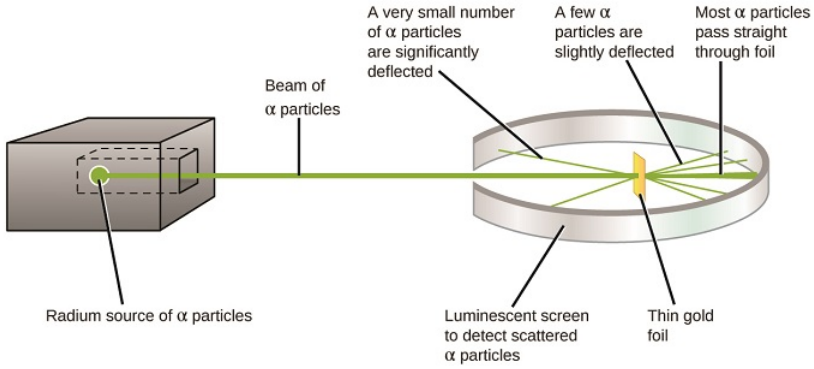


Figure* 2.1.8*: *Geiger and Rutherford fired α particles at a piece of gold foil and detected where those particles went, as shown in this schematic diagram of their experiment. Most of the particles passed straight through the foil, but a few were deflected slightly and a very small number were significantly 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.

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 **2.1.5**).

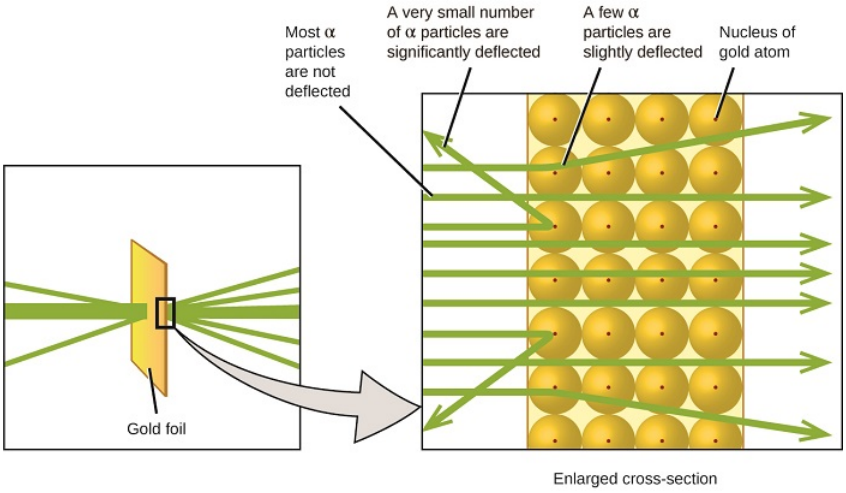
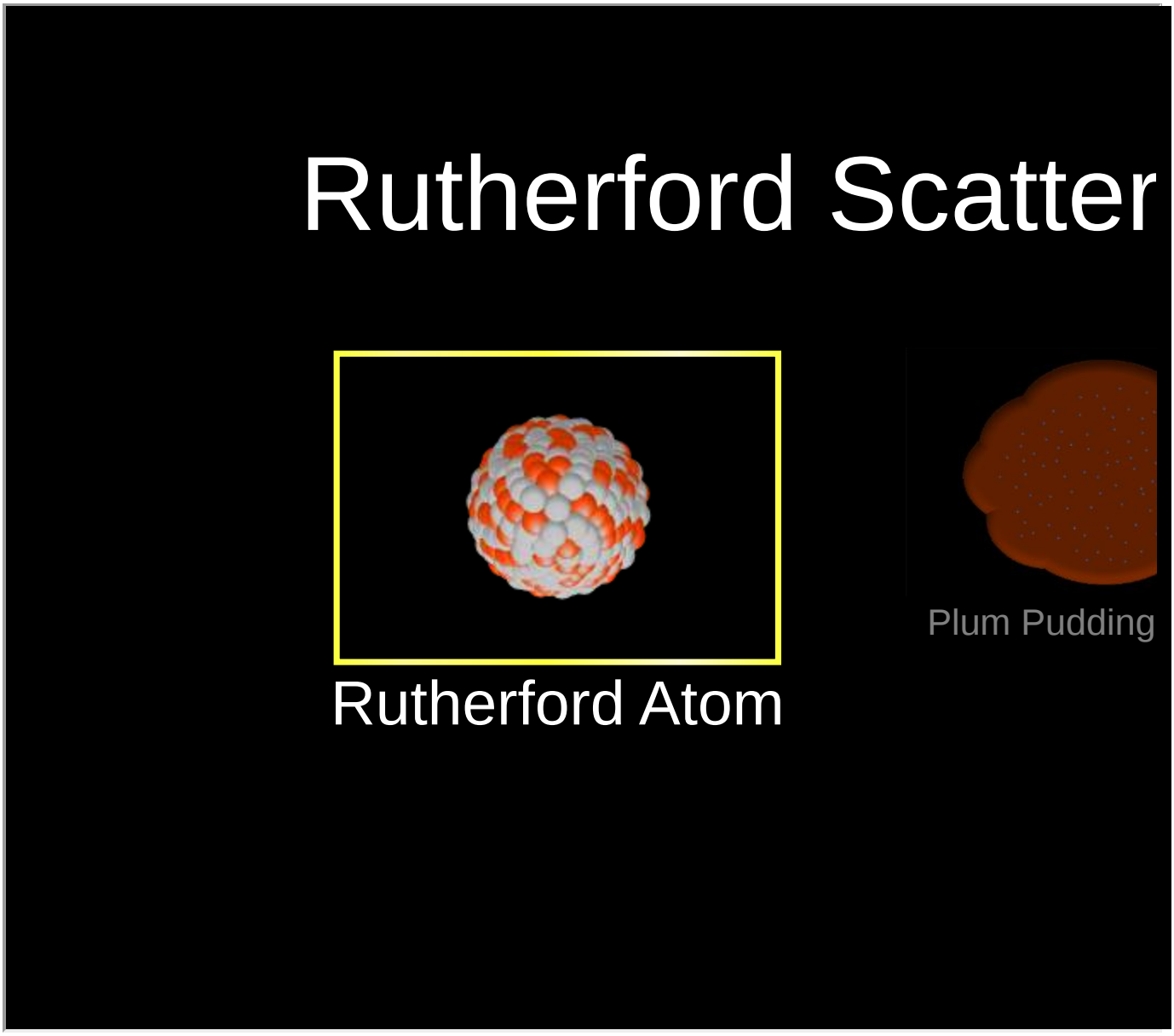


Figure* 2.1.9*: *The α particles are deflected only when they collide with or pass close to the much heavier, positively charged gold nucleus. Because the nucleus is very small compared to the size of an atom, very few α particles are deflected. Most pass through*

the relatively large region occupied by electrons, which are too light to deflect the rapidly moving particles.

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.



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 unit.



Video* 2.1.2*: An Introduction to Subatomic Particles

Summary



***Video* 2.1.3*:** *A summary of discoveries in atomic theory.*



***Video* 2.1.4*:** *A different summary of discoveries in atomic theory.*

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.

Footnotes

1. Ernest 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.

Glossary

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

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 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

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

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

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

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

neutron
uncharged, subatomic particle located in the nucleus

proton
positively charged, subatomic particle located in the nucleus

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

Contributors

- Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).
- Adelaide Clark, Oregon Institute of Technology
- Crash Course Chemistry: Crash Course is a division of Complexly and videos are free to stream for educational purposes.
- TED-Ed's commitment to creating lessons worth sharing is an extension of TED's mission of spreading great ideas. Within TED-Ed's growing library of TED-Ed animations, you will find carefully curated educational videos, many of which represent collaborations between talented educators and animators nominated through the TED-Ed website.

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2.1.1: The Periodic Table

Learning Objectives

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

The modern periodic table has evolved through a long history of attempts by chemists to arrange the elements according to their reactivity and other properties as an aid in predicting chemical behavior. Now that we have arranged the table according to electronic structure, it makes sense to go back and look at earlier efforts in the light of what we know about electronic structure.

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

By the mid-19th century, the atomic masses of many of the elements had been determined. The English chemist John Newlands (1838–1898), hypothesizing that the chemistry of the elements might be related to their masses, arranged the known elements in order of increasing atomic mass and discovered that every seventh element had similar properties (Figure 3.4.1). Newlands therefore suggested that the elements could be classified into octaves: a group of seven elements (not counting the noble gases, which were unknown at the time) that correspond to the *horizontal* rows in the main group elements. Unfortunately, Newlands's "law of octaves" did not seem to work for elements heavier than calcium, and his idea was publicly ridiculed. At one scientific meeting, Newlands was asked why he didn't arrange the elements in alphabetical order instead of by atomic mass, since that would make just as much sense! Actually, Newlands was on the right track—with only a few exceptions, atomic mass does increase with atomic number, and similar properties occur every time a set of ns^2np^6 subshells is filled. Despite the fact that Newlands's table had no logical place for the *d*-block elements, he was honored for his idea by the Royal Society of London in 1887.

John Newlands (1838–1898)

Newlands noticed that elemental properties repeated every seventh (or multiple of seven) element, as musical notes repeat every eighth note.

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

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

Figure 3.4.1 The arrangement of the elements into octaves as proposed by **Newlands:** *The table shown here accompanied a letter from a 27-year-old Newlands to the editor of the journal Chemical News in which he wrote: "If the elements are arranged in the order of their equivalents, with a few slight transpositions, as in the accompanying table, it will be observed that elements belonging to the same group usually appear on the same horizontal line. It will also be seen that the numbers of analogous elements generally differ either by 7 or by some multiple of seven; in other words, members of the same group stand to each other in the same relation as the extremities of one or more octaves in music. Thus, in the nitrogen group, between nitrogen and phosphorus there are 7 elements; between phosphorus and arsenic, 14; between arsenic and antimony, 14; and lastly, between antimony and bismuth, 14 also. This peculiar relationship I propose to provisionally term the Law of Octaves. I am, &c. John A. R. Newlands, F.C.S. Laboratory, 19, Great St. Helen's, E.C., August 8, 1865."*

The periodic table achieved its modern form through the work of the German chemist Julius Lothar Meyer (1830–1895) and the Russian chemist Dimitri Mendeleev (1834–1907), both of whom focused on the relationships between atomic mass and various physical and chemical properties. In 1869, they independently proposed essentially identical arrangements of the elements. Meyer aligned the elements in his table according to periodic variations in simple atomic properties, such as "atomic volume" (Figure

3.4.2), which he obtained by dividing the atomic mass (molar mass) in grams per mole by the density of the element in grams per cubic centimeter. This property is equivalent to what is today defined as molar volume, the molar mass of an element divided by its density (measured in cubic centimeters per mole):

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

As shown in Figure 3.4.2 , the alkali metals have the highest molar volumes of the solid elements. In Meyer's plot of atomic volume versus atomic mass, the nonmetals occur on the rising portion of the graph, and metals occur at the peaks, in the valleys, and on the down slopes.

Dimitri Mendeleev (1834–1907)

When his family's glass factory was destroyed by fire, Mendeleev moved to St. Petersburg, Russia, to study science. He became ill and was not expected to recover, but he finished his PhD with the help of his professors and fellow students. In addition to the periodic table, another of Mendeleev's contributions to science was an outstanding textbook, *The Principles of Chemistry*, which was used for many years.

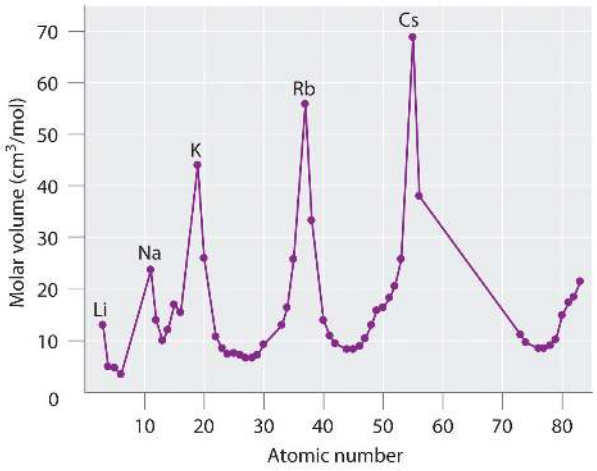


Figure 3.4.2 Variation of atomic volume with atomic number, adapted from Meyer's plot of **1870:** *Note the periodic increase and decrease in atomic volume. Because the noble gases had not yet been discovered at the time this graph was formulated, the peaks correspond to the alkali metals (group 1).*

Mendeleev's Periodic Table

Mendeleev, who first published his periodic table in 1869 (Figure 3.4.3), is usually credited with the origin of the modern periodic table. The key difference between his arrangement of the elements and that of Meyer and others is that Mendeleev did not assume that all the elements had been discovered (actually, only about two-thirds of the naturally occurring elements were known at the time). Instead, he deliberately left blanks in his table at atomic masses 44, 68, 72, and 100, in the expectation that elements with those atomic masses would be discovered. Those blanks correspond to the elements we now know as scandium, gallium, germanium, and technetium.

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

Figure 3.4.3 Mendeleev's periodic table, as published in the German journal *Annalen der Chemie und Pharmacie* in 1872: *The column headings "Reihen" and "Gruppe" are German for "row" and "group." Formulas indicate the type of compounds formed by each group, with "R" standing for "any element" and superscripts used where we now use subscripts. Atomic masses are shown after equal signs and increase across each row from left to right.*

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

The most convincing evidence in support of Mendeleev's arrangement of the elements was the discovery of two previously unknown elements whose properties closely corresponded with his predictions (Table 3.4.1). Two of the blanks Mendeleev had left in his original table were below aluminum and silicon, awaiting the discovery of two as-yet-unknown elements, *eka*-aluminum and *eka*-silicon (from the Sanskrit *eka*, meaning "one," as in "one beyond aluminum"). The observed properties of gallium and germanium matched those of *eka*-aluminum and *eka*-silicon so well that once they were discovered, Mendeleev's periodic table rapidly gained acceptance.



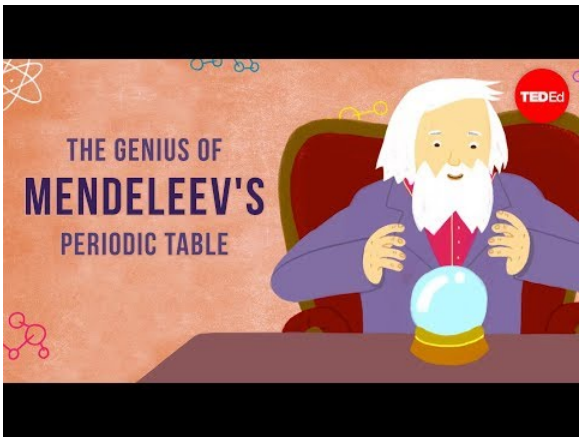


Table 3.4.1 Comparison of the properties predicted by Mendeleev in 1869 for *eka*-aluminum and *eka*-silicon with the properties of gallium (discovered in 1875) and germanium (discovered in 1886)

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

*mp = melting point; bp = boiling point.

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

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

The Role of the Atomic Number in the Periodic Table

Despite its usefulness, Mendeleev's periodic table was based entirely on empirical observation supported by very little understanding. It was not until 1913, when a young British physicist, H. G. J. Moseley (1887–1915), while analyzing the frequencies of x-rays emitted by the elements, discovered that the underlying foundation of the order of the elements was the

atomic number, not the atomic mass. Moseley hypothesized that the placement of each element in his series corresponded to its atomic number *Z*, which is the number of positive charges (protons) in its nucleus. Argon, for example, although having an atomic mass greater than that of potassium (39.9 amu versus 39.1 amu, respectively), was placed *before* potassium in the periodic table. While analyzing the frequencies of the emitted x-rays, Moseley noticed that the atomic number of argon is 18, whereas that of potassium is 19, which indicated that they were indeed placed correctly. Moseley also noticed three gaps in his table of x-ray frequencies, so he predicted the existence of three unknown elements: technetium (Z = 43), discovered in 1937; promethium (Z = 61), discovered in 1945; and rhenium (Z = 75), discovered in 1925.

H. G. J. Moseley (1887–1915)

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

Example 3.4.1

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

Given: atomic number

Asked for: name using prefix *eka*-

Strategy:

A Using the periodic table locate the n = 7 row. Identify the location of the unknown element with Z = 114; then identify the known element that is directly above this location.

B Name the unknown element by using the prefix *eka*- before the name of the known element.

Solution:

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

Exercise

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

Answer: *eka*-mercury

Summary

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

Key Takeaways

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

Conceptual Problems

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

Numerical Problem

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

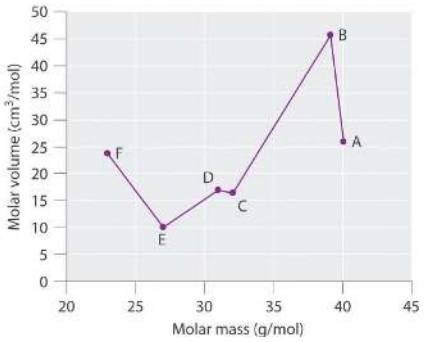
Species	Molar Mass (g/mol)	Density (g/cm^3)	Molar Volume (cm^3/mol)
A	40.078		25.85
B	39.09	0.856	
C	32.065		16.35
D		1.823	16.98
E	26.98		9.992
F	22.98	0.968	

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

Answer

1.

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



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

Contributors and Attributions

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2.1.2: Discovery of Subatomic Particles and the Bohr Atom

Hydrogen Absorption and Emission Spectra

When a high-voltage electrical discharge is passed through a sample of hydrogen gas (H_2) at low pressure, the result is individual isolated hydrogen atoms that emit a red light. Unlike blackbody radiation, the color of the light emitted by the hydrogen atoms does not depend greatly on the temperature of the gas in the tube. When the emitted light is passed through a prism, only a few narrow lines of particular wavelengths, called a line spectrum, are observed rather than a continuous range of wavelengths (Figure **2.1.2.1**). The light emitted by hydrogen atoms is red because, of its four characteristic lines, the most intense line in its spectrum is in the red portion of the visible spectrum, at 656 nm.

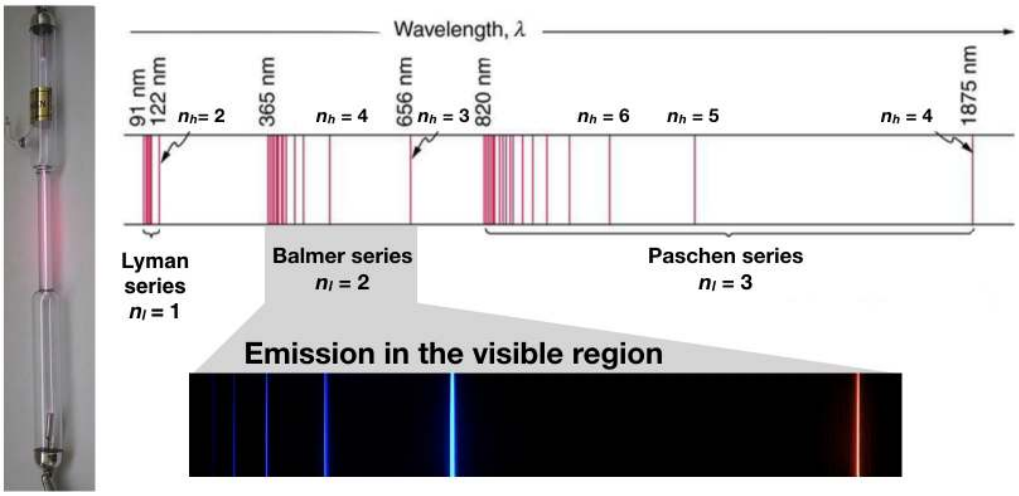


Figure **2.1.2.1**: The emission of light by hydrogen atoms. (left) A sample of excited hydrogen atoms emits a characteristic red light. (bottom) When the light emitted by a sample of excited hydrogen atoms is split into its component wavelengths by a prism, four characteristic violet, blue, green, and red emission lines can be observed, with the most intense at 656 nm. (top) A diagram showing extended regions of the electromagnetic spectrum and the hydrogen line spectra that are observed. (Kathryn Haas; CC-BY-SA)

The Balmer Series

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

$$u = constant\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \tag{2.1.2.1}$$

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

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_l^2} - \frac{1}{n_h^2}\right) \tag{2.1.2.2}$$

,

where n_l and n_h are positive integers, $n_h > n_l$, and R_H, the *Rydberg constant*, has a value of 1.09737 × 10^7 m^{-1}. Like Balmer's equation, Rydberg's simple equation described the wavelengths of the visible lines in the emission spectrum of hydrogen (with $n_l = 2, n_h = 3, 4, 5, ...$). More importantly, Rydberg's equation also predicted the wavelengths of other series of lines that would be observed in the emission spectrum of hydrogen: one in the ultraviolet ($n_l = 1, n_h = 2, 3, 4, ...$) and one in the infrared ($n_l = 3, n_h = 4, 5, 6$).

Other Series

The results given by Balmer and Rydberg for the spectrum in the visible region of the electromagnetic spectrum start with $n_h = 3$, and $n_l = 2$.

Is there a different series with the following formula (e.g., $n_l = 1$)?

$$\frac{1}{\lambda} = R_H \left(\frac{1}{1^2} - \frac{1}{n^2} \right) \tag{2.1.2.3}$$

The values for n_h and wavenumber u for this series would be:

Table 2.1.2.1: The Lyman Series of Hydrogen Emission Lines ($n_l = 1$)

n_h	2	3	4	5
λ (nm)	121	102	97	94
$\tilde{u}$ (cm^{-1})	82,2291	97,530	102,864	105,332

Do you know what region of the electromagnetic radiation these lines are in? Of course, these lines are in the UV region, and they are not visible, but they are detected by instruments; these lines form a **Lyman series**. The existences of the Lyman series and Balmer's series suggest the existence of more series. For example, the series with $n_2^2 = 3$ and n_1^2 = 4, 5, 6, 7, ... is called the **Pashen series**.

Multiple series

The spectral lines are grouped into series according to n_1 values. Lines are named sequentially starting from the longest wavelength/lowest frequency of the series using Greek letters within each series. For example, the ($n_1 = 1/n_2 = 2$) line is called "Lyman-alpha" (Ly-α), while the ($n_1 = 3/n_2 = 7$) line is called "Paschen-delta" (Pa-δ). The first six series have specific names:

- Lyman series with $n_1 = 1$
- Balmer series with $n_1 = 2$
- Paschen series (or Bohr series) with $n_1 = 3$
- Brackett series with $n_1 = 4$
- Pfund series with $n_1 = 5$
- Humphreys series with $n_1 = 6$



The spectral series of hydrogen based on the Rydberg Equation (on a logarithmic scale).

Example 2.1.2.1: The Lyman Series

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

Given: lowest-energy orbit in the Lyman series

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

Strategy:

A. Substitute the appropriate values into Equation ***Ref*2.1.2.2** (the Rydberg equation) and solve for λ.
B. Locate the region of the electromagnetic spectrum corresponding to the calculated wavelength.

Solution:

We can use the Rydberg equation (Equation $\mathbf{Ref2.1.2.2}$ to calculate the wavelength:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_l^2} - \frac{1}{n_h^2} \right)$$

A For the Lyman series, $n_1 = 1$.

$$\begin{aligned} \frac{1}{\lambda} &= R_H \left(\frac{1}{n_l^2} - \frac{1}{n_h^2} \right) \\ &= 1.097 \times m^{-1} \left(\frac{1}{1} - \frac{1}{4} \right) \\ &= 8.228 \times 10^6 \; m^{-1} \end{aligned}$$

Spectroscopists often talk about energy and frequency as equivalent. The cm^{-1} unit (wavenumbers) is particularly convenient. We can convert the answer in part A to cm^{-1}.

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

and

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

This emission line is called Lyman alpha and is the strongest atomic emission line from the sun; it drives the chemistry of the upper atmosphere of all the planets producing ions by stripping electrons from atoms and molecules. It is completely absorbed by oxygen in the upper stratosphere, dissociating O_2 molecules to O atoms, which react with other O_2 molecules to form stratospheric ozone (O_3).

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

? Exercise 2.1.2.1: The Pfund Series

The Pfund series of lines in the emission spectrum of hydrogen corresponds to transitions from higher excited states to $n_1 = 5$. Calculate the wavelength of the *second* line in the Pfund series to three significant figures. In which region of the spectrum does it lie?

Answer

$4.65 \times 10^3 \; nm$; infrared

The above discussion presents only a phenomenological description of hydrogen emission lines. Balmer and Rydberg could predict where emission lines could occur, but they could not explain why lines followed this pattern using any useful theory. For an explanation of why atoms demonstrate discrete emission spectra, quantum theories were developed.

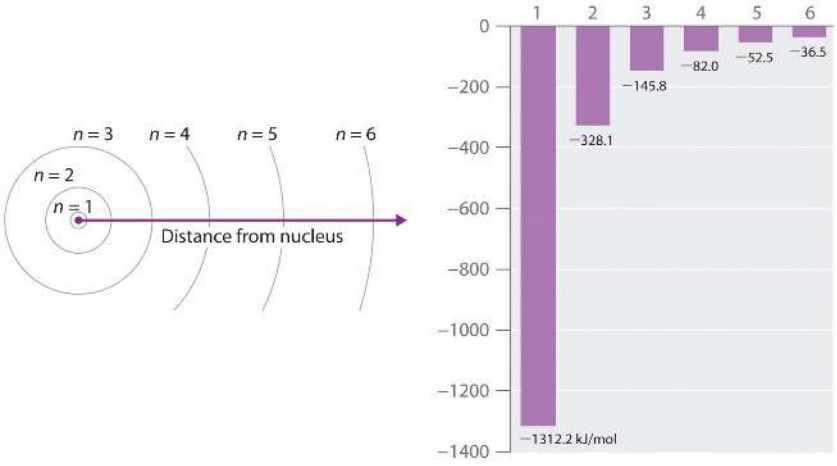
The Bohr Model

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

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

$$E_n = \frac{-R_H hc}{n^2} \tag{2.1.2.4}$$

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

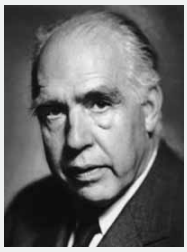


(a) Hydrogen orbits (Bohr model). Orbits are not drawn to scale. **(b) Hydrogen orbit energy (kJ/mol) vs. *n***

Figure **2.1.2.2**: *The Bohr Model of the hydrogen atom (a) The distance of the orbit from the nucleus increases with increasing n. (b) The energy of the orbit becomes increasingly less negative with increasing n.*

Niels Bohr (1885–1962)

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



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

As n decreases, the energy holding the electron and the nucleus together becomes increasingly negative; the radius of the orbit shrinks and more energy is needed to ionize the atom. The orbit with n = 1 is the lowest lying and most tightly bound. The negative sign in Equation ??? indicates that the electron-nucleus pair is more tightly bound (i.e. at a lower potential energy) when they are near each other than when they are far apart. Because a hydrogen atom with its one electron in this orbit has the lowest possible energy, this is the **ground state** (the most stable arrangement of electrons for an element or a compound) for a hydrogen atom. As n increases, the radius of the orbit increases; the electron is farther from the proton, which results in a less stable arrangement with higher potential energy (Figure **2.1.2.2***a*). A hydrogen atom with an electron in an orbit with n > 1 is therefore in an **excited state**, defined as any arrangement of electrons that is higher in energy than the ground state. When an atom in an excited state undergoes a transition to the ground state in a process called decay, it loses energy by emitting a photon whose energy corresponds to the *difference* in energy between the two states (Figure **2.1.2.1**).

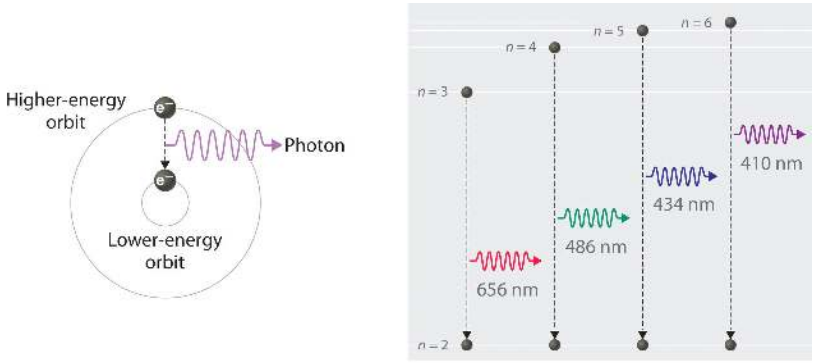


Figure **2.1.2.3**: *The emission of light by a hydrogen atom in an excited state. (a) Light is emitted when the electron undergoes a transition from an orbit with a higher value of n (at a higher energy) to an orbit with a lower value of n (at lower energy). (b) The Balmer series of emission lines is due to transitions from orbits with n ≥ 3 to the orbit with n = 2. The differences in energy between these levels correspond to light in the visible portion of the electromagnetic spectrum.*

So the difference in energy (ΔE) between any two orbits or energy levels is given by $\Delta E = E_{n_l} - E_{n_h}$, where n_l is the final orbit and n_h the initial orbit. Substituting from Bohr's equation (Equation 2.1.2.4) for each energy value gives

$$\Delta E = E_{final} - E_{initial} = -\frac{R_H hc}{n_h^2} - \left(-\frac{R_H hc}{n_l^2}\right) = -R_H hc\left(\frac{1}{n_h^2} - \frac{1}{n_l^2}\right) \tag{2.1.2.5}$$

If $n_h > n_l$, the transition is from a higher energy state (larger-radius orbit) to a lower energy state (smaller-radius orbit), as shown by the dashed arrow in part (a) in Figure **2.1.2.3**. Substituting hc/λ for ΔE gives

$$\Delta E = \frac{hc}{\lambda} = -R_H hc\left(\frac{1}{n_h^2} - \frac{1}{n_l^2}\right) \tag{2.1.2.6}$$

Canceling *hc* on both sides gives

$$\frac{1}{\lambda} = -R_H\left(\frac{1}{n_h^2} - \frac{1}{n_l^2}\right) \tag{2.1.2.7}$$

Except for the negative sign, this is the same equation that Rydberg obtained experimentally. The negative sign in Equations 2.1.2.6 and 2.1.2.7 indicates that energy is released as the electron moves from orbit n_h to orbit n_l because orbit n_h is at a higher energy than orbit n_l. Bohr calculated the value of R_H from fundamental constants such as the charge and mass of the electron and Planck's constant and obtained a value of $1.0974 \times 10^7\ m^{-1}$, the same number Rydberg had obtained by analyzing the emission spectra.

We can now understand the physical basis for the Balmer series of lines in the emission spectrum of hydrogen (**2.1.2.3***b*); the lines in this series correspond to transitions from higher-energy orbits (n > 2) to the second orbit (n = 2). Thus, the hydrogen atoms in the sample have absorbed energy from the electrical discharge and decayed from a higher-energy excited state (n > 2) to a lower-energy state (n = 2) by emitting a photon of electromagnetic radiation whose energy corresponds exactly to the difference in energy between the two states (Figure **2.1.2.3***a*). The n = 3 to n = 2 transition gives rise to the line at 656 nm (red), the n = 4 to n = 2 transition to the line at 486 nm (green), the n = 5 to n = 2 transition to the line at 434 nm (blue), and the n = 6 to n = 2 transition to the line at 410 nm (violet). Because a sample of hydrogen contains a large number of atoms, the intensity of the various lines in a line spectrum depends on the number of atoms in each excited state. At the temperature in the gas discharge tube, more atoms are in the n = 3 than the n ≥ 4 levels. Consequently, the n = 3 to n = 2 transition is the most intense line, producing the characteristic red color of a hydrogen discharge (Figure **2.1.2.1***a*). Other families of lines are produced by transitions from excited states with n > 1 to the orbit with n = 1 or to orbits with n ≥ 3. These transitions are shown schematically in Figure **2.1.2.4** :

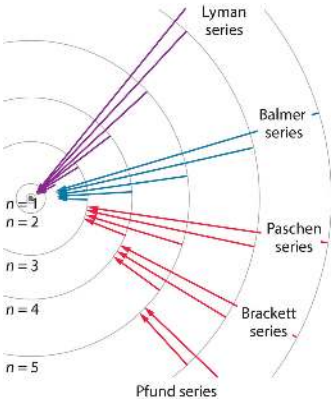


Figure **2.1.2.4**: Electron transitions responsible for the various series of lines observed in the emission spectrum of hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (n = 1); these transitions release a great deal of energy, corresponding to radiation in the ultraviolet portion of the electromagnetic spectrum. The Paschen, Brackett, and Pfund series of lines are due to transitions from higher-energy orbits to orbits with n = 3, 4, and 5, respectively; these transitions release substantially less energy, corresponding to infrared radiation. (Orbits are not drawn to scale.)

Using Atoms to Time

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

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

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

Example 2.1.2.1: The Lyman Series

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

Given: lowest-energy orbit in the Lyman series

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

Strategy:

A. Substitute the appropriate values into Equation 2.1.2.4 (the Rydberg equation) and solve for λ.
B. Use Figure 2.2.1 to locate the region of the electromagnetic spectrum corresponding to the calculated wavelength.

Solution:

We can use the Rydberg equation to calculate the wavelength:

$$\frac{1}{\lambda} = -R_H \left(\frac{1}{n_h^2} - \frac{1}{n_l^2} \right)$$

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

$$\frac{1}{\lambda} = -R_H \left(\frac{1}{n_h^2} - \frac{1}{n_l^2} \right) = 1.097 \times m^{-1} \left(\frac{1}{1} - \frac{1}{4} \right) = 8.228 \times 10^6 \; m^{-1}$$

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

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

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

and

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

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

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

? Exercise 2.1.2.1: The Pfund Series

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

Answer

4.65×10^3 nm; infrared

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

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

Unfortunately, Bohr could not explain *why* the electron should be restricted to particular orbits. Also, despite a great deal of conjecturing, such as assuming that orbits could be ellipses rather than circles, his model could not quantitatively explain the emission spectra of any element other than hydrogen (Figure **2.1.2.5**). In fact, Bohr's model worked only for species that contained just one electron: H, He^+, Li^{2+}, and so forth. Scientists needed a fundamental change in their way of thinking about the electronic structure of atoms to advance beyond the Bohr model.

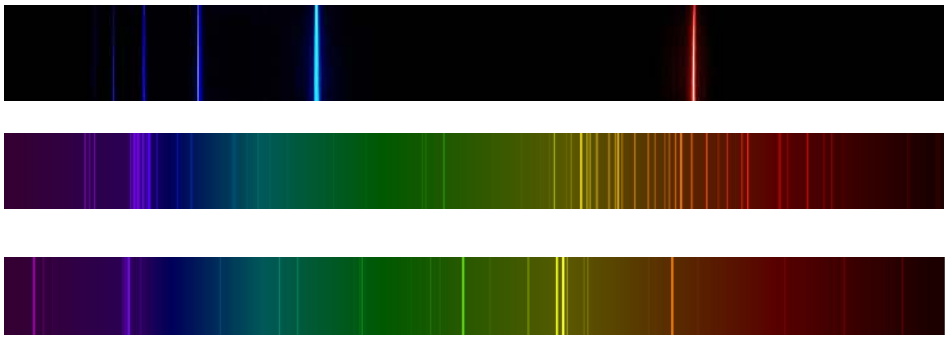


Figure 2.1.2.5: The emission spectra of elements compared to hydrogen. **Top:** hydrogen gas (atomized to hydrogen atoms in the discharge tube). **Middle:** neon. **Bottom:** mercury. The strongest lines in the hydrogen spectrum are in the far UV Lyman series starting at 124 nm and below. The strongest lines in the mercury spectrum are at 181 and 254 nm, also in the UV. These are not shown. Attribution: Hydrogen (Jan Homann / CC BY-SA); Neon (Teravolt at en.Wikipedia / Public domain); Mercury (Teravolt at en.Wikipedia / Public domain)

The Energy States of the Hydrogen Atom

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

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

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

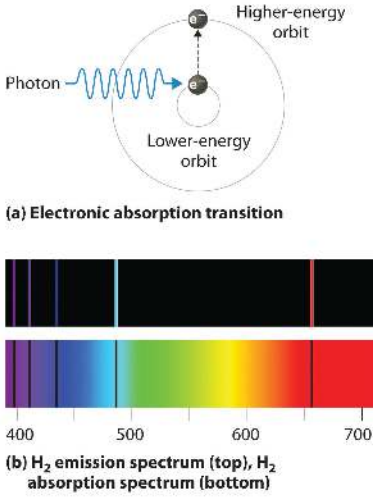


Figure 2.1.2.6: Absorption and emission spectra. Absorption of light by a hydrogen atom. (a) When a hydrogen atom absorbs a photon of light, an electron is excited to an orbit that has a higher energy and larger value of n. (b) Images of the emission and absorption spectra of hydrogen are shown here.

Emission and absorption spectra form the basis of *spectroscopy*, which uses spectra to provide information about the structure and the composition of a substance or an object. In particular, astronomers use emission and absorption spectra to determine the composition of stars and interstellar matter. As an example, consider the spectrum of sunlight shown in Figure 2.1.2.7. Since the sun is very hot, it emits light in the form of a continuous emission spectrum. Superimposed on the spectrum, however, is a series of

dark lines primarily resulting from the absorption of specific frequencies of light by cooler atoms in the outer atmosphere of the sun. By comparing these lines with the spectra of elements measured on Earth, we now know that the sun contains large amounts of hydrogen, iron, and carbon, along with smaller amounts of other elements. During the solar eclipse of 1868, the French astronomer Pierre Janssen (1824–1907) observed a set of lines that did not match those of any known element. He suggested that they were due to the presence of a new element, which he named *helium*, from the Greek *helios*, meaning "sun." Helium (He) was finally discovered in uranium ores on Earth in 1895. Alpha particles are helium nuclei. Alpha particles emitted by radioactive uranium nuclei pick up electrons from the rocks to form helium atoms.

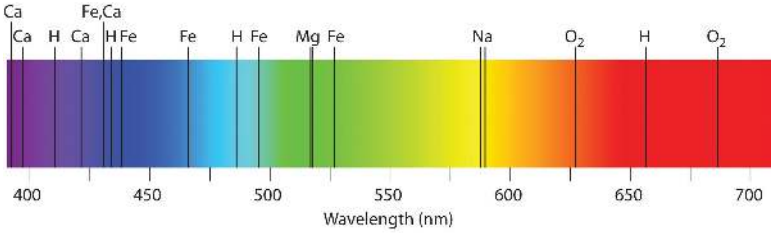


Figure **2.1.2.7**: *The visible spectrum of sunlight. The characteristic dark lines are mostly due to the absorption of light by elements that are present in the cooler outer part of the sun's atmosphere; specific elements are indicated by the labels. The lines at 628 and 687 nm, however, are due to the absorption of light by oxygen molecules in Earth's atmosphere.*

The familiar red color of neon signs used in advertising is due to the emission spectrum of neon shown in part (b) in Figure **2.1.2.5**. Similarly, the blue and yellow colors of certain street lights are caused, respectively, by mercury and sodium discharges. In all these cases, an electrical discharge excites neutral atoms to a higher energy state, and light is emitted when the atoms decay to the ground state. In the case of mercury, most of the emission lines are below 450 nm, which produces a blue light (part (c) in Figure **2.1.2.5**). In the case of sodium, the most intense emission lines are at 589 nm, which produces an intense yellow light.

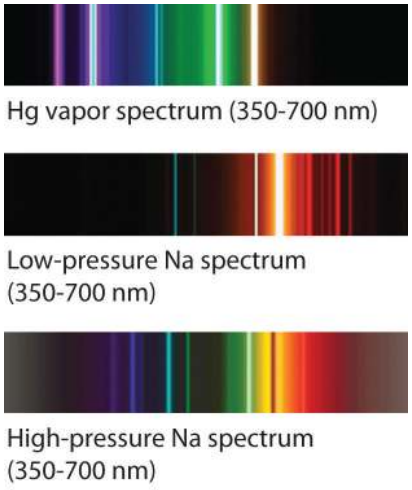


Figure **2.1.2.8**: *The emission spectra of sodium and mercury. Many street lights use bulbs that contain sodium or mercury vapor. Due to the very different emission spectra of these elements, they emit light of different colors. The lines in the sodium lamp are broadened by collisions. The dark line in the center of the high pressure sodium lamp where the low pressure lamp is strongest is caused by absorption of light in the cooler outer part of the lamp.*

Summary

There is an intimate connection between the atomic structure of an atom and its spectral characteristics. Atoms of individual elements emit light at only specific wavelengths, producing a **line spectrum** rather than the continuous spectrum of all wavelengths produced by a hot object. Niels Bohr explained the line spectrum of the hydrogen atom by assuming that the electron moved in circular orbits and that orbits with only certain radii were allowed. Lines in the spectrum were due to transitions in which an electron moved from a higher-energy orbit with a larger radius to a lower-energy orbit with smaller radius. The orbit closest to the nucleus represented the **ground state** of the atom and was most stable; orbits farther away were higher-energy **excited states**. Transitions from an excited state to a lower-energy state resulted in the emission of light with only a limited number of wavelengths. Atoms can also absorb light of certain energies, resulting in a transition from the ground state or a lower-energy

excited state to a higher-energy excited state. This produces an **absorption spectrum**, which has dark lines in the same position as the bright lines in the **emission spectrum** of an element. Bohr's model revolutionized the understanding of the atom but could not explain the spectra of atoms heavier than hydrogen.

Contributors and Attributions

- Modified by Joshua Halpern (Howard University)

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2.2: The Schrödinger equation, particle in a box, and atomic wavefunctions

Considering the failures of the Bohr model, Erwin Schrödinger and Werner Heisenberg proposed a major change in the paradigm regarding the electron. In several breakthrough papers (1925-1927) they attributed wave properties to electrons and they each received Nobel prizes for developing the theories of Wave Mechanics (or the "New Quantum Mechanics"). This approach treated electrons as having "dual" nature: possessing properties of *both* waves and particles.

Schrödinger's Equation describes the behavior of the electron (in a hydrogen atom) in three dimensions. It is a mathematical equation that defines the electron's position, mass, total energy, and potential energy. The simplest form of the Schrödinger Equation is as follows:

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

where $\hat{H}$ is the **Hamiltonian operator**, E is the **energy of the electron**, and ψ is the **wavefunction**.

The Hamiltonian, $\hat{H}$

The Hamiltonian operator is like a set of instructions that tells us what to do with the function that follows it. A Hamiltonian operator is a function over three-dimensional space that corresponds to the sum of kinetic energies and potential energies of the particles in a system, one electron and its nucleus in this case. The Hamiltonian operator for a one-electron system is:

$$\hat{H} = \frac{-h^2}{8\pi^2 m_e}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{Ze^2}{4\pi\epsilon_0 r},$$

where h is Planck's constant, m_e is the mass of the electron, e is the charge of the electron, r is the distance from the nucleus ($r = \sqrt{x^2+y^2+z^2}$), Z is the charge of the nucleus, and $4\pi\epsilon_0$ is the permittivity of a vacuum.

Kinetic Energy

The first part of the Hamiltonian written above, $\frac{-h^2}{8\pi^2 m_e}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$ describes the kinetic energy of the electron. This is the energy due to motion of the electron.

Potential energy

The second part written above, $\frac{-Ze^2}{4\pi\epsilon_0 r}$, describes the potential energy of the electron, and is commonly written as $V(r)$ or $V(x,y,z)$.

$$V(x,y,x) = \frac{-Ze^2}{4\pi\epsilon_0 r} = \frac{-Ze^2}{4\pi\epsilon_0\sqrt{x^2+y^2+z^2}}$$

The potential energy depends on the attractive electrostatic force between the electron and the nucleus. You might notice that this attraction is essentially the same as the electrostatic force defined by Coulomb's law. And, just as in Coulomb's law, when two opposite charges are attracted to one another, the potential energy of the force is negative. Thus, when an electron is close to the nucleus, the potential energy is a large negative number corresponding to a strong attractive force. When an electron is farther from the nucleus, the potential energy is still negative but with a smaller magnitude, corresponding to a weaker attractive force. If the electron is very far from the nucleus ($r = \infty$) then the attractive force, and the potential energy, is zero.

The Wavefunction, ψ

In simple terms, the wavefunction (ψ) of an electron describes the electron's position in space, relative to the nucleus. The square of the ψ describes an atomic orbital. We can't define the position too exactly because we would violate the Heisenberg Uncertainty principle, but we can define its wave. A simple example of a ψ is described in the next section: Particle in a Box. Here, we will describe the ψ in general terms. Generally, in a one-electron atom, the electron ψ is defined by the wave's distance from the nucleus and its angle with respect to the x, y, and z axes of the atom's Cartesian coordinates (the nucleus is at the origin). The general form of the (ψ) for an electron in a hydrogen atom can be written as follows:

$$\psi_{n,l,m_l} = R_{n,l}(r) + Y_{l,m_l}(\theta,\phi)$$

Quantum Numbers define ψ

The (ψ) is defined by three of the quantum numbers: n, l, and m_l. These quantum numbers will be discussed more in a later section (2.2.2) The radial variation, R, depends on the electron's distance from the nucleus. The quantum numbers n (energy level) and l (orbital type) define R. Since n must be an integer, there are only certain allowed values for the solution to the wavefunction.

The angular variation, Y, depends on the angle with respect to the x, y, and z coordinates, and depends on the quantum numbers l (the orbital type) and m_l (the angular momentum, or the specific orbital). For example p_x lies along the x axis, while p_y points in a different direction in space.

For review, a list of the quantum numbers, their values, and meanings are in the table below.

SYMBOL	NAME	VALUES	MEANING
n	principal	$1, 2, 3...$(any integer)	energy level, shell
l	angular momentum	$0 \rightarrow n-1$	subshell, $0 = s, 1 = p, 2 = d, 3 = f...$ this is the angular dependence of the orbital, shape of the orbital *letters have historical meaning, sharp, principle, diffuse, fundamental
m_l	magnetic	$+l \rightarrow -l$	orientation of angular momentum in space, orbital
m_s	spin	$+\frac{1}{2}, -\frac{1}{2}$	the imaginary property we call "spin", up or down

Some important considerations and limitations

Although it might seem like there could be any value of x, y, and z for the Hamiltonian, these values are limited by the allowed positions of electrons according to ψ, which is limited by integer values of n. In other words the allowed solutions are *quantized*. However, there are an infinite number of values for n from $n = 1 \rightarrow \infty$, so there are also infinite solutions to the Schrödinger equation.

The ψ describes the wave properties of an electron. The probability of finding the electron somewhere in space is the square of the wavefunction (ψ^2 or $\psi\psi^*$). In other words, ψ^2 describes the shape and size of an electron's orbital (the shapes you already know).

There are some requirements for a physically realistic and meaningful solution for ψ, and thus ψ^2.

1. There is only one possible value for ψ for any set of the three quantum numbers n, l, m_l.
2. The ψ approaches zero as r approaches infinity, and so ψ^2 also approaches zero as $r \rightarrow \infty$.
3. The wavefunction must be normalized. In other words, the total probability of finding the electron in all of space must be 1.

$$\int_{\text{all space}} \psi_A \psi_A^* d\tau = 1$$

4. Any two orbitals must not occupy the same space. In other words, any two orbitals in an atom are orthogonal. If ψ_A and ψ_B are wavefunctions for different orbitals in the same atom,

$$\int_{\text{all space}} \psi_A \psi_B^* d\tau = 0$$

5. The probability of finding the electron anywhere in infinite space must be defined. This means that the wave functions and their first derivatives must be continuous (i.e. not change abruptly from one point to the next).

Awesome Sources for further reading

- +Plus: https://plus.maths.org/content/schrodinger-1

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2.2.1: Particle in a Box

The particle in the box is a model that can illustrate how a wave equation works. Although it does not represent a real situation, we can limit our model to just one dimension (the x-dimension, for instance) such that the Schrödinger equation becomes significantly simplified. Despite being unrealistic, this simplification is quite useful for gaining an understanding of the Schrödinger equation.

The model of a particle in a box

The particle in the box is a hypothetical situation with a particle trapped in a one-dimensional "box". Let's not get hung-up on the fact that the common object called a "box" is typically an object with three dimensions instead of just one dimension. And let's also not get hung up on the word "particle". This is a particle that has properties of a wave…so it is unlike the macroscopic particle that you're probably imagining. This "box" is more like a line, or an x-axis; it is just a one-dimensional space in which a particle-wave is trapped.

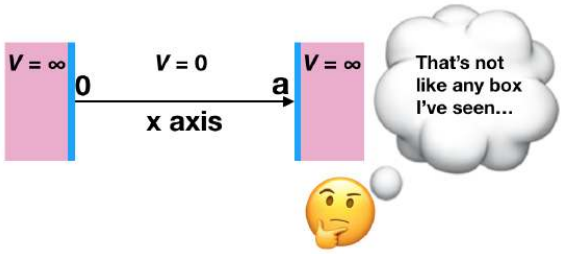


Figure 2.2.1.1. An illustration of the particle in the box model (particle not shown). The box is actually just a one-dimensional space, often assigned to the x-dimension (the x-axis). The particle has wave properties and is trapped in the box. Since no forces act on the particle inside the box, the particle's potential energy inside the box is zero ($V = 0$) and its potential energy outside the box is infinite ($V = \infty$). (CC-BY-NC-SA; Kathryn Haas)

The particle-wave can only exist inside the walls (where $0 < x < a$), along the x axis in the figure shown above. In terms of energy, the potential energy is zero ($V = 0$) because the particle is in an energetically-favorable position here. On the other hand, outside the box, the particle cannot exist and the potential energy is infinitely large ($V = \infty$) outside the walls (where $x < 0$ or $x > a$). This means that it is infinitely unfavorable for the particle-wave to exist outside the box, and so it never does. The particle-wave is trapped between the walls, along the 1-dimensional x axis, and there are no forces acting on the particle-wave inside this "box".

The Schrödinger wave equation for a particle in a box

The particle in a box model lets us consider a simple version of the Schrödinger equation. Before we simplify, let's take another look at the full Hamiltonian for a particle-wave in three dimensions (see equation 2.2.2) and the simplest form of the Schrödinger equation (see equation 2.2.1). Both of these equations are described in the previous section and are written below for convenience.

The Schrödinger Equation (from equation 2.2.1): $\hat{H}\psi = E\psi$

The Hamiltonian in three dimensions (from equation 2.2.2):

$$\hat{H} = \frac{-h^2}{8\pi^2 m_e}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{Ze^2}{4\pi\epsilon_0 r}$$

In the particle in a box model, there is only one dimension, x. Because the y and z values are zero, we can drop y and z out of our Hamiltonian equation. And, since $V = 0$ inside the box, we can drop the whole part of the Hamiltonian equation that describes the potential energy ($\frac{-Ze^2}{4\pi\epsilon_0 r}$). This leaves us with a much simplified Hamiltonian operator, which we can then use to write the Schrödinger wave equation for a particle moving in one dimension. One last thing we'll do is use a more general value m for the mass of the particle, rather than m_e that specifically represents the mass of an electron. The Schrödinger equation for a particle-wave in a one-dimensional box is:

$$\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2\psi(x)}{\partial x^2}\right) = E\psi \qquad (2.2.1.1)$$

? Exercise 2.2.1.1

Follow the steps that were described in the last paragraph to find Equation 2.2.1.1 from equation 2.2.1 and 2.2.2. In other words, derive the Schrödinger Equation for the particle in a box given the three-dimensional Hamiltonian and Schrödinger Equations.

Answer

Here is the Hamitlonian Equation for in three dimensions.

$$\hat{H} = \frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{Ze^2}{4\pi\epsilon_0 r}$$

There are two parts to this equation: the kinetic energy contribution and the potential energy contribution. While the first part of this expression, $\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$, is the **kinetic energy** contribution, the second part of the expression, $-\frac{Ze^2}{4\pi\epsilon_0 r}$, is the **potential energy (V)** contribution.

(1) Simplify the expression for kinetic energy

Your particle-wave is moving in only one dimension. We can arbitrarily choose the dimension x. This means that x is a variable and will have some value from 0 to a. On the other hand, the particle does not move in the other two dimensions, y and z. You can assign the position of the particle along x and y axes as zero or you can just understand that they do not exist in any significant capacity in our 1-D space. Either way, you can just drop them out of the kinetic energy part of the Hamiltonian, as so:

When $y = z = 0$ and the particle-wave only exists/moves in the x dimension, $\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) = \frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}\right)$

And the overall Hamiltonian is simplified:

$$\hat{H} = \frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}\right) - \frac{Ze^2}{4\pi\epsilon_0 r}$$

(2) Simplify the expression for potential energy (V).

The particle's potential energy inside the box is zero ($V = 0$). Therefore, $V = -\frac{Ze^2}{4\pi\epsilon_0 r} = 0$. We can simply drop the potential energy portion from the Hamiltonian because its value is zero.

The simplified Hamiltonian is now:

$$\hat{H} = \frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2}{\partial x^2}\right)$$

(3) Substitute the simplified Hamiltonian into the Schrödinger Equation.

The Schrödinger is: $\hat{H}\psi = E\psi$

When the simplified Hamiltonian is substituted into this equation, the result is the 1-D Schrödinger Equation 2.2.1.1.

$$\left(\frac{-h^2}{8\pi^2 m}\left(\frac{\partial^2 \psi(x)}{\partial x^2}\right)\right) = E\psi$$

The wavefunction of a one-dimensional wave

Although we've simplified the Schrödinger Equation by considering the particle in the box, Equation 2.2.1.1 may still look mysterious to you. But it's simpler than you might realize. Let's unpack it! Here we'll go through the steps of deriving the 1-dimensional wavefunction for the particle in a box. We won't try to derive a three-dimensional wavefunction for a "real" electron, but when you understand how to find the 1-dimensional wavefunction, and what it tells us, then you can conceptually extend this to understand what the wavefunction tells us about electrons in three dimensions.

Let's dissect Equation 2.2.1.1. Here it is again for reference:

$$\frac{-h^2}{8\pi^2 m_e}\left(\frac{\partial^2\psi(x)}{\partial x^2}\right) = E\psi$$

The expression $\frac{-h^2}{8\pi^2 m_e}$ is just a negative constant. This negative constant is multiplied by the second derivative of the wavefunction in the expression above. And E is a constant multiplied by that same function. We can rearrange this equation as follows:

$$\frac{\partial^2\psi(x)}{\partial x^2} = \frac{-8\pi^2 m_e E}{h^2}\psi = -C\psi \tag{2.2.1.2}$$

where C is just the constant; $C = \frac{8\pi^2 m_e E}{h^2}$

To an expert in the mathematical field of Differential Equations, this expression 2.2.1.1 follows a familiar pattern that makes it easy to translate. If you're not an expert in differential equations, that is OK; you'll just have to bear with this while things get a little "hand-wavy" and try Exercise 2.2.1.2 to prove it to yourself that the following "hand waviness" is true. An expert in differential equations could tell you that when the second derivative of a function is equal to a negative constant times that same function, the function can be written in terms of *sin* and *cos*, as shown in Equation 2.2.1.3 (that was the hand-wavy part...see, not so bad):

$$\psi = A\sin(rx) + B\cos(sx) \tag{2.2.1.3}$$

A, B, r, and s are constants in Equation 2.2.1.3. This expression is useful because it is in a form that we could plot with a graphing program (or calculator). However, to do so we must know the constants A, B, r, and s.

What are r and s?

If we substitute expression 2.2.1.3 into Equation 2.2.1.1 and solve for r and s, we find the expressions below.

$$r = s = \sqrt{2m_e E}\left(\frac{2\pi}{h}\right) \tag{2.2.1.4}$$

This shows us that r and s are equal and constant; we know the values for π, h, and m_e, and we can solve for the constant E.

? Exercise 2.2.1.2: Prove that Equation 2.2.1.3 is true

Show that Equation 2.2.1.3 is true in the case that Equation 2.2.1.2 ($\frac{\partial^2\psi(x)}{\partial x^2} = -C\psi$) is true. Also consider Equation 2.2.1.4 (r, s are constants and $r = s$) and explain why the constant r must equal s.

To do this problem, you'll also need to know the basic differentiation rules of **sin** and **cos** functions, given below for convenience.

Differentiation Rules for *sin* and *cos*:

$\frac{d}{dx}\left(\sin(rx)\right) = r\cos(rx)$, where r is a constant.

$\frac{d}{dx}\left(\cos(rx)\right) = -r\sin(rx)$, where r is a constant.

Answer

You can show that 2.2.1.3 is true by substituting 2.2.1.3 back into Equation 2.2.1.2; in other words take the second derivative of the function, $\psi = A\sin(rx) + B\cos(sx)$ to show that $\frac{\partial^2\psi(x)}{\partial x^2} = -C\psi$. C, r, and s are arbitrary constants, and $r = s$. The actual value of these constants is irrelevant for this problem. Here is one way to approach the problem:

(1) Substitute $\psi = A\sin(rx) + B\cos(sx)$ into $\frac{\partial^2\psi(x)}{\partial x^2} = -C\psi$.

$\frac{\partial^2}{\partial x^2}\left(A\sin(rx) + B\cos(sx)\right) = -C\psi$

(2) Take the first and second derivative of $A\sin(rx) + B\cos(sx)$.

The result of taking the first derivative...

$\frac{\partial}{\partial x}\left(rA\cos(rx) - sB\sin(sx)\right) = -C\psi$

...and the second derivative...

$-r^2 A\sin(rx) - s^2 B\cos(sx) = -C\psi$

This is where we see that the only way $\psi = A\sin(rx) + B\cos(sx)$ is if we can factor the values r^2 and s^2 out of the left side. We have a hint that $r = s$ from the discussion above and Equation 2.2.1.4. Now we see that this is a necessary condition for the expression $-r^2 A\sin(rx) - s^2 B\cos(sx) = -C\psi$ to be true.

(3) Simplify

If $r = s$, then $r^2 = s^2$ and we can replace s with r in the equation above, as so...

$$-r^2 A\sin(rx) - r^2 B\cos(sx) = -C\psi$$

Now, we can factor the constant, $-r^2$ out of the left side of this expression,

$$-r^2\left(A\sin(rx) + B\cos(sx)\right) = -C\psi$$

Now we see that $\psi = A\sin(rx) + B\cos(sx)$ when $-C = -r^2$. In other words, we have shown that $\psi = A\sin(rx) + B\cos(sx)$ is true.

Why is this a useful exercise?

Although it is difficult to explain the derivation of the expression $\psi = A\sin(rx) + B\cos(sx)$ without differential equations and only knowing that $\frac{\partial^2\psi(x)}{\partial x^2} = -C\psi$, to show this is true is as simple as solving this exercise. This exercise is here to help you review your calculus and to show you that the "hand waving" in the text above is not magic, but it is coming from math that you have seen in your calculus courses. Math is crucial for explaining the nature of the universe! Eat your vegetables and practice your math.

? Exercise 2.2.1.4

*Complete Exercise **2.2.1.2** before attempting this one.

Derive the expression for r below (from Equation 2.2.1.4) using the 1-D wavefunction (2.2.1.3: $\psi = A\sin(rx) + B\cos(sx)$) and the 1-D Schrödinger equation (2.2.1.1: $\left(\frac{-h^2}{8\pi^2 m_e}\left(\frac{\partial^2\psi(x)}{\partial x^2}\right) = E\psi\right)$).

$$r = \frac{2\pi}{h}\sqrt{2m_e E}$$

Answer

The steps below could be carried out in a different sequence:

(1) Rearrange

Let's move **all constants** to the right side of 2.2.1.1 so that we arrive at the expression that is shown in part of Equation 2.2.1.2 .

$$\frac{\partial^2\psi(x)}{\partial x^2} = \frac{-8\pi^2 m_e E}{h^2}\psi$$

(2) Take the second derivative of ψ, which we found in Exercise **2.2.1.2**.

$$\frac{\partial^2\psi(x)}{\partial x^2} = -r^2\left(A\sin(rx) + B\cos(sx)\right) = \frac{-8\pi^2 m_e E}{h^2}\psi$$

And since $\psi = A\sin(rx) + B\cos(sx)$, we can simplify this by dividing both sides by ψ (or by $A\sin(rx) + B\cos(sx)$).

**recall that $s = r$. So, you could have substituted r for s in the expression above, and you'd still be on the right track.*

$$-r^2 = \frac{-8\pi^2 m_e E}{h^2}$$

(3) Solve for r (*we already showed $r = s$ in the Exercise **2.2.1.2**).

$$r = \sqrt{\frac{8\pi^2 m_e E}{h^2}} = \frac{2\pi}{h}\sqrt{2m_e E}$$

What are A and B?

We can find the possible values of A and B by looking at the possible extremes for the value of x. In our model in Figure 2.2.1.1, we can see that x can have values from $0 \rightarrow a$. The two extremes, where $x = 0$ and $x = a$, lie at the walls of the box. The electron cannot exist beyond these values because it is trapped inside the walls, so its wavefunction must be zero at $x = 0$ and $x = a$.

The case where $x = 0$ can help us find the value of B. We just said that the wavefunction must be zero where $x = 0$. This means:

$$\psi_{x=0} = A\sin(rx) + B\cos(sx) = A\sin(0) + B\cos(0) = 0$$

Because $A\sin(0) = 0$, the expression can be simplified to:

$$\psi_{x=0} = B\cos(0) = B(1) = 0$$

Now we can see that there is only one possible value for the constant, B, that would allow this expression to be true, $B = 0$. And since B is constant then it will always be zero despite the value of x. This simplifies our 1-D wavefunction:

$$\psi = A\sin(rx) \tag{2.2.1.5}$$

The case where $x = a$ can help us find the value for A. Since the wavefunction must be zero where $x = a$:

$$\psi_{x=a} = A\sin(rx) = A\sin(ra) = 0$$

In this case, A cannot be zero because if both A and B are zero, the wavefunction is zero at all values of x, and so our wavefunction would not exist inside the box. So, let's assume A is not zero. Then, it must be the case that

$$\sin(ra) = 0$$

and then because of the way that $\sin$ functions work, the quantity ra must be an integer value of π if $\sin(ra) = 0$.

$$ra = \pm n\pi$$

where $n = 1, 2, 3...$ any non-zero integer. We can ignore negative values here since both positive and negative values of r will give the same value for $\sin(ra)$. We can then solve for r:

$$r = \frac{n\pi}{a} \tag{2.2.1.6}$$

and substitute the value $r = \frac{n\pi}{a}$ into Equation 2.2.1.5 to get:

$$\psi = A\sin\left(\frac{n\pi x}{a}\right) \tag{2.2.1.7}$$

Recall that the square of the wavefunction (ψ^2) gives the probability of finding the electron anywhere in space. In our model, the probability of finding the particle-wave inside the box is unity (it is 1). Mathematically, this is the normalizing requirement (expressed as $\int \psi_A \psi_A^* d\tau = 1$), which can be solved to find the value of A.

$$A = \sqrt{\frac{2}{a}}$$

Now, we can substitute the value of A into expression 2.2.1.7, and we have a wavefunction that can be visualized using any graphing program/calculator!

$$\psi = \sqrt{\frac{2}{a}}\left(\sin\left(\frac{n\pi x}{a}\right)\right) \tag{2.2.1.8}$$

What is the energy (E) of a particle in the box?

So, now you can see how a 1-D wavefunction can be solved. But how do we find the E of the electron from this? Well, in order to not distract you earlier, we skipped over a very simple way to do this. The E falls right out of the equations you just saw. We can set the two expressions we found above for the constant r, (equations 2.2.1.4 and 2.2.1.6) equal to one another and then solve for E:

$$r = \frac{n\pi}{a} = \sqrt{2mE}\left(\frac{2\pi}{h}\right)$$

$$E = \frac{n^2h^2}{8ma^2} \tag{2.2.1.9}$$

Expression 2.2.1.9 can be used to calculate the energy of a particle in a one-dimensional box of length a, given its integer energy level, n. Here we can see that the energy is quantized because n is an integer ($n = 1, 2, 3...$). In other words, n is a **quantum number**.

Making sense of the particle in a box: plotting the 1-D ψ and ψ^2.

No matter whether you're dealing with a 1-dimensional or 3-dimensional wave equation, the wavefunction itself (ψ) describes the particle's wave properties. This ψ doesn't have actual physical meaning, so it's hard to imagine what it "looks like" other than just plotting its function. However, the probability of finding the particle-wave at any specific position along the x-axis between $x = 0$ and $x = a$ is more physically meaningful. The probability of finding the particle is proportional to the square of the wave function, which is represented by either ψ^2 or, sometimes, $\psi\psi^*$. The plots of the functions for ψ and ψ^2 for the first three possible values of n are shown below in Figure 2.2.1.2. You could create plots similar to these simply by plotting the function shown in Equation 2.2.1.8. To plot, you just need to assign a value of n, and it is convenient to assign the length of the box as $a = 1$. The plot generated would have the general ratio of $\frac{x}{a}$ on the x axis, and thus would be relevant for any length box.

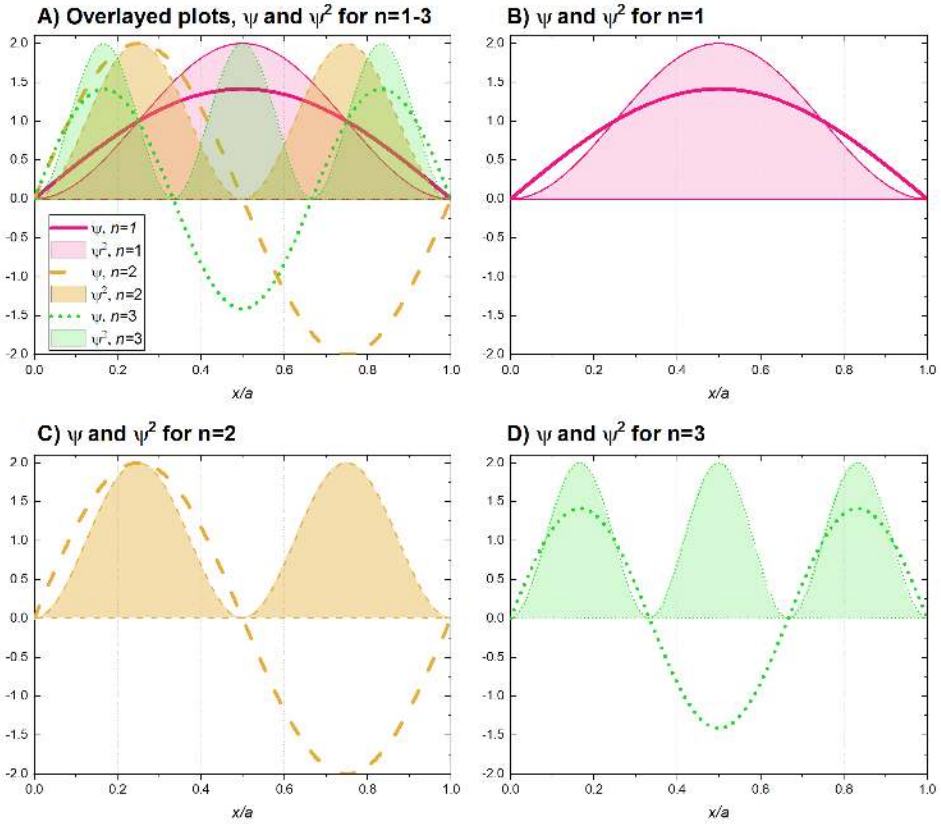


Figure 2.2.1.2. Plots of the 1-D ψ and ψ^2 for $n = 1$, $n = 2$, and $n = 3$ of a box of length a. The wavefunction (ψ) is plotted as a thick solid, dashed, or dotted line. The square of the wavefunction (ψ), which represents the probability of finding the particle at position x, is plotted as the thinner lines and is shaded. Solid lines represent $n = 1$, dashed lines represent $n = 2$, and dotted lines represent $n = 3$. (CC-BY-NC-SA; Kathryn Haas)

The graphs above represent "solutions" to the wave function. For example, the solution $n = 1$ gives the plot shown in Figure 2.2.1.2 B. The solution of $n = 2$ is plotted in Figure 2.2.1.2 C, and so on. These values for n are some of the possible solutions to the 1-dimensional ψ, and they yield descriptions of the wave behavior and probability of finding a particle in 1-dimensional space.

How does this apply to atoms?

The 1-dimensional particle in a box does not represent a real situation; but rather, it is a simple model that we can use to understand a more complex system, like a electron orbiting the nucleus in three dimensions. It's useful to recognize the analogies here that might represent something familiar in a real situation.

$x = 0$ is analogous to the nucleus in an atom. Here in the particle in a box model, $\psi = 0$ and there is zero probability of finding an electron. When this is extended to an atom, this position is analogous to the nucleus (at the origin of a coordinate system where $x = y = z = 0$. A 3-dimensional ψ is also zero at the nucleus and the electron cannot exist there; also, ψ approaches zero as it approaches this position in both the particle in a box model and in a more realistic case of an electron in an atom.

$x = a$ is analogous to a boundary surface far from the nucleus. In the particle in a box model, the 1-dimensional ψ is zero at $x = a$. This is analogous to an electron's ψ approaching zero as it gets further from the nucleus. There will be a more in depth description of boundary surface in the next section (2.2.2). You already know this as the outermost surface of an electron orbital. One minor but notable difference between the 1-dimensional particle in a box and the case of a real atom is that the ψ in three dimensions approaches but never quite reaches zero as distance from the nucleus increases, while $\psi = 0$ for $x = a$ in the more simple case of a 1-dimensional particle in a box.

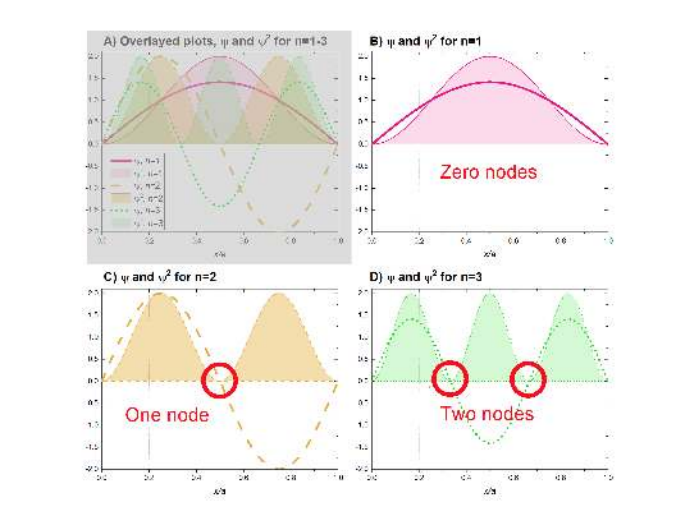
A change in sign of the ψ (and where both $psi = 0$ and $\psi^2 = 0$) is a node. In both the 1-dimensional particle in a box model and in the more realistic 3-dimensional case, a node is found where the ψ changes sign. At this point, $\psi = \psi^2 = 0$; in other words there is zero probability of finding the particle or electron at these points. It is easy to spot these points in the plots above because the wave function crosses the x-axis and the ψ^2 meets zero.

? Exercise 2.2.1.4

Identify the points on plots B, C, and D in Figure **2.2.1.2** that are nodes. How many nodes are there for $n = 1, n = 2,$ and $n = 3$?

Answer

The nodes are annotated with red circles on the figure below. **Panel B** ($n = 1$) has zero nodes. There are two points where $\psi = 0$ in the case of $n = 1$, but these points are at the walls of the box and they are not nodes. The walls of the box are analogous to the nucleus and the boundary surface of an electron orbital. **Panel C** ($n = 2$) has one node where the ψ crosses zero. **Panel D** ($n = 3$) shows two nodes.



? Exercise 2.2.1.5

Use a graphing program to plot the 1-dimensional ψ and ψ^2 for $n = 1, 2, 3, 4$. How many nodes are there for $n = 4$? Is this expected? Predict how many nodes we should expect for $n = 5$.

You can use any plotting program to do this, and if you aren't familiar with any, try this one: Desmos

Answer

You can use any plotting program to do this. This is the function you should plot (it is Equation 2.2.1.8):

$\psi = \sqrt{\frac{2}{a}}\left(\sin\left(\frac{n\pi x}{a}\right)\right)$

For n=1: Assign a value of $n = 1$, as stated in the problem. In the text above, it also states that it is convenient to assign a value of $a = 1$. Assigning these values results in the following function:

$\psi = \sqrt{\frac{2}{1}}\left(\sin\left(\frac{1\pi x}{1}\right)\right)$ and simplifying leads to $\psi = \sqrt{2}\left(\sin\left(\pi x\right)\right)$

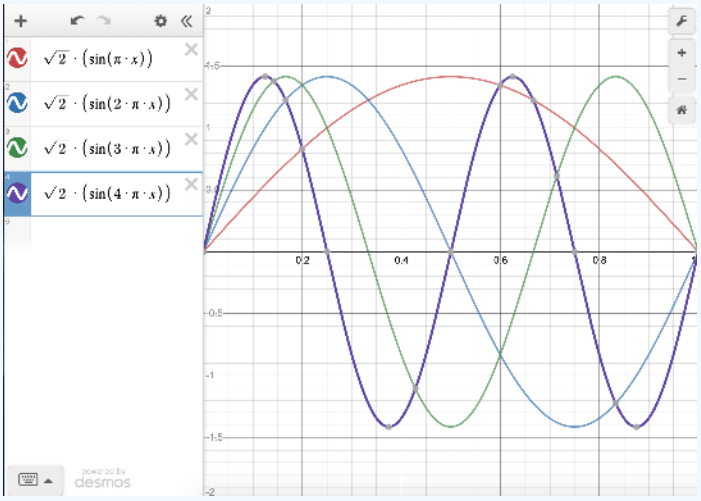
For n=2,3,4 you would repeat the process above. You will get the following functions:

For n=2: $\psi = \sqrt{2}\left(\sin\left(2\pi x\right)\right)$

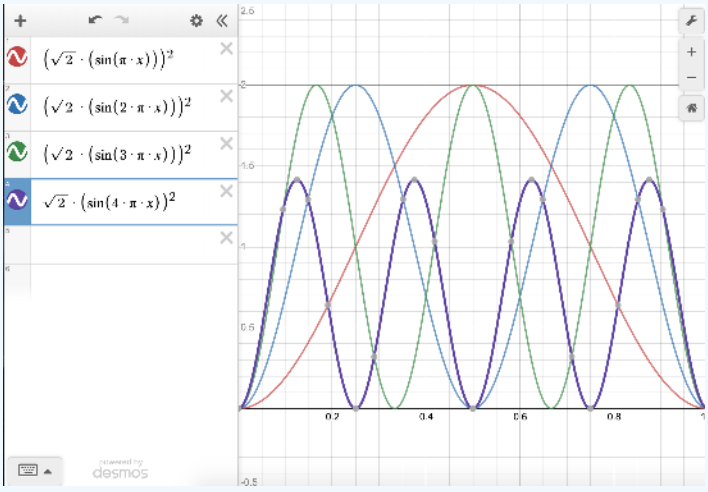
For n=3: $\psi = \sqrt{2}\left(\sin\left(3\pi x\right)\right)$

For n=4: $\psi = \sqrt{2}\left(\sin\left(4\pi x\right)\right)$

In a program like Desmos, you need to input the function correctly. It's useful to know the code for at least one graphing program. For Desmos, and most others, you can find help online. For example, the correct input for Desmos for the n=4 case is sqrt(2)*(sin(4*pi*x)). But, you have to type it in because copy/paste doesn't work. You'll also want to display your graph only from $x = 0$ to $x = 1$ by hitting the settings button (a little wrench in the upper right corner) and changing the x scale. Go ahead and change the y scale too, to $y = -2$ to $y = 2$. If you do this, you should get something that looks like this:



To graph the square of each wavefunction, you'd just square the functions that we just plotted:



> In both the case of ψ and ψ^2, the $n = 4$ function shows three nodes (see the bolded purple line, where nodes are tiny grey spots on the axis). This follows a pattern that you might have noticed with the cases of $n = 1, 2,$ and 3 where the number of nodes is $n - 1$ (nodes = $n - 1$). We should expect three nodes for $n = 4$ based on this pattern, and four nodes for $n = 5$.

In the next section, we will extend these ideas qualitatively to three dimensions. While there is only one quantum number in one dimension, there are three quantum numbers in three dimensions that (when combined) give discrete descriptions of an electron in three-dimensional space (plus a fourth quantum number that explains other properties of the electron).

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2.2.2: Quantum Numbers and Atomic Wave Functions

The one-dimensional particle in a box model from the previous section shows us how a wavefunction works in one dimension (the x-dimension). In one dimension, the wavefunction requires only one quantum number, n. A full explanation of the three-dimensional wavefunction for an electron is outside of the scope of this course. Instead, we will focus on gaining a conceptual understanding by extending knowledge of the one-dimensional wavefunction to a three-dimensional space.

Quantum numbers

Extending the wavefunction to three dimensions requires a total of three quantum numbers. In addition to n, which we saw in the one-dimensional case, we also need l and m_l to express the wavefunction in three dimensions. A complete solution to the Schrödinger equation, both the three-dimensional wavefunction and energy, includes a set of three quantum numbers (n, l, m_l). The wavefunction describes what we know as an atomic orbital; it defines the region in space where the electron is located. Additionally, there is a fourth quantum number, m_s. The m_s quantum number accounts for the observed interaction of electrons with an applied magnetic field; it is an additional postulate that is not part of the wavefunction. These four quantum numbers are described below.

The quantum number, n: This is the principle quantum number. This number represents the shell, including both the overall energy of the electron in that shell and the size of that shell. An allowed value for n is any non-zero, positive integer (1, 2, 3, 4, ... etc are allowed, but 4.1 is not allowed).

The quantum number, l: This is the angular momentum quantum number that corresponds to the subshell and its shape. It represents the angular dependence of the subshell, or the "shape" of the orbitals within a subshell. The allowed values of l depend on n. The allowed values of l for an electron in shell n are integer values between 0 to $n-1$, or $l = 0 \rightarrow n-1$. These values correspond to the orbital shape where $l = 0$ is an s-orbital, $l = 1$ is a p-orbital, $l = 2$ is a d-orbital, and $l = 3$ is an f-orbital.

The quantum number m_l: This is the magnetic quantum number. Its possible values give the number of orbitals within a subshell and its specific value gives the orbital's orientation in space. The allowed values of m_l depend on the value of l. The value of m_l is allowed to be any positive or negative integer between $+l$ and $-l$. In other terms, $m_l = +l \rightarrow -l$. For example, if the electron is in a 3-p-orbital, then $n = 3, l = 1$, and the possible values of m_l are $-1, 0,$ and $+1$. Since there are three possible values of m_l there are three orbitals in the p subshell. The specific m_l value defines in which of the three possible p-orbitals (p_x, p_y, or p_z) the electron exists. In the case of the s subshell, there is only one value, $m_l = 0$ because $l = 0$. The one value corresponds to the fact that there is only one s orbital in any shell.

The quantum number m_s: This quantum number accounts for the electron's "spin". In short, electrons interact with magnetic fields in a way that is similar to how a tiny bar magnet would interact with a magnetic field. The allowed values for m_s are $+\frac{1}{2}$ and $-\frac{1}{2}$.

Table 2.2.2.1. Quantum Numbers

SYMBOL	NAME	VALUES	MEANING
n	principal	$1, 2, 3...$(any integer)	energy level, shell
l	angular momentum	$0 \rightarrow n-1$	subshell, $0 = s, 1 = p, 2 = d, 3 = f...$ this is the angular dependence of the orbital, shape of the orbital *letters have historical meaning, sharp, principle, diffuse, fundamental
m_l	magnetic	$+l \rightarrow -l$	orientation of angular momentum in space, orbital
m_s	spin	$+\frac{1}{2}, -\frac{1}{2}$	the imaginary property we call "spin", up or down

1-Electron Wavefunctions (Atomic orbitals)

One simplified representation of the three-dimensional wavefunction is shown below. This representation breaks the wavefunction into two parts: the **radial contribution** ($R_{n,l}(r)$) and the **angular contribution** ($Y_{l,m_l}(\theta,\phi)$).

$$\psi_{(n,l,m_l)} = R_{n,l}(r) \times Y_{l,m_l}(\theta,\phi) \tag{2.2.2.1}$$

Allowed Energies

From the wavefunction, we can find the allowed energies of an electron in an atom. We have not given you the more complex form of the wavefunction where you'd need to derive 2.2.2.2 from 2.2.2.1 because it is outside the scope of this course. Instead, consider the process that we used to derive the energy of a particle in a one-dimensional box in the previous section. A similar process can be used to find the energy of an electron in three dimensions, shown in 2.2.2.2.

$$E_n = -\frac{hcRZ^2}{n^2} = -(13.607\,eV)\left(\frac{Z}{n}\right)^2 \tag{2.2.2.2}$$

,

where n is the principle quantum number, h is Planck's constant, c is the speed of light, R is the Rydberg constant, and Z is the charge of the nucleus. It is useful to know that the value of $hcR = 13.6eV$. This is also the value of the ionization energy of an electron in a hydrogen atom. This equation only works for **hydrogenic atoms** (atoms or ions that are "like" hydrogen in that they have only one electron).

? Exercise 2.2.2.1

The energy that it takes to eject a ground-state electron from a hydrogen atom (its ionization energy, IE) is measured to be approximately 13.6 eV, while the IE energy of a He^+ ion is four times greater at 54.4 eV. These values can be predicted using both Equation 2.2.2.2 and the Rydberg equation.

a. Using Equation 2.2.2.2 for allowed energies of electrons in a hydrogen atom, derive the energy of the ground state electron in H. Then repeat this process for a He^+ ion. What do the values indicate about the relative attraction between an electron and the nuclei of these two hydrogenic atoms?
b. Show that the IE of H's 1s electron can also be predicted by the Rydberg formula (equation 2.1.2.2).

Answer (a)

Use Equation 2.2.2.2 . For a hydrogen atom with one proton, $Z = 1$, and the ground state energy level is the lowest energy level, $n = 1$. Therefore, the energy of an electron in the ground state of a H atom is:

$E_n = -\frac{hcRZ^2}{n^2} = -13.607\ eV(\frac{1}{1})^2 = -13.607\ eV$, or *approximately* $-13.6\ eV$. Thus, the IE (energy necessary to remove that electron) is +13.6 eV.

We can use the same process to find the ground state energy of an electron in He^+. This time, $Z = 2$ because helium has two protons in its nucleus, and as before, the ground state is $n = 1$.

$E_n = -\frac{hcRZ^2}{n^2} = -13.607\,eV(\frac{2}{1})^2 = -54.428eV$, or *approximately* $-54.4\,eV$. Thus, the IE is +54.4 eV.

These ground-state energies are the same as the energy required to remove the ground state electron from H and He^+. In other words, these are the predicted ground state IE values for one electron in H and He^+. The *measured* IEs for these two species are in fact 13.6 eV and 54.4 eV, respectively.

The He^+ ion has a more negative value for its ground state energy with a magnitude four times greater than that of the ground state H electron. This means that the He^+ electron is more strongly attracted to the (+2) nucleus than the H electron is attracted to the (+1) nucleus, and more energy is required to eject the He^+ electron than the H electron. It takes more energy to remove the electron from He^+ than from H. This makes sense in light of Coulomb's law: The attractive force between the H nucleus (+1) and an electron (-1) would be weaker than that of a He nucleus (+2) and an electron (-1) because the positive charge of the He nucleus has a greater magnitude.

Answer (b)

The Rydberg equation is: $\frac{1}{\lambda} = E(cm^{-1}) = R_H \left(\frac{1}{n_l^2} - \frac{1}{n_h^2}\right)$ where n_l and n_h are positive integers, $n_h > n_l$, and the *Rydberg constant* (R_H), has a value of 1.09737 × $10^7 m^{-1}$. We should set $n_l = 1$ to represent the initial ground state, and $n_h = \infty$ to represent the removal of the electron from the atom.

Step 1.

Calculate Energy (in m^{-1}) using the Rydberg equation:

$$E = R_H \left(\frac{1}{n_l^2} - \frac{1}{n_h^2}\right) = 1.09737 \times 10^7 m^{-1} \left(\frac{1}{1^2} - \frac{1}{\infty^2}\right) = 1.09737 \times 10^7 m^{-1} (1 - 0) = 1.09737 \times 10^7 m^{-1}$$

Ultimately, we want a value of energy in units of eV so we can compare it to the answers in part (a), but our value here is in units of inverse meters (m^{-1}). A quick internet search can tell you the conversion between inverse centimeters (cm^{-1}) and eV is $1eV = 8065.6 cm^{-1}$.

Step 2.

Convert from m^{-1} to cm^{-1} to eV so that we can compare to the answer in part (a):

$1.09737 \times 10^7 \frac{1}{m} \times \frac{1m}{100cm} \times \frac{1eV}{8065.6 \frac{1}{cm}} = 13.6056eV$, or approximately 13.6 eV.

Exercise 2.2.2.2

Which of the following are hydrogenic atoms? H, H^+, H^-, He, He^{2+}, He^+, He^-, Li, Li^{3+}, Li^{2+}, Li^+, Li^- .

Answer

Hydrogenic atoms are atoms or ions that contain only one electron. H, He^+, and Li^{2+} are hydrogenic atoms/ions that contain only one electron.

Radial and Angular contributions to the wavefunction:

Radial contribution, $R_{n,l}(r)$

The radial part of the wavefunction, $R_{n,l}(r)$ gives the radial variation of ψ. In other words, $R_{n,l}(r)$ defines how the wavefunction depends on the distance of the electron from the nucleus (the radius). The $R_{n,l}(r)$ parts of the wavefunction for a hydrogenic atom are listed in Table **2.2.2.2**, and they are plotted in Figure **2.2.2.1**. Notice that the $R_{n,l}(r)$ of all s-orbitals (solid lines) reaches a maximum at $r = 0$. This is unique to the s-orbitals' $R_{n,l}(r)$. The $R_{n,l}(r)$ of p- and d-orbitals orbitals approaches zero as r approaches zero. This has important consequences for how closely an electron in these orbitals can approach the nucleus.

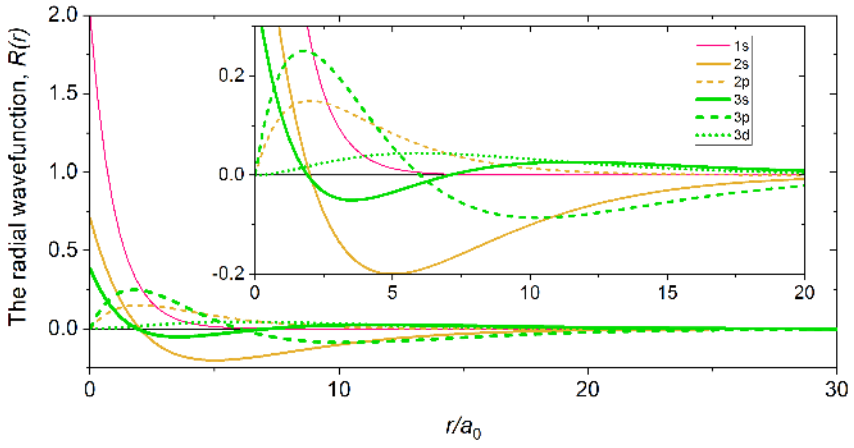


Figure **2.2.2.1**. Plots of the radial wavefunction, $R_{n,l}(r)$, for the first three shells. The wavefunctions are plotted relative to $\frac{r}{a_0}$, where $a_0 = 52.9pm = 0.529\text{Å}$ is the Bohr Radius (the radius of a hydrogen 1s orbital). The expressions for these radial wavefunctions ($R_{n,l}(r)$) are shown in Table **2.2.2.2**. (Kathryn Haas; CC-NC-BY-SA)

Table 2.2.2.2. Radial wavefunctions ($R(r)$) for the first three shells of a hydrogen atom. Z is the nuclear charge, and $a_0 = 52.9pm = 0.529\text{Å}$ is the Bohr radius (the radius of a hydrogen 1s orbital). For the H atom, $Z = 1$ (the nuclear charge of hydrogen). Plotting of the functions can be simplified if we set $a_0 = 1$ and plot the functions with respect to r/a_0, which was done to find the plots shown in Figure 2.2.2.1.

Orbital	n	l	$R_{n,l}(r)$
1s	1	0	$2\left[\frac{Z}{a_0}\right]^{3/2} e^{-Zr/a_0}$
2s	2	0	$2\left[\frac{Z}{2a_0}\right]^{3/2}\left(2-\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$
2p	2	1	$\frac{1}{\sqrt{3}}\left[\frac{Z}{3a_0}\right]^{3/2}\left(\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$
3s	3	0	$\frac{2}{27}\left[\frac{Z}{3a_0}\right]^{3/2}\left(27-18\frac{Zr}{a_0}-2(\frac{Zr}{a_0})^2\right) e^{-Zr}$
3p	3	1	$\frac{1}{81\sqrt{3}}\left[\frac{2Z}{a_0}\right]^{3/2}\left(6-\frac{Zr}{a_0}\right)(\frac{Zr}{a_0})e^{-Zr/3a_0}$
3d	3	2	$\frac{1}{81\sqrt{15}}\left[\frac{2Z}{a_0}\right]^{3/2}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$

Radial probability function, $4\pi r^2(R_{n,l}(r))^2$

Just like in the particle-in-a-box model, the square of the wavefunction is proportional to the probability of finding a particle (electron) at some point in space. The square of the radial part of the wavefunction is called the radial distribution function $4\pi r^2(R_{n,l}(r))^2$, and it describes the probability of locating the electron at some distance r away from the nucleus. When we normalize the probability functions by dividing the function by its integral over all space, we get the plots shown in Figure 2.2.2.2. The normalized probability functions are compared to the original radial part of the wavefunctions in Figure 2.2.2.3. The most probable distance for finding an electron is shown by the maximum value of the function. For an electron in the 1s orbital of H, the most probable distance from the nucleus occurs at $r = 1a_0$. This is the Bohr Radius, and it has a value of $a_0 = 52.9pm = 0.529\text{Å}$. It is convenient to plot the functions of the hydrogen atomic orbitals relative to the size of its smallest orbital, the 1s orbital; this is the reason we plot $R_{n,l}(r)$ and $4\pi r^2(R_{n,l}(r))^2$ relative to $\frac{r}{a_0}$.

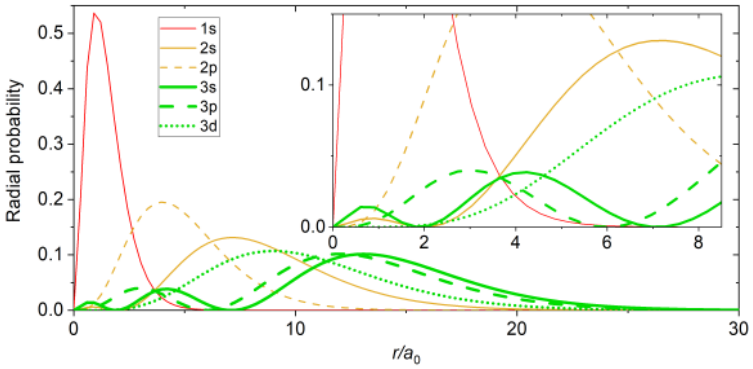


Figure 2.2.2.2: Plots of the normalized radial probability functions for the first three shells. The radial wavefunctions ($R_{n,l}(r)$) are shown in Table 2.2.2.2. (Kathryn Haas; CC-NC-BY-SA)

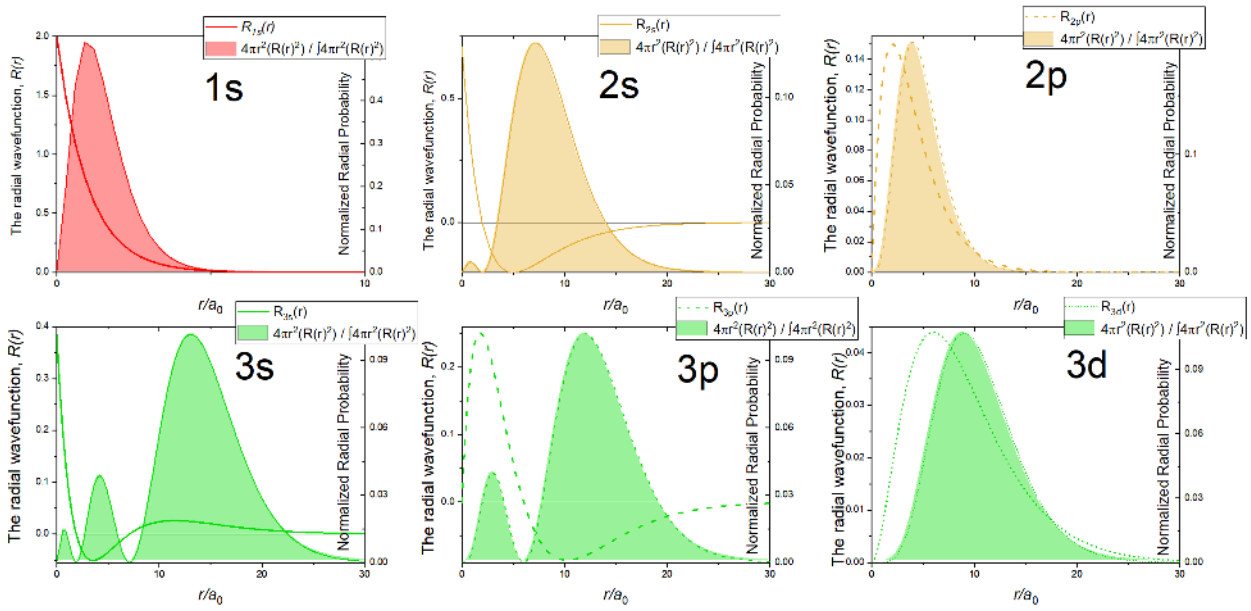


Figure **2.2.2.2**. Plots of the normalized radial probability function for each orbital in the first three shells (shaded curves). The radial wavefunctions are also shown (Table **2.2.2.2**). The y-axis on the left of each plot corresponds to the radial wavefunction (line); the y-axis on the right of each plot corresponds to the radial probability function (shaded). (Kathryn Haas; CC-NC-BY-SA)

Radial nodes

From the discussion of the 1-dimensional particle in a box, we learned that nodes exist where $\psi = 0$. In the case of the 3-dimensional wavefunction, there are two different types of nodes: radial nodes and angular nodes. **Radial nodes occur where the radial part of the wavefunction is zero ($R(x) = 0$)**. These are easy to find by plotting the radial part of the wavefunction and finding where the radial part of the wavefunction (and the radial probability function) is zero (where $R_{n,l}(r) = 0$) and where $4\pi r^2 (R_{n,l}(r))^2 = 0$. These nodes are spherical in shape and depend on the energy level and subshell (the values of n and l). **The number of radial nodes is $n - l - 1$**. An example of a radial node is the single node that occurs in the **2*s*** orbital ($2 - 0 - 1 = 1$ node). In contrast, the 1s orbital has zero radial nodes ($1 - 0 - 1 = 0$ nodes). Where there is a node, there is zero probability of finding an electron.

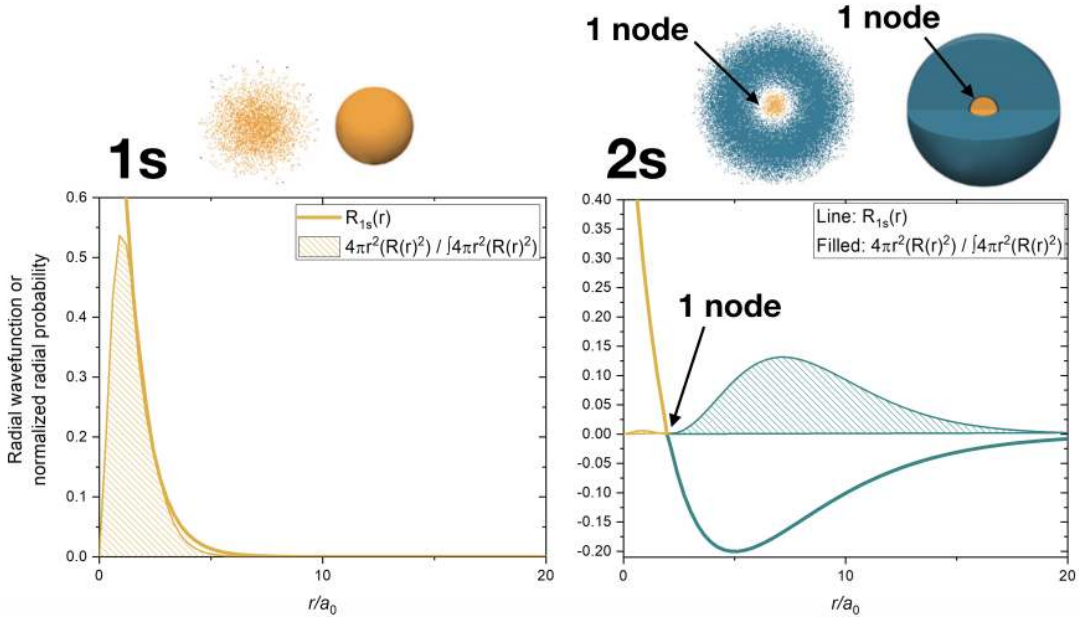


Figure **2.2.2.3**: Visualization of the 1s and 2s atomic orbitals. Each orbital is shown as both an electron probability density plot and a contour plot above its wavefunction and probability density function. The 1s orbital has zero radial nodes. The 2s orbital has one radial node where its wavefunction changes sign and its radial probability function is zero. (Kathryn Haas; CC-BY-SA)

Boundary surfaces

A true node occurs where the probability of finding an electron is zero. Nodes occur where $\psi = \psi^2 = 0$. Far from the nucleus, the probability of finding the electron rapidly approaches zero, but is never *exactly* zero. What this means is that it is rather improbable to find the electron at far distances from the nucleus, but it's not impossible. The rapid fall of probability creates a boundary surface rather than a node. The boundary surface represents the area around the nucleus where the electron exists most of the time.

? Exercise 2.2.2.1

How many radial nodes are in the s, p, d, and f orbitals in the first four shells? $n = 1, 2, 3, 4$?

Answer

You can approach this answer by using the mathematical relationship between the number of radial nodes and the values of n and l: **number of radial nodes is $n - 1 - l$**. You could also notice the pattern that the first orbital of any type (1s, 2p, 3d...) has zero radial nodes, the second orbital of a type (2s, 3p, 4d...) has one radial node, the third orbital of a type has two radial nodes (3s, 4p, 5d...)...etc.

A full list of all of the orbitals in the first four shells and their number of radial nodes is below. It's a good idea to prove to yourself that the numbers given below are consistent with the plots of the orbitals' wavefunctions for those orbitals in the first three shells:

s-orbitals:

1s: $n - 1 - l = 1 - 1 - 0 = 0$, zero radial nodes

2s: $n - 1 - l = 2 - 1 - 0 = 1$, one radial node

3s: $n - 1 - l = 3 - 1 - 0 = 2$, two radial nodes

4s: $n - 1 - l = 4 - 1 - 0 = 3$, three radial nodes

p-orbitals

2p: $n - 1 - l = 2 - 1 - 1 = 0$, zero radial nodes

3p: $n - 1 - l = 3 - 1 - 1 = 1$, one radial node

4p: $n - 1 - l = 4 - 1 - 1 = 2$, two radial nodes

d-orbitals

3d: $n-1-l=3-1-2=0$, zero radial nodes

4d: $n-1-l=4-1-2=1$, one radial nodes

f-orbital

4f: $n-1-l=4-1-3=0$, zero radial nodes

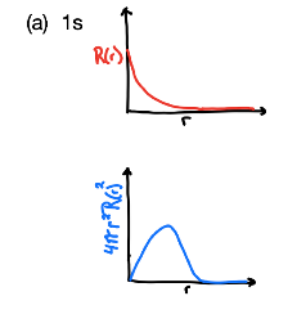
Exercise 2.2.2.1

Draw a rough plot of the following:

a. The radial wavefunction, $R_{n,l}(r)$ and the probability density function, $4\pi r^2(R_{n,l}(r))^2$, for the 1s orbital.
b. The radial wavefunction, $R_{n,l}(r)$ and the probability density function, $4\pi r^2(R_{n,l}(r))^2$, for the 4s orbital.

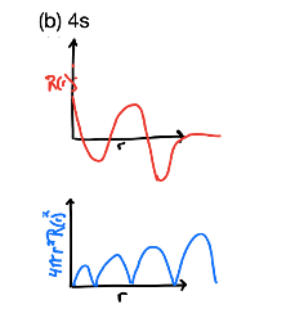
Answer, 1s

The 1s orbital's $R_{n,l}(r)$ reaches a maximum near the origin and approaches zero far from the nucleus. The $4\pi r^2(R_{n,l}(r))^2$ approaches zero at the origin, has a maximum intensity at the Bohr radius, and approaches zero far from the nucleus (its boundary surface).



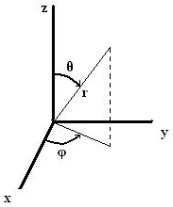
Answer, 4s

Like all s orbitals, the 4s orbital's $R_{n,l}(r)$ reaches a maximum near X=0, but it would be less intense than the function of the 1s, 2s, and 3s orbitals. It should have three radial nodes and so its wavefunction would change sign three times. This would give four regions of electron density in the probability function while the function would approach zero (boundary surface) far from the nucleus.



Angular contribution, $Y_{l,m_l}(\theta,\phi)$, and angular probability function, $(Y_{l,m_l}(\theta,\phi))^2$

The angular contribution to the wavefunction, $Y_{l,m_l}(\theta,\phi)$, describes the wavefunction's shape, or the angle with respect to a coordinate system. To describe the direction in space, we use spherical coordinates that tell us distance *and* orientation in 3-dimensional space. There are three spherical coordinates: r, ϕ, and θ. r is the radius, or the actual distance from the origin. ϕ and θ are angles. ϕ is measured from the positive x axis in the xy plane and may be between 0 and 2π. θ is measured from the positive z axis towards the xy plane and may be between 0 and π.



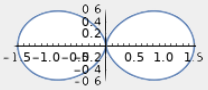
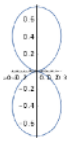
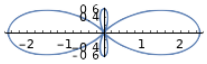
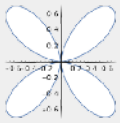
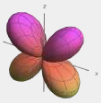
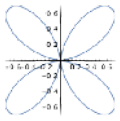
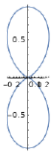
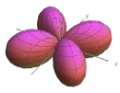
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$$Y_{l,m_l}(\theta,\phi) = \left(\frac{1}{4\pi}\right)^{1/2} y(\theta,\phi)$$

$Y_{l,m_l}(\theta,\phi)$, is slightly more difficult to describe than the radial contribution was. This is partly because $Y_{l,m_l}(\theta,\phi)$ contains imaginary numbers, which have no real, physical meaning. However, the angular part of the wavefunction becomes more "real" when you square it to get angular probability density, a more tangible concept described as the **shapes of orbitals**.

The values of θ, ϕ, and $y(\theta,\phi)$ for orbitals in the hydrogen atom are listed in Table **2.2.2.3**. But $Y_{l,m_l}(\theta,\phi)$ is only a mathematical function and has no real physical meaning. The square of the radial wavefunction, $Y_{l,m_l}(\theta,\phi)^2$, gives the probability of finding the electron at a point in space on a ray described by (ϕ,θ). Thus $Y_{l,m_l}(\theta,\phi)^2$ describes the shape of the orbital.

Table **2.2.2.3**. Components of the angular wavefunction and the resulting orbital shapes. The plots in the two right hand columns were created using Desmos and Mathematica: specifically "Spherical Harmonics" from the Wolfram Demonstrations Project, http://demonstrations.wolfram.com/SphericalHarmonics/ and "Visualizing Atomic Orbitals" demonstrations.wolfram.com/Vi...tomicOrbitals/.

subshell	m_l (orbital)	θ	ϕ	Plots of θ^2	orbital shapes
$l = 0$, s	$m_l = 0$	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2\pi}}$		
$l = 1$, p	$m_l = 0$	$\frac{\sqrt{6}}{2}\cos\theta$	$\frac{1}{\sqrt{2\pi}}$		
$l = 1$, p	$m_l = +1$	$\frac{\sqrt{3}}{2}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{i\phi}$		
$l = 1$, p	$m_l = -1$	$\frac{\sqrt{3}}{2}\sin\theta$	$\frac{1}{\sqrt{2\pi}}e^{-i\phi}$		
$l = 2$, d	0	$\frac{\sqrt{10}}{4}\left(3\cos^2\theta - 1\right)$	$\frac{1}{\sqrt{2\pi}}$		
$l = 2$, d	$m_l = +1$	$\frac{\sqrt{15}}{2}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}e^{i\phi}$		
$l = 2$, d	$m_l = -1$	$\frac{\sqrt{15}}{2}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}e^{-i\phi}$		
$l = 2$, d	$m_l = +2$	$\frac{\sqrt{15}}{4}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{i2\phi}$		
$l = 2$, d	$m_l = -2$	$\frac{\sqrt{15}}{4}\sin^2\theta$	$\frac{1}{\sqrt{2\pi}}e^{-i2\phi}$		

Angular nodes

Angular nodes exist where $(Y_{l,m_l}(\theta,\phi))^2 = 0$. These nodes are planar in shape, and they depend on the value of l. The number of angular nodes in any orbital is equal to l. This means that s-orbitals ($l = 0$) have zero angular nodes, p-orbitals ($l = 1$) have one angular node, d-

orbitals ($l = 2$) have two angular nodes, and so on. Planar nodes can be flat planes (like the nodes in all p orbitals) or they can have a conical shape, like the two angular nodes in the d_{z^2} orbital. Angular nodes in some p and d orbitals are shown in Figure 2.2.2.4.

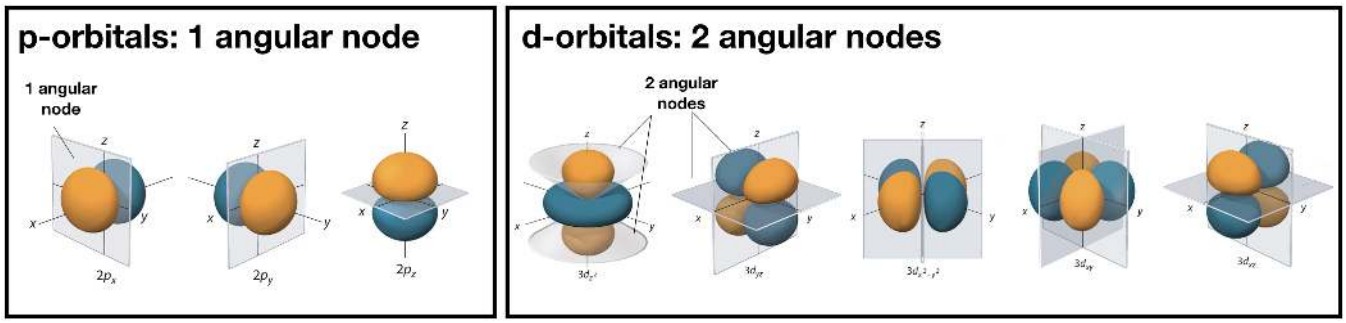
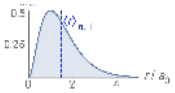
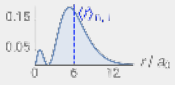
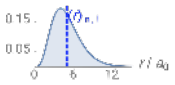
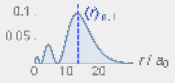
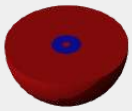
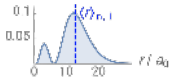
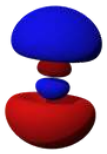
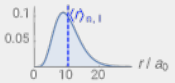
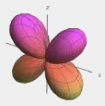


Figure 2.2.2.4: The angular nodes in p-orbitals and d-orbitals are shown. Every p orbital has one angular node, and every d orbital has two angular nodes. The number of angular nodes in any orbital is equal to the value of the quantum number, l. (CC BY-NC-SA; anonymous by request)

Atomic Orbitals

Atomic orbitals result from a combination of both the radial and angular contributions of the wavefunction. Atomic orbitals can have both angular nodes and radial nodes, depending on the values of n and l.

The chart below compares the radial variation, angular variation, and their combinations (orbitals).

Orbital	Radial Probability	Radial Nodes	Angular Probability	Angular Nodes	Combination (Orbital)	Total Nodes
1s		0		0		0
2s		1		0		1
2p		0		1		1
3s		2		0		2
3p		1		1		2
3d		0		2		2

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2.2.3: Aufbau Principle

Introduction

The **Aufbau Principle** (also called the **building-up principle** or the **Aufbau rule**) states that, in the ground state of an atom or ion, electrons fill atomic orbitals of the lowest available energy level before occupying higher-energy levels. In general, an electron will occupy an atomic orbital with the lowest value of n, l, m_l, in that order of priority. The value of m_s for an unpaired electron is conventionally assigned a value of $+\frac{1}{2}$. Each electron in an atom/ion must have a unique set of values for all four quantum numbers.

The Ground State of Hydrogenic Atoms/Ions

In a hydrogenic atom/ion, there is only one electron. In this case, the *only factor determining energy is the value of* n. The ground state will always be the 1s orbital ($n = 1, l = 0, m_l = 0, m_s = +\frac{1}{2}$).

The Ground State of Multi-electron Atoms/Ions

In atoms/ions with two or more electrons, the ground state electron configuration (1) minimizes the total energy of the electrons, (2) obeys the Pauli exclusion principle, (3) obeys Hunds rule of maximum multiplicity, and (4) considers the exchange interaction. These "rules" are described below.

(1) Electrons will occupy the lowest energy orbitals in order to minimize the total energy. The two quantum numbers that are related to energy in multi-electron atoms are n, and l. Thus, orbitals with the lowest values of n and l will fill first.

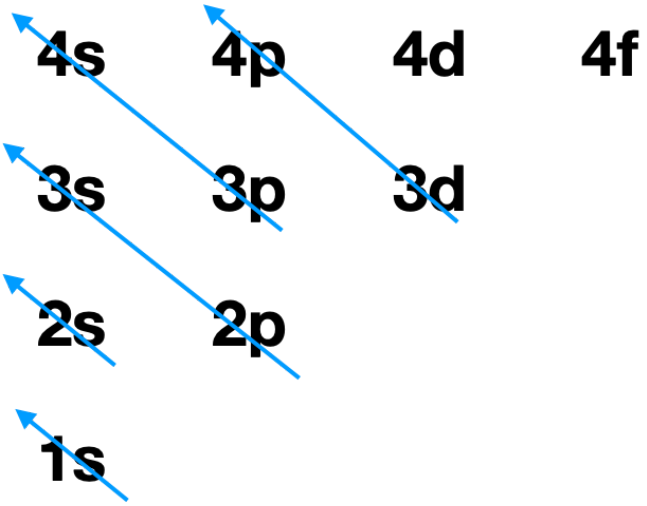


Figure **2.2.3.1**. The order of filling of ground state electron orbitals is 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, etc... (CC-BY-NC-SA; Kathryn Haas)

(2) Hund's rule of maximum multiplicity states that for a given electron configuration, the lowest energy arrangement of electrons in degenerate orbitals is the one with the greatest "multiplicity," where multiplicity is the number of unpaired electrons (n) plus 1 (multiplicity = n + 1). This rule is used to predict the ground state of an atom or molecule with one or more open electronic shells.

Hund's rule is based on empirical observation of atomic spectra, and it is a consequence of the energy required to pair two electrons in the same orbital. This energy of repulsion between two electrons in the same orbitals is a Coulombic energy of repulsion, Π_c, caused by two electrons with like charge sharing the same area of space (an orbital). When more than one electron occupies a set of degenerate orbitals, the most favorable arrangement is one where the number of paired electrons is minimized.

A simplified definition of Hund's rule is that **the lowest energy arrangement is the one with the greatest number of unpaired electrons**. This implies that if two or more orbitals of equal energy are available, electrons will occupy them singly before filling them in pairs. Examples of ground

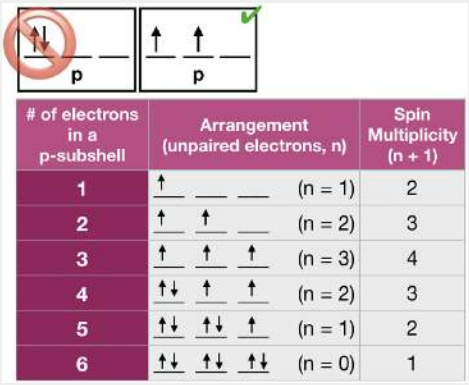


Figure 2.2.3.2. Hund's rule is that spin multiplicity must be maximized in the ground state.

(Kathryn Haas; CC-NC-BY-SA)

state arrangements of electrons in three degenerate p-orbitals is given in the figure shown here.

(3) The Pauli exclusion principle states that it is impossible for two electrons of a multi-electron atom to have the same set of values for all four quantum numbers. Two electrons in different orbitals will have a different set of n, l, and m_l values. When two electrons reside in the same orbital, they posses the same n, l, and m_l values, therefore their m_s must be different. Thus, two electrons in the same orbital must have opposite half-integer spin projections of $+\frac{1}{2}$ and $-\frac{1}{2}$.

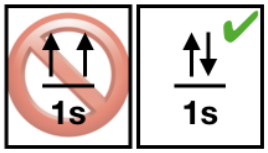


Figure 2.2.3.3. Pauli's principle tells us that paired electrons must have opposite spin. (Kathryn Haas; CC-NC-BY-SA)

(4) The exchange interaction is sometimes called the *exchange energy* or *exchange force*. However, it is not a true energy or force. Rather, it is a quantum mechanical effect that takes place between identical particles. The exchange interaction results in a ground state electron configuration with unpaired electrons all being of the same spin. Unpaired electrons are conventionally written in the "spin up" direction.

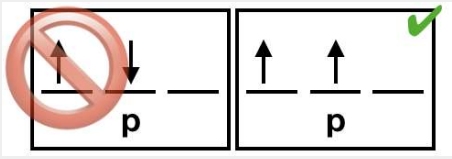


Figure 2.2.3.4. Unpaired electrons should have identical spins due to the exchange interaction. (Kathryn Haas; CC-NC-BY-SA)

Trends in Expected Electron Configuration

The four "rules" above can be used as guidelines to predict the ground state electron configuration of atoms, the filling of subshells, and the configuration of electrons in degenerate orbitals. However, the utility of these guidelines for predicting actual electron configurations requires more nuanced knowledge of the relative energy levels of orbitals.

Generally, orbital energy levels directly correspond to their shell number. Additionally, orbitals within a shell generally follow the energetic trend where s<p<d<f. Although these general trends for relative orbital energy levels hold true for most of the main block elements (the s - and p-blocks), there are important exceptions in the orbital energy levels of transition metal atoms and ions of the d- and f-blocks.

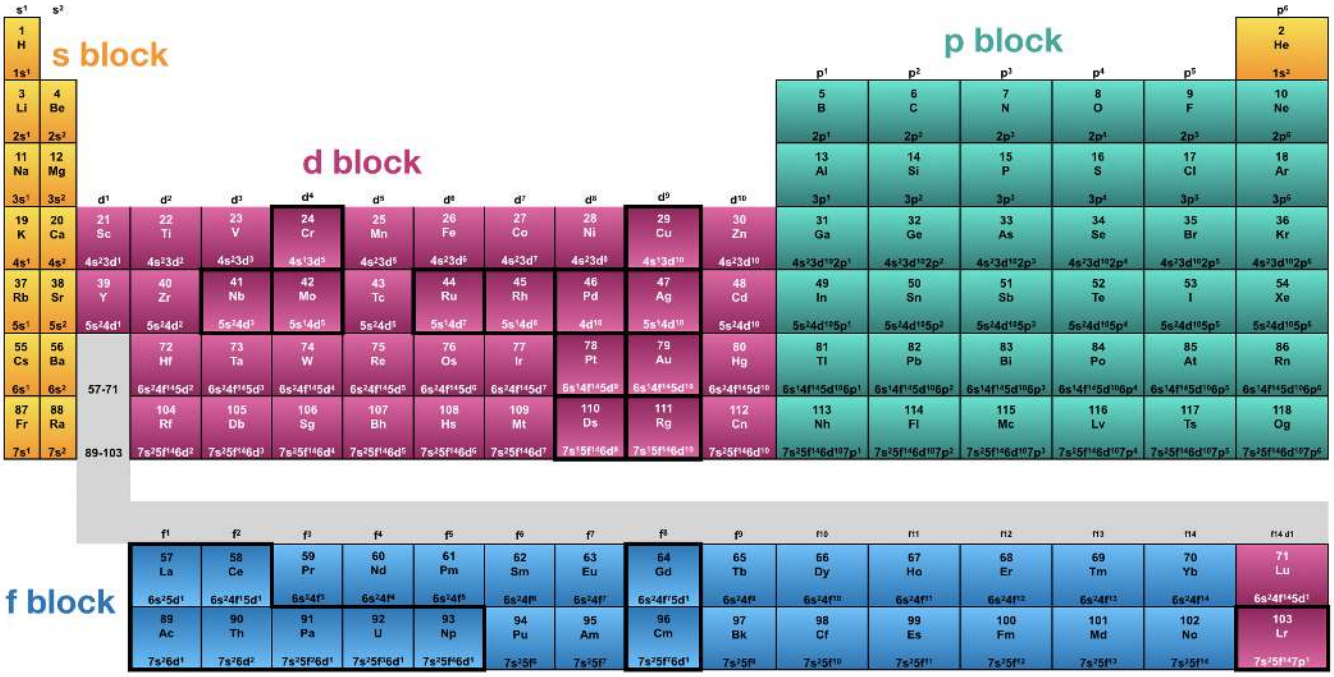


Figure **2.2.3.5**. This is a depiction of the periodic table that highlights the s-, p-, d-, and f- blocks in different colors. Violations of the expected trend in electron configurations are outlined in a heavy black line. Several elements of the d block and f block violate the general trends in electron configuration because their orbital energy levels do not follow *general* trends. (CC-BY-NC-SA; Kathryn Haas)

Elements that violate general trends in electron configuration are outlined with a dark line in Figure **2.2.3.5**. All of the exceptions are within the d- and f- blocks, and the violations are caused by an unexpected order of the orbital energy levels.

In the next section you will learn why the orbital energy levels correlate with shell number and why subshells within a shell usually follow the trend that s<p<d<f. You will also learn why there are occasional exceptions to this trend and how these exceptions influence elemental properties.

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1. Miessler, Gary L., and Donald A. Tarr. *Inorganic Chemistry*. Upper Saddle River, NJ: Pearson Prentice Hall, 2010. Print.
2. Brown, Ian David. *The Chemical Bond in Inorganic Chemistry the Bond Valence Model*. Oxford: Oxford UP, 2006. Print.

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2.2.4: Shielding

Introduction

Coulomb's Law is from classical physics; it tells us that particles with opposite electrostatic charge are attracted to each other, and the larger the charge on either particle or the closer the distance between them, the stronger the attraction. Coulomb's law explains why atomic size decreases as the charge on the nucleus increases, but it can't explain the nuances and variations in size as we go across the periodic table. Coulomb's Law also explains why electrons in different shells (*n*), at different distances from the nucleus, have different energies. But on its own, Coulomb's law doesn't quite explain why electron subshells within a shell (like 2s vs. 2p) would have different energies. To explain these things, we need to consider how both electron **shielding** and **penetration** result in variations in effective nuclear charge (Z*) that depend on shell and subshell.

Effective Nuclear Charge (Z*)

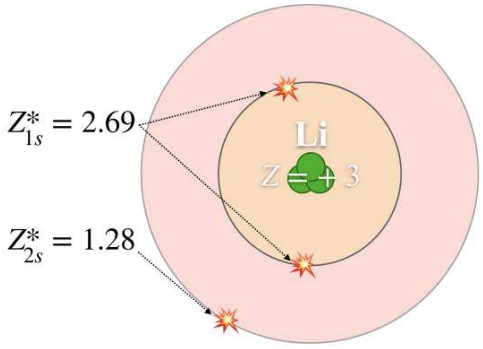


Figure **2.2.4.1**. In a lithium atom, the nuclear charge (Z) is +3. 1s electrons experience an effective nuclear charge (Z*) of +2.69, and 2s electrons experience an Z* of +1.28. (CC-BY-NC-SA; Kathryn Haas)

Coulombs' law works well for predicting the energy of an electron in a hydrogen atom (because H has only one electron). It also works for hydrogen-like atoms: any nucleus with exactly one electron (a He^+ ion, for example, has one electron). However, Coulomb's law is insufficient for predicting the energies of electrons in multi-electron atoms and ions.

Electrons within a multi-electron atom interact with the nucleus and with all other electrons. Each electron in a multi-electron atom experiences both attraction to the nucleus and repulsion from interactions with other electrons. The presence of multiple electrons decreases the nuclear attraction to some extent. Each electron in a multi-electron atom experiences a different magnitude of (and attraction to) the nuclear charge depending on what specific shell and subshell the electron occupies. The amount of positive nuclear charge experienced by any individual electron is the **effective nuclear charge (Z*)**.

For example, in lithium (Li), none of the three electrons "feel" the full +3 charge from the nucleus (see Figure **2.2.4.1**). Rather, each electron "feels" a Z* that is less than the actual Z and that depends on the electron's orbital. The actual nuclear charge in Li is $Z = +3$; the 1s electrons experience a $Z^* = +2.69$, and the 2s electron experiences a $Z^* = +1.28$. In general, core electrons (or the electrons closest to the nucleus), "feel" a Z* that is close to, but less than, Z. On the other hand, outer valence electrons experience a Z* that is much less than Z.

In summary:

- Core electrons: $Z^* \lessapprox Z$
- Valence electrons: $Z^* \ll Z$

Shielding:

Shielding is the reduction of true nuclear charge (Z) to the effective nuclear charge (Z*) by other electrons in a multi-electron atom or ion. Shielding occurs in all atoms and ions that have more than one electron. H is the only atom in which shielding does not occur.

Explanation of shielding: Electrons in a multi-electron atom interact with the nucleus and all other electrons in the atom. To describe shielding, we can use a simplified model of the atom: we will choose an electron-of-interest in a multi-electron atom and treat all the "other" electrons as a group of spherically-distributed negative charge. Classical electrostatics allows us to treat spherical distribution of charge as a point of charge at the center of the distribution. Thus, we consider all the "other" electrons in our atom as a point of negative charge in the center of the atom. While the positive charge of the nucleus provides an attractive force toward our electron, the negative charge distribution at the center of the atom would provide a repulsive force. The attractive and repulsive forces would partially cancel each other; but since there are less "other" electrons than there are protons in our atom, the nuclear charge is never completely canceled. The "other" electrons partially block, or shield, part of the nuclear charge so that our electron-of-interest experiences a partially-reduced nuclear charge, the Z*.

In reality, there is not a one-for-one "canceling" of the nuclear charge by each electron. Partly due to *penetration*, no single electron can completely shield a full unit of positive charge. Core electrons shield valence electrons, but valence electrons have little effect on the Z* of core electrons. The ability to shield, and be shielded by, other electrons strongly depends the electron orbital's average distance from the nucleus and its *penetration*; thus shielding depends on both shell (n) and subshell (l).

Shielding depends on electron penetration

Coulomb's law shows us that distance of an electron from its nucleus is important in determining the electron's energy (its attraction to the nucleus). The shell number (n) determines approximately how far an electron is from the nucleus *on average*. Thus, all orbitals in the same shell (s,p,d) have similar sizes and similar average distance of their electrons from the nucleus. But there is another distance-related factor that plays a critical role in determining orbital energy levels: *penetration*. **Penetration** describes the ability of an electron in a given subshell to penetrate into other shells and subshells to get close to the nucleus. Penetration is the **extent to which an electron can approach the nucleus**. Penetration depends on both the shell (n) and subshell (l).

The penetration of individual orbitals can be visualized using the radial probability functions. For example, Figure **2.2.4.2** below shows plots of the radial probability function of the 1s, 2s, and 2p orbitals. From these plots, we can see that the 1s orbital is able to approach the closest to the nucleus; thus it is the most penetrating. While the 2s and 2p have most of their probability at a farther distance from the nucleus (compared to 1s), the 2s orbital and the 2p orbital have different extents of penetration. Notice that the 2s orbital is able to penetrate the 1s orbital because of the central 2s lobe. The 2p orbital penetrates somewhat into the 1s, but it cannot approach the nucleus as closely as the 2s orbital can. While the 2s orbital penetrates more than 2p (the 2s orbital can approach closer to the nucleus), the 2p is slightly *closer on average* than 2s. The order of Z* in 2s and 2p subshells depends on which factor (average distance or penetration) is more important. In the first two rows of the periodic table, penetration is the dominant factor that results in 2s having a lower energy than 2p (see Figure **2.2.4.4** for values).

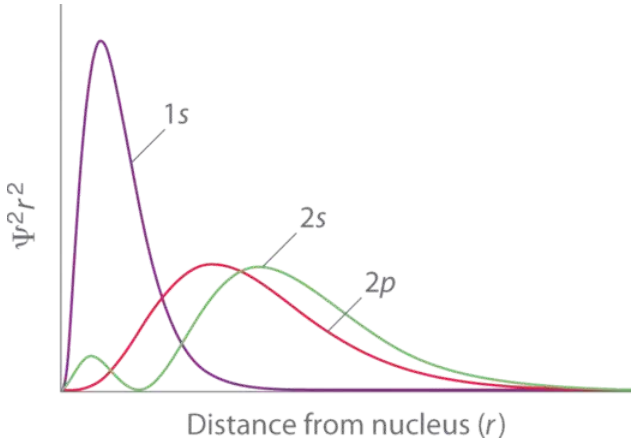


Figure **2.2.4.2**. Orbital Penetration. A comparison of the radial probability distribution of the 2s and 2p orbitals for various states of the hydrogen atom shows that the 2s orbital penetrates inside the 1s orbital more than the 2p orbital does. Consequently, when an electron is in the small inner lobe of the 2s orbital, it experiences a relatively large value of Z*, which causes the energy of the 2s orbital to be lower than the energy of the 2p orbital.

An electron orbital's penetration affects its ability to shield other electrons and affects the extent to which it is shielded by other electrons. In general, electron orbitals that have greater penetration experience stronger attraction to the nucleus and less shielding by other electrons; these electrons thus experience a larger Z*. Electrons in orbitals that have greater penetration also shield other electrons to a greater extent.

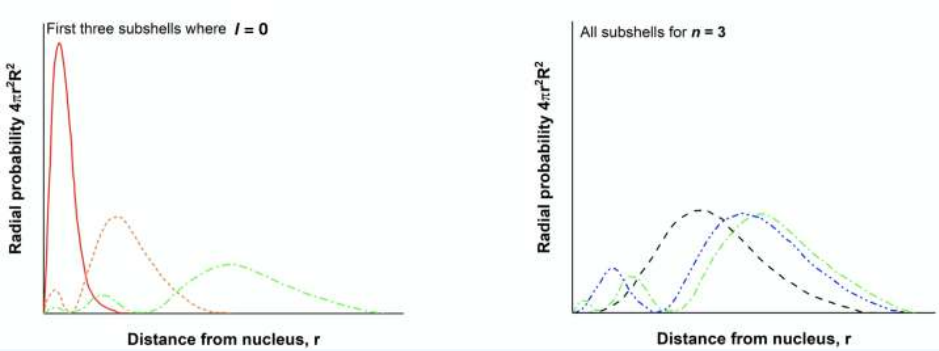
Within the same shell value (n), the penetrating power of an electron follows this trend in subshells (m_l):

s>p>d>f

Exercises

Exercises

1. Compare the 2s and 2p orbitals:
   (a) Which is closer to the nucleus on average?
   (b) Which is more penetrating?
   (c) Which orbital experiences a stronger Z* and is thus lower in energy (consider your experience, but also inspect Figures 1.1.2.3 and 1.1.2.4 from the previous page)? Please explain.
2. Peruse the Hyperphysics page (click) that shows radial probability functions of several orbitals (click around on various orbitals). Compare the 2p and 3s orbitals:
   (a) Which is farther from the nucleus on average?
   (b) Which is more penetrating?
   (c) Which orbital is lower in energy?
3. Which atom, Li, or N, has a stronger valence Z*? Explain why.
4. Explain why 2s and 2p subshells are completely degenerate in a hydrogen atom.
5. Which atom has a smaller radius: Be or F? Explain.
6. Which electrons shield others more effectively: 3p or 3d?
7. Use the clues given in the figures below to label the radial distribution functions shown.



8. Examine the plots on the right in the previous question, above. Note that this is a plot showing the probability density for the 3s, 3p, and 3d subshells.
(a) For which of these three functions is the highest probability density at the smallest r value (which is closest to the nucleus on average)? Is this the same subshell that penetrates most?
(b) Use this example to describe how penetration and shielding result in a splitting of subshell energy level in multi-electron atoms.

9. Explain why the ground state (most energetically favorable) electron configuration of Be is $1s^2 2s^2$ rather than alternative configurations like $1s^2 2s^1 2p^1$ or $1s^2 2p^2$.

Answer 1

(a) The 2s orbital is closer to the nucleus on average.

(b) The 2s orbital is more penetrating than 2p.

(c) You might "know" that the 2s orbital is lower in energy than 2p because 2s fills first. But a close inspection of Figures 1.1.2.3 and 1.1.2.4 from the previous page indicates that while the 2s and 2p elements are degenerate in Ne (element 10), for elements with atomic number 11 and greater 2p has a higher Z* than 2s! This example illustrates that both average distance and penetration are factors in determining Z*, and the factor that is more important may change as we increase in atomic number.

Answer 2

(a) The 3s orbital reaches farther away from the nucleus and is on average farther from the nucleus than 2p.

(b) The 3s orbital is more penetrating than 2p, even though 3s is farther on average!

(c) The 2p orbital is lower in energy than 3s; this is because 2p is still significantly closer to the nucleus on average and experiences a stronger Z*. (Penetration is not the only consideration!)

Answer 3

A nitrogen atom has a stronger effective nuclear charge (Z*) than lithium due to its greater number of protons; even though N also has more electrons that would shield the nuclear charge, each electron only partially shields each proton. This means that atoms with greater atomic number always have greater Z* for any given electron.

Answer 4

The hydrogen atom has only one electron; thus there is no shielding to consider. When there are not other electrons to shield the nucleus, penetration and shielding are irrelevant, and subshells within a shell are degenerate.

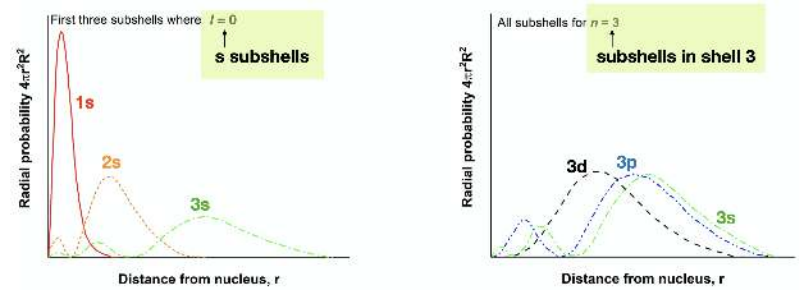
Answer 5

Fluorine has a smaller radius than beryllium because F has a greater valence Z* and therefore pulls the valence electrons closer to the nucleus and provides a smaller atomic radius.

Answer 6

3p shields better than 3d because p orbitals penetrate more than d orbitals within the same shell.

Answer 7



Answer 8

3d is closest on average, but 3s penetrates most. The three subshells of $n = 3$ differ in their average distance and in their ability to penetrate; these factors result in differences in the Z* experienced by electrons in each orbital. We would expect 3s to be lowest in energy followed by 3p and then 3d.

Answer 9

This question is asking why the 2s orbital fills in Be before 2p is occupied. This is a multi-electron atom, therefore core electrons shield the 2s and 2p orbitals to different extents. In Be we expect the 2s orbital to fill before 2p because 2s penetrates more and experiences a higher Z*.

Slater's rules for estimating Z*

The Z* can be estimated using a number of different methods; probably the best known and most commonly used method is known as **Slater's Rules**. Slater developed a set of rules to estimate Z* based on how many other electrons exist in the atom and on the

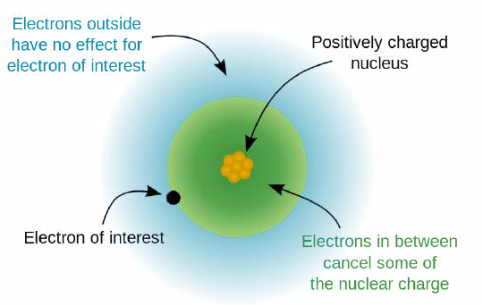


Figure **2.2.4.3**. Diagram illustrating effective nuclear charge according to Slater's rules.

orbital location of the electron-of-interest. These two factors are important determinants in shielding, and they are used to calculate a **shielding constant (S)** used in Slater's formula:

$$Z* = Z - S$$

where Z is the actual nuclear charge (the atomic number) and Z* is the effective nuclear charge.

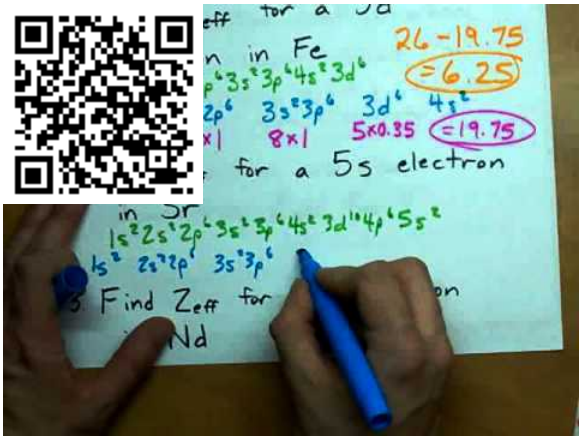
In the calculation of S, it is assumed that electrons closer to the nucleus than our electron-of-interest cancel some of the nuclear charge; those farther from the nucleus have no effect. To calculate S, all the relevant orbitals in an atom are written out in order of increasing energy, separating them into in "groups". Each change in shell number is a new group; s and p subshells are in the same group but d and f orbitals are their own group. You write out all the orbitals using parentheses until you get to the group of the electron-of-interest, like this:

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

**Critical: The orbitals must be written in order of increasing energy!

1. **Electrons in the same Group():** Each other electron (not counting the electron-of-interest) in the same group () as the chosen electron, contributes 0.35 to S.
   Conceptually, this means electrons in the same group shield each other 35%.
2. **Electrons in Groups() to the left:**
   - If the electron-of-interest is in a d or f subshell, every electron in groups () to the left contributes 1.00 to S.
     Conceptually, this means that d and f electrons are shielded 100% by all electrons in the same shell with a smaller value of l*, as well as all electrons in lower shells (*n*).*
   - If the electron-of-interest is in an s or p subshell, all electrons in the next lower shell (n - 1) contribute 0.85 to S. And all the electrons in even lower shells contribute 1.00 to S.
     Conceptually, this means that s and p electrons are shielded 85% by the electrons one shell lower, and 100% by all electrons in shells n - 2 or lower.
3. ***1s electrons:*** *S of a 1s electron is just S=0.3, no matter the element.*

A video explaining how to use Slater's Rules



Example 2.2.4.1: Fluorine, Neon, and Sodium

What is the Z* experienced by the valence electrons in the three isoelectronic species: fluorine anion (F^-), neutral neon atom (Ne), and sodium cation (Na^+)?

Solution

Each species has 10 electrons, and the number of core electrons is 2 (10 total electrons - 8 valence), but the effective nuclear charge varies because each has a different atomic number (Z). The approximate Z* can be found with Slater's Rules. For all of these species, we would calculate the same sigma value:

Calculating S: (1s)(2s,2p), $S = 2(0.85) + 7(0.35) = 1.7 + 2.45 = 4.15$

Fluorine anion: $Z* = 9 - S = 9 - 4.15 = 4.85$

Neon atom: $Z* = 10 - S = 10 - 4.15 = 5.85$

Sodium Cation: $Z* = 11 - S = 11 - 4.15 = 6.85$

So, the sodium cation has the greatest effective nuclear charge.

? Exercise 2.2.4.1

Calculate Z* for a 3d-electron in a zinc (Zn) atom.

Answer

Write out the relevant orbitals: (1s)(2s,2p)(3s,3p)(3d) ~~(4s)~~

Notice that although 4s is fully occupied, we don't include it because in Zn, 4s is higher in energy than 3d. Therefore, 4s is to the right of the d electrons we are considering. The electron-of-interest is in 3d, so the other nine electrons in 3d each contribute 0.35 to the value of S. The other 18 electrons each contribute 1 to the value of S.

$$S = 18(1) + 9(0.35) = 21.15$$

$$Z* = 30 - 21.15 = 8.85$$

So, although the nuclear charge of Zn is 30, the 3d electrons only experience a $Z* \approx 8.85$!

"Best" values for Z*

Slater's rules are a set of simple rules for predicting S and Z* based on empirical evidence from quantum mechanical calculations. In other words, the Z* calculated from Slater's rules are approximate values. The values considered to be the most accurate are derived from quantum mechanical calculations directly. You can find these values in a nice chart on the Wikipedia article of Effective Nuclear Charge. The chart is recreated here in Figure 2.2.4.3 for convenience:

Z or Z_{eff}	H																	He
Z	1.00																	2.00
1s	1.00																	1.69
	Li	Be											B	C	N	O	F	Ne
Z	3.00	4.00											5.00	6.00	7.00	8.00	9.00	10.00
1s	2.69	3.69											4.68	5.67	6.67	7.66	8.65	9.64
2s	1.28	1.91											2.58	3.22	3.85	4.49	5.13	5.76
2p													2.42	3.14	3.83	4.45	5.10	5.76
	Na	Mg											Al	Si	P	S	Cl	Ar
Z	11.00	12.00											13.00	14.00	15.00	16.00	17.00	18.00
1s	10.63	11.61											12.59	13.58	14.56	15.54	16.52	17.51
2s	6.57	7.39											8.21	9.02	9.83	10.63	11.43	12.23
2p	6.80	7.83											8.96	9.95	10.96	11.98	12.99	14.01
3s	2.51	3.31											4.12	4.90	5.64	6.37	7.07	7.76
3p													4.07	4.29	4.89	5.48	6.12	6.76
	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Z	19.00	20.00	21.00	22.00	23.00	24.00	25.00	26.00	27.00	28.00	29.00	30.00	31.00	32.00	33.00	34.00	35.00	36.00
1s	18.49	19.47	20.46	21.44	22.43	23.41	24.40	25.38	26.37	27.35	28.34	29.33	30.31	31.29	32.28	33.26	34.25	35.23
2s	13.01	13.78	14.57	15.38	16.18	16.98	17.79	18.60	19.41	20.21	21.02	21.83	22.60	23.37	24.13	24.89	25.64	26.40
2p	15.03	16.04	17.06	18.07	19.07	20.08	21.08	22.09	23.09	24.10	25.10	26.10	27.09	28.08	29.07	30.07	31.06	32.05
3s	8.68	9.60	10.34	11.03	11.71	12.37	13.02	13.68	14.32	14.96	15.59	16.22	17.00	17.79	18.60	19.40	20.22	21.03
3p	7.73	8.66	9.41	10.10	10.79	11.47	12.11	12.78	13.44	14.09	14.73	15.37	16.20	17.01	17.85	18.71	19.57	20.43
4s	3.50	4.40	4.63	4.82	4.98	5.13	5.28	5.43	5.58	5.71	5.84	5.97	7.07	8.04	8.94	9.76	10.55	11.32
3d			7.12	8.14	8.98	9.76	10.53	11.18	11.86	12.53	13.20	13.88	15.09	16.25	17.38	18.48	19.56	20.63
4p													6.22	6.78	7.45	8.29	9.03	9.34
	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Z	37.00	38.00	39.00	40.00	41.00	42.00	43.00	44.00	45.00	46.00	47.00	48.00	49.00	50.00	51.00	52.00	53.00	54.00
1s	36.21	37.19	38.18	39.16	40.14	41.13	42.11	43.09	44.08	45.06	46.04	47.03	48.01	48.99	49.97	50.96	51.94	52.92
2s	27.16	27.90	28.62	29.37	30.13	30.88	31.63	32.38	33.16	33.88	34.63	35.39	36.12	36.86	37.60	38.33	39.07	39.80
2p	33.04	34.03	35.00	35.99	36.98	37.97	38.94	39.95	40.94	41.93	42.92	43.91	44.90	45.89	46.87	47.86	48.85	49.84
3s	21.84	22.66	23.55	24.36	25.17	25.98	26.79	27.60	28.44	29.22	30.03	30.84	31.63	32.42	33.21	34.00	34.79	35.58
3p	21.30	22.17	23.09	23.85	24.62	25.47	26.38	27.22	28.15	29.02	29.81	30.69	31.52	32.35	33.18	34.01	34.84	35.67
4s	12.39	13.44	14.26	14.90	15.28	16.10	17.20	17.66	18.58	18.99	19.87	20.87	21.76	22.66	23.54	24.41	25.30	26.17
3d	21.68	22.73	25.40	25.57	26.25	27.23	28.35	29.36	30.41	31.45	32.54	33.61	34.68	35.74	36.80	37.84	38.90	39.95
4p	10.88	11.93	12.75	13.46	14.08	14.98	15.81	16.44	17.14	17.72	18.56	19.41	20.37	21.27	22.18	23.12	24.03	24.96
5s	4.99	6.07	6.26	6.45	5.92	6.11	7.23	6.49	6.64	(empty)	6.76	8.19	9.51	10.63	11.62	12.54	13.40	14.22
4d			15.96	13.07	11.24	11.39	12.88	12.81	13.44	13.62	14.76	15.88	16.94	17.97	18.97	19.96	20.93	21.89
5p													8.47	9.10	10.00	10.81	11.61	12.43

Figure 2.2.4.4. This chart shows Z* values calculated by Clementi et al. in 1963 and 1967 that are consistent with SCF Calculations. This chart was created using data from the Wikipedia article on Effective Nuclear Charge. (Kathryn Haas; CC-NC-BY-SA)

Z* modulates attraction

When valence electrons experience less nuclear charge than core electrons, different electrons experience different magnitudes of attraction to the nucleus. A modified form of Coulomb's Law is written below, where e is the charge of an electron, Z* is the effective nuclear charge experienced by that electron, and r is the radius (distance of the electron from the nucleus).

$$F_{eff} = k\frac{Z* e^2}{r^2}$$

This formula suggests that if we can estimate Z*, then we can predict the attractive force experienced by, and the energy of, an electron in a multi-electron atom (ex. Li).

The attraction of the nucleus to valence electrons determines the atomic or ionic size, ionization energy, electron affinity, and electronegativity. The stronger the attraction, and the stronger Z*, the closer the electrons are pulled toward the nucleus. This in turn results in a smaller size, higher ionization energy, higher electron affinity, and stronger electronegativity.

General Periodic Trends in Z*

Close inspection of Figure **2.2.4.3** and analysis of Slater's rules indicate that there are some predictable trends in Z*. The data from Figure **2.2.4.3** is plotted below in Figure **2.2.4.4** to provide a visual aid to the discussion below.

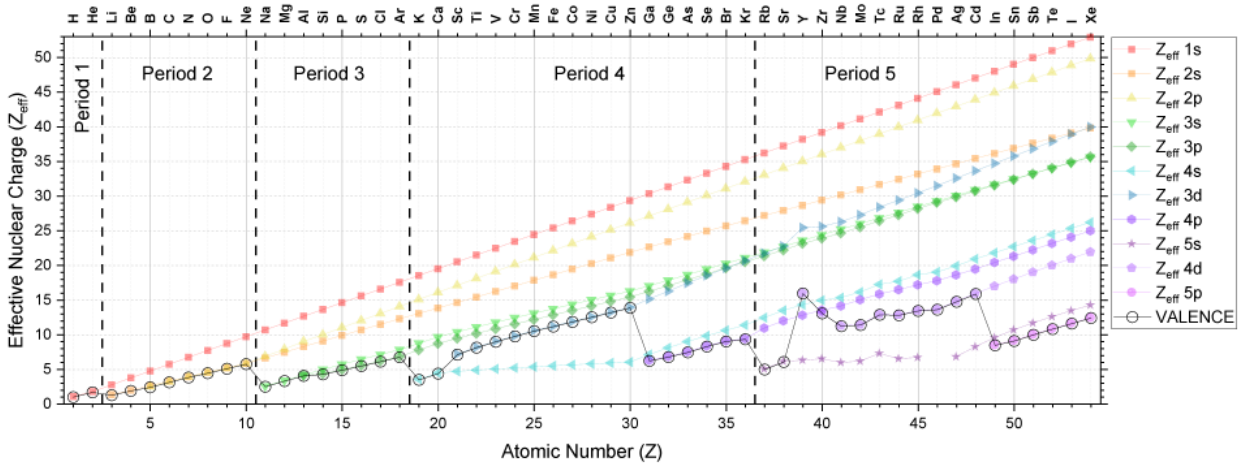


Figure **2.2.4.5**: The Z* values for electrons in each subshell of the first 54 elements (H to Xe). Each subshell is plotted as a different series (see legend) and the valence shell is highlighted by a solid black line with open circles. (Kathryn Haas; CC-NC-BY-SA)

Trends in Z* for electrons in a specific shell and subshell

The Z* for electrons in a given shell and subshell generally increases as atomic number increases; this trend holds true going across the periodic table and down the periodic table. Convince yourself that this is true for any subshell by examining Figure **2.2.4.4**. (CC-BY-NC-SA; Kathryn Haas)

Do you notice any exceptions to this general trend?

Inspection of Figure **2.2.4.4** should confirm for you that the Z* increases as Z increases for electrons in any subshell (like the 1s subshell for example, which is plotted above as a red line with square points). You can see this trend as the positive slope in each series. There is one obvious exception in Period 5 in elements 39 (Y) to 41 (Nb; the Z* of 4s actually decreases across these three elements as atomic number increases. There is also an exception between Y and Zr in the 3d subshell, and between Tc and Ru in the 5s subshell.

For valence electrons:

It is useful to understand trends in valence Z* because the valence Z* determines atomic/ionic properties and chemical reactivity. The trends in the valence Z* are not simple because as atomic number increases, the valence shell and/or subshell also changes. The valence Z* is indicated in Figure **2.2.4.4** as a black line with open circles.

Down the table: As we go down a column of the periodic table, the valence Z* increases. This is a simple trend because type of subshell is consistent and there is an increase only in shell and in atomic number, Z. This trend is best illustrated by inspection of Figure **2.2.4.3**.

Across the table: the trend depends on shell and subshell, but generally Z* increases across a period.

Periods 1-3 (s and p only): As we go across the table in periods 1-3, the shell stays constant as Z increases and the subshell changes from s to p. In these periods, there is a gradual increase in valence Z* as we move across any of the

first three periods.

Periods 4 and 5 (s, p, and d): Now we have some more complex trends because valence subshell and shell are changing as we increase in atomic number. Notice that the valence Z* generally increases going across a period as long as the subshell isn't changing; the exception is within the 4d subshell (elements 39-44 or Y-Ru). In general, going from an $(n)s$ subshell to an $(n-1)d$ subshell, there a relatively large increase in valence Z*. And in going from an $(n-1$d\) subshell to an $(n)p$ subshell, there is a relatively large decrease in Z*.

From one period to another: From Figure **2.2.4.4**, we can see that as we increase Z by one proton, going from one period to the next, there is a relatively large decrease in Z* (from Ne to Na, for example). This is because as Z increases by a small interval, the shell number increases, and so the electrons in the valence shell are much farther from the nucleus and are more shielded by all the electrons in the lower shell numbers.

Exercises

? Exercise 2.2.4.2

1. Compare trends in Z* and atomic size. Explain how and why atomic size depends on Z*.
2. Compare trends in Z* and ionization energy. Explain how and why ionization energy depends on Z*.

Answer

1. On the periodic table, atomic radius generally decreases across the periods (left to right) and increases down the groups. As atomic number increases across the periodic table, nuclear charge (Z) increases and Z* increases. In turn, the atomic radius decreases because the higher nuclear charge (and thus higher Z*) pulls electrons closer to the nucleus. Atomic radius increases down the periodic table because the shell number increases. Despite an increase in Z* going down the periodic table, larger atomic radii result from electrons occupying higher shells.

2. Ionization energies (IE) are inversely related to atomic radius; IE increases across the periods and decreases down the groups. Since the nucleus holds valence electrons more strongly (due to higher Z*) across the periods, IE increases because valence electrons are harder to remove. Down the periodic table, larger atomic radii cause electrons in valence orbitals to be shielded by core electrons. Recall that shielding reduces the nuclear charge available to electrons in higher orbital levels, resulting in a lower Z*. With more shielding and lower Z*, the valence electrons are held less tightly by the nucleus such that ionization energy decreases (i.e., valence electrons are easier to remove).

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2. Raymond Chang. Physical Chemistry for Biological Sciences. Sausalito, California: University Science Books, 2005
3. R. S. Mulliken, Electronic Structures of Molecules and Valence. II General Considerations, Physical Review, vol. 41, pp. 49-71 (1932)
4. Anastopoulos, Charis (2008). *Particle Or Wave: The Evolution of the Concept of Matter in Modern Physics*. Princeton University Press. pp. 236–237. ISBN 0691135126. http://books.google.com/?id=rDEvQZhpltEC&pg=PA236.

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SECTION OVERVIEW

2.3: Periodic Properties of Atoms

General periodic trends are specific patterns that are present within the periodic table; these are patterns in properties like electronegativity, ionization energy, electron affinity, atomic radius, melting point, and metallic character. General periodic trends provide chemists with an invaluable tool to quickly predict an element's properties. These trends exist because of the similar atomic structure of the elements within their respective group families or periods, and because of the periodic nature of the elements. Some of the general periodic trends are described in this section.

2.3.1: Ionization energy

2.3.2: Electron Affinity

2.3.3: Covalent and Ionic Radii

References

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3. Atkins, Peter et. al, *Physical Chemistry*, 7th Edition, 2002, W.H Freeman and Company, New York, pg. 390.
4. Alberty, Robert A. et. al, *Physical Chemistry*, 3rd Edition, 2001, John Wiley & Sons, Inc, pg. 380.
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2.3.1: Ionization energy

Ionization energy (IE) is the energy required to **remove an electron from a neutral atom or cation in its gaseous phase**. IE is also known as *ionization potential*.

$$A^{n+}_{(g)} \longrightarrow A^{(n+1)+}_{(g)} + e^- \qquad IE = \Delta U$$

Conceptually, ionization energy is the affinity of an element for its outermost electron (an electron it already has in its valence shell).

1st, 2nd, and 3rd Ionization Energies

The symbol I_1 stands for the ***first ionization energy*** (energy required to take away an electron from a neutral atom, where $n = 0$). The symbol I_2 stands for the ***second ionization energy*** (energy required to take away an electron from an atom with a +1 charge, $n = 2$.)

- **First Ionization Energy,** I_1 (general element, A):

$$A_{(g)} \rightarrow A^{1+}_{(g)} + e^-$$

- **Second Ionization Energy,** I_2 (general element, A):

$$A^{1+}_{(g)} \rightarrow A^{2+}_{(g)} + e^-$$

- **Third Ionization Energy,** I_3 (general element, A):

$$A^{2+}_{(g)} \rightarrow A^{3+}_{(g)} + e^-$$

Each succeeding ionization energy is larger than the preceding energy. This means that $I_1 < I_2 < I_3 < ... < I_n$ will always be true. For example, ionization energy increases as succeeding electrons are taken away from **Mg**.

$$Mg_{\,(g)} \rightarrow Mg^{+}{}_{(g)} + e^- \quad I_1 = 738\,kJ/mol$$

$$Mg^{+}{}_{(g)} \rightarrow Mg^{2+}{}_{(g)} + e^- \quad I_2 = 1451\,kJ/mol$$

Ionization energy is correlated with the strength of attraction between the positively-charged nucleus and the negatively-charged valence electrons. The higher the ionization energy, the stronger the attractive force between nucleus and valence electrons, and the more energy is required to remove a valence electron. The lower the ionization energy, the weaker the attractive force between nucleus and valence electrons, and the less energy required to remove a valence electron.

General periodic trends in electron affinity

In general, ionization energies increase from left to right and decrease down a group; however, there are variations in these trends that would be expected from the effects of penetration and shielding. The trends in **first ionization energy** are shown in Figure **2.3.1.1** and are summarized below.

- **Across a period:** As Z* increases across a period, the ionization energy of the elements generally increases from left to right. However there are breaks or variation in the trends in the following cases:
  - IE is especially low when removal of an electron creates a newly empty p subshell (examples include I_1 of B, Al, Sc)
  - IE energy is especially low where removal of an electron results in a half-filled p or d subshell (examples include I_1 of O, S)
  - IE increases more gradually across the d- and f-subshells compared to s- and p- subshells. This is because d- and f- electrons are weakly penetrating and experience especially low Z*.
- **From one period to the next:** There is an especially large decrease in IE with the start of every new period (from He to Li or from Ne to Na for example). This is consistent with the idea that IE is especially low when removal of an electron creates a newly empty s-subshell.
- **Noble gases:** The noble gases posses very high ionization energies. Note that helium has the highest ionization energy of all the elements.

- **Down a group:** Although Z* increases going down a group, there is no reliable trend in IE going down any group; in some cases IE increases going down a group, while in other cases IE decreases going down a group.

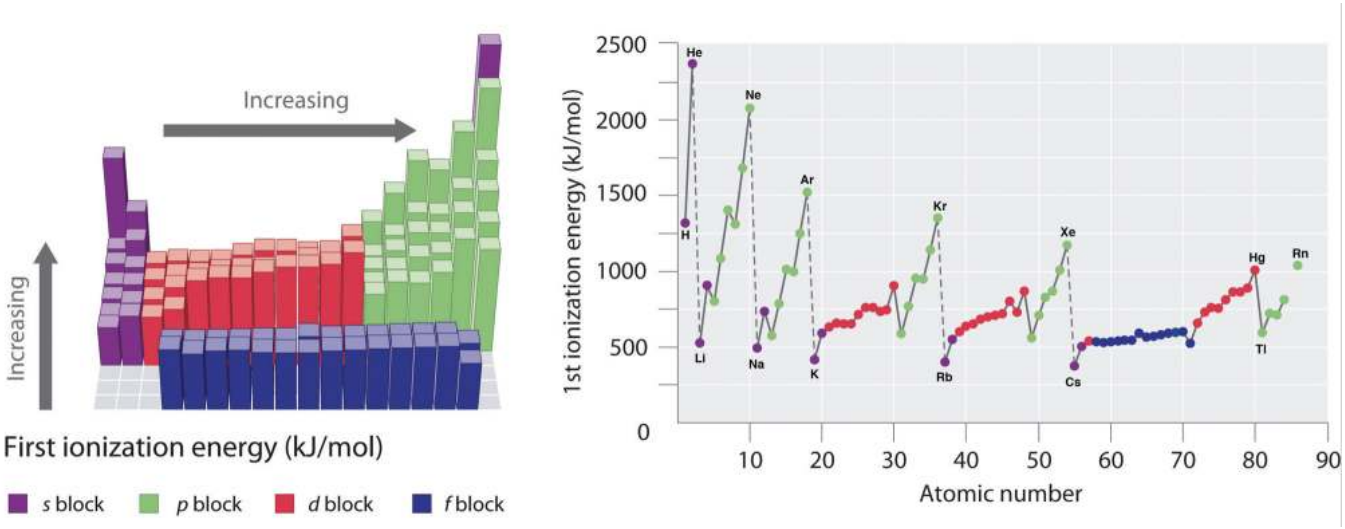


Figure 2.3.1.1: Graph showing the First Ionization Energy of the Elements. Left: ionization energies are mapped onto the periodic table, where the magnitude of ionization energy is depicted as a bar graph. Right: the first ionization energy is plotted against atomic number. In both panels the elements of the s-block are shown in purple, p-block are shown in green, d-block are shown in red, and f-block are shown in blue. (CC BY-NC-SA 3.0; anonymous)

Plots of the I_1, I_2, and I_3 of elements from hydrogen to krypton (first four periods) are shown in Figure 2.3.1.2. Notice that $I_3 > I_2 > I_1$. Also notice that trends mentioned above for I_1 hold true for subsequent ionizations when electron configurations are considered!

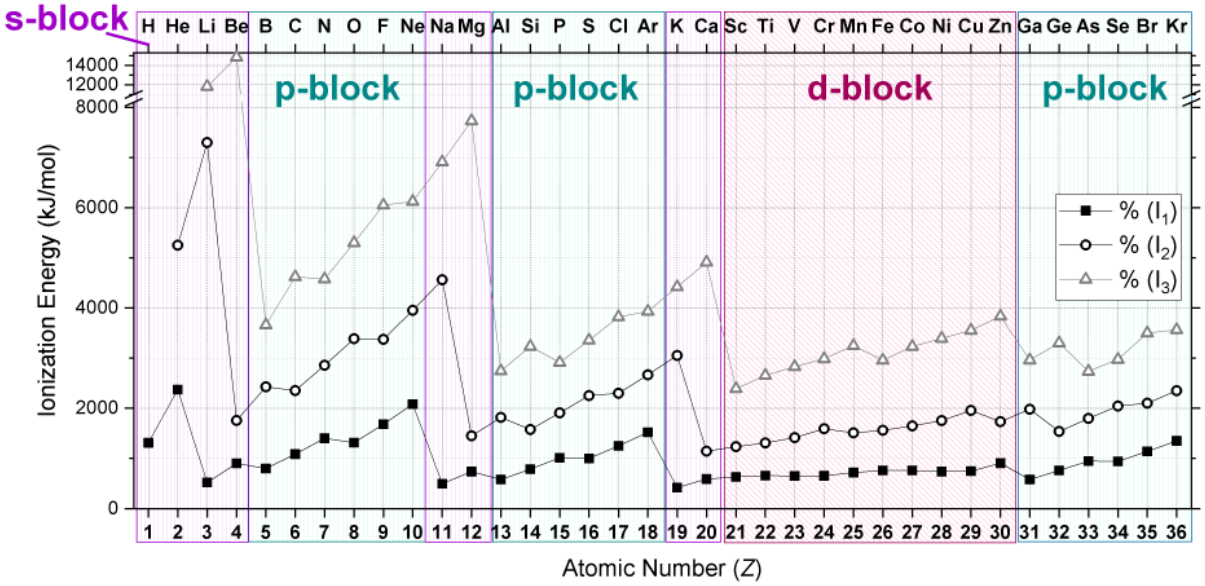


Figure 2.3.1.2. The first (I_1), second (I_2), and third (I_3) ionization energies plotted for elements with Z = 1 to 36 (H to Kr). The position of each element in its atomic form is indicated as s- p- or d-block. (CC-BY-NC-SA; Kathryn Haas)

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2.3.2: Electron Affinity

Definitions of Electron Affinity

According to IUPAC, there are two different, but equivalent, definitions of **electron affinity (EA)**.[1]

Definition: Electron Affinity defined as removal of an electron

Electron affinity can be defined as the energy *required* when an electron is removed from a gaseous anion. The reaction as shown in equation 2.3.2.1 is *endothermic* (positive ΔU) for elements except noble gases and alkaline earth metals. Under this definition, the more positive the EA value, the higher an atom's affinity for electrons.

$$A^-_{(g)} \longrightarrow A_{(g)} + e^- \qquad EA = \Delta U \tag{2.3.2.1}$$

The reaction shown in Equation 2.3.2.1 is similar those that define ionization energy. For this reason, the EA is also described as the *zeroth ionization energy*.

Definition: Electron Affinity defined as addition of an electron

An alternate and more common definition is the microscopic reverse of Equation 2.3.2.1. This more common definition states that electron affinity is the energy *released* when an electron is added to a gaseous atom, as shown in Equation 2.3.2.2. The reaction as shown in equation 2.3.2.2 is *exothermic* (negative ΔU) for elements except noble gases and alkaline earth metals. The more negative this EA value, the higher an atom's affinity for electrons.

$$A_{(g)} + e^- \longrightarrow A^-_{(g)} \qquad EA = \Delta U \tag{2.3.2.2}$$

Conceptually, this second definition is quite similar to the concept of electronegativity; but unlike electronegativity, EA is a well-defined quantitative measurement.

Trends in Electron Affinity

For this discussion, we will use the definition of EA that is consistent with it being a *zeroth ionization energy:* a more positive (larger) value means that the EA is higher (meaning stronger affinity toward an electron).

- **Across a period**: Similar to ionization energy, EA generally increases across a row of the periodic table; this observation is consistent with the increase in effective nuclear charge (Z*) from left to right across a period. However, there are variations across a period that are similar to variations in ionization energy and that can be explained by shielding, penetration, and electron configuration.
- **Down a group**: Like the case of ionization energy trends, EA does not consistently decrease going down a column of the periodic table despite the fact that Z^* increases down a group.

The trend in EA follows a zig-zag pattern similar to the one seen with ionization energies, except that it is displaced by one unit from the trend in I_1, two units from I_2, and so on. For example, EA peaks at F, while I_1 peaks at Ne, I_2 peaks at Na, and I_3 peaks at Mg. A plot of EA for the first 13 elements is shown overlaid on plots of I_1, I_2 and I_3 in Figure 2.3.2.1., where the shifts in the peaks and valleys within each zig-zag trend are indicated.

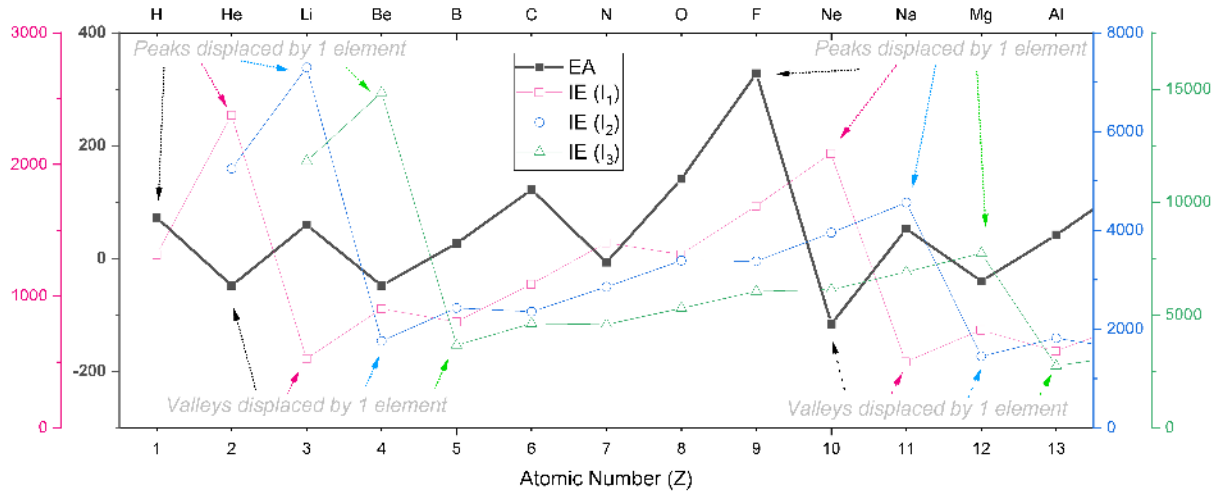


Figure **2.3.2.1**. A plot of electron affinity (the zeroth ionization energy) is overlaid on plots of the first (I_1), second (I_2), and third (I_3) ionization energies. Each plot is shown using separate y-axes. Trends in EA are similar to those in ionization energies, except that the peaks and valleys of the trends are shifted by one unit, as indicated. These plots are shown in units of kJ/mole. (CC-BY-NC-SA; Kathryn Haas)

Sources

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2.3.3: Covalent and Ionic Radii

Measurement of Radius

There are several methods that can be used to determine radii of atoms and ions:

- **Nonpolar atomic radii:** The radius of an atom is derived from the bond lengths within nonpolar molecules; one-half the distance between the nuclei of two atoms within a covalent bond.
- **van der Waals radius:** The radius of an atom is determined by collision with other atoms.
- **Crystal radii**: The atomic or ionic radius is determined using electron density maps from X-ray data.

The measurement of atomic or ionic size will depend on a number of factors, including the covalent character of bonding in any particular molecule, coordination number, physical state (liquid, solid, gas), the identity of nearby atoms/ions, variation in crystal structure, and distortions within regular crystal structures. You should keep in mind that the size of an atom or ion is a "fuzzy" measure, and the radius under a different set of conditions will probably change slightly.

Regardless, measured atomic and ionic radii reveal obvious trends across the periodic table and between atoms and ions. The relative atomic sizes shown in Figure **2.3.3.1** were derived from crystallographic data.[1]

Trends in Atomic Radius

Atomic size generally decreases gradually from left to right across a period of elements. As nuclear charge (Z) increases, we expect the effective nuclear charge (Z*) of the valence electrons to also increase. Increasing Z pulls electrons closer to the nucleus. However, with each additional unit of Z, there is also an additional electron. The change in size is a balance of a compression caused by increasing Z and an expansion in the number of electrons. As a result, the atomic radius decreases *gradually* across a period.

Atomic size generally increases going down a group. As valence electrons occupy higher level shells due to the increasing quantum number (n), size increases despite the fact that Z and Z* are increasing going down the group.

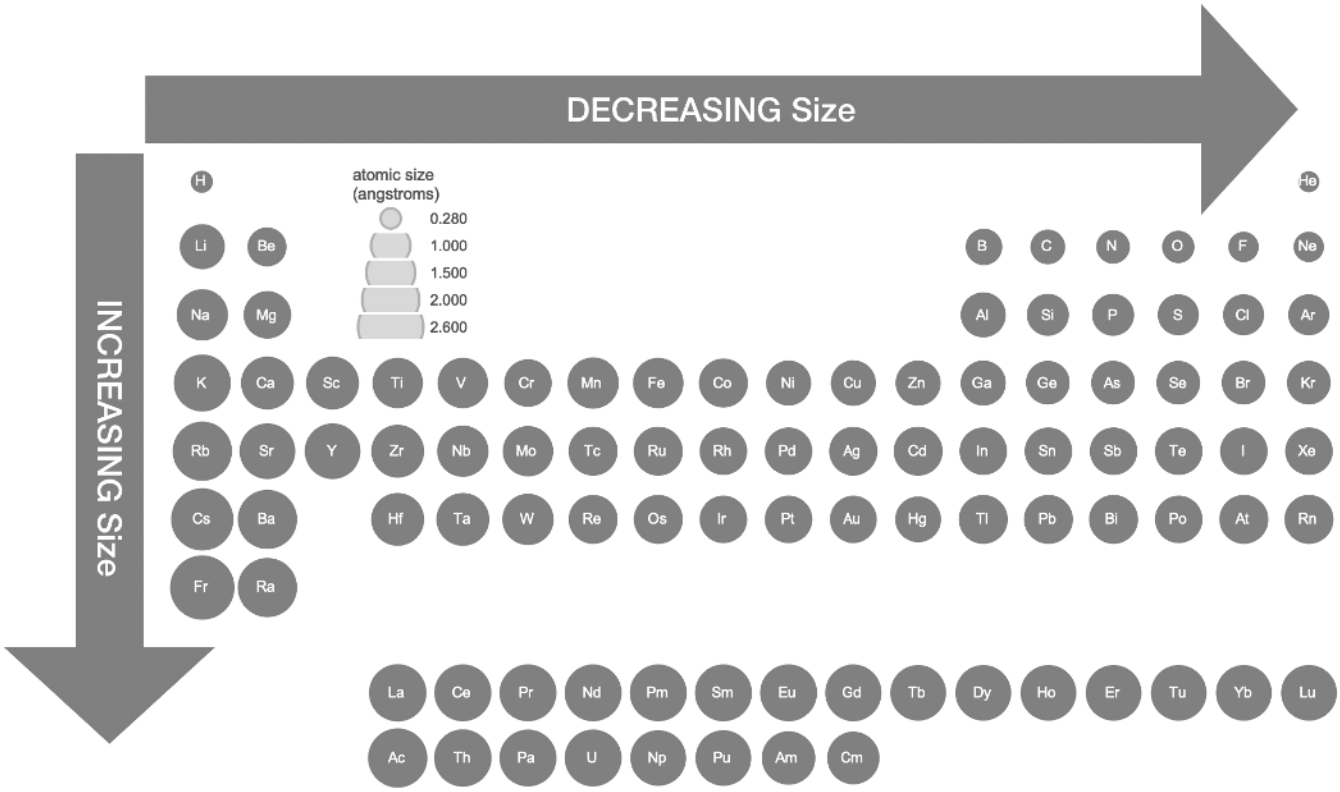


Figure **2.3.3.1**. *Atomic Radii Calculated from Crystalographic Data. Data from Cordero, Beatriz, Veronica Gomez, Ana E. Platero-Prats, Marc Reves, Jorge Echeverria, Eduard Cremades, Flavia Barragan, and Santiago Alvarez. "Covalent Radii Revisited." Dalton Transactions, no. 21 (2008): 2832–38. doi:10.1039/b801115j.* (Kathryn Haas; CC-NC-BY-SA)

Trends in Ionic Radius

Trends in ionic radius follow general trends in atomic radius for ions of the same charge. Ionic radius varies with the charge of the ion (and number of electrons) and the electron configuration (e.g. high spin or low spin).

Cations

Compared to their atoms, cations have the same Z but fewer electrons. Removal of electrons from an atom to form a cation results in a significant increase in effective nuclear charge, resulting in all other electrons being more strongly attracted to the nucleus, and having a lower energy level. The result is a contraction in size from the atom to cation. Figure **2.3.3.2** visually illustrates the relative size of atoms and some cations of the first four periods; the data is available in tabular format in Figure **2.3.3.3**.

Anions

Compared to their atoms, anions have the same Z but more electrons. Addition of electrons to an atom to form an anion results in a decrease in effective nuclear charge, which corresponds to a decrease in attractive force between the nucleus and electrons. Lower attractive force leads to expansion, where the size of the atom becomes larger in the formation of an anion. Figure **2.3.3.2** visually illustrates the relative size of atoms and some anions of the first four periods, while the data is available in tabular format in Figure **2.3.3.3**.

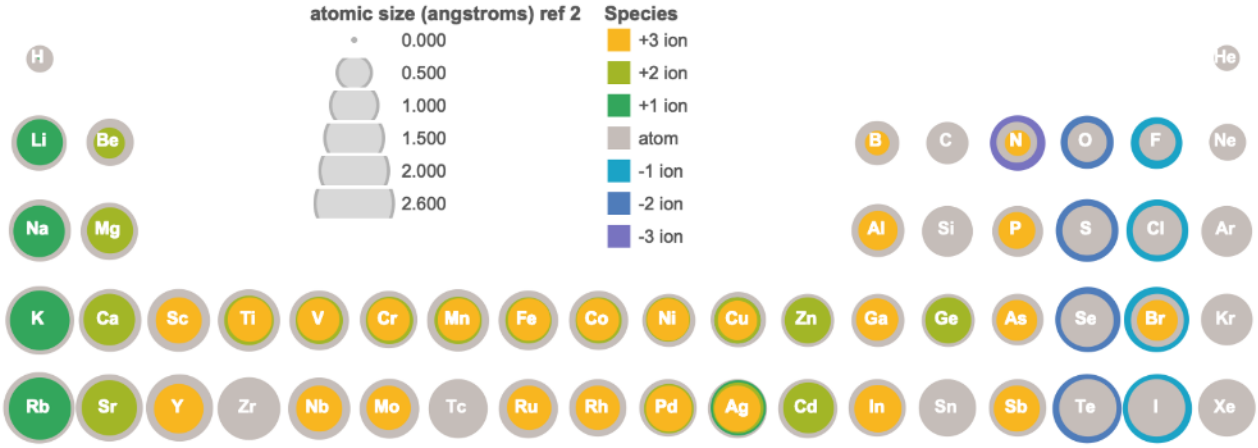


Figure **2.3.3.2**. This figure illustrates relative size of atoms and ions of the first four periods of the periodic table. Atomic radius is indicated by grey circles. Radius of cations is shown in green (+1), lime (+2), and yellow (+3) circles. Radius of anions are shown as aqua (-1), blue (-2), and purple (-3) circles. Data from sources 1-3. (Kathryn Haas; CC-NC-BY-SA)

H																	He
0.31 (atom) 0 (+1)																	0.28 (atom)
Li	Be											B	C	N	O	F	Ne
1.28 (atom) 0.9 (+1) -	0.96 (atom) 0.41 (+2) -											0.84 (atom) 0.25 (+1)	0.76 (atom) 0.29 (+4)	1.32 (-3) 0.71 (atom) 0.3 (+3) 0.27 (+5)	1.21 (-2) 0.66 (atom)	1.145 (-1) 0.57 (atom)	0.58 (atom)
Na	Mg											Al	Si	P	S	Cl	Ar
1.66 (atom) 1.16 (+1)	1.41 (atom) 0.86 (+2)											1.21 (atom) 0.675 (+3)	1.11 (atom) 0.4 (+4)	1.07 (atom) 0.58 (+3) 0.31 (+5)	1.7 (-2) 1.05 (atom) 0.51 (+4) 0.26 (+6)	1.67 (-1) 1.02 (atom)	1.06 (atom)
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
2.03 (atom) 1.52 (+1)	1.76 (atom) 1.14 (+2)	1.7 (atom) 0.885 (+3)	1.6 (atom) 1 (+2) 0.81 (+3) 0.745 (+4)	1.53 (atom) 0.93 (+2) 0.78 (+3) 0.72 (+4)	1.39 (atom) 0.94 (+2 hs) 0.87 (+2 ls) 0.7555 (+3) 0.69 (+4) 0.63 (+5) 0.58 (+6)	1.61 (atom) 0.97 (+2 hs) 0.81 (+2 ls) 0.785 (+3 hs) 0.72 (+3 ls) 0.67 (+4) 0.47 (+5) 0.395 (+6) 0.39 (+7)	1.52 (atom) 0.92 (+2 hs) 0.765 (+3 hs) 0.75 (+2 ls) 0.725 (+4) 0.69 (+3 ls) 0.39 (+6)	1.5 (atom) 0.885 (+2 hs) 0.79 (+2 ls) 0.75 (+3 hs) 0.685 (+3 ls) 0.67 (+4 hs)	1.24 (atom) 0.83 (+2) 0.74 (+3 hs) 0.7 (+3 ls) 0.62 (+4)	1.32 (atom) 0.91 (+1, cn6) 0.87 (+2, cn6) 0.68 (+3, cn6)	1.22 (atom) 0.88 (+2)	1.22 (atom) 0.76 (+3)	1.2 (atom) 0.87 (+2) 0.67 (+4)	1.19 (atom) 0.72 (+3) 0.6 (+5)	1.84 (-2) 1.2 (atom) 0.64 (+4) 0.56 (+6)	1.82 (-1) 1.2 (atom) 0.73 (+3) 0.53 (+7) 0.45 (+5)	1.16 (atom)
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
2.2 (atom) 1.66 (+1)	1.95 (atom) 1.32 (+2)	1.9 (atom) 1.04 (+3)	1.75 (atom) 0.86 (+4)	1.64 (atom) 0.86 (+3) 0.82 (+4) 0.78 (+5)	1.54 (atom) 0.83 (+3) 0.79 (+4) 0.75 (+5) 0.73 (+6)	1.47 (atom) 0.785 (+4) 0.74 (+5) 0.7 (+7)	1.46 (atom) 0.82 (+3) 0.76 (+4) 0.705 (+5) 0.52 (+7) 0.5 (+8)	1.42 (atom) 0.805 (+3) 0.74 (+4) 0.69 (+5)	1.39 (atom) 0.73 (+1) 1 (+2) 0.9 (+3) 0.755 (+4)	1.45 (atom) 1.29 (+1) 1.08 (+2) 0.89 (+3)	1.44 (atom) 1.09 (+2)	1.42 (atom) 0.94 (+3)	1.39 (atom) 0.83 (+4)	1.39 (atom) 0.9 (+3) 0.74 (+5)	2.07 (-2) 1.38 (atom) 1.1 (+4) 0.7 (+6)	2.06 (-1) 1.39 (atom) 1.09 (+5) 0.67 (+7)	1.4 (atom) 0.62 (+8)

Figure 2.3.3.3.

This figure shows radii (in Angstroms) of atoms and ions of the first four periods of the periodic table. Radii from each element are listed from largest to smallest, ionic charge indicated in parentheses (); hs = high spin, ls = low spin, cn6 = coordination number is 6. Data from sources 1-3. (Kathryn Haas; CC-NC-BY-SA)

References

1. Cordero, Beatriz, Veronica Gomez, Ana E. Platero-Prats, Marc Reves, Jorge Echeverria, Eduard Cremades, Flavia Barragan, and Santiago Alvarez. *"Covalent Radii Revisited." Dalton Transactions, no. 21 (2008): 2832–38. doi:10.1039/b801115j.*
2. R. D. Shannon (1976). "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides". *Acta Crystallogr A.* **32** (5): 751–767. Bibcode:1976AcCrA..32..751S. doi:10.1107/S0567739476001551.
3. Wikipedia articles on Atomic Radius and Ionic Radius.

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2.4: Problems

Example Exercises

The following series of problems reviews general understanding of the aforementioned material.

? Exercises

1. Based on the periodic trends for ionization energy, which element has the highest ionization energy?
2. Which has a larger atomic radius: nitrogen or oxygen?
3. Which element is more electronegative, sulfur (S) or selenium (Se)?
4. Why is the electronegativity value of most noble gases zero?
5. Rewrite the following list in order of decreasing electron affinity: fluorine (F), phosphorous (P), sulfur (S), boron (B).
6. Which of these elements has a smaller atomic radius than sulfur (S): O, Cl, Ca, Li

Answer 1

Helium (He).

Answer 2

Atomic radius increases from right to left on the periodic table. Therefore, nitrogen is larger than oxygen.

Answer 3

Sulfur (S). Note that sulfur and selenium share the same column. Electronegativity increases up a column. This indicates that sulfur is more electronegative than selenium.

Answer 4

Because of their full valence electron shell, the noble gases are extremely stable and do not readily lose or gain electrons.

Answer 5

Fluorine (F)>Sulfur (S)>Phosphorous (P)>Boron (B). Explanation: Electron affinity generally increases from left to right and from bottom to top.

Answer 6

Oxygen (O) is the only element in the list with a smaller atomic radius than S. Periodic trends indicate that atomic radius increases down a group (from top to bottom) and from left to right across a period.

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CHAPTER OVERVIEW

3: Simple Bonding Theory

3.1: Lewis Electron-Dot Diagrams

3.1.1: Resonance

3.1.2: Breaking the octet rule with higher electron counts (hypervalent atoms)

3.1.3: Formal Charge

3.1.4: Lewis Fails to Predict Unusual Cases - Boron and Beryllium

3.2: Valence Shell Electron-Pair Repulsion

3.2.1: Lone Pair Repulsion

3.2.2: Multiple Bonds

3.2.3: Electronegativity and Atomic Size Effects

3.2.4: Ligand Close Packing

3.3: Molecular Polarity

3.4: Hydrogen Bonding

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3.1: Lewis Electron-Dot Diagrams

In 1916, Gilbert Lewis Newton introduced a simple way to show the bonding between atoms in a molecule though Lewis electron dot diagrams. Creating Lewis diagrams is rather simple and requires only a few steps and some accounting of the valence electrons on each atom. Valence electrons are represented as dots. When two electrons are paired (lone pairs), they are represented by two adjacent dots located on an atom, and when two paired electrons are shared between atoms (bonds), they are shown as lines. For example, below are the electron dot structures of atoms and the Lewis electron dot structures of the molecules.

These diagrams are helpful because they allow us to show how atoms are connected, and when coupled with Valence Shell Electron Repulsion Theory (VSEPR), we can use Lewis structures to predict the shape of the molecule.

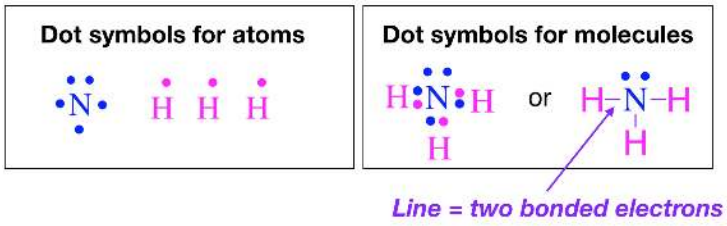


Figure 3.1.1: Lewis dot structure of atoms comprising ammonia and the dot structure of the molecule. (Kathryn Haas; CC-NC-BY-SA)

The drawing of Lewis electron-dot structures is guided largely by the **octet rule**: that atoms form bonds to achieve eight electrons in their valence shell. For many elements, a full valence shell has an electron configuration of s^2p^6, or eight electrons. A common exception to this rule is the first row elements, H and He. These two elements have $n = 1$ as their valence shell, and so they have only two electrons in a full valence shell ($1s^2$ electron configuration). Although H and He are exceptions to the "octet rule", they still form bonds to achieve a full valence shell. It may be better to think of this as the "full valence" rule of bonding. We will see many more violations to the "octet" rule as we progress through this course. In the case of metals and metalloids, breaking of the rules is particularly common. (CC-BY-NC-SA; Kathryn Haas)

Common violations of the octet rule

- **Less than eight electrons (hypovalency)**: H and He are examples of elements that cannot have more than two electrons in their full valence shell. Additionally, there are cases where a valid Lewis structure contains atoms with ***hypovalency:*** *partially-filled valence shells*. An example of this is a *carbocation, a positively charged carbon with only six electrons in its valence shell.* Carbocations are important intermediates in organic chemistry, and they are highly reactive (unstable) Lewis acids (electrophiles). Another example of hypovalency is the Lewis structure for BH_3, which shows boron with three bonds, and only six electrons in its valence shell. Boron hydride is a strong Lewis Acid. (Side note: the actual chemical form of BH_3 is not well-predicted by the Lewis structure and we'll see more about this in Section 3.1.4.)
- **More than eight electrons (hypervalency)**: This is a case where an element has more than eight electrons in its valence shell. It is common for larger atoms ($n \geq 3$), and it is discussed further in Section 3.1.2.

Pitfall alert! There are different rules for counting electrons depending on the purpose of the counting. These are the rules for counting for "octets". The rules for counting for calculation of an atom's formal charge are !!different!! and are described in Section 3.1.1. When an atom is part of a molecule, all electrons that are associated with the atom are counted as contributing to the atom's valence. This includes electrons that are lone pairs on the atoms, and *all* electrons that are shared in bonds. If four electrons are shared between two atoms, it is a double bond. If six electrons are shared between atoms, it is a triple bond.

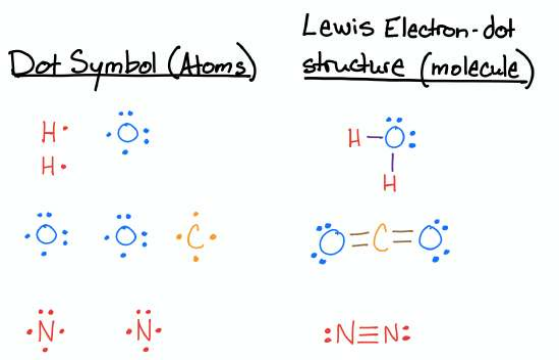
Electrons in valence (octet) = total unbonded electrons on the atom + total bonded electrons (2 electrons per bond)

Even if you're an old pro at drawing Lewis structures, it's a good idea to polish up. Please complete the practice exercises below. You should get out an actual piece of paper (I know...just do it. It's good for you.) and a writing tool and try to complete each problem before checking the answer.

Exercise 3.1.1

Draw the Lewis structures for H_2O, CO_2, and N_2.

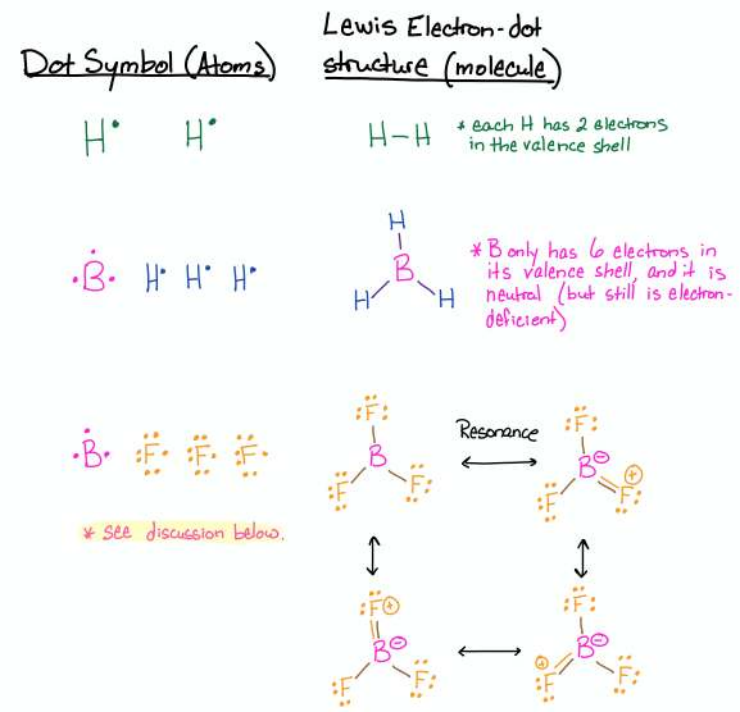
Answer



Exercise 3.1.2

Draw the Lewis structures for H_2, BH_3 and BF_3.

Answer



These three examples include atoms that have less than eight electrons in their valence shell. In the case of H, it is satisfied with only two electrons in its valence, as was discussed earlier in this section. The case of BH_3 was also discussed above. In the Lewis structure of BH_3, the boron can only have six electrons in its octet and it is neutral in charge. The boron is electron deficient even though it has neutral charge.

The case of BF_3 deserves a discussion: If you are unfamiliar with resonance and formal charge, see Sections 3.1.1 (Resonance) and 3.1.3 (Formal Charge) first and come back to this afterward. You might have drawn the BF_3 structure similar to the one that is drawn for BH_3, where boron has three bonds and only six electrons in its valence shell. If you did that, then you are correct; but if you only gave this structure, then your answer is not complete. There are three other correct

ways to draw the structure. Since F has lone pairs of electrons, other valid Lewis structures would each have a double bond to one of the fluorines (three total). All of these structures are called resonance structures, and based on the four of them, we could predict that BF_3 would have B-F bonds that have some double-bond character. If fact, this is the case for BF_3; it has bond lengths that are shorter than single bonds, but longer than double bonds. Read more about it on its Wikipedia page here (click).

Outside Links

- en.Wikipedia.org/wiki/Lewis_structures
- http://www.ausetute.com.au/lewisstr.html
- cost.georgiasouthern.edu/chem...cule/lewis.htm

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3.1.1: Resonance

Learning Objectives

- To understand the concept of resonance.

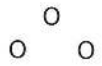
Resonance structures are a set of two or more Lewis Structures that collectively describe the electronic bonding of a single polyatomic species including fractional bonds and fractional charges. Resonance structures are capable of describing delocalized electrons that cannot be expressed by a single Lewis formula with an integral number of covalent bonds.

Sometimes one Lewis Structure is not Enough

Sometimes, even when formal charges are considered, the bonding in some molecules or ions cannot be described by a single Lewis structure. Resonance is a way of describing delocalized electrons within certain molecules or polyatomic ions where the bonding cannot be expressed by a single Lewis formula. A molecule or ion with such delocalized electrons is represented by several contributing structures (also called resonance structures or canonical forms). Such is the case for ozone ($\mathbf{O_3}$), an allotrope of oxygen with a V-shaped structure and an O–O–O angle of 117.5°.

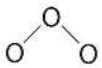
Ozone (O_3)

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



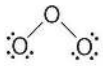
2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

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



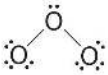
with 14 electrons left over.

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

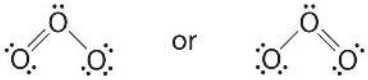


and have 2 electrons left over.

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

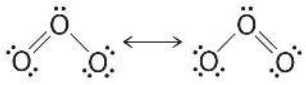


6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons —but which one? Depending on which one we choose, we obtain either



Which is correct? In fact, neither is correct. Both predict one O–O single bond and one O=O double bond. As you will learn, if the bonds were of different types (one single and one double, for example), they would have different lengths. It turns out, however, that both O–O bond distances are identical, 127.2 pm, which is shorter than a typical O–O single bond (148 pm) and longer than the O=O double bond in O_2 (120.7 pm).

Equivalent Lewis dot structures, such as those of ozone, are called **resonance structures**. The position of the *atoms* is the same in the various resonance structures of a compound, but the position of the *electrons* is different. Double-headed arrows link the different resonance structures of a compound:



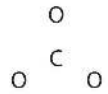
The double-headed arrow indicates that the actual electronic structure is an *average* of those shown, not that the molecule oscillates between the two structures.

> *When it is possible to write more than one equivalent resonance structure for a molecule or ion, the actual structure is the average of the resonance structures.*

The Carbonate (CO_3^{2-}) Ion

Like ozone, the electronic structure of the carbonate ion cannot be described by a single Lewis electron structure. Unlike O_3, though, the actual structure of CO_3^{2-} is an average of *three* resonance structures.

1. Because carbon is the least electronegative element, we place it in the central position:



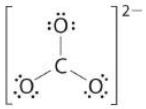
The three oxygens are drawn in the shape of a triangle with the carbon at the center of the triangle.

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

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



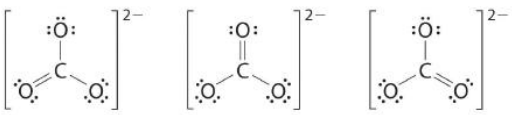
4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the −2 charge:



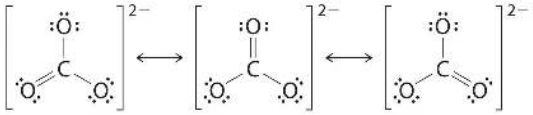
The Lewis dot structure has a central carbon that is bonded to 3 oxygens. Each oxygen has 3 lone pairs. The molecule is inside square brackets and has a charge of minus 2.

5. No electrons are left for the central atom.

6. At this point, the carbon atom has only 6 valence electrons, so we must take one lone pair from an oxygen and use it to form a carbon–oxygen double bond. In this case, however, there are *three* possible choices:



As with ozone, none of these structures describes the bonding exactly. Each predicts one carbon–oxygen double bond and two carbon–oxygen single bonds, but experimentally all C–O bond lengths are identical. We can write resonance structures (in this case, three of them) for the carbonate ion:



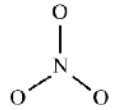
The resonance structure includes all three Lewis dot structures with double headed arrows between them.

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

The Nitrate (NO_3^-) ion

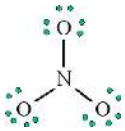
1. Count up the valence electrons: (1*5) + (3*6) + 1(ion) = **24** electrons

2. Draw the bond connectivities:

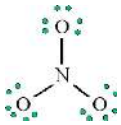


The three oxygens are drawn in the shape of a triangle with the nitrogen at the center of the triangle.

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

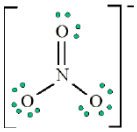


4. Place any leftover electrons (24-24 = **0**) on the center atom:



5. Does the central atom have an octet?

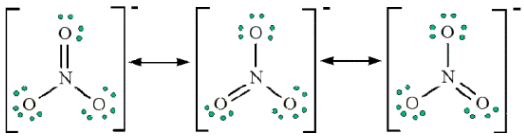
- **NO**, it has 6 electrons
- Add a multiple bond (first try a double bond) to see if the central atom can achieve an octet:



A double bond is added between one oxygen and the central nitrogen. The molecule has a negative charge.

6. Does the central atom have an octet?

- YES
- Are there possible resonance structures? YES



Note: We would expect that the bond lengths in the $\mathbf{NO_3^-}$ ion to be somewhat shorter than a single bond.



Example 3.1.1.1: Benzene

Benzene is a common organic solvent that was previously used in gasoline; it is no longer used for this purpose, however, because it is now known to be a carcinogen. The benzene molecule (C_6H_6) consists of a regular hexagon of carbon atoms, each of which is also bonded to a hydrogen atom. Use resonance structures to describe the bonding in benzene.

Given: molecular formula and molecular geometry

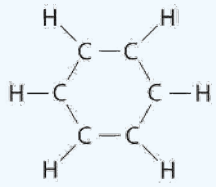
Asked for: resonance structures

Strategy:

A. Draw a structure for benzene illustrating the bonded atoms. Then calculate the number of valence electrons used in this drawing.
B. Subtract this number from the total number of valence electrons in benzene and then locate the remaining electrons such that each atom in the structure reaches an octet.
C. Draw the resonance structures for benzene.

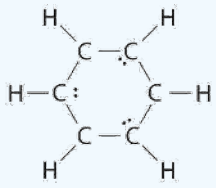
Solution:

A Each hydrogen atom contributes 1 valence electron, and each carbon atom contributes 4 valence electrons, for a total of (6 × 1) + (6 × 4) = 30 valence electrons. If we place a single bonding electron pair between each pair of carbon atoms and between each carbon and a hydrogen atom, we obtain the following:



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

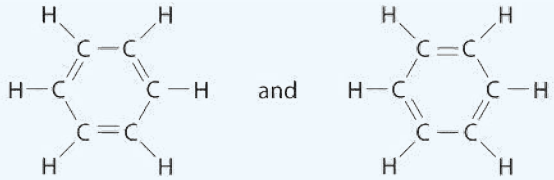
B If the 6 remaining electrons are uniformly distributed pairwise on alternate carbon atoms, we obtain the following:



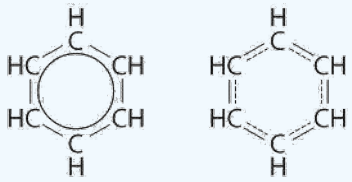
Three carbon atoms now have an octet configuration and a formal charge of −1, while three carbon atoms have only 6 electrons and a formal charge of +1. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of

electrons and a formal charge of 0, by making three C=C double bonds.

C There are, however, two ways to do this:



Each structure has alternating double and single bonds, but experimentation shows that each carbon–carbon bond in benzene is identical, with bond lengths (139.9 pm) intermediate between those typically found for a C–C single bond (154 pm) and a C=C double bond (134 pm). We can describe the bonding in benzene using the two resonance structures, but the actual electronic structure is an average of the two. The existence of multiple resonance structures for aromatic hydrocarbons like benzene is often indicated by drawing either a circle or dashed lines inside the hexagon:

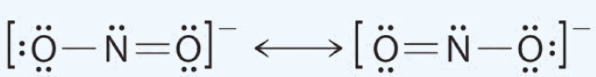


Benzene

Exercise 3.1.1.1: Nitrite Ion

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

Answer



There is a double bond between one oxygen and the nitrogen, It can be found on the left oxygen or the right oxygen.

Resonance structures are particularly common in oxoanions of the *p*-block elements, such as sulfate and phosphate, and in aromatic hydrocarbons, such as benzene and naphthalene.

Warning

If several reasonable resonance forms for a molecule exists, the "actual electronic structure" of the molecule will probably be intermediate between all the forms that you can draw. The classic example is benzene in Example **3.1.1.1**. One would expect the double bonds to be shorter than the single bonds, but if one overlays the two structures, you see that one structure has a single bond where the other structure has a double bond. The best measurements that we can make of benzene do not show two bond lengths - instead, they show that the bond length is intermediate between the two resonance structures.

Resonance structures is a mechanism that allows us to use all of the possible resonance structures to try to predict what the actual form of the molecule would be. Single bonds, double bonds, triple bonds, +1 charges, -1 charges, these are our limitations in explaining the structures, and the true forms can be in between - a carbon-carbon bond could be mostly single bond with a little bit of double bond character and a partial negative charge, for example.

Summary

Some molecules have two or more chemically equivalent Lewis electron structures, called resonance structures. Resonance is a mental exercise and method within the Valence Bond Theory of bonding that describes the delocalization of electrons within molecules. These structures are written with a **double-headed arrow** between them, indicating that none of the Lewis structures accurately describes the bonding but that the actual structure is an average of the individual resonance structures. Resonance

structures are used when one Lewis structure for a single molecule cannot fully describe the bonding that takes place between neighboring atoms relative to the empirical data for the actual bond lengths between those atoms. The net sum of valid resonance structures is defined as a resonance hybrid, which represents the overall delocalization of electrons within the molecule. A molecule that has several resonance structures is more stable than one with fewer. Some resonance structures are more favorable than others.

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3.1.2: Breaking the octet rule with higher electron counts (hypervalent atoms)

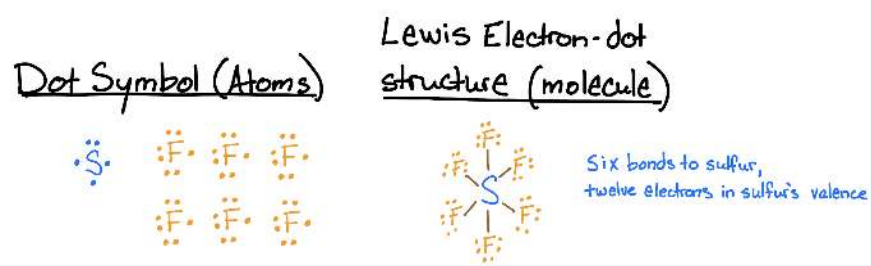
The octet rule applies well to atoms in the second row of the periodic table, where a full valence shell includes eight electrons with an electron configuration of s^2p^6. Even elements in the third and fourth row are known to follow this rule *sometimes*, but not always. In larger atoms, where $n \geq 3$ the valence shell contains additional subshells: the $d, f, g...$ subshells. Therefore, atoms with $n \geq 3$ can have higher valence shell counts by "expanding" into these additional subshells. When atoms contain more than eight electrons in their valence shell, they are said to be **hypervalent**. Hypervalency allows atoms with $n \geq 3$ to break the octet rule by having more than eight electrons. This also means they can have five or more bonds; something that is nearly unheard of for atoms with $n \leq 2$. Complete the exercises below to see examples of molecules containing hypervalent atoms.

? Exercise 3.1.2.1

Draw the Lewis structures for sulfur hexafluoride (SF_6).

Answer

Each fluorine atom has one valence electron and will make one bond each. The sulfur has six valence electrons, and must make six bonds to form a molecule with the six fluorine atoms. The molecular structure has six bonds to sulfur, with twelve valence electrons. The sulfur is hypervalent.

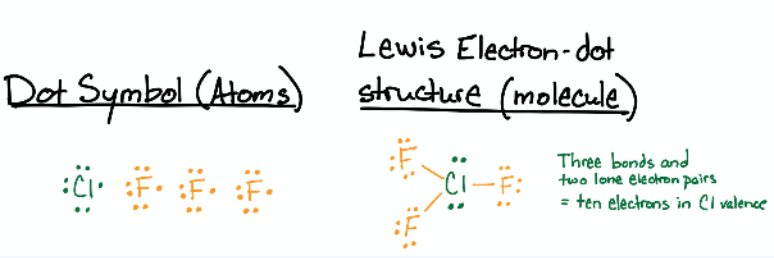


? Exercise 3.1.2.1

Draw the Lewis structure for chlorine trifluoride (ClF_3.

Answer

All atoms are halogens and each has seven valence electrons. Chlorine is capable of hypervalency because it is in the third row of the periodic table; however fluorine cannot have more than eight valence electrons in its valence because it is in the second row. The structure has the three fluorine atoms bonded to a central chlorine atom. The chlorine has a valence of ten electrons due to its three bonds and two lone pairs.



Is hypervalency real? Not exactly. Hypervalency is a concept associated with hybrid orbital theory and Lewis theory. It's useful for some simple things, like predicting how atoms are connected and predicting molecular shape. But the idea that the d-orbitals are involved in bonding isn't accurate according to wave mechanics.

For main group molecules, chemists (like Pauling) thought a long time ago that hypervalence is due to expanded s^2p^6 octets. The consensus is now clear that d orbitals are NOT involved in bonding in molecules like SF_6 any more than they are in SF_4 and SF_2. In all three cases, there is a small and roughly identical participation of d-orbitals in the wavefunctions. This has been established in both MO and VB theory. However, using hybrid orbitals with d-orbital contributions equips us with a language which can pragmatically describe the geometries of highly coordinated substances.

While hybrid orbitals are a powerful tool to describe the geometries and shape of molecules and metal complexes, in "real" molecules their significance may be debated. Often a more realistic molecular orbitals approach is needed. However, from an epistemologically simple point of view, bonding theories can only be judged by their predictions. To the extent that hybridization can explain the shapes of PF_5 and SF_6, valence bond theory is a perfectly good theory. To the extent that if you write out the valence bond wavefunction using hybridized orbitals and calculate energies and other properties à la Pauling (i.e., ionization energy and electron affinities) and find them to be off from experimental results (by tens of kcals/mol), then valence bond theory is not accurate.

> *Bonding theories can only be judged by their predictions.*

A simple explanation that can be given is that molecular wavefunctions constructed out of hybridized atomic orbitals are accurate enough to predict some things, but not others. Predictions of any theory must be compared with empirical evidence to assess when they work and when they fail. When a theory gives the wrong answer, at least one assumption must not hold. In this case, the valence bond wavefunction is not accurate enough to capture some important features of a system's electronic structure. It may not be the most intellectually satisfying answer, but to say more would result in a much more complicated answer and certainly far beyond the level reasonably expected from general chemistry discussions.

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3.1.3: 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.

Calculating Formal Charges

We calculate the formal charge of an atom in a molecule or polyatomic ions as follows:

Formal Charge = (valence electrons of the "free" element) - (unshared electrons) - (bonds).

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.

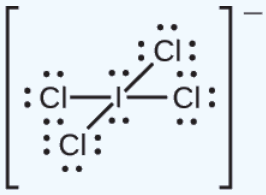
We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen ion ICl_4^-.

Solution

We divide the bonding electron pairs equally for all I–Cl bonds:



We assign lone pairs of electrons to their atoms. Each Cl atom now has seven electrons assigned to it, and the I atom has eight.

Subtract this number from the number of valence electrons for the neutral atom:

- I: 7 – 8 = –1
- Cl: 7 – 7 = 0

The sum of the formal charges of all the atoms equals –1, which is identical to the charge of the ion (–1).

Exercise 3.1.3.1

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



Answer

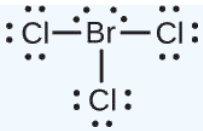
C −1, O +1

Example: Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen molecule $BrCl_3$.

Solution

Assign one of the electrons in each Br–Cl bond to the Br atom and one to the Cl atom in that bond:



Assign the lone pairs to their atom. Now each Cl atom has seven electrons and the Br atom has seven electrons.

Subtract this number from the number of valence electrons for the neutral atom. This gives the formal charge:

- Br: 7 – 7 = 0
- Cl: 7 – 7 = 0

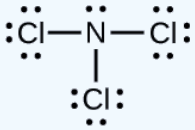
All atoms in $\mathbf{BrCl_3}$ have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

? Exercise 3.1.3.2

Determine the formal charge for each atom in $\mathbf{NCl_3}$.

Answer

N: 0; all three Cl atoms: 0



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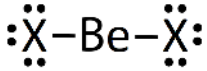
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3.1.4: Lewis Fails to Predict Unusual Cases - Boron and Beryllium

Two notable cases where Lewis theory fails to predict structure are the cases of beryllium (**Be**) and boron (**B**). These two atoms are in period 2 ($n = 2$) of the periodic table and their atoms have the valence electron configurations of $2s^2$ and $2s^2 2p^1$, respectively.

Beryllium

The Lewis electron dot structures are shown below for BeX_2, where **X** is one of the halogens, **F** or **Cl**.



Each of the structures above would predict a linear geometry for the BeX_2 molecule. Together the three resonance structures suggest partial double-bond character in the Be-X bond, which results in an intermediate bond length between a single and double bond.

There are issues with each of these resonance structures. The structure on the left would predict only four electrons around **Be**; thus, the atom does not fulfill the octet rule. The structure on the left suggests multiple bonds for the halogen (**X**) and high separation of charge with formal charge on each atom. The structure in the middle is a mix of these problems. None of these situations is ideal according to Lewis theory. Further, experimental data is not consistent with any of these structures or their resonance hybrid (except in the case of $BeCl_2$ at very high temperatures).

It turns out that the monomer of BeX_2 does exist, but only at very high temperatures and low pressures. Even under extreme conditions, the monomer is not particularly stable due to the electron deficiency around **Be**.

BeF_2

At ambient temperature and pressure, BeF_2 is a solid that looks similar to quartz (Figure **3.1.4.1**) The Be is four-coordinate with tetrahedral geometry; each F is two-coordinate and the Be-F bond length is 1.54 Å. This structure is possible due to an extended 3-dimensional network in the solid where adjacent BeF_2 units are bonded to one another, as shown in Figure **3.1.4.1**.

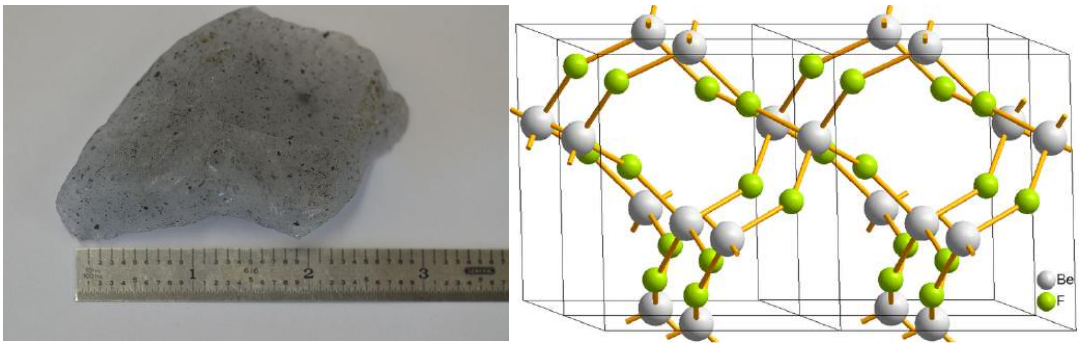


Figure **3.1.4.1**: (left) A nugget of beryllium fluoride obtained from Materion. Black spots are carbon (CC BY-SA 3.0; Bckelleher via Wikipedia). (right) BeF2 structure (CC BY-SA 3.0 Unported; Materialscientist via Wikipedia)

In the liquid phase, BeF_2 has a fluctuating tetrahedral structure where Be and F ions exchange. The vapor phase is reached at temperatures higher than 1000 °C (at ~ 1 atm). In the vapor phase, BeF_2 exists as a monomer with linear geometry and a bond length of 1.43 Å, consistent with a double bond between **Be** and **F**.

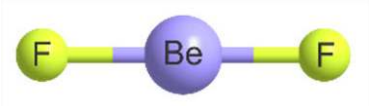


Figure **3.1.4.2**: Geometries of BeF_2. (CC BY; Ibon Alkorta and Anthony C. Legoe via Inorganics)

$BeCl_2$

At ambient temperature and pressure, $BeCl_2$ is a solid. As in BeF_2 described above, $BeCl_2$ has four-coordinate, tetrahedral Be and two-coordinate Cl. In contrast to BeF_2, solid $BeCl_2$ is a 1-dimensional polymer consisting of edge-shared tetrahedral.

In the gas phase, $BeCl_2$ exists as a dimer with two chlorine atoms bridging two Be atoms. In the dimer, the Be atoms are 3-coordinate. Bridging Cl atoms are two-coordinate, while terminal Cl atoms are one-coordinate. At higher temperatures in the vapor phase, the linear monomer also exists.

Boron ($2s^2 2p^1$)

Prediction based on Lewis structures:

Lewis structures of $\mathbf{BH_3}$ and $\mathbf{BF_3}$ were described in Exercise 3.1.2, and are drawn again below for convenience.

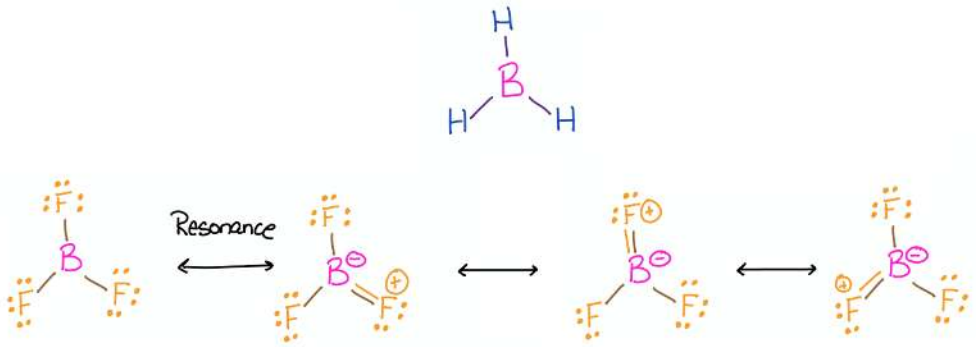


Figure **3.1.4.2**: Lewis structures of $\mathbf{BH_3}$ and $\mathbf{BF_3}$. (Kathryn Haas; CC-NC-BY-SA)

Boron trihalides

Boron trihalides, like $\mathbf{BF_3}$, have properties that are largely predicted by Lewis structures and VSEPR theory. The Lewis structure for $\mathbf{BF_3}$ includes several resonance structures. The structure with only single bonds is the most common representation for this molecule because the charge separation shown in the other structures is considered to be unfavorable. The highly polarized B-F bond has a dipole moment that lies opposite to the indicated formal charges shown in the resonance structures with double bonds between boron and fluorine.

The resonance hybrid of $\mathbf{BF_3}$ predicts partial double bond character between boron and fluorine, thus a bond length shorter than a single bond. Using the Lewis structures and VSEPR theory, we would predict a trigonal planar geometry around boron. In fact, the actual structure of $\mathbf{BF_3}$ is a monomer with trigonal planar geometry and with bond length that is shorter than a single bond. The case is similar to structures of other boron trihalides as well.

Boron trihalides are electron deficient at the boron center and react readily with Lewis bases. In other words they are strong Lewis acids (electrophiles).

Boron trihydride (BH_3 is really B_2H_6)

The properties of boron trihydride ($\mathbf{BH_3}$) are not predicted by the simple predictions made through Lewis structures and VSEPR. The monomer, BH_3, is not stable, but when dissolved in the presence of a Lewis base, BH_3 can form a stable acid-base adduct. In its pure form, the compound actually exists as a dimeric gas with a molecular unit of B_2H_6 (try drawing a valid Lewis structure for that!). Its unexpected structure includes two H's that bridge the two boron atoms in 3-center-2-electron bonds. You can read more about B_2H_6 on the Wikipedia page for Diborane(6). The unique bonding observed for boron is described more in Chapter 8 and Chapter 15.

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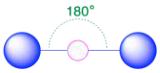
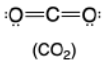
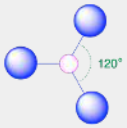
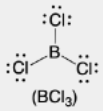
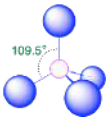
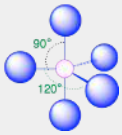
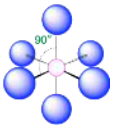
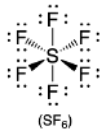
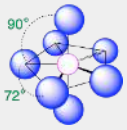
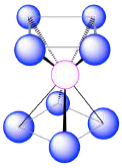
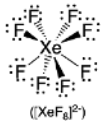
3.2: Valence Shell Electron-Pair Repulsion

Introduction to VSEPR

The **Valence Shell Electron Repulsion (VSEPR)** model can predict the structure of most molecules and polyatomic ions in which the central atom is a nonmetal; it also works for some structures in which the central atom is a metal. VSEPR builds on Lewis electron dot structures (discussed in Section 3.1(opens in new window)); Lewis structures alone predict only connectivity while the Lewis structure and VSEPR together can predict the geometry of each atom in a molecule. The main idea of VSEPR theory is that pairs of electrons (in bonds and in lone pairs) repel each other. The pairs of electrons (in bonds and in lone pairs) are called "groups". Because electrons repel each other electrostatically, the most stable arrangement of electron groups (i.e., the one with the lowest energy) is the one that minimizes repulsion. Groups are positioned around the central atom in a way that produces the molecular structure with the lowest energy. In other words, the repulsion between groups around an atom favors a geometry in which the groups are as far apart from each other as possible. Although VSEPR is simplistic because it does not account for the subtleties of orbital interactions that influence molecular shapes, it accurately predicts the three-dimensional structures of a large number of compounds.

We can use the VSEPR model to predict the geometry around the atoms in a polyatomic molecule or ion by focusing on the number of electron pairs (groups) around a *central atom* of interest. Groups include bonded and unbonded electrons; a single bond, a double bond, a triple bond, a lone pair of electrons, or even a single unpaired electron each count as one group. The molecule or polyatomic ion is given an AX_mE_n designation, where **A is the central atom**, **X is a bonded atom**, **E is a nonbonding** valence electron group (usually a lone pair of electrons), and m and n are integers. The number of groups is equal to the sum of m and n. Using this information, we can describe the molecular geometry around a central atom, that is, the arrangement of the *bonded atoms* in a molecule or polyatomic ion. The geometries that are predicted from VSEPR when a central atom has only bonded groups ($n = 0$) are listed below in Table **3.2.1**. The cases where lone pairs contribute to the total groups ($n \geq 1$) are discussed in the next section about lone pair repulsion(opens in new window).

Table **3.2.1**. Geometries predicted using VSEPR theory (bonded groups only).

Groups around central atom (m + n)	Geometry Name	Geometry Sketch	Predicted bond Angle	Example
2	linear		180°	
3	trigonal plane(opens in new window)		120°	
4	tetrahedron		109.5°	
5	trigonal bipyramid		90° and 120°	
6	octahedron		90°	
7	pentagonal bipyramid		90° and 72°	
8	square antiprism		70.5°, 99.6° and 109.5°	

Practice

VSEPR to predict Molecular Geometry

You can follow these four steps to predict the geometry around an atom using VSEPR:

1. Draw the Lewis electron structure of the molecule or polyatomic ion.
2. For the central atom of interest, assign the AX_mE_n designation and the total number of groups (m+n).
3. Determine the electron group arrangement around the central atom that minimizes repulsions.
4. Describe the molecular geometry.

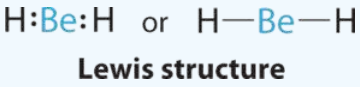
Use the procedure above to complete the exercises below

Exercise 3.2.1

Predict the geometry around the central atom in BeH_2 and CO_2.

Answer BeH_2

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



Lewis structure

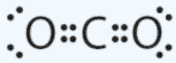
2. There are two groups around the central atom, and both groups are single bonds. Thus BeH_2 is designated as AX_2.

3. We see from Table **3.2.1** that the arrangement that minimizes repulsions places the groups 180° apart.

4. From Table **3.2.1** we see that with two bonding pairs, the molecular geometry that minimizes repulsions in BeH_2 is *linear.*

Answer CO_2

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



2. The carbon atom forms two double bonds. Each double bond is counted as one group, so there are two groups around the central atom. Once again, both groups around the central atom are bonds, so CO_2 is designated as AX_2.

3. Like BeH_2, the arrangement that minimizes repulsions places the groups 180° apart.

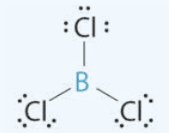
4. VSEPR only recognizes groups around the *central* atom (the carbon). Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonded groups on the central atom and no lone pairs, the molecular geometry of CO_2 is linear (Table **3.2.1**). The structure of CO_2 is shown in Table **3.2.1**.

? Exercise 3.2.2

Predict the geometry around the central atom in BCl_3 and CO_3^{2-}.

Answer BCl_3

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



Lewis structure

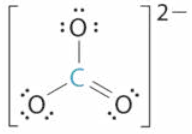
2. There are three groups around the central atom and all are single bonds. The structure is designated as AX_3.

3. To minimize repulsions, the groups are placed 120° apart (Table **3.2.1**).

4. From Table **3.2.1** we see that with three bonding pairs around the central atom, the molecular geometry of BCl_3 is *trigonal planar*.

Answer CO_3^{2-}

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

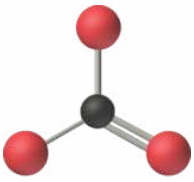


Lewis structure

2. The structure of CO_3^{2-} is a resonance hybrid. It has three identical bonds, each with a bond order of $1\frac{1}{3}$. All electron groups are bonds. With three bonding groups around the central atom, the structure is designated as AX_3.

3. We minimize repulsions by placing the three groups 120° apart (Table **3.2.1**).

4. We see from Table **3.2.1** that the molecular geometry of CO_3^{2-} is trigonal planar with bond angles of 120°.



Molecular geometry
(trigonal planar)

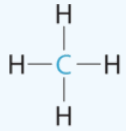
In our next example we encounter the effects of lone pairs and multiple bonds on molecular geometry for the first time.

? Exercise 3.2.3

Predict the geometry around the central atom in CH_4, PCl_5 and SF_6.

Answer CH_4

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

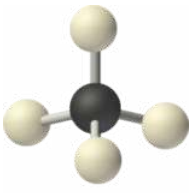


Lewis structure

2. There are four electron groups around the central atom. All electron groups are bonding pairs, so the structure is designated as AX_4.

3. As shown in Table **3.2.1**, repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5°.

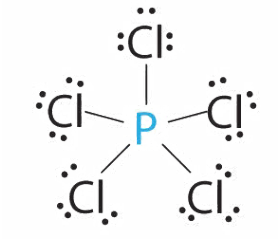
4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Table **3.2.1**).



Molecular geometry
(tetrahedral)

Answer PCl_5

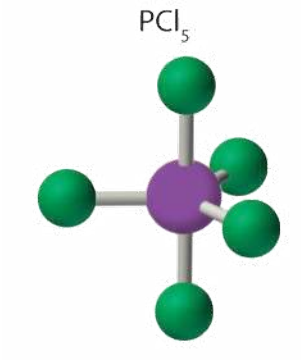
1. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron structure of PCl_5 is



2. There are five bonding groups around phosphorus, the central atom. All electron groups are bonds, so the structure is designated as AX_5.

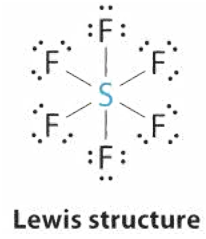
3. The structure that minimizes repulsions is a *trigonal bipyramid*, which consists of two trigonal pyramids that share a base (Table **3.2.1**).

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



Answer SF_6

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

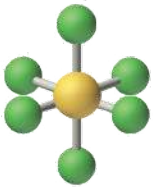


With an expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the central atom, each a bonding pair. We see from Figure **3.2.2** that the geometry that minimizes repulsions is *octahedral*.

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

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



Molecular geometry
(octahedral)

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3.2.1: Lone Pair Repulsion

In the previous section, we saw how to use VSEPR to predict the geometry around a central atom based on the number of groups attached to a central atom. However, our previous discussion was limited to the simple cases where all of the groups were bonded groups (i.e., in the designation AX_mE_n , n=0). When all of the groups are bonds, the geometries can be predicted using information in Table 3.2.1 in the previous section. Now we will consider cases where one or more of these groups are lone pairs.

Lone pairs have stronger repulsive forces than bonded groups.

When one or more of the groups is a lone pair of electrons (non-bonded electrons), the experimentally-observed geometry around an atom is slightly different than in the case where all groups are bonds. The actual bond angles are similar, but not exactly the same, as those predicted based on the *total number of groups* (the "parent" geometry). When there is a mixture of group types (**lone pairs (E)** ***and*** **bonded groups (X)**) there are three different types of angles to consider: bond angles between two bonded atoms (**X-X** angles), angles between a bonded atom and a lone pair (**X-E** angles), and angles between two lone pairs (**E-E** angles). Empirical evidence shows the following trend in the degree of bond angles around atoms with a mixture of group types:

Trend in bond angles:

E-E >**X-E** >**X-X**

Using empirical evidence as a guide, we can predict that lone pairs repel other electron groups more strongly than bonded pairs. The molecular geometry of molecules with lone pairs of electrons is better predicted when we consider that electronic repulsion created by lone pairs is stronger than the repulsion from bonded groups. It is difficult to predict the exact bond angle based on this principle, but we can predict approximate angles, as described and summarized below in Table **3.2.1.1**.

Table **3.2.1.1**: Predictions of molecular geometry and bond angles around atoms with a mixture of bonded (X) and unbonded (E) electron groups.

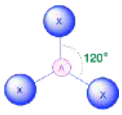
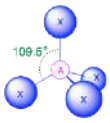
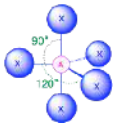
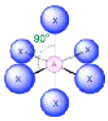
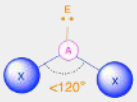
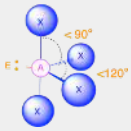
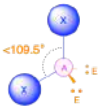
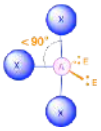
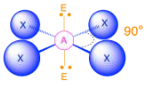
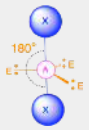
Electron Groups (m + n)					
	2 (steric number = 2)	**3** (steric number = 3)	**4** (steric number = 4)	**5** (steric number = 5)	**6** (steric number = 6)
Parent Geometry (0 lone pairs) AX_m	 AX_2, linear 180°	 AX_3, trig. plane 120°	 $AX4$, tetrahedron 109.5°	 AX_5, trig. bipyramid 90°, 120°	 AX_6, octahedron 90°
1 lone pair AX_mE_1		 $AX2E_1$, bent <120°	 AX_3E_1, trig. pyramid <109.5°	 AX_4E_1, see-saw <90°, <120°	 AX_5E_1, square pyramid 90°, <90°
2 lone pairs AX_mE_2			 AX_2E_2, bent <109.5°	 AX_3E_2, T-shape <90°	 AX_4E_2, square plane 90°
3 lone pairs AX_mE_3				 AX_2E_3, linear 180°	

Table **3.2.1.1** summarizes the geometries and bond angles predicted for nearest-neighbor bonded groups on central atoms with a mixture of lone pairs and bonded groups. The table does not cover all possible situations; it only includes cases where there are two bonded groups in which an X-X angle is measurable between nearest-neighbors. A more detailed description of some selected cases is given below.

Two Electron Groups (m + n = 2)

(Steric number = 2) In the case that there are only two electron groups around a central atom, those groups will lie 180° from one another. This results in a linear molecular geometry with 180° bond angles.

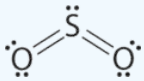
Three Electron Groups (m + n = 3)

(Steric number = 3) In the case that there are three electron groups around a central atom, those groups will lie approximately 120° from one another in space. This results in an electronic geometry that is approximately **trigonal planar**. There are two different molecular geometries that are possible in this category:

- When all of the electron groups are bonds (m = 3 or AX_3), the molecular geometry is a ***trigonal plane*** with **120°** bond angles.
- When there is one lone pair (m=2, n=1 or AX_2E_1), the molecular geometry is ***bent*** with a bond angle that is slightly **less than 120°**.

✔ AX_2E Molecules: Example SO_2

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



2. There are three electron groups around the central atom: two double bonds and one lone pair. We initially place the groups in a trigonal planar arrangement to minimize repulsions (Table **3.2.1.1**).

3. With two bonding pairs and one lone pair, the structure is designated as AX_2E. This designation has a total of three electron pairs, two X and one E. The lone pair occupies more space around the central atom than a bonding pair (even double bonds!). Bonding pairs and lone pairs repel each other electrostatically in the order BP–BP < LP–BP < LP–LP. In SO_2, we have one BP–BP interaction and two LP–BP interactions.

4. The molecular geometry is described only by the positions of the nuclei, *not* by the positions of the lone pairs. Thus, with two nuclei and one lone pair the shape is *bent*, or *V shaped*, which can be viewed as a trigonal planar arrangement with a missing vertex. The O-S-O bond angle is expected to be *less than* 120° because of the extra space taken up by the lone pair.

Four Electron Groups (m + n = 4)

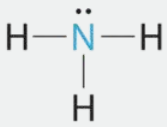
(Steric number = 4) In the case that there are four electron groups around a central atom, those groups will lie approximately 109.5° from one another in space. This results in an electronic geometry that is approximately **tetrahedral**. There are three different molecular geometries that are possible in this category:

- When all electron groups are bonds (m=4 or AX_4), the molecular geometry is a ***tetrahedron*** with bond angles of **109.5°**.
- When there is one lone pair (m=3, n=1 or AX_3E_1), the molecular geometry is a ***trigonal pyramid*** with bond angles of **slightly less than 109.5°**.
- When there are two lone pairs (m=2, n=2 or AX_2E_2), the molecular geometry is ***bent*** with bond angles of **slightly less than 109.5°**.

📌 AX_3E Molecules: Example NH_3

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

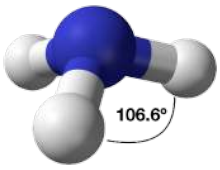
1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure



Lewis structure

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

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



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

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

4. There are three nuclei and one lone pair, so the molecular geometry is *trigonal pyramidal*. In essence, this is a tetrahedron with a vertex missing. However, the H–N–H bond angles are less than the ideal angle of 109.5° because of LP–BP repulsion. The bond angles in ammonia are 106.6°.

AX_2E_2 Molecules: Example H_2O

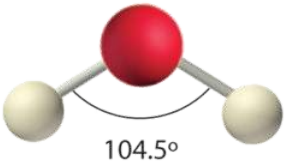
1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure



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

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

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



Five Electron Groups (m + n = 5)

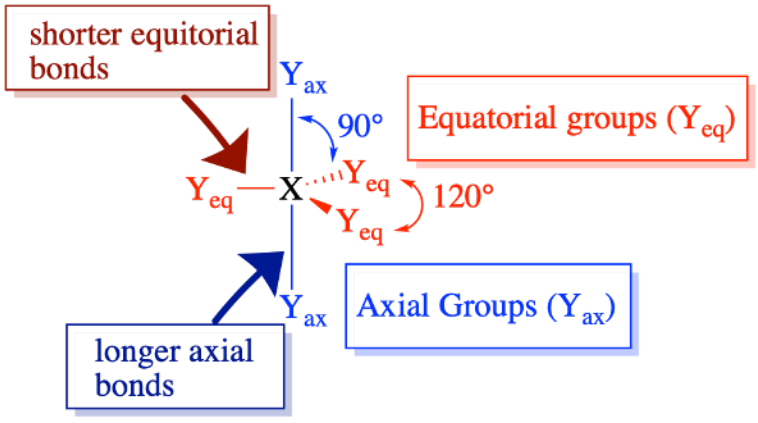


Figure: Trigonal pyramidal molecules (steric number 5) possess different bond angles and lengths for axial (ax) and equatorial (eq) pendant atoms. (CC-BY-NC-SA; Kathryn Haas).

(Steric number = 5) In the case that there are five electron groups around a central atom, there are two different types of positions around the central atom: equatorial positions and axial positions. The three equatorial ligands are 120° from one another and are 90° from each of the two axial ligands. The axial positions have three adjacent groups oriented 90° away in space. Axial groups are thus more crowded than the equatorial positions with only two adjacent groups at 90°. The crowding of axial positions results in slight differences in bond distances; crowded axial groups have longer bonds than the less crowded equatorial groups. Lone pairs of electrons generally prefer to occupy equatorial positions rather than axial positions. The justification for this preference, according to VSEPR theory, is that the lone electron pairs are more repulsive than bonding electron pairs, and thus the lone pairs prefer the less crowded equatorial positions.

The arrangement of five groups around a central atom results in a **trigonal bipyramidal** electronic geometry. There are four different molecular geometries that are possible in this category, depending upon the number of bonded groups and lone pairs of electrons:

- When all electron groups are bonds (m=5 or AX_5), the molecular geometry is a ***trigonal bipyramid*** with bond angles of **120°** and **90°** between adjacent ligands.
- When there is one lone pair (m=4, n=1 or AX_4E_1), the lone pair occupies one of the equatorial positions. The molecular geometry is called a ***see saw*** with bond angles of **slightly less than 120°** and **slightly less than 90°**.
- When there are two lone pairs (m=3, n=2 or AX_3E_2), each lone pair occupies one of the three equatorial positions. The molecular geometry is ***T-shaped*** with bond angles of **slightly less than 120°** and **slightly less than 90°**.
- When there are three lone pairs (m=1, n=3 or AX_3E_2), the lone pairs occupy the three equatorial positions. The molecular geometry is ***linear*** with bond angles of **180°**.

AX_4E Molecules: SF_4

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



Lewis structure

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

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

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

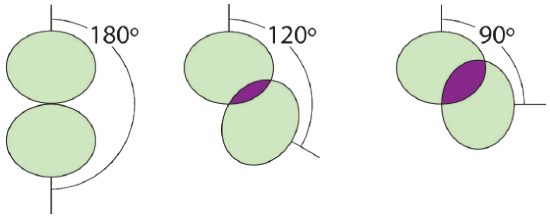
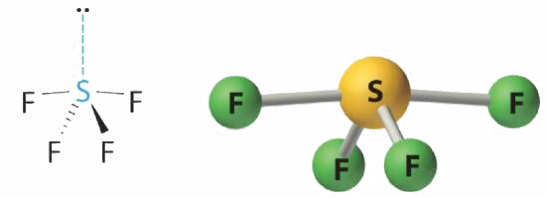


Illustration of the Area Shared by Two Electron Pairs versus the Angle between Them

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

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

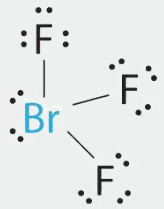
in the equatorial plane.



Molecular geometry (seesaw)

AX_3E_2 Molecules: BrF_3

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



Lewis structure

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

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

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



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

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

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

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

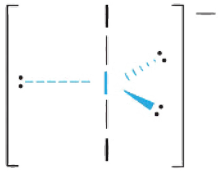
AX_2E_3 Molecules: I_3^-

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



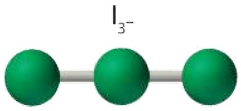
2. There are five electron groups about the central atom in I_3^-, two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

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



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

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



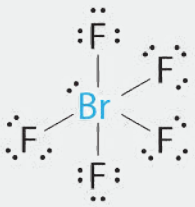
Six Electron Groups (m + n = 6)

(Steric number = 6) In the case that there are six electron groups around a central atom, the nearest groups will lie approximately 90° from one another in space. This results in an electronic geometry that is approximately **octahedral**. There are three relevant molecular geometries in this category:

- When all electron groups are bonds (m=6 or AX_6), the molecular geometry is an ***octahedron*** with bond angles of **90°** between adjacent bonds.
- When there is one lone pair (m=5, n=1 or AX_5E_1) we now distinguish between the axial and equitorial positions; the lone pair is considered to be in one of the axial positions, while the bond directly opposite of the lone pair is the axial bond. The molecular geometry is a ***square pyramid*** with bond angles of **90°** between adjacent equatorial bonds and **slightly less than 90°** between the axial bond and equatorial groups.
- When there are two lone pairs (m=4, n=2 or AX_4E_2), the lone pairs are opposite of one another and each occupy an axial position. The molecular geometry is ***square planar*** with bond angles of **90°**.

AX_5E Molecules: BrF_5

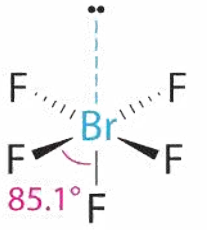
1. The central atom, bromine, has seven valence electrons, as does each fluorine, so the Lewis electron structure is



Lewis structure

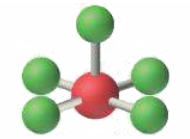
With its expanded valence, this species is an exception to the octet rule.

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



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

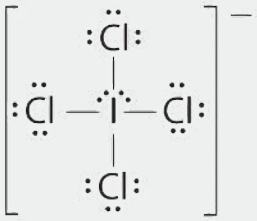
4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is *square pyramidal*. The F_{axial}–B–$F_{equatorial}$ angles are 85.1°, less than 90° because of LP–BP repulsions.



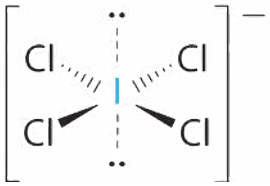
Molecular geometry
(square pyramidal)

AX_4E_2 Molecules: ICl_4^-

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

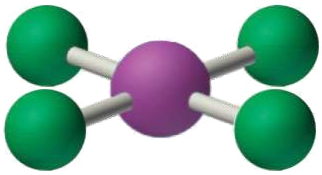


2. There are six electron groups around the central atom, four bonding pairs and two lone pairs. The structure that minimizes LP–LP, LP–BP, and BP–BP repulsions is



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

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



Summary

The arrangement of bonded atoms in a molecule or polyatomic ion is crucial to understanding the chemistry of a molecule, but Lewis electron structures give no information about **molecular geometry**. The **valence-shell electron-pair repulsion (VSEPR) model** allows us to predict which of the possible structures is actually observed in most cases. VSEPR is based on the assumption that pairs of electrons occupy space, and the lowest-energy structure is the one that minimizes repulsions between electron pairs. In the VSEPR model, the molecule or polyatomic ion is given an AX_mE_n designation, where A is the central atom, X is a bonded atom, E is a nonbonding valence electron group (usually a lone pair of electrons), and *m* and *n* are integers. Each group around the central atom is designated as a bonding pair (BP) or lone (nonbonding) pair (LP). From the BP and LP interactions we can predict both the relative positions of the atoms and the angles between the bonds, called the **bond angles**. From this we can describe the **molecular geometry**. The VSEPR model can be used to predict the shapes of many molecules and polyatomic ions, but it gives no information about bond lengths and the presence of multiple bonds. A combination of VSEPR and a bonding model, such as Lewis electron structures, is necessary to understand the presence of multiple bonds.

The relationship between the number of electron groups around a central atom, the number of lone pairs of electrons, and the molecular geometry is summarized in Table **3.2.1.1**.

Example Excercises

✔ Example 3.2.1.1

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

1. PF_5 (phosphorus pentafluoride, a catalyst used in certain organic reactions)
2. H_3O^+ (hydronium ion)

Given: two chemical species

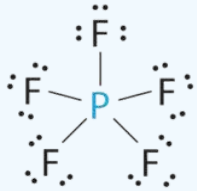
Asked for: molecular geometry

Strategy:

A. Draw the Lewis electron structure of the molecule or polyatomic ion.
B. Determine the electron group arrangement around the central atom that minimizes repulsions.
C. Assign an AX_mE_n designation; then identify the LP–LP, LP–BP, or BP–BP interactions and predict deviations in bond angles.
D. Describe the molecular geometry.

Solution:

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



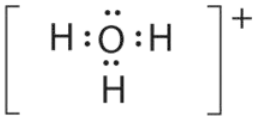
B There are five bonding groups about phosphorus. The structure that minimizes repulsions is a trigonal bipyramid.

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

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



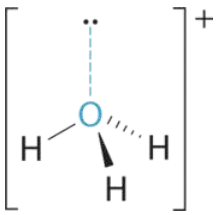
- **A** The central atom, O, has six valence electrons, and each H atom contributes one valence electron. Subtracting one electron for the positive charge gives a total of eight valence electrons, so the Lewis electron structure is



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

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

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



? Exercise 3.2.1.1

Using the VSEPR model, predict the molecular geometry of each molecule or ion.

a. XeO_3
b. PF_6^-
c. NO_2^+

Answer a

trigonal pyramidal

Answer b

octahedral

Answer c

linear

Example 3.2.1.2

Predict the molecular geometry of each molecule.

1. XeF_2
2. $SnCl_2$

Given: two chemical compounds

Asked for: molecular geometry

Strategy:

Use the strategy given in Example 3.2.1.1.

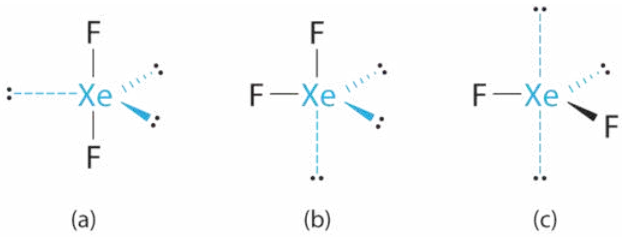
Solution:

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



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

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

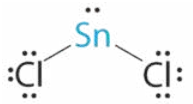


Interactions			
90 LP–LP	0	2	2

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

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

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



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

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

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

? Exercise 3.2.1.2

Predict the molecular geometry of each molecule.

a. SO_3
b. XeF_4

Answer a

trigonal planar

Answer b

square planar

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- **3.2.2: Multiple Bonds** by Kathryn Haas is licensed CC BY-NC-SA 4.0.

3.2.2: Multiple Bonds

In the previous sections, we saw how to predict the approximate geometry around an atom using VSEPR theory, and we learned that lone pairs of electrons slightly distort bond angles from the "parent" geometry. This page discusses the effect of multiple (double and triple) bonds between bonded atoms.

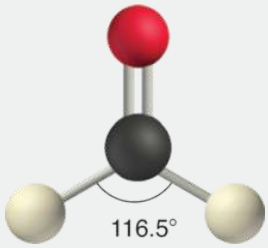
Double and triple bonds are more repulsive than single bonds

VSEPR theory predicts that double and triple bonds have stronger repulsive forces than single bonds. Like lone pairs of electrons, multiple bonds occupy more space around the central atom than a single bond. The result is that bond angles are slightly distorted compared to the parent geometry. Since a multiple bond has a higher electron density than a single bond, its electrons occupy more space than those of a single bond. Double and triple bonds distort bond angles in a way similar to what lone pairs do. Due to the stronger repulsion, double and triple bonds occupy positions similar to those of lone pairs in groups with 5 and 6 electron groups.

Examples 3.2.2.1

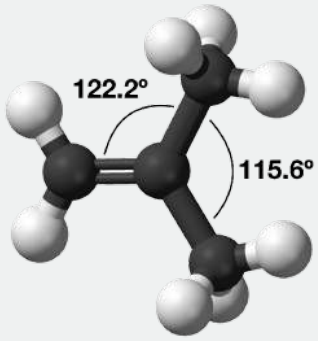
CH_2O

In a molecule such as CH_2O (AX_3), whose structure is shown below, the double bond repels the single bonds more strongly than the single bonds repel each other. This causes a deviation from ideal geometry (an H–C–H bond angle of 116.5° rather than 120°).



2-methybutene

In the molecule, $CH_2C(CH_3)_2$, the methyl—C—methyl bond angle is 115.6°, which is less than the 120° bond angle that would be expected of the parent geometry. On the other hand, the acetyl—C—methyl bond angle is greater than 120°, with an actual bond angle of 122.2°.



Atoms with both lone pairs and multiple bonds

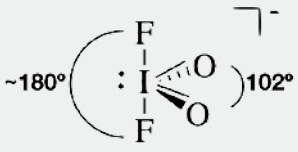
In general, we expect that a lone pair has slightly greater repulsive force than a multiple bond, and that a multiple bond has slightly greater repulsive force than a single bond. The **order of expected repulsive force** is:

$$\text{lone pair} > \text{double or triple bond} > \text{single bond}$$

Examples3.2.2.1

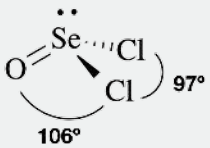
$IO_2F_2^-$

With five electron groups, the IO_2F_2 molecule has an approximately trigonal bipyramidal electronic (parent) geometry. The central iodine atom has a single bond to each of the fluorine atoms, a double bond to each oxygen, and a lone pair. The lone pair and the double bonds will occupy more space around iodine than each of the single bonds. Thus, we expect the lone pair and double bonds to occupy equatorial positions around the central iodine. The O=I=O bond angle is 102° (*much* smaller than the 120° angle expected from the parent geometry). This dramatically smaller angle is a result of the increased repulsion between the lone pair and the double bond.



$SeOCl_2$

With four electron groups, the $SeOCl_2$ molecule has four electron groups and approximately tetrahedral electronic (parent) geometry. It has both a lone pair and a double bond on the central selenium atom. The two chlorine atoms are singly bonded to selenium, while the oxygen is double bonded. The lone pair is most repulsive, followed by the double bonded oxygen, and then the chlorine bonds. This gives a Cl—Se—Cl bond angle of 97° and a Cl—Se—O bond angle of 106°; both angles are less than the 109.5° angles expected for the ideal tetrahedral geometry.



Practice

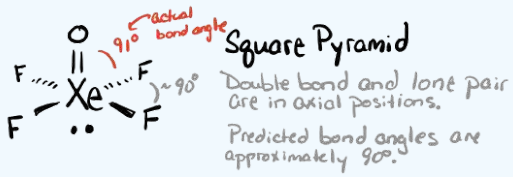
Exercise 3.2.2.1

Use VSEPR theory to predict the geometries and draw the structures of the following.

a. $XeOF_4$
b. NO_2^-
c. $SOCl_2$
d. IOF_3^-

Answer a

This molecule has six electron groups around the central Xe atom (steric number 6), and thus has an approximately octahdral electronic (parent) geometry. There is a double bond to O and a lone pair, both of which are more strongly repulsive than the single bonds to F. The double bond and lone pair will be directly opposite to each other, designated as axial positions. The result is a square pyramidal molecular geometry. VSEPR theory predicts F—Xe—F bond angles of 90°. As a general rule, lone pairs are slightly more repulsive than multiple bonds, and so we might expect the O—Xe—F bond angles to be <90°; *however in this case the actual O—Xe—F bond angle is observed to be 91°* (you could not have predicted the latter).



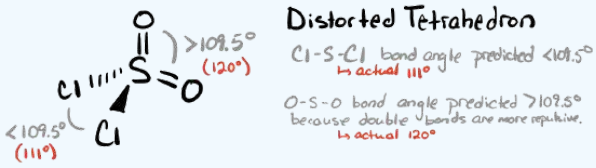
Answer b

This molecule has three electron groups around the central atom: one lone pair and two double bonds to oxygen atoms. This results in an approximately trigonal planar electronic (parent geometry). We expect the lone pair to be slightly more repulsive than double bonds, and so we expect the O—N—O bond angle to be slightly less than 120°. *The actual O—N—O angle is 115°.*



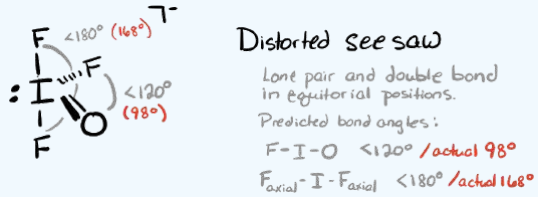
Answer c

This molecule has four electron groups (steric number 4) with an approximately tetrahedral electronic (parent) geometry. Each double bonded oxygen will take up more space around the central S than the single bonded Cl atoms. We should expect the double bonds to repel each other more strongly than they repel each single bond, with the least repulsive interaction being between the two single bonds. The bond angle for Cl—S—Cl is expected to be <109.5° according to VSEPR theory (however, it is actually 111°). We would expect the bond angle for O—S—O to be larger than the angle for Cl—S—Cl and for Cl—S—O. The O—S—O bond angle is predicted to be >109.5° (and the actual bond angle is 120°). The molecular geometry is a distorted tetrahedron.



Answer d

This molecule has five electron groups (steric number 5) with an approximately trigonal bipyramidal electronic (parent) geometry. There is one lone pair, a double bond to O, and three single bonds to F atoms around the central I atom. The lone pair and double bond are most repulsive, and should occupy the less crowded equatorial positions rather than the more crowded axial positions. This results in a seesaw molecular geometry. With the more repulsive lone pair and the strongest equatorial repulsive force being between the double bond and lone pair, we should expect the $F_{equatorial}$—I—O bond angle to be less than the 120° angle expected for the parent geometry (*it is actually much less, at 98°*). Due to repulsion between the axial F atoms and both the lone pair and double bond, we should expect the F—S—F bond angles to be compressed. The F_{axial}—I—F_{axial} is actually 168°.



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3.2.3: Electronegativity and Atomic Size Effects

Introduction

We saw in previous sections how lone pairs of electrons and multiple bonds distort bond angles between non-central atoms (ligands) around a central atom. This section describes how ligand **electronegativity and size also influence bond angles and molecular geometry**. Electronegativity is generally correlated with atomic size going down any group of the periodic table. There are some cases where bond angles can be predicted by these correlations. However, size and electronegativity can also work as competing factors in determining bond angles.

Definitions of Electronegativity

Linus Pauling introduced the first electronegativity scale in 1932 in order to explain the extra stability of molecules with polar bonds.[1] The electronegativity of an atom, represented by the Greek letter χ (chi), can be defined as the tendency of an atom to draw electrons to itself in a chemical bond. On the Pauling scale, the electronegativity difference between two atoms A and B was defined in terms of the dissociation energies E_d of the A-A, B-B, and A-B bonds:

$$\chi_A - \chi_B = \sqrt{E_d(AB) - [E_d(AA) + E_d(BB)]/2}$$

where the energies are expressed in electron volts. Pauling's scale of electronegativity ranges from Fluorine (most electronegative = 4.0) to Francium (least electronegative = 0.7). [2,3] The polarity of bonds and assignment of formal charges is predicted by electronegativity differences.

Periodic table of electronegativity using the Pauling scale

→ Atomic radius decreases → Ionization energy increases → Electronegativity increases →

Group →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
↓ Period																		
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.60
6	Cs 0.79	Ba 0.89	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 1.87	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
7	Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo
* Lanthanoids			La 1.1	Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27	
** Actinoids			Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.3	

Figure **3.2.3.1**: Table of Pauling electronegativities from Wikipedia's Electronegativity page (click).

While directly relevant to the strength of chemical bonds, the Pauling definition of electronegativity has a significant limitation: calculating each value requires data from several compounds in which specific atoms are bonded. This means that the scale cannot be successfully applied to all situations. To overcome this limitation, alternative electronegativity scales were developed based on different thermochemical measurements or calculations. These other scales are listed in the table below. More thorough descriptions of how values in each scale are calculated are described on Wikipedia's Electronegativity page (click) and a concise history of electronegativity scales is summarized in ref 4.

Scale Developer	Year first described	Characteristics
Linus Pauling[1]	1932	Based on bond energies
Robert S. Mulliken[5,6]	1934	Based on valence electron properties of atoms (electron affinity and ionization energy)
Louis Allred & Eugene G. Rochow[7]	1958	Based on electrostatic force (effective nuclear charge)
Robert T. Sanderson[8]	1983	Based on atomic electron density
Ralph G. Pearson[9]	1985	Related to Hard-Soft Acid-Based theory
Leland C. Allen, Joseph Mann, Terry L. Meek[10,11,12]	1989, 2000	Average ionization energies of valence shell electrons, configuration energies (CE) $$\mathrm{CE} = \frac{n\varepsilon_s + m\varepsilon_p}{n+m}$$ n = number of s electrons m = number of p electrons $\varepsilon_s, \varepsilon_p$ = experimental 1-electron s and p energies

The primary advantage to this scale developed by Mann, Meek, and Allen[12] is that it is based on configuration energy (CE), the average ionization energies of valence electrons in ground state free atoms. A scale based on ionization energies can be calculated more directly for any element. However, a critique of all electronegativity scales, including this one, is that they are all based on assumptions that fail in some cases.

There is a relationship between electronegativity and atomic size because both are related to ionization energy. Like ionization energy, there is a general trend across the periodic table for both electronegativity and atomic size; in general, smaller atoms toward the top right-hand side of the periodic table have greater electronegativity values and smaller atomic size. We will see below that both electronegativity and atomic size influence bond angles and absolute molecular geometry around a central atom. In some cases, the size and electronegativity affects are aligned; in some cases these effects compete.

Electronegativity and Size Influence Bond Angles

Let's begin by examining the bond angles of several trigonal pyramidal molecules. The molecules shown in Figure **3.2.3.2** each have three identical "pendant groups" on the central atom (Figure **3.2.3.2**). *Pendant atoms* or *pendant groups* are the atoms, or groups of atoms, that are bonded directly to the central atom. The molecules shown here are arranged according to the size of the central and pendant atoms. Central atoms increase in size going down this figure, and pendant atoms increase in size going across from left to right. The bond angles and bond lengths are labeled in each case.

What trends can you identify?

Trends in Size

First, let's examine how the size of the central and pendant groups might influence bond angle. In VSEPR theory, **the size of atoms (or groups of atoms) will affect bond angles due to changes in steric interactions between pendant groups.**

Size of the central atom

Examine the relationship between the size of the central atom and the bond angles in Figure **3.2.3.2** (go down any column in the figure). For example, compare NH_3, PH_3, AsH_3, and SbH_3, with bond angles 106.6°, 93.2°, 92.1°, and 91.6°, respectively. In this series, the size of the central atom increases from N to Sb while the size of the pendant atom (hydrogen) remains constant. *As the size of the central atom increases, the bond angles decrease; thus, we observe a negative relationship between size of the central atom and the bond angle in these molecules*. This relationship is explained by sterics. As the central atom increases in size, the

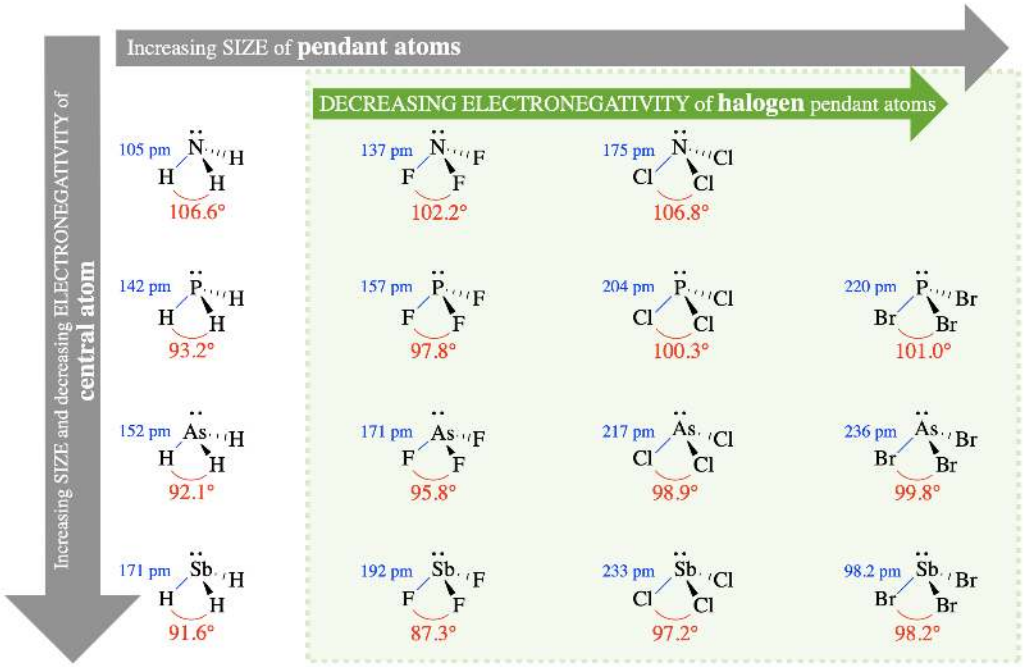


Figure **3.2.3.2**: Several molecules with trigonal pyramidal electronic geometry are shown arranged according to size of the central atom (increasing size of central atom from top to bottom) and pendant atom (increasing size of pendant atoms from left to right). Bond angles and bond lengths are indicated. (Kathryn Haas; CC-NC-BY-SA)

bond lengths also increase and the pendant atoms are farther from each other in space. In VSEPR theory, this will reduce steric interactions between the pendant groups. Since the lone pair on these molecules is more repulsive than bonded groups, the decrease in steric interactions between bonded groups results in a decrease in bond angles.

Size of the pendant atoms (or groups)

Examine the relationships between size of the halogen pendant atoms and bond angle in Figure **3.2.3.2** (go across any row within the shaded region). For example, compare PF_3, PCl_3, and PBr_3, with bond angles 97.8°, 100.3°, and 101.0°, respectively. In this series, the size of the pendant atom increases from F to Br while the central atom remains constant (phosphorous). *As the size of pendant atoms increases, the bond angle increases; thus, we observe a direct relationship between size of the pendant group and the bond angle in these molecules*. Again, we can explain this using sterics. As the size of the pendant atoms increases, sterics between the pendant groups will increase (despite small changes in bond length). Increased steric interactions between pendant groups will prefer larger bond angles between the groups.

This trend fails, however, if we consider the molecules with hydrogen as the pendant atoms. Notice, for example, that H is the smallest pendant atom. If we consider the trend described above, we should assume that XH_3 (where X is a variable atom) would have the smallest bond angle in the series of XH_3, XF_3, XCl_3, and XBr_3. However this is not the case of NH_3, NF_3, and NCl_3, with bond angles 106.6°, 102.2°, and 106.8°, respectively. To explain the variation in these bond angles, we need to consider electronegativity.

Trends in Electronegativity

Now let's examine how electronegativity influences bond angles around a central atom. In VSEPR theory, **electronegativity of atoms/groups will affect bond angles due to changes in the distribution of electron pairs around the central atom (and thus changes in the severity of electron pair repulsion).** This really comes down to bond polarity caused by the difference in electronegativity between the central atom and pendant groups (bond polarity in the context of valence bond theory). In a polar bond, the more electronegative atom will pull electron density towards itself. When a pendant atom is more electronegative, it will pull the bonded electron pair towards itself and away from the central atom; this will reduce the electron pair repulsion between bonded electron pairs on the central atom. A decrease in electron pair repulsion on the central atom should decrease bond angles between the groups (Figure **3.2.3.3**).

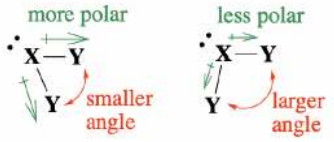


Figure **3.2.3.3**. When electron pairs are distributed away from the central atom, repulsions are decreased, allowing smaller bond angles. (Kathryn Haas; CC-NC-BY-SA)

Electronegativity is an alternative explanation to the trends we already examined above in Figure **3.2.3.2** . For example, when we compare the halogen pendant atoms (shaded region in Figure **3.2.3.2**) , the electronegativity of pendant groups decreases, bond polarity of the bonds decreases, and bond angles increase going from left to right and from F to Br. As more electron density remains on the central atom, electron repulsion between the bonded pairs increases and bond angles increase.

The electronegativity argument can also be used to explain the fact that NH_3 (106.6°) has a larger bond angle than NF_3 (102.2°). This particular case illustrates how electronegativity and size can be competing factors. While electronegativity differences seem to dominate in the case of NH_3 (106.6°) compared to NF_3 (102.2°), size differences still dominate in the cases of other XH_3 and XF_3 examples in Figure **3.2.3.2**).

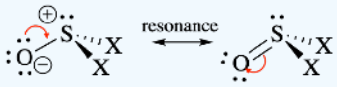
? Exercise 3.2.3.1

Predict the geometry and approximate bond angles. Then put the molecules in each series in order of smallest to largest bond angle. Defend your answer.

a. The X-S-X bond angle in OSF_2, $OSCl_2$, $OSBr_2$
b. H_2O, H_2S, H_2Se, H_2Te
c. H_2O, OF_2, OCl_2

Answer (a)

Geometry and predicted bond angles: These are molecules with steric number 4. They can be written as two different resonance structures, and the resonance hybrid would have double bond character between S and O.



We would expect a trigonal pyramidal geometry with all bond angles <109.5° because the lone pair is more repulsive than bonds. Because the double bond is more repulsive than single bonds, we should also expect the O-S-X bond angles to be greater than the X-S-X bond angles.

Trend: This is a series of molecules that varies in the identity of the pendant atoms; the variation is within the halogens. The size of the halogens increases, and the electronegativity decreases in the order F, Cl, Br. Both size and electronegativity would lead us to conclude that the X-S-X bond angles would increase in the order $OSF_2 < OSCl_2 < OSBr_2$

Explanation: (1) Increasing electonegativity of the pendant atom (F > Cl > Br) increases the polarity of the bond and reduces the electron density of the bonded pair on the central atom. This reduces the e-e repulsions of adjacent bonded electron pairs on S, allowing the halogens to become closer. The more electronegative pendant atoms can have smaller bond angles. (2) Increasing size of pendant atoms (F < Cl < Br) increases steric repulsions and increases bond angle. Both explanations lead to the same predicted trend.

The actual measured X-S-X bond angles are OSF_2 (92.3°) / $OSCl_2$ (96.2°) / $OSBr_2$ (98.2°). The trend in these bond angles is consistent with the prediction.

Answer (b)

Geometry and predicted bond angles: These are molecules with steric number 4, bent molecular geometry, with predicted bond angles <109.5° because the two lone pairs are each more repulsive than the bonds. There are two lone pairs and two single bonds to H around each central atom.

Trend: This is a series of molecules that varies in the identity of the central atom. The central atom increases in the order O < S < Se < Te, where Te is the largest element and O is the smallest. Arguments based on size would lead us to predict that the pendant groups of H_2Te would be less sterically crowded and thus have a smaller bond angle than the pendant groups of H_2O. The electronegativity decreases in the order O > S > Se > Te, where O is the most electronegative element and Te is the least. Thus, we expect the bonding electro pairs to be closer to the central atom on O than they would be on Te; we should expect H_2Te to have the least electron pair repulsions and thus smallest bond angle in this series, while H_2O would have the strongest electron pair repulsions and largest bond angles.

Both arguments lead to the same conclusion, that the order of increasing bond angle is $H_2Te < H_2Se < H_2S < H_2O$.

The actual measured bond angles are H_2Te (90.2°) / H_2Se (90.6°) / H_2S (92.1°) / H_2O (104.5). The trend in these bond angles is consistent with prediction.

Answer (c)

Geometry and predicted bond angles: These are molecules with steric number 4, bent molecular geometry, with predicted bond angles <109.5° because the two lone pairs are each more repulsive than the bonds. There are two lone pairs and two single bonds to H around each central atom. (This is similar to the case in (b)).

Trend: This is a series of molecules that varies in the identity of the pendant atoms; two of the molecules have halogens, and the other has hydrogen pendant atoms. This is a case where size and electronegativity will be conflicting factors because trends in electronegativity do not mirror the trend in size.

- *Size:* The size of pendant atoms increases in the order H < F < Cl where H is smallest and Cl is largest. Prediction of bond angles based on size alone would lead to the predicted order of increasing bond angle $H_2O < OF_2 < OCl_2$.
- *Electronegativity*: The electronegativity decreases in the order F > Cl > H where F has the greatest electronegativity and H has the least. Since we expect the most electronegative pendant atoms to have the smallest bond angles, prediction based on electronegativity alone would lead to the predicted order of increasing bond angle $OF_2 < OCl_2 < H_2O$.

The points above illustrate how the two different arguments would lead to different predictions about the trend in bond angle. This makes it difficult to predict the actual order of increasing bond angle. However, we saw above in the example of NH_3 vs NF_3 that electronegativity is more important than size; yet in the case of NH_3 vs NCl_3, the much larger size of the pendant atom is more important. If we apply this lesson to the current problem, we might predict the order $OF_2 < H_2O < OCl_2$, and in fact this more nuanced prediction, based on a similar case, matches the actual order for measured bond angles: OF_2 (103.3°) < H_2O (104.5°) < OCl_2 (110.9°).

Group Electronegativities

You probably heard the terms "electron donating group" and "electron withdrawing group" from your coursework in Organic Chemistry. For example, the acid trifluoroacetic acid (TFA) is more acidic than acetic acid due to the electron withdrawing effects of the CF_3 group compared to CH_3. CF_3 is an electron withdrawing group, while CH_3 is an electron donating group. In other words, CF_3 is more electronegative than CH_3.

The electron withdrawing ability (electronegativity) of groups can be estimated and compared, just as they are with atoms. Although there is no one scale that is used for group electronegativities, and published values even for the same groups vary widely, there are reliable trends within similar groups. The same size and electronegativity factors discussed above that affect bond angles for *pendant atoms*, also can be used to rationalize distorted bond angles for *pendant groups* around a central atom.

? Exercise 3.2.3.2

Consider the relative electronegativities and sizes of the pendant atoms/groups in the following examples. Is the trend in bond angles what you would expect from the relative group electronegativities and relative sizes? What, if any, is the more dominant factor in determining the trend?

a. $N(CH_3)_3$ has an C-N-C bond angle of 110.9°, while $N(CF_3)_3$ has a bond angle of 117.9°.
b. The X-S-X bond angles in molecules of the form $SO_2(X)_2$ are: $SO_2(OH)_2$ 101.3°; $SO_2(CF_3)_2$ 102.0°; $SO_2(CH_3)_2$ 102.6°.

Answer (a)

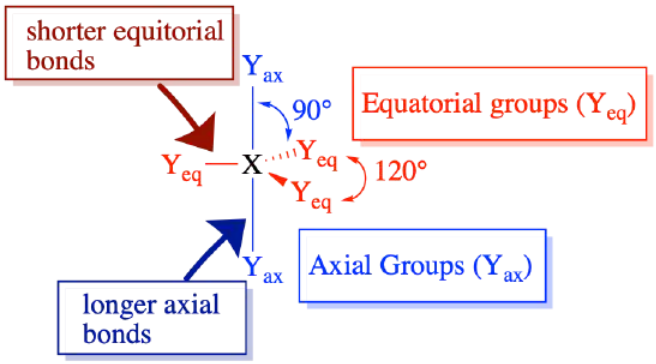
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Answer (b)

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Special case of electronegativity and size in steric number 5 (trigonal bypyramid)

Molecules with steric number 5 are interesting because they posses two different types of positions (equatorial and axial). These positions have unique bond angles and bond lengths. Pendant atoms/groups have different preferences for the axial and equatorial positions that depend somewhat on their electronegativity.



Molecules with steric number 5 possess different bond angles and lengths for axial (ax) and equatorial (eq) pendant atoms. (CC-BY-NC-SA; Kathryn Haas)

In a previous section, we discussed the preference of lone pairs and multiple bonds for the equatorial positions in trigonal bipyramidal molecules. VSEPR theory rationalizes this by assuming that lone pairs and multiple bonds are more repulsive than the electron pairs in single bonds. Equatorial positions are less crowded (with only two closest neighbors at 90°, and two farther neighbors at 120°) compared to axial positions (with three closest neighbors at 90°), thus the more repulsive groups prefer the less crowded equatorial positions.

Pendant groups that are more electronegative result in weaker electron pair repulsion around the central atom, while groups that are less electronegative result in stronger electron-pair repulsion around the central atom (as described above). The result for steric number 5: **bonding pairs to *less electronegative elements* are *more repulsive,* and *generally prefer equatorial* positions.** Still, lone pairs and multiple bonds are more repulsive than single bonds and would show a stronger preference for equatorial positions.

Examples and Nuances

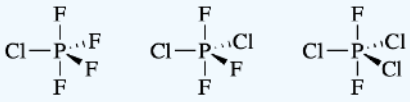
? Exercise 3.2.3.3

Some examples of molecule that demonstrate the equatorial preference of less electronegative groups are below. Predict (draw) their structures.

a. PF_4Cl, PF_3Cl_2, and PF_2Cl_3
b. $PF_4(CH_3)$ $PF_3(CH_3)_2$, and $PF_2(CH_3)_3$

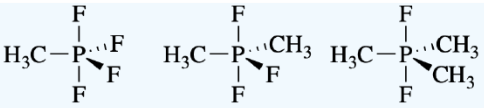
Answer (a)

Cl is less electronegative than F; thus we expect Cl to have stronger preference for the equatorial positions.

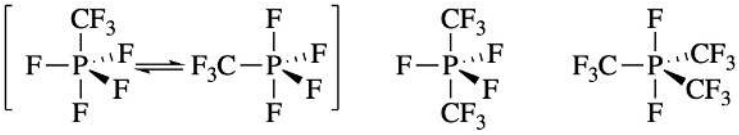


Answer (b)

CH_3, an electron donating group, is less electronegative than F. We expect CH_3 to have a stronger preference for the equatorial positions.



In the exercise above, the structures can be explained by the electronegativity of the pendant groups; less electronegative groups prefer the equatorial positions. There are other similar molecules for which explanations (or predictions) are difficult. For example, the series of molecules below seems to have completely random placement of F and CF_3 groups. **These structures could not be predicted based on VSEPR theory.** It seems that in this case, the more symmetrical arrangements of pendant groups is preferred.



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3.2.4: Ligand Close Packing

Introduction

Ligand Close Packing (LCP) theory is complimentary to VSEPR, except that LCP focuses on repulsions between pendant *atoms* ("outer" atoms that are not directly bonded to one another), rather than focusing on the chemical environment around the central atom in a molecule. Both LCP and the VSEPR models were developed by Robert Gillespie.

The LCP model assumes that ligands (or pendant atoms) "pack" as closely as possible around a central atom. A given ligand will have a specific atomic radius when bound to a central atom. The distance between two ligands around the same central atom is simply the sum of the atomic radii of the pendant atoms. Therefore for a specific set of ligands around a specific central atom, the ligand-ligand distances are constant despite the coordination number or bond angles. In other words, for a series of similar molecules with the same central atom, while bond angles and bond distances of pendant atoms may change, the distances between two pendant atoms remain the same.

Ligand Close Packing Theory

According to LCP, distances between two pendant atoms are similar...

- even when steric number changes
- even when bond angles change
- Reason: pendant atoms "pack" around the central atom.

Ligand Close Packing and Bond Distances

If the distance between non-bonded atoms remains constant even while bond angles change, then the bond length between the pendant and central atom must change to accommodate. For example, $\mathbf{PF_4^+}$ and $\mathbf{PF_3O}$ have almost identical $\mathbf{F-F}$ distances of 238 and 237 pm, respectively. As expected from VSEPR, the $\mathbf{F-P-F}$ bond angle in $\mathbf{PF_4^+}$ is 109.5°. The $\mathbf{F-P-F}$ bond angle in $\mathbf{PF_3O}$ (101.1°) is smaller due to the increased repulsion of the oxygen double bond. Therefore the P-F bond lengths must be different. In fact, the P-F bond distances are 145.7 pm in $\mathbf{PF_4^+}$ and 154 pm in $\mathbf{PF_3O}$.

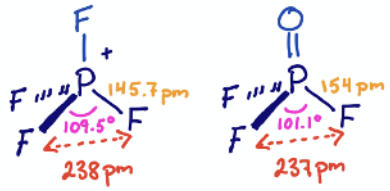


Figure **3.2.4.1**: The molecular structures of $\mathbf{PF_4^+}$ and $\mathbf{PF_3O}$. The distances between neighboring F atoms are similar in the two molecules, while bond lengths and angles differ. The $\mathbf{PF_4^+}$ ion has a $\mathbf{P-F}$ bond length of 145.7 pm, an $\mathbf{F-P-F}$ bond angle of 109.5°, and a distance of 238 pm between neighboring F atoms. The $\mathbf{PF_3O}$ molecule has a $\mathbf{P-F}$ bond length of 154 pm, an $\mathbf{F-P-F}$ bond angle of 101.1°, and a distance of 237 pm between neighboring F atoms. (CC-BY-NC-SA; Kathryn Haas)

The relationship between bond angles, bond lengths, and close-packing distance is described by right angle trigonometry (recall SOA-CAH-TOA). In a right triangle, the hypotenuse is the longest side, opposite to the right angle. For either of the other two angles in the triangle, the angle (θ) and lengths of the sides (*opposite* and *adjacent* to θ) are related by the trigometric functions shown in Figure **3.2.4.2** .



Figure **3.2.4.2**: Visual depiction of SOA-CAH-TOA. (CC-BY-NC-SA; Kathryn Haas)

In the case of a molecule, we can apply right angle trigonometry by imagining that the bond angle is divided into two right angles, as illustrated in Figure **3.2.4.2**. The hypotenuse of the triangles is the bond length, the opposite side is one half of the close-packing

distance, and θ is one half the bond angle.

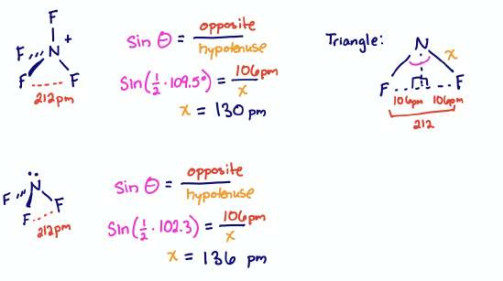


Figure 3.2.4.1: Illustration of how right angle trigonometry can be applied to determine bond angle, bond length, or distance between neighboring atoms: any bond angle can be divided into two right angles where the bond length is the hypotenuse, the distance between neighbors is twice the opposite side, and the bond angle is twice θ. (CC-BY-NC-SA; Kathryn Haas)

Exercise 3.2.4.1

The distance between F atoms is 212 pm in both NF_4^+ and NF_3. The bond angles are 109.5° and 102.3°, respectively. What are the expected $N-F$ bond lengths?

Answer



The actual measured bond lengths are 130 pm for NF_4^+ and 136.5 pm for NF_3.

Sources and Resources

- https://en.Wikipedia.org/wiki/LCP_th...ieNyholm1957-3

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3.3: Molecular Polarity

Dipole moments occur when there is a separation of charge. They can occur between two ions in an ionic bond or between atoms in a covalent bond; dipole moments arise from differences in electronegativity. The larger the difference in electronegativity, the larger the dipole moment. The distance between the charge separation is also a deciding factor in the size of the dipole moment. The dipole moment is a measure of the polarity of the molecule.

Introduction

When atoms in a molecule share electrons unequally, they create what is called a dipole moment. This occurs when one atom is more electronegative than another, resulting in that atom pulling more tightly on the shared pair of electrons, or when one atom has a lone pair of electrons and the difference of electronegativity vector points in the same way. One of the most common examples is the water molecule, made up of one oxygen atom and two hydrogen atoms. The differences in electronegativity and lone electrons give oxygen a partial negative charge and each hydrogen a partial positive charge.

Dipole Moment

When two electrical charges, of opposite sign and equal magnitude, are separated by a distance, an electric dipole is established. The size of a dipole is measured by its dipole moment (μ). Dipole moment is measured in Debye units, which is equal to the distance between the charges multiplied by the charge (1 Debye equals $3.34 \times 10^{-30}\ C\,m$). The dipole moment of a molecule can be calculated by Equation 3.3.1:

$$\vec{\mu} = \sum_i q_i \vec{r}_i \tag{3.3.1}$$

where

- $\vec{\mu}$ is the dipole moment vector
- q_i is the magnitude of the ith charge, and
- $\vec{r}_i$ is the vector representing the position of ith charge.

The dipole moment acts in the direction of the vector quantity. An example of a polar molecule is H_2O. Because of the lone pair on oxygen, the structure of H_2O is bent (via VSEPR theory), which means that the vectors representing the dipole moment of each bond do not cancel each other out. Hence, water is polar.

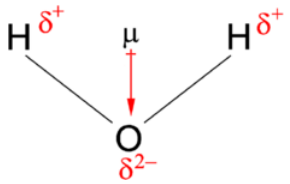


Figure 3.3.1: Dipole moment of water. The convention in chemistry is that the arrow representing the dipole moment goes from positive to negative. Physicist tend to use the opposite orientation.

The vector points from positive to negative, on both the molecular (net) dipole moment and the individual bond dipoles. Table A2 shows the electronegativity of some of the common elements. The larger the difference in electronegativity between the two atoms, the more electronegative that bond is. To be considered a polar bond, the difference in electronegativity must be large. The dipole moment points in the direction of the vector quantity of each of the bond electronegativities added together.

It is relatively easy to measure dipole moments: just place a substance between charged plates (Figure 3.3.2); polar molecules increase the charge stored on the plates, and the dipole moment can be obtained (i.e., via the capacitance of the system). Nonpolar CCl_4 is not deflected; moderately polar acetone deflects slightly; highly polar water deflects strongly. In general, polar molecules will align themselves: (1) in an electric field, (2) with respect to one another, or (3) with respect to ions (Figure 3.3.2).

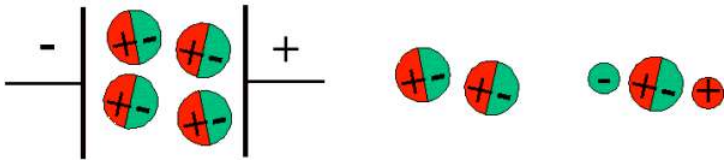


Figure **3.3.2**: Polar molecules align themselves in an electric field (left), with respect to one another (middle), and with respect to ions (right)

Equation 3.3.1 can be simplified for a simple separated two-charge system like diatomic molecules or when considering a bond dipole within a molecule

$$\mu_{diatomic} = Q \times r \tag{3.3.2}$$

This bond dipole is interpreted as the dipole from a charge separation over a distance r between the partial charges Q^+ and Q^- (or the more commonly used terms δ^+ - δ^-); the orientation of the dipole is along the axis of the bond. Consider a simple system of a single electron and proton separated by a fixed distance. When the proton and electron are close together, the dipole moment (degree of polarity) decreases. However, as the proton and electron get farther apart, the dipole moment increases. In this case, the dipole moment is calculated as (via Equation 3.3.2):

$$\begin{aligned}\mu &= Qr \\ &= (1.60 \times 10^{-19}\, C)(1.00 \times 10^{-10}\, m) \\ &= 1.60 \times 10^{-29}\, C \cdot m\end{aligned}$$

The Debye characterizes the size of the dipole moment. When a proton and electron are 100 pm apart, the dipole moment is $4.80\ D$:

$$\begin{aligned}\mu &= (1.60 \times 10^{-29}\, C \cdot m)\left(\frac{1\ D}{3.336 \times 10^{-30}\, C \cdot m}\right) \\ &= 4.80\ D\end{aligned}$$

$4.80\ D$ is a key reference value and represents a pure charge of +1 and -1 separated by 100 pm. If the charge separation is increased then the dipole moment increases (linearly):

- If the proton and electron are separated by 120 pm:

$$\mu = \frac{120}{100}(4.80\ D) = 5.76\ D \tag{3.3.3}$$

- If the proton and electron are separated by 150 pm:

$$\mu = \frac{150}{100}(4.80\ D) = 7.20\ D \tag{3.3.4}$$

- If the proton and electron are separated by 200 pm:

$$\mu = \frac{200}{100}(4.80\ D) = 9.60\ D \tag{3.3.5}$$

Example 3.3.1: Water

The water molecule in Figure **3.3.1** can be used to determine the direction and magnitude of the dipole moment. From the electronegativities of oxygen and hydrogen, the difference in electronegativity is 1.2e for each of the hydrogen-oxygen bonds. Next, because the oxygen is the more electronegative atom, it exerts a greater pull on the shared electrons; it also has two lone pairs of electrons. From this, it can be concluded that the dipole moment points from between the two hydrogen atoms toward the oxygen atom. Using the equation above, the dipole moment is calculated to be 1.85 D by multiplying the distance between the oxygen and hydrogen atoms by the charge difference between them and then finding the components of each that point in the direction of the net dipole moment (the angle of the molecule is 104.5˚).

The bond moment of the O-H bond =1.5 D, so the net dipole moment is

$$\mu = 2(1.5)\cos\left(\frac{104.5^\circ}{2}\right) = 1.84\ D$$

Polarity and Structure of Molecules

The shape of a molecule and the polarity of its bonds determine the OVERALL POLARITY of that molecule. A molecule that contains polar bonds might not have any overall polarity, depending upon its shape. The simple definition of whether a complex molecule is polar or not depends upon whether its overall centers of positive and negative charges overlap. If these centers lie at the same point in space, then the molecule has no overall polarity (and is non polar). If a molecule is completely symmetric, then the dipole moment vectors on each molecule will cancel each other out, making the molecule nonpolar. A molecule can only be polar if the structure of that molecule is not symmetric.

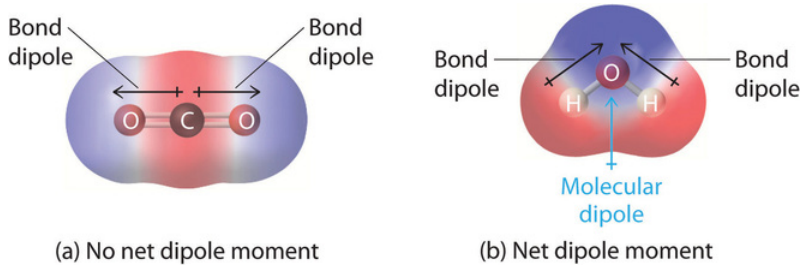


Figure 3.3.3: Charge distributions of CO_2 and H_2O\). Blue and red colored regions are negatively and positively signed regions, respectively. (CC BY-SA-NC 3.0; anonymous)

A good example of a nonpolar molecule that contains polar bonds is carbon dioxide (Figure 3.3.3*a*). This is a linear molecule and each C=O bond is, in fact, polar. The central carbon will have a net positive charge, and the two outer oxygen atoms a net negative charge. However, since the molecule is linear, these two bond dipoles cancel each other out (i.e. the vector addition of the dipoles equals zero) and the overall molecule has a zero dipole moment ($\mu = 0$).

> *Although a polar bond is a prerequisite for a molecule to have a dipole, not all molecules with polar bonds exhibit dipoles*

For AB_n molecules, where A is the central atom and B are all the same types of atoms, there are certain molecular geometries which are symmetric. Therefore, they will have no dipole even if the bonds are polar. These geometries include linear, trigonal planar, tetrahedral, octahedral and trigonal bipyramid.

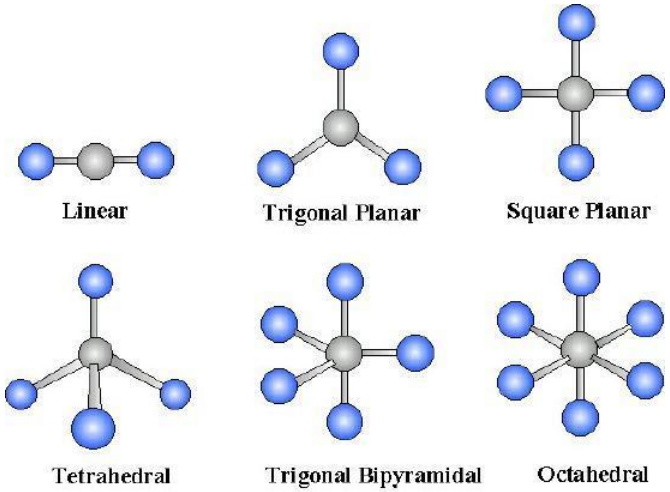
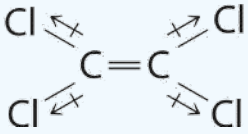


Figure 3.3.4: Molecular geometries with exact cancellation of polar bonding to generate a non-polar molecule ($\mu = 0$)

Example 3.3.3: C_2Cl_4

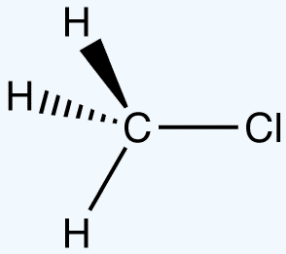
Although the C–Cl bonds are rather polar, the individual bond dipoles cancel one another in this symmetrical structure, and $Cl_2C{=}CCl_2$ does not have a net dipole moment.



Example 3.3.3: CH_3Cl

C-Cl, the key polar bond, is 178 pm. Measurement reveals 1.87 D. From this data, % ionic character can be computed. If this bond were 100% ionic (based on proton & electron),

$$\mu = \frac{178}{100}(4.80\ D)$$
$$= 8.54\ D$$



Although the bond length is ***increasing***, the dipole is ***decreasing*** as you move down the halogen group. The electronegativity decreases as we move down the group. Thus, the greater influence is the electronegativity of the two atoms (which influences the ***charge*** at the ends of the dipole).

Table **3.3.1**: Relationship between Bond length, Electronegativity and Dipole moments in simple Diatomics

Compound	Bond Length (Å)	Electronegativity Difference	Dipole Moment (D)
HF	0.92	1.9	1.82
HCl	1.27	0.9	1.08
HBr	1.41	0.7	0.82
HI	1.61	0.4	0.44

References

1. *Housecroft, Catherine E. and Alan G. Sharpe. Inorganic Chemistry. 3rd ed. Harlow: Pearson Education, 2008. Print. (Pages 44-46)*
2. *Tro, Nivaldo J. Chemistry: A Molecular Approach. Upper Saddle River: Pearson Education, 2008. Print. (Pages 379-386)*

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3.4: Hydrogen Bonding

A hydrogen bond is an intermolecular force (IMF) that forms a special type of dipole-dipole attraction when a hydrogen atom bonded to a strongly electronegative atom exists in the vicinity of another electronegative atom with a lone pair of electrons. Intermolecular forces (IMFs) occur between molecules. Other examples include ordinary dipole-dipole interactions and dispersion forces. Hydrogen bonds are are generally stronger than ordinary dipole-dipole and dispersion forces, but weaker than true covalent and ionic bonds.

The evidence for hydrogen bonding

Many elements form compounds with hydrogen. If you plot the boiling points of the compounds of the group 14 elements with hydrogen, you find that the boiling points increase as you go down the group.

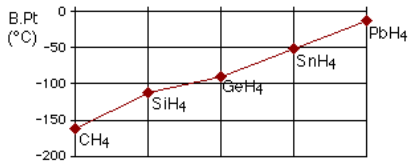


Figure 1: Boiling points of group 14 elemental halides.

The increase in boiling point happens because the molecules are getting larger with more electrons, and so van der Waals dispersion forces become greater. If you repeat this exercise with the compounds of the elements in groups 15, 16, and 17 with hydrogen, something odd happens.

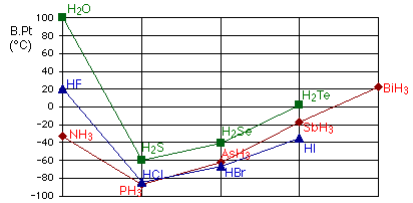


Figure 2: Boiling points of group 15-17 elemental halides.

Although the same reasoning applies for group 4 of the periodic table, the boiling point of the compound of hydrogen with the first element in each group is abnormally high. In the cases of NH_3, H_2O and HF there must be some additional intermolecular forces of attraction, requiring significantly more heat energy to break the IMFs. These relatively powerful intermolecular forces are described as hydrogen bonds.

Origin of Hydrogen Bonding

The molecules capable of hydrogen bonding include the following:

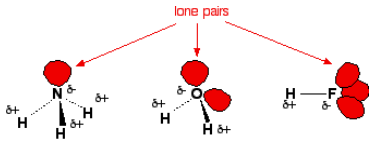


Figure 3: The lone pairs responsible for hydrogen bonding in NH_3, H_2O, and HF. The solid line represents a bond in the plane of the screen or paper. Dotted bonds are going back into the screen or paper away from you, and wedge-shaped ones are coming out towards you.

Notice that in each of these molecules:

- The hydrogen is attached directly to a highly electronegative atoms, causing the hydrogen to acquire a highly positive charge.
- Each of the highly electronegative atoms attains a high negative charge and has at least one "active" lone pair. Lone pairs at the 2-level have electrons contained in a relatively small volume of space, resulting in a high negative charge density. Lone pairs at higher levels are more diffuse and, resulting in a lower charge density and lower affinity for positive charge.

> *If you are not familiar with electronegativity, you should follow this link before you go on.*

Consider two water molecules coming close together.

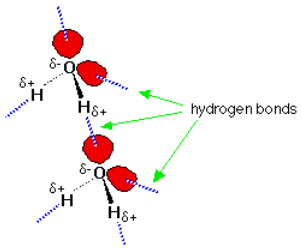


Figure 4: Hydrogen bonding in water

The δ^+ hydrogen is so strongly attracted to the lone pair that it is almost as if you were beginning to form a co-ordinate (dative covalent) bond. It doesn't go that far, but the attraction is significantly stronger than an ordinary dipole-dipole interaction. Hydrogen bonds have about a tenth of the strength of an average covalent bond, and are constantly broken and reformed in liquid water. If you liken the covalent bond between the oxygen and hydrogen to a stable marriage, the hydrogen bond has "just good friends" status.

Water is an ideal example of hydrogen bonding. Notice that each water molecule can potentially form four hydrogen bonds with surrounding water molecules: two with the hydrogen atoms and two with the with the oxygen atoms. There are exactly the right numbers of δ^+ hydrogens and lone pairs for every one of them to be involved in hydrogen bonding.

This is why the boiling point of water is higher than that of ammonia or hydrogen fluoride. In the case of ammonia, the amount of hydrogen bonding is limited by the fact that each nitrogen only has one lone pair. In a group of ammonia molecules, there are not enough lone pairs to go around to satisfy all the hydrogens. In hydrogen fluoride, the problem is a shortage of hydrogens. In water, two hydrogen bonds and two lone pairs allow formation of hydrogen bond interactions in a lattice of water molecules. Water is thus considered an ideal hydrogen bonded system.

More complex examples of hydrogen bonding

The hydration of negative ions

When an ionic substance dissolves in water, water molecules cluster around the separated ions. This process is called hydration. Water frequently attaches to positive ions by co-ordinate (dative covalent) bonds. It bonds to negative ions using hydrogen bonds.

> *If you are interested in the bonding in hydrated positive ions, you could follow this link to co-ordinate (dative covalent) bonding.*

The diagram shows the potential hydrogen bonds formed with a chloride ion, Cl-. Although the lone pairs in the chloride ion are at the 3-level and would not normally be active enough to form hydrogen bonds, they are made more attractive by the full negative charge on the chlorine in this case.

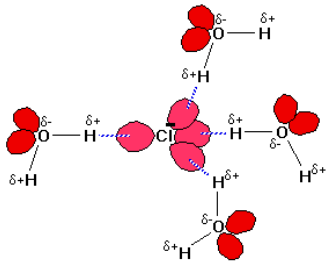


Figure 5: Hydrogen bonding between chloride ions and water.

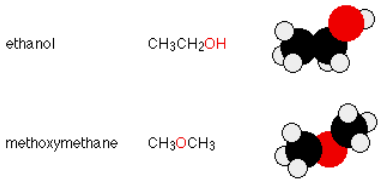
However complicated the negative ion, there will always be lone pairs that the hydrogen atoms from the water molecules can hydrogen bond to.

Hydrogen bonding in alcohols

An alcohol is an organic molecule containing an -OH group. Any molecule which has a hydrogen atom attached directly to an oxygen or a nitrogen is capable of hydrogen bonding. Hydrogen bonds also occur when hydrogen is bonded to fluorine, but the HF

group does not appear in other molecules. Molecules with hydrogen bonds will always have higher boiling points than similarly sized molecules which don't have an -O-H or an -N-H group. The hydrogen bonding makes the molecules "stickier," such that more heat (energy) is required to separate them. This phenomenon can be used to analyze boiling point of different molecules, defined as the temperature at which a phase change from liquid to gas occurs.

Ethanol, $\mathbf{CH_3CH_2{-}O{-}H}$, and methoxymethane, $\mathbf{CH_3{-}O{-}CH_3}$, both have the same molecular formula, $\mathbf{C_2H_6O}$.

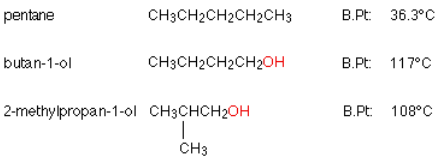


They have the same number of electrons, and a similar length. The van der Waals attractions (both dispersion forces and dipole-dipole attractions) in each will be similar. However, ethanol has a hydrogen atom attached directly to an oxygen; here the oxygen still has two lone pairs like a water molecule. Hydrogen bonding can occur between ethanol molecules, although not as effectively as in water. The hydrogen bonding is limited by the fact that there is only one hydrogen in each ethanol molecule with sufficient $\delta+$ charge.

In methoxymethane, the lone pairs on the oxygen are still there, but the hydrogens are not sufficiently $\delta+$ for hydrogen bonds to form. Except in some rather unusual cases, the hydrogen atom has to be attached directly to the very electronegative element for hydrogen bonding to occur. The boiling points of ethanol and methoxymethane show the dramatic effect that the hydrogen bonding has on the stickiness of the ethanol molecules:

ethanol (with hydrogen bonding)	78.5°C
methoxymethane (without hydrogen bonding)	-24.8°C

The hydrogen bonding in the ethanol has lifted its boiling point about 100°C. It is important to realize that hydrogen bonding exists in addition to van der Waals attractions. For example, all the following molecules contain the same number of electrons, and the first two have similar chain lengths. The higher boiling point of the butan-1-ol is due to the additional hydrogen bonding.



Comparing the two alcohols (containing -OH groups), both boiling points are high because of the additional hydrogen bonding; however, the values are not the same. The boiling point of the 2-methylpropan-1-ol isn't as high as the butan-1-ol because the branching in the molecule makes the van der Waals attractions less effective than in the longer butan-1-ol.

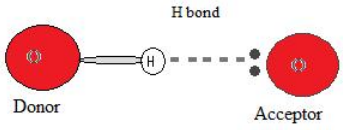
Hydrogen bonding in organic molecules containing nitrogen

Hydrogen bonding also occurs in organic molecules containing N-H groups; recall the hydrogen bonds that occur with ammonia. Examples range from simple molecules like CH_3NH_2 (methylamine) to large molecules like proteins and DNA. The two strands of the famous double helix in DNA are held together by hydrogen bonds between hydrogen atoms attached to nitrogen on one strand, and lone pairs on another nitrogen or an oxygen on the other one.

Donors and Acceptors

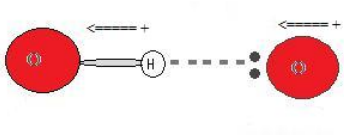
In order for a hydrogen bond to occur there must be both a hydrogen donor and an acceptor present. The donor in a hydrogen bond is usually a strongly electronegative atom such as N, O, or F that is covalently bonded to a hydrogen bond.

The hydrogen acceptor is an electronegative atom of a neighboring molecule or ion that contains a lone pair that participates in the hydrogen bond.



Why does a hydrogen bond occur?

Since the hydrogen donor (N, O, or F) is strongly electronegative, it pulls the covalently bonded electron pair closer to its nucleus, and away from the hydrogen atom. The hydrogen atom is then left with a partial positive charge, creating a dipole-dipole attraction between the hydrogen atom bonded to the donor and the lone electron pair of the acceptor. This results in a hydrogen bond.(see Interactions Between Molecules With Permanent Dipoles)

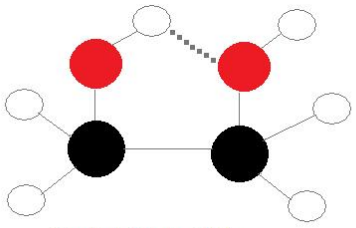


Types of hydrogen bonds

Although hydrogen bonds are well-known as a type of IMF, these bonds can also occur within a single molecule, between two identical molecules, or between two dissimilar molecules.

Intramolecular hydrogen bonds

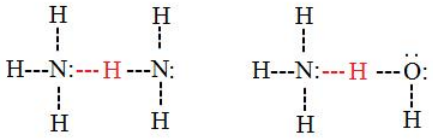
Intramolecular hydrogen bonds are those which occur *within* one single molecule. This occurs when two functional groups of a molecule can form hydrogen bonds with each other. In order for this to happen, both a hydrogen donor a hydrogen acceptor must be present within one molecule, and they must be within close proximity of each other in the molecule. For example, intramolecular hydrogen bonding occurs in ethylene glycol ($C_2H_4(OH)_2$) between its two hydroxyl groups due to the molecular geometry.



Intramolecular h-bonding in Ethylene Glycol molecule

Intermolecular hydrogen bonds

Intermolecular hydrogen bonds occur *between* separate molecules in a substance. They can occur between any number of like or unlike molecules as long as hydrogen donors and acceptors are present in positions where they can interact with one another. For example, intermolecular hydrogen bonds can occur between NH_3 molecules alone, between H_2O molecules alone, or between NH_3 and H_2O molecules.



Properties and effects of hydrogen bonds

On Boiling Point

When we consider the boiling points of molecules, we usually expect molecules with larger molar masses to have higher normal boiling points than molecules with smaller molar masses. This, without taking hydrogen bonds into account, is due to greater dispersion forces (see Interactions Between Nonpolar Molecules). Larger molecules have more space for electron distribution and thus more possibilities for an instantaneous dipole moment. However, when we consider the table below, we see that this is not always the case.

Compound	Molar Mass	Normal Boiling Point
H_2O	18 g/mol	373 K
HF	20 g/mol	292.5 K
NH_3	17 g/mol	239.8 K
H_2S	34 g/mol	212.9 K
HCl	36.4 g/mol	197.9 K
PH_3	34 g/mol	185.2 K

We see that H_2O, HF, and NH_3 each have higher boiling points than the same compound formed between hydrogen and the next element moving down its respective group, indicating that the former have greater intermolecular forces. This is because H_2O, HF, and NH_3 all exhibit hydrogen bonding, whereas the others do not. Furthermore, H_2O has a smaller molar mass than HF but partakes in more hydrogen bonds per molecule, so its boiling point is higher.

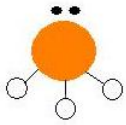
On Viscosity

The same effect that is seen on boiling point as a result of hydrogen bonding can also be observed in the viscosity of certain substances. Substances capable of forming hydrogen bonds tend to have a higher viscosity than those that do not form hydrogen bonds. Generally, substances that have the possibility for multiple hydrogen bonds exhibit even higher viscosities.

Factors preventing Hydrogen bonding

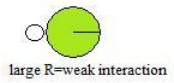
Electronegativity

Hydrogen bonding cannot occur without significant electronegativity differences between hydrogen and the atom it is bonded to. Thus, we see molecules such as PH_3, which do not participate in hydrogen bonding. PH_3 exhibits a trigonal pyramidal molecular geometry like that of ammonia, but unlike NH_3 it cannot hydrogen bond. This is due to the similarity in the electronegativities of phosphorous and hydrogen. Both atoms have an electronegativity of 2.1, and thus, there is no dipole moment. This prevents the hydrogen atom from acquiring the partial positive charge needed to hydrogen bond with the lone electron pair in another molecule. (see Polarizability)



Atom Size

The size of donors and acceptors can also affect the ability to hydrogen bond. This can account for the relatively low ability of Cl to form hydrogen bonds. When the radii of two atoms differ greatly or are large, their nuclei cannot achieve close proximity when they interact, resulting in a weak interaction.

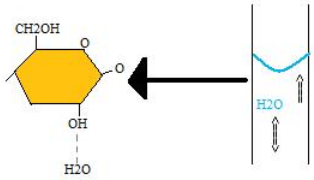


Hydrogen Bonding in Nature

Hydrogen bonding plays a crucial role in many biological processes and can account for many natural phenomena such as the Unusual properties of Water. In addition to being present in water, hydrogen bonding is also important in the water transport system of plants, secondary and tertiary protein structure, and DNA base pairing.

Plants

The cohesion-adhesion theory of transport in vascular plants uses hydrogen bonding to explain many key components of water movement through the plant's xylem and other vessels. Within a vessel, water molecules hydrogen bond not only to each other, but also to the cellulose chain that comprises the wall of plant cells. Since the vessel is relatively small, the attraction of the water to the cellulose wall creates a sort of capillary tube that allows for capillary action. This mechanism allows plants to pull water up into their roots. Furthermore, hydrogen bonding can create a long chain of water molecules, which can overcome the force of gravity and travel up to the high altitudes of leaves.



Proteins

Hydrogen bonding is present abundantly in the secondary structure of proteins, and also sparingly in tertiary conformation. The secondary structure of a protein involves interactions (mainly hydrogen bonds) between neighboring polypeptide backbones which contain nitrogen-hydrogen bonded pairs and oxygen atoms. Since both N and O are strongly electronegative, the hydrogen atoms bonded to nitrogen in one polypeptide backbone can hydrogen bond to the oxygen atoms in another chain and vice-versa. Though they are relatively weak, these bonds offer substantial stability to secondary protein structure because they repeat many times and work collectively.

In tertiary protein structure, interactions are primarily between functional R groups of a polypeptide chain; one such interaction is called a hydrophobic interaction. These interactions occur because of hydrogen bonding between water molecules around the hydrophobe that further reinforces protein conformation.

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1. Brown, et al. Chemistry:The Central Science. 11th ed. Upper Saddle River, New Jersey: Pearson/Prentice Hall, 2008.
2. Chang, Raymond. General Chemistry:The Essential Concepts. 3rd ed. New York: Mcgraw Hill, 2003
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CHAPTER OVERVIEW

4: Symmetry and Group Theory

- 4.1: Symmetry Elements and Operations
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- 4.3: Properties and Representations of Groups
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  - 4.3.2: Representations of Point Groups
  - 4.3.3: Character Tables
- 4.4: Examples and Applications of Symmetry
  - 4.4.1: Chirality
  - 4.4.2: Molecular Vibrations
- 4.P: Problems (under construction)

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4.1: Symmetry Elements and Operations

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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 **4.1.1**). In this example, the symmetry operation is the rotation and the symmetry element is the axis of rotation.

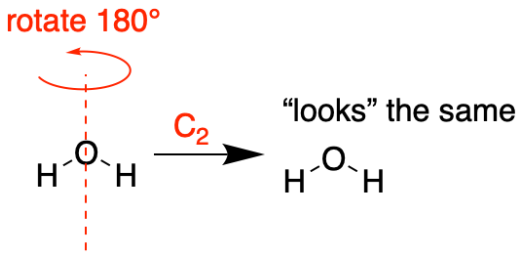


Figure **4.1.1**: An example of a symmetry operation is a 180° rotation where the resulting position is indistinguishable from the original. A 180° rotation is called a C_2 operation; the axis of rotation is the symmetry element. (Kathryn Haas; CC-NC-BY-SA)

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 **4.1.1**.

Table **4.1.1**: 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.

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4.2: Point Groups

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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.

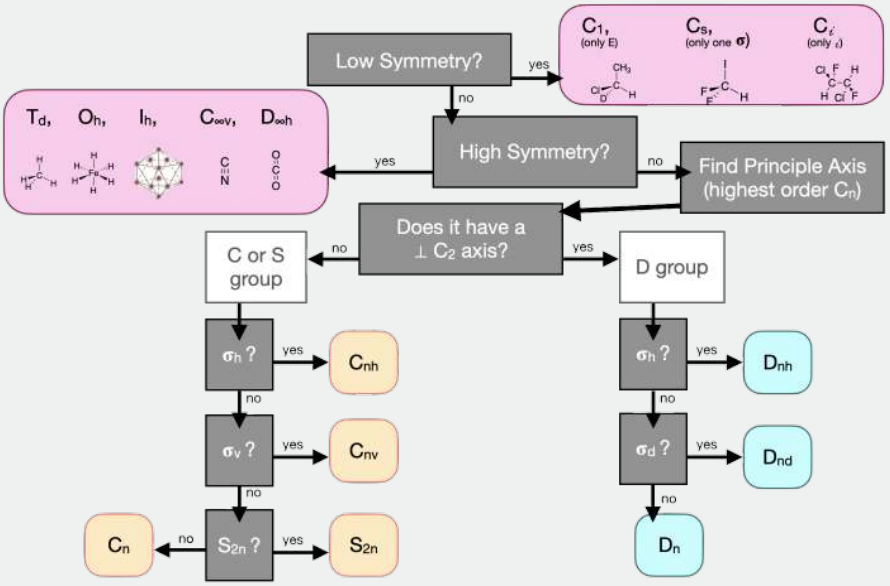


Figure **4.2.1**: Decision tree for determining a molecule's point group (CC-BY-NC-SA; Kathryn Haas)

Example 4.2.1

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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4.2.1: 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

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4.2.2: 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

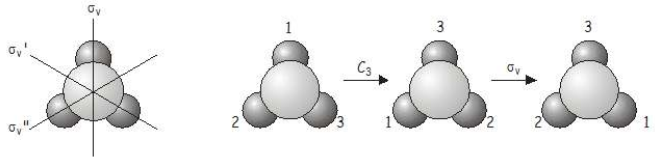
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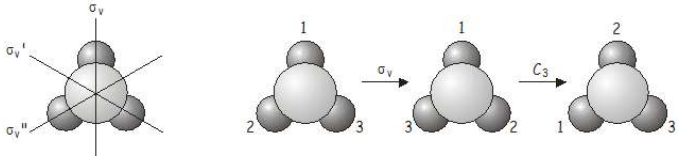
4.3: Properties and Representations of Groups

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_3rotation (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, $EA_i = A_i$ 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.

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4.3.1: 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}.

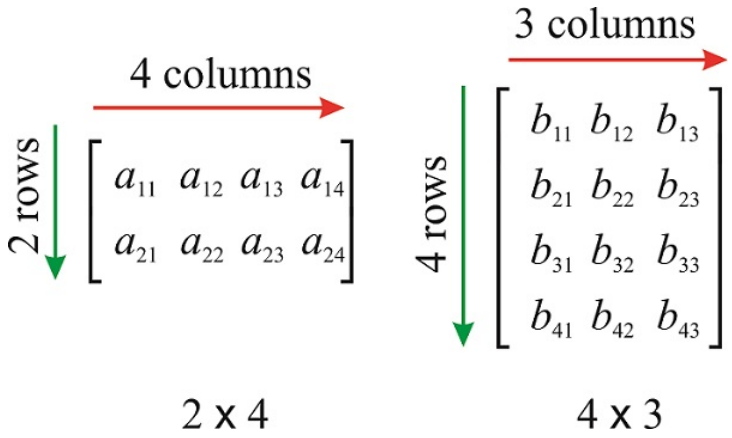


Figure **4.3.1.1**: Matrices of different dimensions

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 $\mathbf{AB}$ 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:

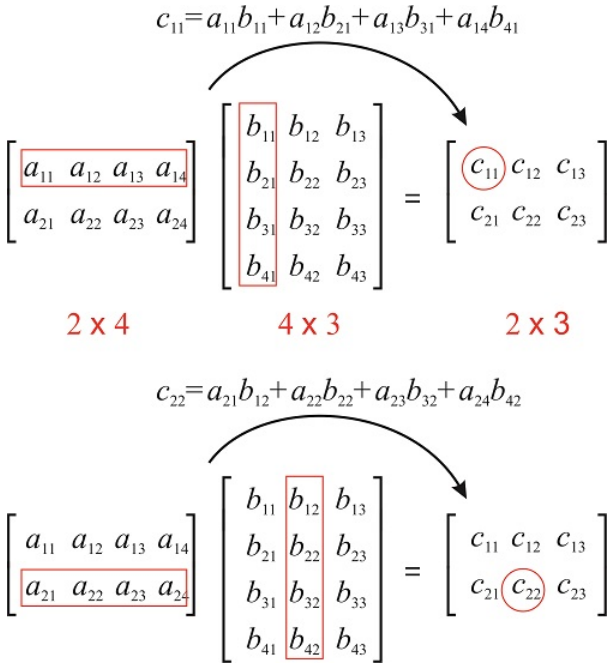


Figure 4.3.1.1: Matrix multiplication

Example 4.3.1.1

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 4.3.1.2

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:

$$[\mathbf{A}, \mathbf{B}] = \mathbf{AB} - \mathbf{BA}$$

Example 4.3.1.3

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

$$[\mathbf{A}, \mathbf{B}] = \mathbf{AB} - \mathbf{BA}$$

$$\mathbf{AB} = \begin{pmatrix} 3 & 1 \\ 2 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ -1 & 2 \end{pmatrix} = \begin{pmatrix} 3 \times 1 + 1 \times (-1) & 3 \times 0 + 1 \times 2 \\ 2 \times 1 + 0 \times (-1) & 2 \times 0 + 0 \times 2 \end{pmatrix} = \begin{pmatrix} 2 & 2 \\ 2 & 0 \end{pmatrix}$$

$$\mathbf{BA} = \begin{pmatrix} 1 & 0 \\ -1 & 2 \end{pmatrix} \begin{pmatrix} 3 & 1 \\ 2 & 0 \end{pmatrix} = \begin{pmatrix} 1 \times 3 + 0 \times 2 & 1 \times 1 + 0 \times 0 \\ -1 \times 3 + 2 \times 2 & -1 \times 1 + 2 \times 0 \end{pmatrix} = \begin{pmatrix} 3 & 1 \\ 1 & -1 \end{pmatrix}$$

$$[\mathbf{A}, \mathbf{B}] = \mathbf{AB} - \mathbf{BA} = \begin{pmatrix} 2 & 2 \\ 2 & 0 \end{pmatrix} - \begin{pmatrix} 3 & 1 \\ 1 & -1 \end{pmatrix} = \begin{pmatrix} -1 & 1 \\ 1 & 1 \end{pmatrix}$$

$$[\mathbf{A}, \mathbf{B}] = \begin{pmatrix} -1 & 1 \\ 1 & 1 \end{pmatrix}$$

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]).

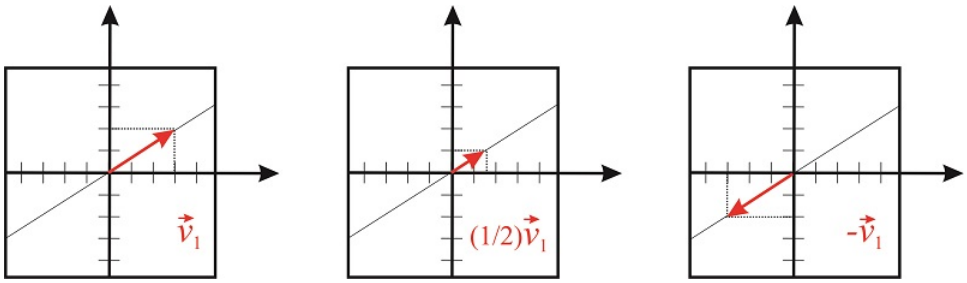


Figure **4.3.1.2**: Multiplication of a vector by a scalar

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 **4.3.1.3**).

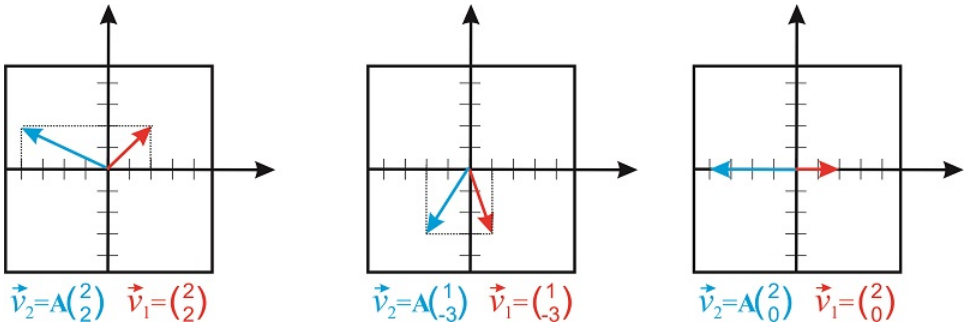


Figure **4.3.1.3**: Multiplication of a vector by a square matrix

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.

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4.3.2: 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 **4.3.2.1**).

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 **4.3.2.1** 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:

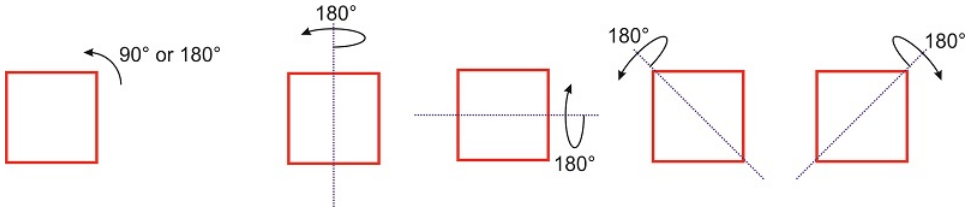


Figure **4.3.2.1**: Symmetry operations performed on a square

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 **4.3.2.2** 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 "C_2 axis." It also has two mirror planes, one that contains the two hydrogen atoms (σ_{yz}), and another one perpendicular to it (σ_{xz}). Both planes contain the C_2 axis.

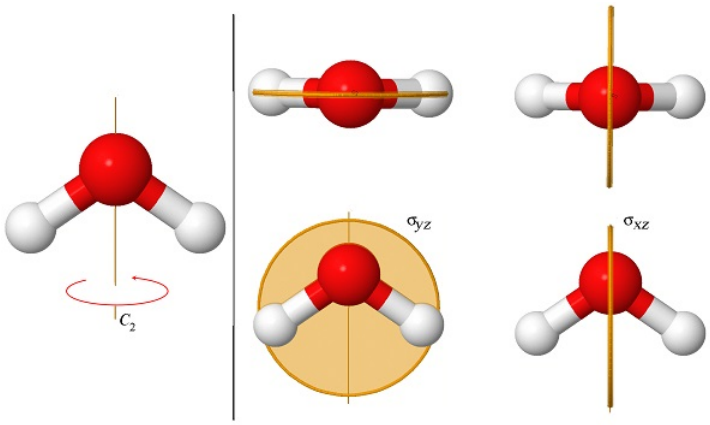


Figure **4.3.2.2**: The symmetry elements of the molecule of water

Transformation Matrix of 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 **4.3.2.3**). By convention, rotations are always taken in the counterclockwise direction.

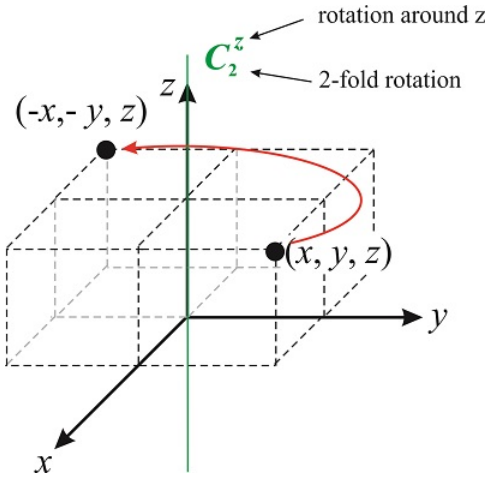


Figure 4.3.2.3: A 2-fold rotation around the z-axis

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:

$$C_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Transformation Matrix of σ_{xz} reflection

Rotations are not the only symmetry operations we can perform on a molecule. Figure 4.3.2.4 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 $\hat{\sigma}_{xz}$:

$$\sigma_{xz}(x, y, z) = (x, -y, z)$$

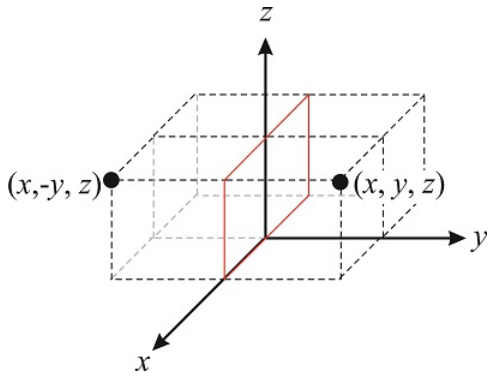


Figure 4.3.2.3: A reflection through the xz plane

Following the same logic we used for the rotation matrix, we can write the σ_{xz} transformation matrix as:

$$\sigma_{x,z} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

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 4.3.2.1

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 $\sigma_{v(yz)''}$ 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 4.3.2.1

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.

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4.3.3: 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:

$$x' = x\cos\theta + y\sin\theta$$
$$y' = -x\sin\theta + y\cos\theta$$

For a C_3 rotation counterclockwise through 120° (or $\frac{2\pi}{3}$):

$$x' = x\cos(2\pi/3) + y\sin(2\pi/3) = -\tfrac{1}{2}x - \tfrac{\sqrt{3}}{2}y$$
$$y' = -x\sin(2\pi/3) + y\cos(2\pi/3) = \tfrac{\sqrt{3}}{2}x - \tfrac{1}{2}y$$

The transformation matrices for symmetry operations of C_{3v} are as follows:

$$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad C_3 = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \sigma'_{v(xz)} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

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 **4.3.3.1**):

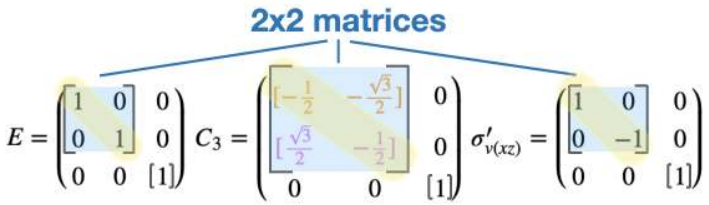


Figure **4.3.3.1**: The C_3 transformation matrix contains off-diagonal entries, and therefore it cannot be block diagonalized as 1x1 matrices. However, the first two lines can be diagonalized as a 2x2 and the last line as a 1x1 matrix. (CC-BY-NC-SA; Kathryn Haas)

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 $-\frac{1}{2} + -\frac{1}{2}$).

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 $\sigma_v$or perpendicular to C_2
2	anti-symmetric to $\sigma_v$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 **4.3.3.2**. Character tables for common point groups are given in the References section of LibreTexts Bookshelves.

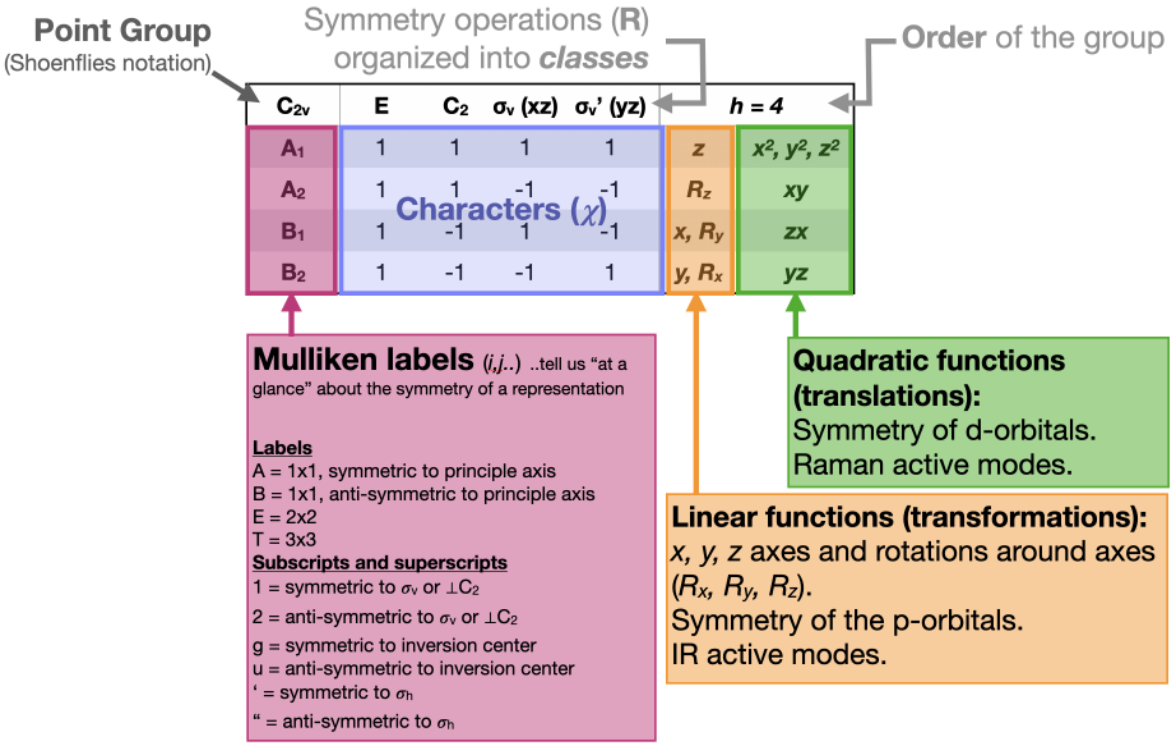


Figure **4.3.3.2**: Visual summary of the sections of a character table and their meaning. (CC-BY-NC-SA; Kathryn Haas)

Contributors and Attributions

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SECTION OVERVIEW

4.4: 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.

4.4.1: Chirality

4.4.2: Molecular Vibrations

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4.4.1: 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.

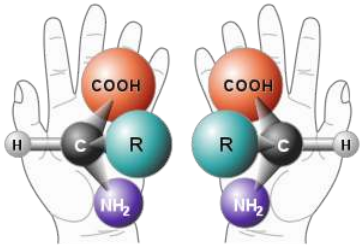


Figure 4.4.1.1: Two enantiomers of an amino acid (with side chain R).

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 4.4.1.1). Figure 4.4.1.1 shows the two enantiomers of tris(ethylenediamine)cobalt(III): the **Δ** and **Λ** isomers.

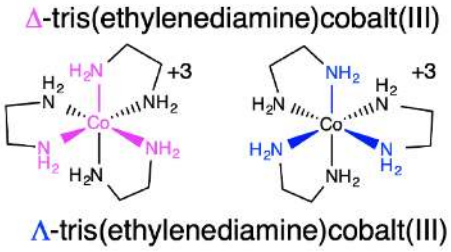


Figure 4.4.1.2: Two chiral enantiomers of tris(ethylenediamine)coalt(III).

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 4.4.1.1

Which point groups are possible for chiral molecules?

Answer

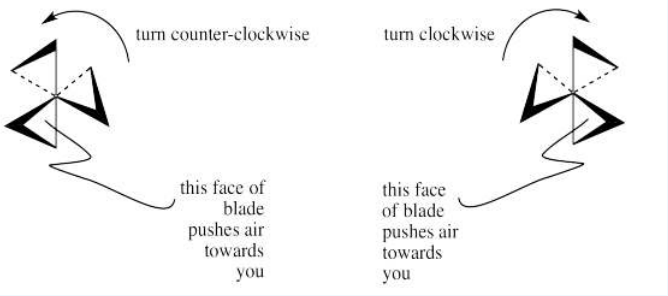


Figure **4.4.1.3**: Another way of thinking about the chirality of the two chiral enantiomers of tris(ethylenediamine)coalt(III) shown in Figure **4.4.1.2**. This figure was taken from Structure and Reactivity in Organic, Biological, and Inorganic Chemistry.

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.

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4.4.2: 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 4.4.2.1).

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}.

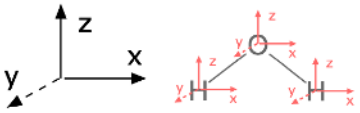


Figure 4.4.2.1: The first step to finding normal modes is to assign a consistent axis system to the entire molecule and to each atom. (CC-BY-SA; Kathryn Haas)

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:

$$\begin{aligned} \text{Linear Molecule Degrees of Freedom} &= 3N-5 \\ \text{Non-Linear Molecule Degrees of Freedom} &= 3N-6 \end{aligned}$$

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 4.4.2.1).

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 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 $\chi = 9$ for the Γ_{modes}.

For the operation 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 $\chi = -1$ 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.

C_{2v}	E	C_2	σ_v	σ'_v
Γ_{modes}	9	−1	3	1

(4.4.2.1)

STEP 2: Break Γ_{modes} into its component irreducible representations.

Now that we've found the Γ_{modes} (4.4.2.1), 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:

Misplaced '#'

In other words, the number of irreducible representations of type i is equal to the sum of the number of operations in the class × the character of the Γ_{modes} × the character of i, and that sum is divided by the order of the group (h).

Using equation ???, we find that for all normal modes of H_2O:

$$\Gamma_{modes} = 3A_1 + 1A_2 + 3B_1 + 2B_2 \tag{4.4.2.2}$$

.

Notice there are 9 irreducible representations in Equation 4.4.2.2. These irreducible representations represent the symmetries of all 9 motions of the molecule: vibrations, rotations, and translations.

? Exercise 4.4.2.1: Derive the irreducible representation in equation 4.4.2.2.

Derive the nine irreducible representations of Γ_{modes} for H_2O, expression 4.4.2.2.

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 (4.4.2.1), the C_{2v} character table (below), and equation ???.

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 ???) 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 4.4.2.2, and therefore the vibrational degrees of freedom can be found by:

$$H_2O \text{ vibrations} = (3A_1 + 1A_2 + 3B_1 + 2B_2) - \text{Rotations} - \text{Translations} \tag{4.4.2.3}$$

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, yz), 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.

$$\begin{aligned} H_2O \text{ vibrations} &= \Gamma_{modes} - \text{ Rotations } - \text{ Translations} \\ &= (3A_1 + 1A_2 + 3B_1 + 2B_2) - (A_1 + B_1 + B_2) - (A_2 + B_1 + B_2) \\ &= 2A_1 + 1B_1 \end{aligned}$$

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.

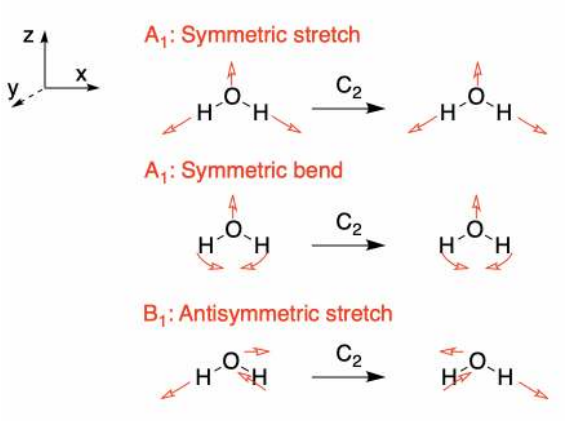


Figure 4.4.2.2: Illustration of the vibrational motions of water. The antisymmetric stretch has B_1 symmetry, while the symmetric stretch and symmetric bend both have A_1 symmetry. (Click here to see animation) (CC-BY-NC-SA; Kathryn Haas)

Table 4.4.2.1: 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
$3A_1$	$1A_1$		$2A_1$	One is a symmetric stretch. The other is a symmetric bend. Both are *IR-active* and *Raman-active*
A_2		$1A_2$		
$3B_1$	$1B_1$	$1B_1$	$1B_1$	Antisymmetric stretch that is *IR-active* and *Raman-active*.
$2B_2$	$1B_2$	$1B_2$		

? Exercise 4.4.2.2

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 $[PtCl_4]^{2-}$ 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

(4.4.2.4)

.

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.

Selected Vibrational Modes

The interpretation of CO stretching vibrations in an IR spectrum is particularly useful. Symmetry and group theory can be applied to predict the number of CO stretching bands that appear in a vibrational spectrum for a given metal coordination complex. A classic example of this application is in distinguishing isomers of metal-carbonyl complexes. For example, the *cis*- and *trans*-isomers of square planar metal dicarbonyl complexes ($ML_2(CO)_2$) have a different number of IR stretches that can be predicted and interpreted using symmetry and group theory. Another example is the case of *mer*- and *fac*- isomers of octahedral metal tricarbonyl complexes ($ML_3(CO)_3$). Structures of the two types of metal carbonyl configurations and their isomers are shown in Figure **4.4.2.1**. The isomers in each case can be distinguished using vibrational spectroscopy.

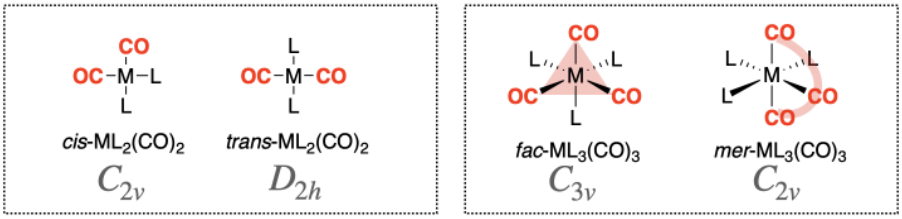


Figure **4.4.2.3**: Cis- and *trans*- isomers of square planar metal dicarbonyl complexes ($ML_2(CO)_2$) are shown in the left box. *Mer*- and *fac*- isomers of octahedral metal tricarbonyl complexes ($ML_3(CO)_3$) are shown in the right box. The point group for each of the general structures is also shown. (CC-BY-NC-SA; Kathryn Haas)

EXAMPLE 1: Distinguishing *cis*- and *trans*- isomers of square planar metal dicarbonyl complexes

General structures of the *cis*- and *trans*- isomers of square planar metal dicarbonyl complexes ($ML_2(CO)_2$) are shown in the left box in Figure **4.4.2.1**. We can use symmetry and group theory to predict how many carbonyl stretches we should expect for each isomer following the steps below.

Step 1: Assign the point group and Cartesian coordinates for each isomer.

The *cis*-isomer has C_{2v} symmetry and the *trans*-isomer has D_{2h} symmetry. We assign the Cartesian coordinates so that z is colinear with the principle axis in each case. For the D_2h isomer, there are several orientations of the z axis possible. The axes shown in Figure **4.4.2.2** will be used here.



Figure **4.4.2.4**: Cis- and *trans*- isomers of square planar metal dicarbonyl complexes ($ML_2(CO)_2$) are shown and oriented with respect to the Cartesian coordinates shown at the left so that the highest-order rotation axis is colinear with z and the molecule is co-planar with the xz plane. The vector along each C—O bond is shown using a red arrow (→). These vectors represent the direction of C—O stretching motions. (CC-BY-NC-SA; Kathryn Haas)

Step 2: Produce a reducible representation (Γ) for CO stretches in each isomer

First, assign a vector along each C—O bond in the molecule to represent the direction of C—O stretching motions, as shown in Figure **4.4.2.2** (red arrows →). These vectors are used to produce a reducible representation (**Γ**) for the C—O stretching motions in each molecule. Using the symmetry operations under the appropriate character table, assign a value of 1 to each vector that remains in place during the operation, and a value of 0 if the vector moves out of place. There will be no occasion where a vector remains in place but is inverted, so a value of -1 will not occur.

cis- $ML_2(CO)_2$:

For *cis*- $ML_2(CO)_2$, the point group is C_{2v} and so we use the operations under the C_{2v} character table to create the Γ_{cis-CO}.

$\mathbf{C_{2v}}$	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
$\mathbf{\Gamma_{cis-CO}}$	2	0	2	0

trans- $ML_2(CO)_2$:

For trans- $ML_2(CO)_2$, the point group is D_{2h} and so we use the operations under the D_{2h} character table to create the $\Gamma_{trans-CO}$.

$\mathbf{D_{2h}}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\mathbf{\Gamma_{trans-CO}}$	2	0	0	2	0	2	2	0

Step 3: Break each Γ into its component irreducible representations

Each Γ can be reduced using inspection or by the systematic method described previously.

In the case of the *cis*- $ML_2(CO)_2$, the CO stretching vibrations are represented by A_1 and B_1 irreducible representations:

$\mathbf{C_{2v}}$	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
$\mathbf{\Gamma_{cis-CO}}$	2	0	2	0		
A_1	1	1	1	1	z	x^2, y^2, z^2
B_1	1	−1	1	−1	x, R_y	xz

(4.4.2.5)

In the case of *trans*- $ML_2(CO)_2$, the CO stretching vibrations are represented by A_1 and B_{3u} irreducible representations:

$\mathbf{D_{2h}}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
$\mathbf{\Gamma_{trans-CO}}$	2	0	0	2	0	2	2	0	
A_g	1	1	1	1	1	1	1	1	$x^2,\ y^2,\ z^2$
B_{3u}	1	−1	−1	1	−1	1	1	−1	x

These irreducible representations correspond to the symmetries of only the selected C—O vibrations. Since these motions are isolated to the C—O group, they do not include any rotations or translations of the entire molecule, and so we do not need to find and subtract rotationals or translations (unlike the previous cases where all motions were considered).

Step 4: Determine which vibrational modes are IR-active and/or Raman-active

Apply the infrared selection rules described previously to determine which of the CO vibrational motions are IR-active and Raman-active. The two isomers of $ML_2(CO)_2$ are described below.

In the case of the *cis*- $ML_2(CO)_2$, the CO stretching vibrations are represented by A_1 and B_1 irreducible representations. The characters of both representations and their functions are shown above, in 4.4.2.5 (and can be found in the C_{2v} character table). Under C_{2v}, both the A_1 and B_1 CO vibrational modes are IR-active and Raman-active. Therefore, two bands in the IR spectrum and two bands in the Raman spectrum are possible.

In the case of the trans- $ML_2(CO)_2$, the CO stretching vibrations are represented by A_g and B_{3u} irreducible representations. The characters of both representations and their functions are shown above, in 4.4.2.5 (and can be found in the D_{2h} character table). Under D_{2h}, the A_g vibrational mode is is Raman-active only, while the B_{3u} vibrational mode is IR-active only. Therefore, only one IR band and one Raman band are possible for this isomer.

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*-$ML_2(CO)_2$.

? Exercise 4.4.2.3

Repeat the steps outlined above to determine how many CO vibrations are possible for *mer*-$ML_3(CO)_3$ and *fac*-$ML_3(CO)_3$ isomers (see Figure **4.4.2.1**) in both IR and Raman spectra. Could either of these vibrational spectroscopies be used to distinguish the two isomers?

Answer

Step 1: Assign the point group and Cartesian coordinates for each isomer.
The *fac*-isomer is C_{3v}. The *mer*-isomer is C_{2v}.

Step 2: Produce a reducible representation for CO stretches in each isomer.

Step 3: Break each into its component irreducible representations.

Step 4: Determine which vibrational modes are IR-active and/or Raman-active.

***For fac*-$ML_3(CO)_3$**, the point group is C_{3v} and so we use the operations under the C_{3v} character table to create the Γ_{fac-CO}. Then break it into its irreducible representations and determine which are IR and Raman active:

C_{3v}	E	$2C_2$	$3\sigma_v$
Γ_{fac-CO}	3	0	1

This reduces to $A_1 + E$. Both of these are IR active, and since one is singly degenerate while the other is doubly degenerate, we expect three possible IR bands from this isomer. Both vibrational modes are also Raman active, and again we would expect three possible bands in the Raman spectrum.

For mer-$ML_3(CO)_3$, the point group is C_{2v} and so we use the operations under the C_{2v} character table to create the Γ_{mer-CO}. Then break it into its irreducible representations and determine which are IR and Raman active:

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
Γ_{mer-CO}	3	1	3	1

This reduces to $2A_1 + B_1$; both A_1 and B_1 are IR and Raman active. So this isomer would have three possible IR bands and three possible Raman Bands.

These two isomers have the same number of possible bands in both IR and Raman spectroscopy. It would not be straightforward to distinguish them from each other based on the number of possible bands in the vibrational spectrum.

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4.P: Problems (under construction)

Problems

1. Chlorophyll *a* is a green pigment that is found in plants. Its molecular formula is $C_{55}H_{77}O_5N_4Mg$. How many degrees of freedom does this molecule possess? How many vibrational degrees of freedom does it have?
2. CCl_4 was commonly used as an organic solvent until its severe carcinogenic properties were discovered. How many vibrational modes does CCl_4 have? Are they IR and/or Raman active?
3. The same vibrational modes in H_2O are IR and Raman active. WF_6^- has IR active modes that are not Raman active and vice versa. Explain why this is the case.
4. How many IR peaks do you expect from SO_3? Estimate where these peaks are positioned in an IR spectrum.
5. Calculate the symmetries of the normal coordinates of planar BF_3.

Answers to Problems

1. Chlorophyll *a* has 426 degrees of freedom and 420 vibrational modes.
2. The point group is T_d, $T_{vib} = a_1 + e + 2t_2$; a_1 and e are Raman active, t_2 is both IR and Raman active.
3. For molecules that possess a center of inversion i, modes cannot be simultaneously IR and Raman active.
4. Point group is D_{3h}; one would expect three IR active peaks. Asymmetric stretch highest (1391 cm^{-1}), two bending modes (both around 500 cm^{-1}). The symmetric stretch is IR inactive.
5. $T_{3N} = A_1' + A_2' + 3E' + 2\,A_2'' + E''$ and $T_{vib} = A_1' + 2E' + A_2''$

Contributors and Attributions

- Kristin Kowolik, University of California, Davis

Problems

1. The water molecule H_2O was used as an example; it was mentioned that when water was rotated 180 degrees around an axis bisecting the oxygen, the molecule was superimposable on the original water molecule. How about CO_2? Will it be like the water molecule since CO_2 also has 2 atoms of oxygen?

Of course not, because every molecule has a different molecular shape. To recognize the symmetry of any molecule, the structure and the molecular shape of that molecule should be defined. The water molecule is bent but CO_2 is not, and if CO_2 is rotated 360 degrees around the axis bisecting the C atom, then it can be superimposed on the original molecule. We then see the symmetry for the CO_2.

2. Why should all of the five symmetry elements be done on a molecule in order to find the point group the molecule belongs to? Why is performing only one or two of the symmetry elements not enough for recognizing the point group?

One or two of the symmetry elements will not be able to tell us everything about the molecule's symmetry, since those one or two properties do not tell us everything about the molecule. Also, while different molecules may have one or two symmetrical properties in common, the five properties will not be the same for all molecules.

3. What does the symbol C_n stand for and what does n represent? Why is it important to identify n?

C is the axis of rotation and n is the order of the axis.

4. How are the character tables helpful?

The character table tells us about all the operational elements performed on the molecule and indicates whether we have forgotten to perform any of the symmetry elements. The tables serve as a checklist because all the operational elements should be done on the molecule in order to find the point group of the molecule.

5. Why is important to find symmetry in molecules?

Symmetry tells us about bonding for that molecule.

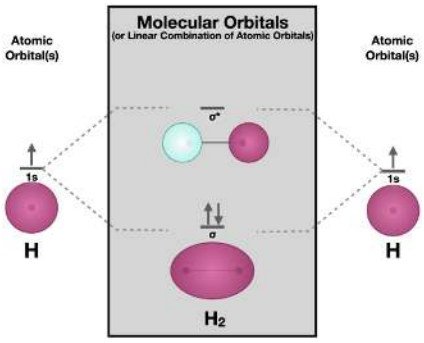
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CHAPTER OVERVIEW

5: Molecular Orbitals

Molecular Orbital Theory



Molecular Orbital (MO) Theory is a sophisticated bonding model. It is generally considered to be more powerful than *Lewis* and *Valence Bond Theories* for predicting molecular properties; however, this power comes at the price of complexity. In its full development, MO Theory requires complex mathematics, though the ideas behind it are simple. Atomic orbitals (AOs) that are localized on individual atoms combine to make molecular orbitals (MOs) that are distributed over the molecule. The simplest example is the molecule dihydrogen (H_2), in which two independent hydrogen 1s orbitals combine to form the σ bonding MO and the σ antibonding MO of the dihydrogen molecule (see figure). The MO's are also called Linear Combinations of Atomic Orbitals (LCAO).

5.1: Formation of Molecular Orbitals from Atomic Orbitals
- 5.1.1: Molecular Orbitals from s Orbitals
- 5.1.2: Molecular Orbitals from p Orbitals
- 5.1.3: Molecular orbitals from d orbitals
- 5.1.4: Nonbonding Orbitals and Other Factors

5.2: Homonuclear Diatomic Molecules
- 5.2.1: Molecular Orbitals
- 5.2.2: Orbital Mixing
- 5.2.3: Diatomic Molecules of the First and Second Periods
- 5.2.4: Photoelectron Spectroscopy

5.3: Heteronuclear Diatomic Molecules
- 5.3.1: Orbital ionization energies
- 5.3.2: Polar bonds
- 5.3.3: Ionic Compounds and Molecular Orbitals

5.4: Larger (Polyatomic) Molecules
- 5.4.1: Bifluoride anion
- 5.4.2: Carbon Dioxide
- 5.4.3: H_2O
- 5.4.4: NH_3
- 5.4.5: CO_2 (Revisted with Projection Operators)
- 5.4.6: BF_3

5.P: Problems

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5.1: Formation of Molecular Orbitals from Atomic Orbitals

Molecular orbital theory extends from quantum theory and the atomic orbital wavefunctions (ψ) described by the Schrödinger equation. While the Schrödinger equation defines a Ψ for electrons in individual atoms, we can approximate the molecular wavefunction (what Ψ would look like if we combined the ψ of individual atoms). The addition or subtraction of wavefunctions is termed **linear combination of atomic orbitals** (LCAO). Molecular orbital theory is applied to LCAO to describe bonding.

The LCAO for the wavefunction of two atoms (ψ_a and ψ_b) is represented by the general expression below. The coefficients c_a and c_b quantify the contribution of each atomic ψ to the molecular Ψ.

$$\Psi = c_a\psi_a + c_b\psi_b$$

For two atomic ψs to form a bond, three conditions must be satisfied:

- First, the **distance between the atoms** must be small enough to provide good overlap. This is because the two orbitals must be able to overlap using regions of ψ^2 where the probability of finding electrons is significant. If atoms are not close enough, ψ_a and ψ_b cannot interact productively. At the same time, the atoms must be far enough apart that their nuclei do not repel each other.
- The **symmetry of the orbitals** must be compatible such that regions of ψ_a and ψ_b with the same sign constructively interfere more than regions with opposite sign destructively interfere. In other words, for a productive interaction, there must be a relatively high probability of finding an electron between the two nuclei, and this depends on the symmetry (and sign of the ψ) of the atomic orbitals.
- Third, the **energies of the atomic orbitals** must be similar. Orbitals with similar energy combine to make the most stable bonding molecular orbitals. Atomic orbitals with very different energies form less stable bonding interactions, and the larger the difference in the atomic orbitals, the weaker the bonding interaction will be.

Atomic orbitals combine to form molecular orbitals when these three conditions are met. The result is a set of bonding molecular orbitals that are lower in energy than the original atomic orbital energies.

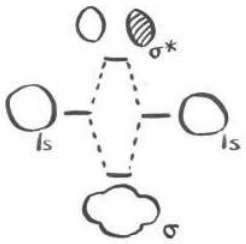
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5.1.1: Molecular Orbitals from s Orbitals

In the case of the hydrogen molecule, we took two atomic orbitals and combined them to form two molecular orbitals. These new molecular orbitals had different wavelengths than the two atomic orbitals: one had a longer wavelength and was a little lower in energy, while the other had a shorter wavelength and was a little higher in energy. If we take into account the energy of the two original atomic wavefunctions, and compare them to the total energy of the two new molecular wavefunctions, there is no change overall.

We started with two atomic orbitals, and by combining them we produced two molecular orbitals. Both of these ideas are useful in considering the formation of more complex molecules from individual atoms.

- - The average energy of the orbitals has remained almost constant.
  - Also, the number of wavefunctions has remained constant.
  - 

Of course, from the point of view of the two real electrons, some remarkable changes have occurred. Both of these electrons have adopted a longer wavelength and a lower energy and that has made all the difference. There is an occupied molecular orbital and an unoccupied molecular orbital; only the occupied orbital makes a real energetic contribution to the overall stability of the molecule. The unoccupied orbital is completely imaginary.

A bonding picture of He_2 would look exactly the same, because it would also involve the overlap of 1s electrons on one atom with 1s electrons on the other atom. There would be a different electronic energy, however. That difference would affect the prospects of helium-helium bond formation.

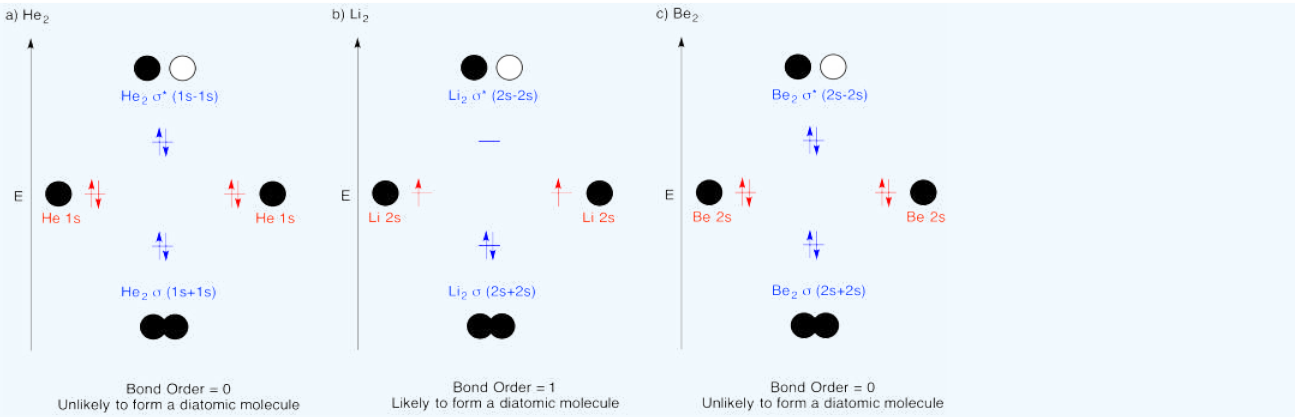
- The electrons have lower kinetic energy in the bond than they had before bonding.
- Electronic energy has decreased. A stable bond has formed.

? Exercise 5.1.1.1

Construct molecular orbital diagrams for the following diatomic species and discuss the likelihood of bond formation in each case.

a. He_2.
b. Li_2.
c. Be_2.

Answer



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5.1.2: Molecular Orbitals from p Orbitals

Bonding with P-orbitals

Sigma bonding with p-orbitals

Other diatomic molecules in the upper right corner of the periodic table can be constructed in a similar way. Look at dinitrogen, N_2.

We can think about how dinitrogen would form if two nitrogen atoms were placed close enough together to share electrons. Nitrogen has more electrons than hydrogen, so this interaction is more complicated.

In our qualitative examination of bonding in main group diatomics, we will take the approach used in Lewis structures and just look at the valence electrons. A quantitative molecular orbital calculation with a computer would not take this shortcut, but would include all of the electrons in the atoms that are bonding together.

Nitrogen has five valence electrons, and these electrons are found in the 2s and 2p levels. There are three possible atomic orbitals in the 2p level where some of these electrons could be found: p_x, p_y and p_z. We need to look at the interaction between the s and p_x, p_y and p_z orbitals on one nitrogen atom with the s and p_x, p_y and p_z orbitals on the other nitrogen. That process could be extremely complicated, but:

- Orbital interactions are governed by symmetry.

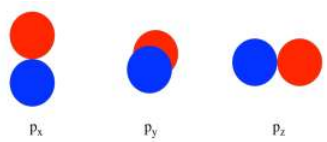
Orbitals interact most easily with other orbitals that have the same element of symmetry. For now, we can simplify and say that orbitals on one atom only interact with the same type of orbitals on the other atom.

- s orbitals interact with s orbitals. We can already see how that will work out in dinitrogen, because that is what happened in dihydrogen.
- p_x orbitals interact with p_x orbitals.
- p_y orbitals interact with p_y orbitals.
- p_z orbitals interact with p_z orbitals.

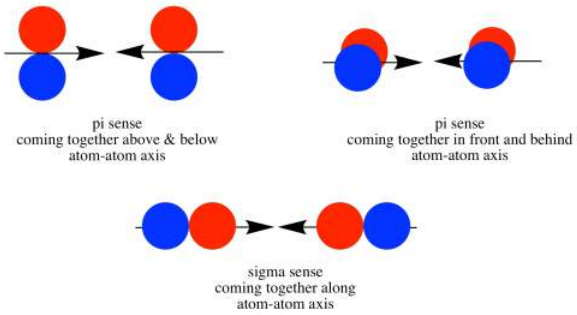
Another complication here is that the s and p orbitals do not start out at the same energy level. When the orbitals mix, one combination goes up in energy and one goes down. Does the s antibonding combination go higher in energy than the combinations from p orbitals? Do the p bonding combinations go lower in energy than the combinations from s orbitals? We will **simplify** and **assume** that the s and p levels remain completely separate from each other. This is not always true, but the situation varies depending on what atoms we are dealing with.

- The combination of one s orbital with another is just like in hydrogen. Two original orbitals will combine and rearrange to produce two new orbitals.
- There is a bonding combination in which the orbitals are in phase. The new orbital produced has a longer wavelength than the original orbital. It is lower in energy.
- There is an antibonding combination in which the orbitals are out of phase. The new orbital produced has a shorter wavelength than the original orbital. It is higher in energy.

In considering the interaction of two p orbitals, we have to keep in mind that p orbitals are directional. A p orbital lies along a particular axis: x, y or z. The three p orbitals on nitrogen are all mutually perpendicular (or orthogonal) to each other. That situation is in contrast to s orbitals, which are spherical and thus look the same from any direction.

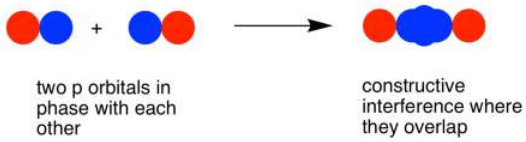


We first need to define one axis as lying along the N-N bond. It does not really matter which one. We arbitrarily say the N-N bond lies along the z axis. The p_z orbitals have a different spatial relationship to each other compared to the p_y and p_x. The p_z orbitals lie along the bond axis, whereas the p_y and p_x are orthogonal to it.

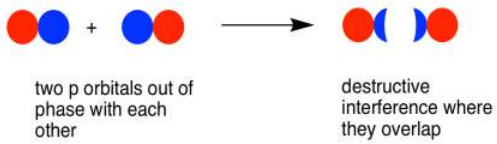


As the nitrogen atoms are brought together, one lobe on one p_z orbital overlaps strongly with one lobe on the other p_z orbital. The other lobes point away from each other and do not interact in any obvious way.

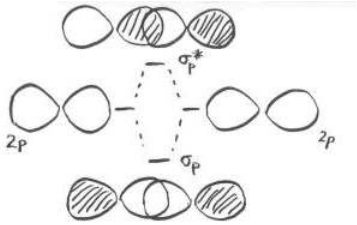
As with the s orbital, the p_z orbitals can be in-phase or out-of-phase. The in-phase combination results in constructive interference. (Here, "in-phase" means the lobes that overlap are in-phase; for that to happen the two p orbitals are actually completely out-of-phase with each other mathematically, so that one orbital is the mirror image of the other.) This combination is at a longer wavelength than the original orbital. It is a lower energy combination.



The out-of-phase combination (meaning in this case that the overlapping lobes are out-of-phase) results in destructive interference. This combination is at shorter wavelength than the original orbital. It is a higher energy combination.



As a result, we have two different combinations stemming from two different p orbitals coming together in two different ways. We get a low-energy, in-phase, bonding combination and a high-energy, out-of-phase, antibonding combination.

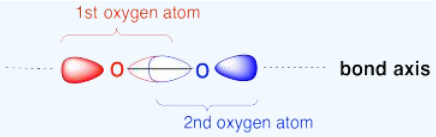


What about those other p orbitals, the ones that do not lie along the bond axis? We'll take a look at that problem on the next page.

? Exercise 5.1.2.2

Draw an MO cartoon of a sigma bonding orbital formed by the overlap of two p orbitals between two oxygen atoms. Label the positions of the oxygen nuclei with the symbol "O". Label the O-O bond axis.

Answer



Exercise 5.1.2.3

Chemical reactions can be described by MO diagrams too! Consider the following reaction in which a new sigma bond is formed.



Draw an MO diagram for the reaction above. In other words, start from the one frontier MO on each reactant to build the MO's of the new sigma bond in the product.

o Draw the orbital from the base (hydroxide) that is likely to donate its electrons.

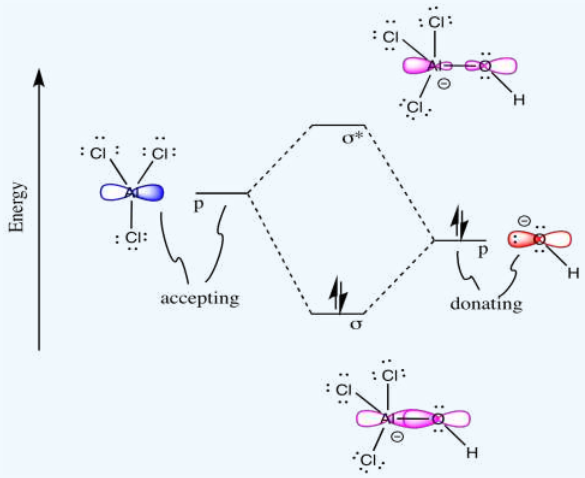
o Draw the orbital from the acid (aluminum chloride) that is likely to accept electrons.

o Complete the MO mixing diagram of these two orbitals:

- Label the electron donating orbital
- Label the electron accepting orbital
- Populate the MO mixing diagram with electrons

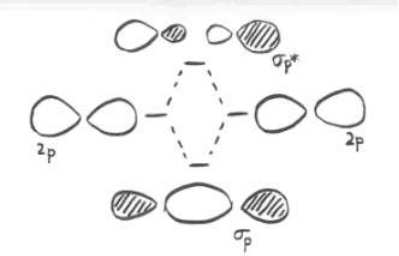
o Draw a cartoon showing each reactant and product MO that contributes to the bonding interaction.

Answer



Pi-bonding with p-orbitals

Earlier, we saw that p orbitals that lie along the same axis can interact to form bonds.



Parallel, but not collinear, p orbitals can also interact with each other. They would approach each other side by side, above and below the bond axis between the two atoms. They can be close enough to each other to overlap, although they do not overlap as strongly as orbitals lying along the bond axis. They can make an in-phase combination, as shown below.

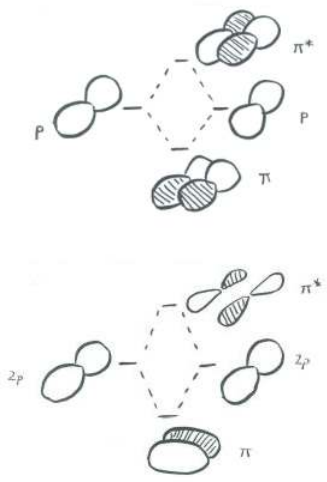


They could also make an out-of-phase combination, as shown below.



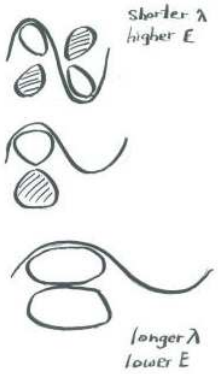
- parallel p orbitals can overlap to produce bonding and antibonding combinations.
- the resulting orbitals contain nodes along the bond axis.
- the electron density is found above and below the bond axis.
- this is called a p (pi) bond.

The illustration above is for one set of p orbitals that are orthogonal to the bond axis. The second picture shows the result of the constructive (or destructive) interference. A similar picture could be shown for the other set of p orbitals.

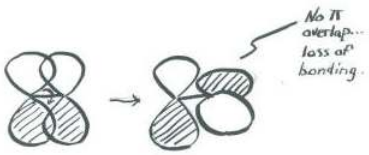


In a main group diatomic species like dinitrogen, one p orbital lying along the bond axis can engage in s bonding. The two p orbitals orthogonal to the bond axis can engage in p bonding. There will be both bonding and antibonding combinations.

Just as the sigma-bonding orbitals display progressively shorter wavelengths along the bonding axis as they go to higher energy, so do the pi bonding orbitals. In other words, there are more nodes in the higher-energy orbitals than in the lower-energy ones.



An important consequence of the spatial distribution or "shape" of a p orbital is that it is not symmetric with respect to the bond axis. An s orbital is not affected when the atom at one end of the bond is rotated with respect to the other. A p orbital is affected by such a rotation. If one atom turns with respect to the other, the p orbital would have to stretch to maintain the connection. The orbitals would not be able to overlap, so the connection between the atoms would be lost.



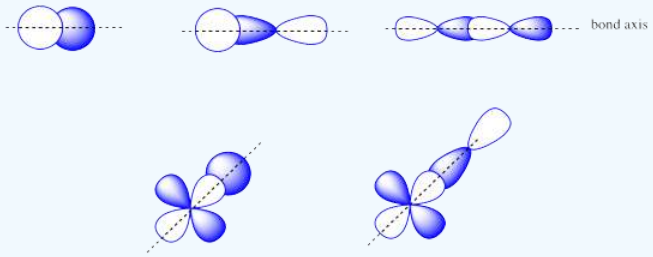
? Exercise 5.1.2.4

The combinations of _____ atomic orbitals leads to σ orbitals.

Draw pictures.

Answer

The combinations of ***s*** + ***s*** OR ***s*** + ***p*** OR ***p*** + ***p*** OR ***s*** + ***d*** OR ***p*** + ***d*** atomic orbitals can lead to σ orbitals.



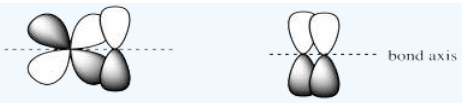
? Exercise 5.1.2.5

The combinations of _____ atomic orbitals leads to π orbitals.

Draw pictures.

Answer

The combinations of side by side p + p or p + d atomic orbitals leads to π orbitals.



Exercise 5.1.2.6

Which molecular orbital is typically the highest in energy?

a. p
b. σ
c. π*
d. π
e. σ*

Answer

e) σ*

Exercise 5.1.2.7

Why would a *core* 1s orbital not interact with a *valence* 2s orbital?

Hint: Why is a Li_2O bond stronger than a K_2O bond?

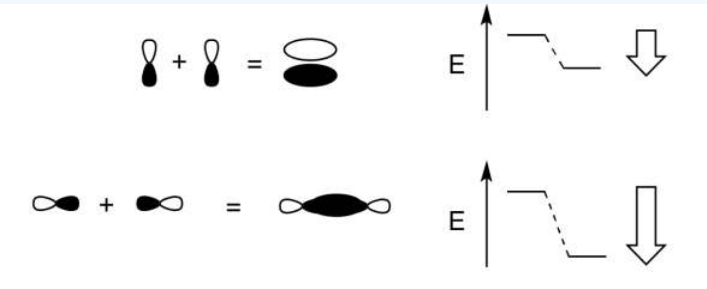
Answer

Li^+ and O^{2-} are more similar in size than K^+ and O^{2-}, so the bond between Li^+ and O^{2-} is stronger.

The energy difference between any core orbitals and valence orbitals is too large, so they cannot interact. In order for orbitals to interact, the orbitals need to have the same symmetry, be in the same plane, and be similar in energy.

Exercise 5.1.2.8

Add a few words to explain the ideas conveyed in these drawings.



Answer

When two parallel p orbitals combine out-of-phase, destructive interference occurs.

There is a node between the atoms.

The energy of the electrons increases.

When two parallel p orbitals combine in-phase, constructive interference occurs.

There is no node between the atoms; the electrons are found above and below the axis connecting the atoms.

The energy of the electrons decreases.

Attribution

Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

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5.1.3: Molecular orbitals from d orbitals

In transition metals and other heavier elements, the d orbitals may combine with other orbitals of compatible symmetry (and energy) to form molecular orbitals. Generally, there are three types of bonding and antibonding interactions that may occur with d orbitals: sigma (σ), pi (π), and delta (δ) bonds.

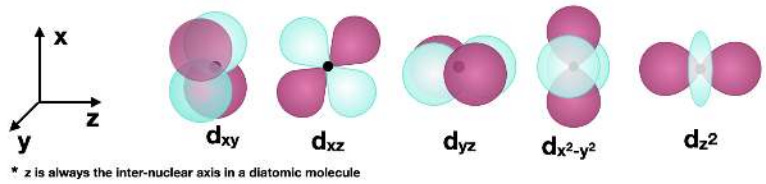


Figure 5.1.3.1: The five $3d$ orbitals are shown. The orientation of the axes is consistent and the z axis is horizontal for convenience in drawing bonding along the z axis (see examples below). (CC-BY-SA; Kathryn Haas)

Sigma (σ) bonding with d orbitals

σ bonds are symmetric with respect to the inter-nuclear axis (in a diatomic molecule, this is the z axis). An example of a σ bond formed by d orbitals is that of two d_{z^2} orbitals (see Figure 5.1.3.2). If a bonded atom is in a position other than on the z axis (in an octahedral geometry, for example), σ bonds can also form. For example, two $d_{x^2-y^2}$ orbitals on atoms bonded along the x or y axes could also form a σ bond.

d orbitals can also form σ bonds with other types of orbitals with the appropriate symmetry. Examples of orbitals with appropriate symmetry are the s orbital and certain p orbitals on another atom, as shown below in Figure 5.1.3.2.

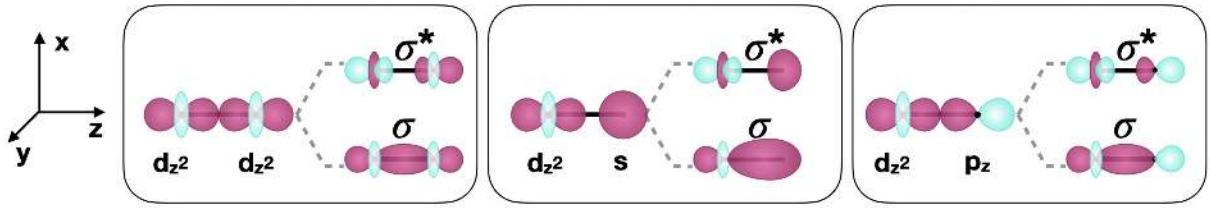


Figure 5.1.3.2: Selected examples of σ bonds involving d orbitals along the z internuclear axis (shown as a bold horizontal line) between two atoms. (CC-BY-SA; Kathryn Haas)

Pi (π) bonding with d orbitals

π bonds are those with one node that is in-plane with the internuclear axis. A π bond can form between two d orbitals or between d orbitals and other types of orbitals with comparable symmetry. An example of a π bond between two d orbitals is that formed by two d_{xz} orbitals along the z axis (shown in Figure 5.1.3.3). d orbitals can also form π bonds using p orbitals with compatible symmetry, as shown in Figure 5.1.3.3.

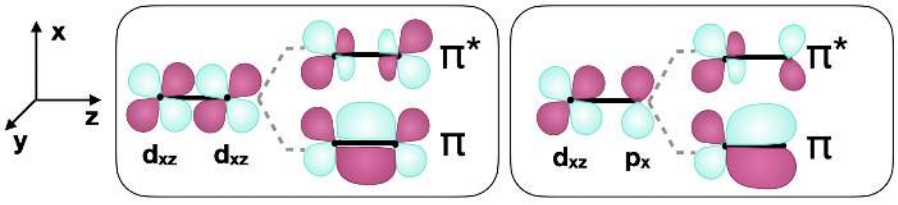


Figure 5.1.3.3: Selected examples of π bonds involving d orbitals along the z internuclear axis (shown as a bold horizontal line) between two atoms. (CC-BY-SA; Kathryn Haas)

Delta (δ) bonding with d orbitals

δ bonds are those with two nodes that are in-plane with the internuclear axis. δ bonds can form between two d orbitals with appropriate symmetry. For example, when two atoms bond along the z axis, the d_{xy} orbitals and the two $d_{x^2-y^2}$ orbitals can form δ bonds (Figure 5.1.3.4).

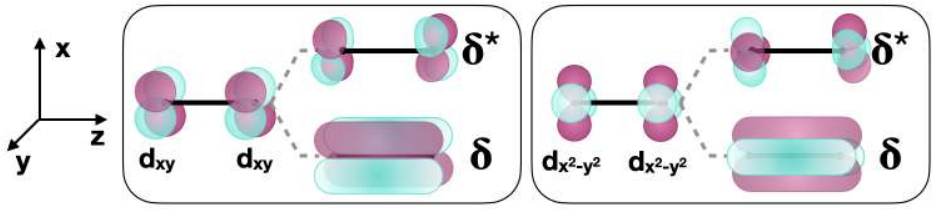


Figure 5.1.3.4: Selected examples of δ bonds involving d orbitals along the z internuclear axis (shown in bold horizontal line) between two atoms. (CC-BY-SA; Kathryn Haas)

Incompatible orbitals

In the descriptions above, we focused on how bonds (and antibonds) can be formed with d orbitals. All bonding and non-bonding interactions require that orbitals have compatible symmetry to form productive interactions. It is worth mentioning that orbitals with symmetry that is incompatible with the d orbitals will not have bonding or antibonding interactions with d orbitals. The figure below shows several sets of orbitals that are incompatible for bonding.

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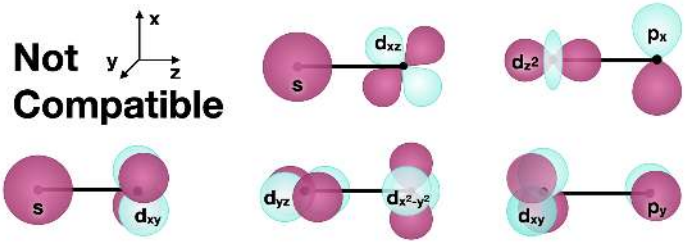


Figure 5.1.3.5: Several incompatible pairs of orbitals. (CC-BY-SA; Kathryn Haas)

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5.1.4: Nonbonding Orbitals and Other Factors

The simplest case is when there is an even number of atomic orbitals that all combine to form strong bonding and antibonding orbitals. But what if there is an uneven number of atomic orbitals? Or what if there are some orbitals that don't meet the criteria for bonding? Or what if the bonding interactions are weak? In these cases, there will be molecular orbitals on the molecule that have non-bonding character.

It is important to note that the bonding, non-bonding, and antibonding nature of orbitals exist on a spectrum. Some bonding and anti-bonding orbitals may have some non-bonding character depending on where their energies lie with respect to the original atomic orbital energies. When molecular orbitals have energies similar to their original atomic orbitals, they will have some non-bonding character. The closer the energies of atomic and molecular orbitals, the more non-bonding the molecular orbitals.

Two major factors to consider

Uneven number of atomic orbitals: In the case that there is an uneven number of atomic orbitals with compatible symmetry, orbitals with non-bonding character will form. For example, in the case where three atomic orbitals combine, the most common result is formation of a low-energy bonding orbital, a high energy antibonding orbital, and a non-bonding orbital of intermediate energy (Figure 5.1.4.1).

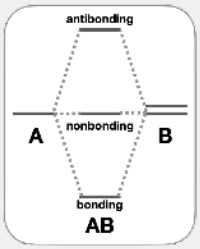


Figure 5.1.4.1. This figure illustrates the most common case for three atomic orbitals that combine to form three molecular orbitals; formation of one low-energy bonding, one high-energy antibonding, and one intermediate energy non-bonding molecular orbital. (CC-BY-NC-SA, Kathryn Haas)

Differences in energy: Combination of orbitals with different energies may lead to orbitals with non-bonding character. Atomic orbitals that have similar energies will have the strongest interactions, and result in bonding molecular orbitals with much lower energies than the component atomic orbitals. On the other hand, atomic orbitals with very unequal energies have a weaker interaction because the molecular orbitals are closer in energy to the atomic orbital energies, thus there is less energy benefit to putting electrons in the bonding molecular orbitals (Figure 5.1.4.2). When bonding or antibonding orbitals are close to the energies of the contributing atomic orbitals, those molecular orbitals may have some non-bonding character.

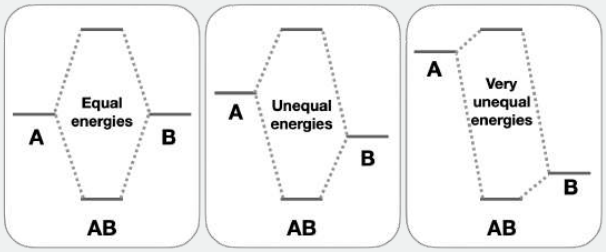


Figure 5.1.4.2. This figure illustrates how relative energies of atomic orbitals result in molecular orbitals that are more or less favorable. The greater the energy difference between atomic orbitals and the bonding molecular orbital, the more eneretically favorable it is for bonding to occur. (CC-BY-NC-SA, Kathryn Haas)

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SECTION OVERVIEW

5.2: Homonuclear Diatomic Molecules

In this section you will be introduced to the molecular orbital diagrams of several homonuclear diatomic molecules. Homonuclear diatomic molecules are molecules made of exactly two identical atoms, and they are relatively simple.

5.2.1: Molecular Orbitals

5.2.2: Orbital Mixing

5.2.3: Diatomic Molecules of the First and Second Periods

5.2.4: Photoelectron Spectroscopy

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5.2.1: Molecular Orbitals

There are several cases where our more elementary models of bonding (like Lewis Theory and Valence Bond Theory) fail to predict the actual molecular properties and reactivity. A classic example is the case of O_2 and its magnetic properties. At very cold temperatures, O_2 is attracted to a magnetic field, and thus it must be paramagnetic (unpaired electrons give rise to magnetism). Watch the video below!



The magnetic properties of O_2 are easily rationalized by its **molecular orbital diagram**. A molecular orbital diagram is a diagram that shows the relative energies and identities of each molecular orbital in a molecule. Figure 5.2.1.1 shows a simplified and generic molecular orbital diagram for a second-row homonuclear diatomic molecule. The diagram is simplified in that it assumes that interactions are limited to degenerate orbitals from two atoms (see next section).

There are some things you should note as you inspect Figure 5.2.1.1 (and keep these in mind as you draw your own diagrams!). First, notice that there are the **same number of molecular orbitals as there are atomic orbitals**. Second, notice that **each orbital in the diagram is rigorously labeled** using labels (σ and π) that include the subscripts u and g. These labels and subscripts indicate the symmetry of the orbitals. The σ symbol indicates that the orbital is symmetric with respect to the internuclear axis, while the π label indicates that there is one node along that axis. The g and u stand for *gerade* and *ungerade*, the German words for *even* and *uneven*, respectively. The subscript g is given to orbitals that are *even*, or *symmetric*, with respect to an inversion center. The subscript u is given to orbitals that are *uneven*, or *antisymetric*, with respect to an inversion center. The pictures of calculated molecular orbitals are shown in Figure 5.2.1.1 to illustrate the symmetry of each orbital.

Another important thing to notice is that the diagram in Figure 5.2.1.1 lacks electrons (because it is generic for any second-row diatomic molecule). If this were a *complete* molecular orbital diagram it would **include the electrons for each atom and for the molecule**. Electrons in molecular orbitals are filled in the same way an atomic orbital diagram would be filled, where electrons occupy lower energy orbitals before higher energy orbitals, and electrons occupy empty degenerate orbitals before pairing. A complete molecular orbital diagram would show whether the molecule is diamagnetic or paramagnetic. It can also be used to calculate the bond order of the molecule (the number of bonds between atoms) using the formula below:

$$\text{Bond order } = \frac{1}{2}\left[\begin{pmatrix}\text{number of electrons}\\ \text{in bonding orbitals}\end{pmatrix} - \begin{pmatrix}\text{number of electrons}\\ \text{in antibonding orbitals}\end{pmatrix}\right]$$

In general, non-valence (core) electrons can be ignored because they contribute nothing to the bond order. In fact, many molecular orbital diagrams will ignore the core orbitals, as they are insignificant for bonding interactions and reactivity.

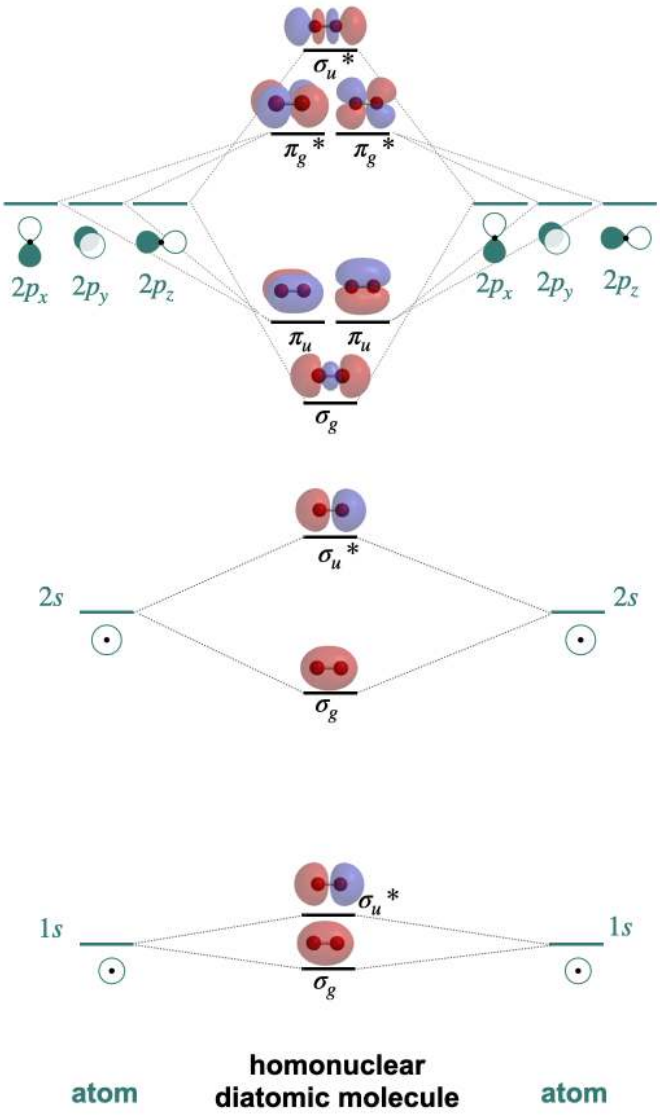


Figure 5.2.1.1: A generic molecular orbital diagram for a homonuclear diatomic molecule of second-row elements assuming no orbital mixing (interactions are formed by orbitals of the same energy from each atom). (CC-BY-NC-SA, Kathryn Haas)

Now, to see how this molecular orbital diagram can explain the magnetic behaviour of O_2, complete the example below.

Example 5.2.1.1

Let's change Figure 5.2.1.1 to make it specific for O_2. Re-draw the MO diagram (no need to draw the shapes of orbitals). Fill in the correct number of electrons for each oxygen atom on either side of the diagram. Then, fill in the total molecular electrons in the center. Calculate the bond order and determine whether it is diamagnetic or paramagnetic.

Solution

The diagram in Figure 5.2.1.1 includes core orbitals (the 1s) and valence electrons (2s, 2p). Therefore, we will consider all the electrons in an oxygen atom and a dioxygen molecule. An oxygen atom has eight total electrons. So we fill eight electrons into the atomic orbitals for the oxygen atom on the right, and eight electrons into the atomic orbitals for oxygen on the left. The total number of electrons for the molecule is sixteen, so fill in 16 electrons into the molecular orbitals, being sure to apply Hund's rule and the Aufbau principle. The result is a diagram that looks like the one drawn below in Figure 5.2.1.2.

The bond order is calculated using the molecular orbitals (we can ignore atomic orbitals). There are 10 electrons in binding orbitals and 6 electrons in antibonding orbitals). This gives a bond order of $\frac{1}{2}(10-6)=2$. This bond order is consistent with valence bond theory!

This diagram indicates that dioxygen is paramagnetic; it has two unpaired electrons in the π^* orbitals. This paramagnetic electron configuration explains why dioxygen is attacted to magnetic fields!

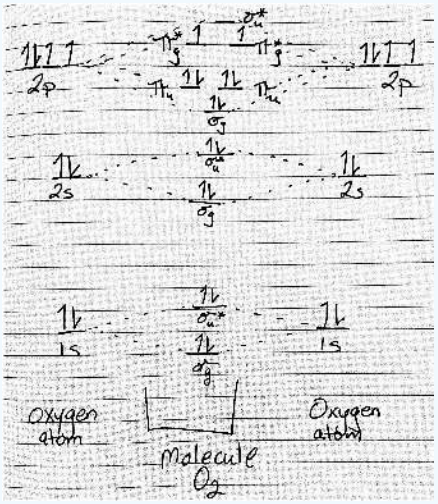


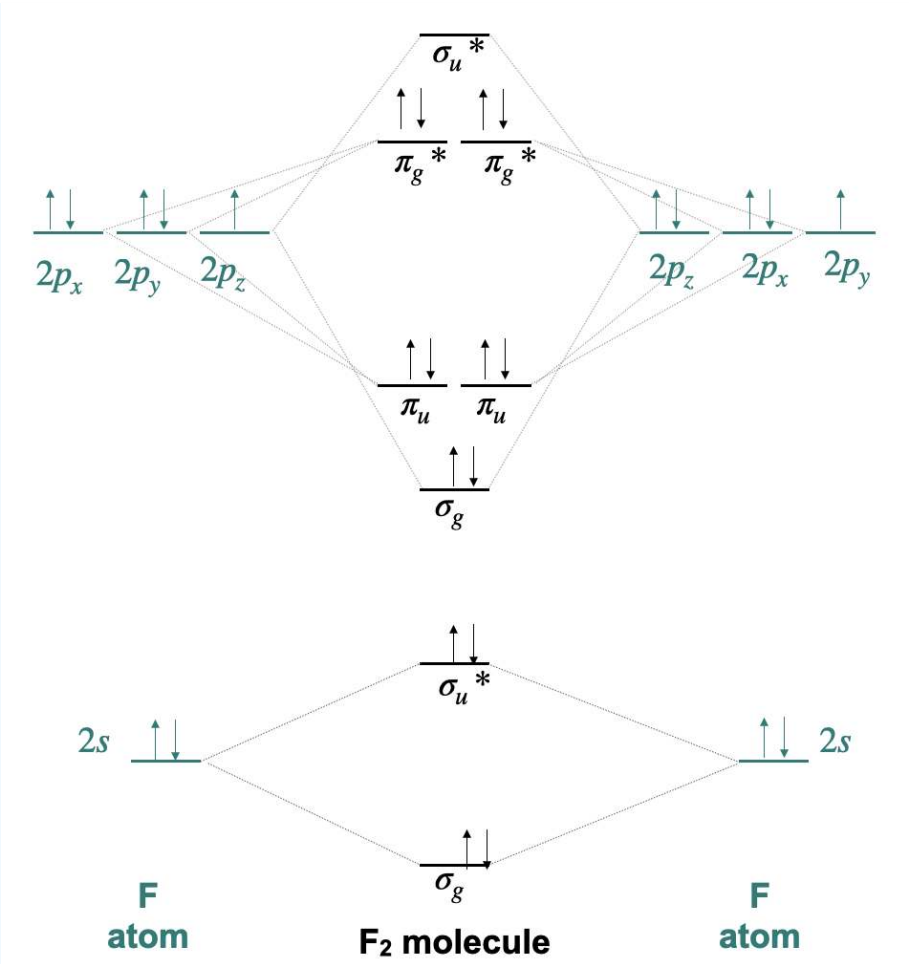
Figure 5.2.1.2: Hand-drawn molecular orbital diagram for dioxygen. (CC-BY-SA; Kathryn Haas)

? Exercise 5.2.1.1

Draw the molecular orbital diagram for $\mathbf{F_2}$; be sure to label your orbitals with the appropriate symmetry and count your orbitals to make sure that the total number of atomic orbitals and molecular orbitals is the same. As a shortcut, include only the valence orbitals and electrons. What is the bond order? Is the molecule diamagnetic or paramagnetic?

Answer

The valence orbitals on an F atom are 2s and 2p. And, there are seven valence electrons in F. This gives fourteen total valence electrons. The MO diagram of the valence molecular orbitals can be constructed by combining the valence 2s and valence 2p orbitals from each F atom. The bond order is 1 and the molecule is diamagnetic.



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5.2.2: Orbital Mixing

In the previous section, we introduced a simplified molecular orbital (MO) diagram, assuming that interactions were limited to degenerate orbitals of compatible symmetry. A version of that *simplified* diagram for second-row homonuclear diatomics is shown on the left side of Figure **5.2.2.1** (only valence orbitals shown).

In reality, orbitals of compatible symmetry can combine, or mix, even when they have different energies. When sets of orbitals mix, it has the effect of decreasing the energy of the lower-energy set and increasing the energy of the higher-energy set. There are two ways to explain mixing, described in the points below. The diagram on the right of side of Figure **5.2.2.1** shows how energy levels are affected by orbital mixing.

- **Starting from the simplified MO diagram and mixing molecular orbitals of like symmetry**: If we start with the "no mixing" simplified diagram shown on the left, we can pick out the orbitals with like symmetry and consider what will happen if these molecular orbitals mix. For example, starting from the MO diagram on the left side of Figure **5.2.2.1**, we see that there are two σ_g orbitals that have identical symmetry (hence they have identical symmetry labels). Upon mixing, the lower-energy $\sigma_g(2s)$ will decrease in energy while the higher-energy $\sigma_g(2p)$ will increase in energy. Likewise, there are two σ_u^* orbitals that will mix, decreasing the energy of $\sigma_u^*(2s)$ while increasing the energy of $\sigma_u^*(2p)$.
- **Starting from and mixing atomic orbitals of compatible symmetry**: Starting from the atomic orbitals, we can select the orbitals that have compatible symmetry to make productive interactions, and combine them as a set to make molecular orbitals. From the two sets of atomic orbitals on the right panel in Figure **5.2.2.1**, there are two sets of four orbitals with compatable symmetry; one is the set of two $2s$ and two $2p_z$ orbitals. These four orbitals can combine to form molecular orbitals with σ symmetry. They combine to form one lowest-energy bonding σ_g, a highest-energy σ_u^*, and two orbitals with intermediate energy (σ_g, and σ_u^*). This treatment can be expressed as the linear combination of four atomic orbitals:

  $$\Psi = c_1\psi(2s_a) \pm c_2\psi(2s_b) \pm c_3\psi(2p_a) \pm c_4\psi(2p_b)$$

  where the coefficients $c_1 = c_2$ and $c_3 = c_4$ for homonuclear diatomic molecules.

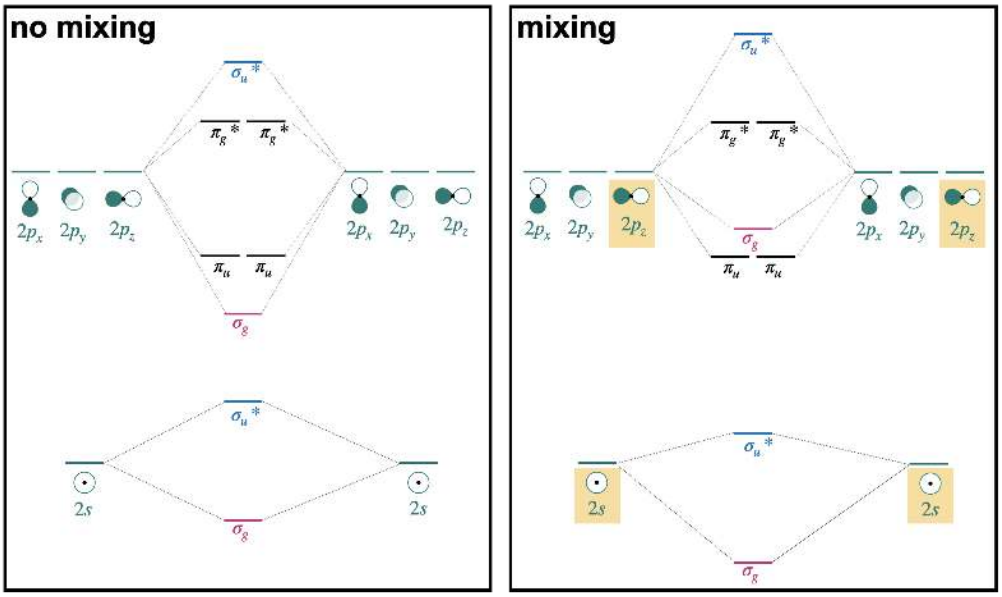


Figure **5.2.2.1**: Mixing of orbitals with like symmetry affects the energies of molecular orbitals. The simplified case where no mixing occurs is shown on the left. The effects of mixing are shown on the right. The σ_g orbitals of like symmetry are highlighted in fuschia and the σ_u^* orbitals of like symmetry are highlighted in blue. A group of atomic orbitals of similar symmetry are highlighted in yellow boxes; these atomic orbitals combine to give all σ molecular orbitals. (CC-BY-SA, Kathryn Haas)

In the case of homonuclear diatomic molecules of the second row, orbital mixing has important consequences for the energetic order of the $\sigma_g(2p)$ and $\pi_u(2p)$ orbitals. This will be discussed in the next section.

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5.2.3: Diatomic Molecules of the First and Second Periods

First Period Homonuclear Diatomic Molecules

In the first row of the periodic table, the valence atomic orbitals are $1s$. There are two possible homonuclear diatomic molecules of the first period:

Dihydrogen, H_2 [$\sigma_g^2(1s)$]: This is the simplest diatomic molecule. It has only two molecular orbitals (σ_g and σ_u^*), two electrons, a bond order of 1, and is diamagnetic. Its bond length is 74 pm. MO theory would lead us to expect bond order to decrease and bond length to increase if we either add or subtract one electron. The calculated bond length for the H_2^+ ion is approximately 105 pm.[1]

Dihelium, He_2 [$\sigma_g^2\sigma_u^{*2}(1s)$]: This molecule has a bond order of zero due to equal number of electrons in bonding and antibonding orbitals. Like other nobel gases, He exists in the atomic form and does not form bonds at ordinary temperatures and pressures.

Exercise 5.2.3.1

Draw the complete molecular orbital diagrams for H_2 and for He_2. Include sketches of the atomic and molecular orbitals.

Answer

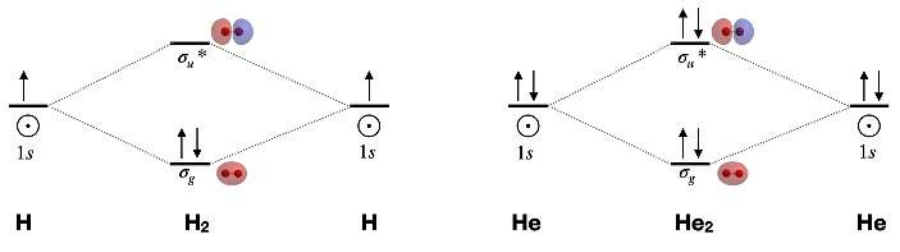


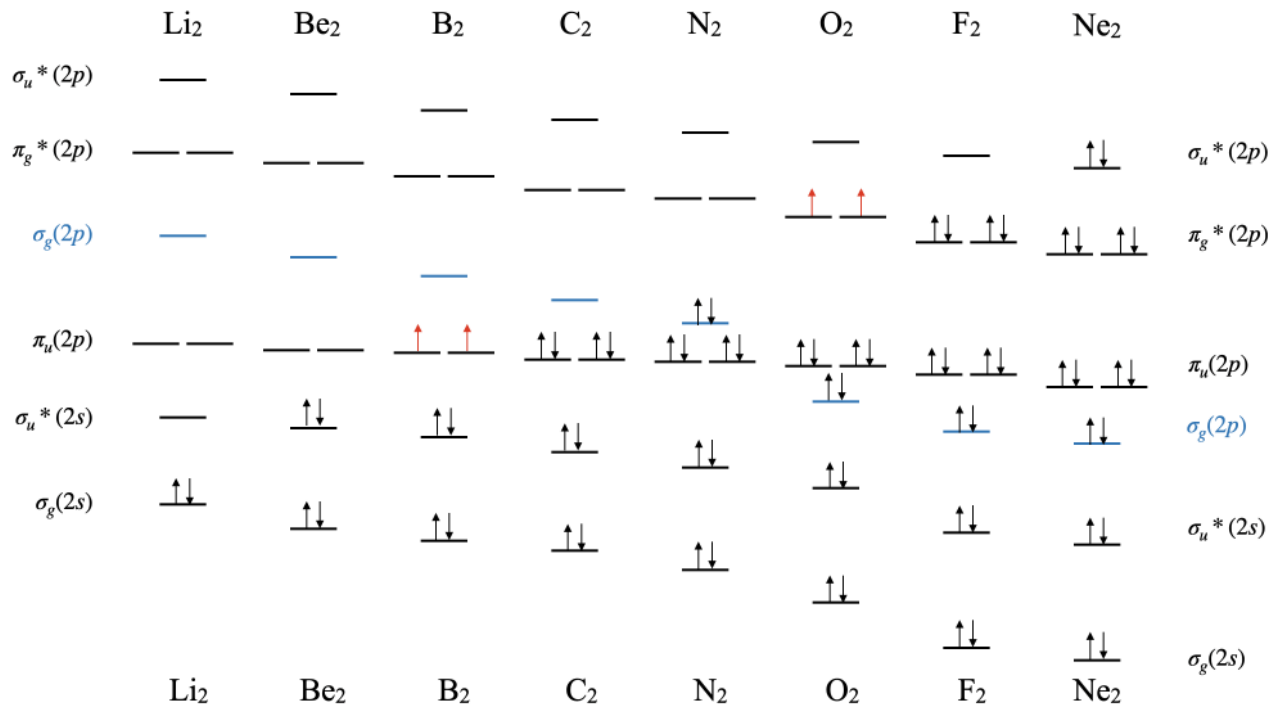
Figure for Exercise 5.2.3.1: Molecular orbital diagrams for dihydrogen and dihelium. Molecular orbital surfaces calculated using Spartan software. (CC-BY-NC-SA; Kathryn Haas)

A complete molecular orbital diagram includes all atomic orbitals and molecular orbitals, their symmetry labels, and electron filling.

Second Period Homonuclear Diatomic Molecules

The second period elements span from Li to Ne. The valence orbitals are 2s and 2p. In their molecular orbital diagrams, non-valence orbitals (1s in this case) are often disregarded in molecular orbital diagrams.

Orbital mixing has significant consequences for the magnetic and spectroscopic properties of second period homonuclear diatomic molecules because it affects the order of filling of the $\sigma_g(2p)$ and $\pi_u(2p)$ orbitals. Early in period 2 (up to and including nitrogen), the $\pi_u(2p)$ orbitals are lower in energy than the $\sigma_g(2p)$ (see Figure 5.2.3.1). However, later in period 2, the $\sigma_g(2p)$ orbitals are pulled to a lower energy. This lowering in energy of $\sigma_g(2p)$ is not unique; all of the σ orbitals in the molecule are pulled to lower energy due to the increasing positive charge of the nucleus. The π orbitals in the molecule are also affected, but to a much lesser extent than σ orbitals. The reason has to do with the high penetration of s atomic orbitals compared to p atomic orbitals (recall our previous discussion on penetration and shielding, and its effect on periodic trends). The σ molecular orbitals have more s character and thus their energy is more influenced by increasing nuclear charge. As nuclear charge increases, the energy of the $\sigma_g(2p)$ orbital is lowered significantly more than the energy of the $\pi_u(2p)$ orbitals (Figure 5.2.3.1).



	Li_2	Be_2	B_2	C_2	N_2	O_2	F_2	Ne_2
Unpaired e⁻	0	0	2	0	0	2	0	0
Bond Order	1	0	1	2	3	2	1	0
Experimental* Bond Length (pm)	267.3	246.0	159.0	124.3	109.8	120.8	141.2	310.0

*Experimental bond lengths from "List of Experimental Diatomic Bond Lengths", NIST, https://cccbdb.nist.gov/diatomicexpbondx.asp

Figure 5.2.3.1: Molecular orbital energy-level diagrams for the diatomic molecules of the period 2 elements. Unlike earlier diagrams, *only the valence molecular orbital energy levels for the **molecules** are shown here (atomic orbitals not shown for simplicity).* For Li_2 through N_2, the $\sigma_g(2p)$ orbital is higher in energy than the $\pi_u(2p)$ orbitals. In contrast, from O_2 onward, the $\sigma_g(2p)$ orbital is *lower* in energy than the $\pi_u(2p)$ orbitals because the nuclear charge increases across the row. The experimental bond lengths correlate with the calculated bond order. (CC-BY-NC-SA, Kathryn Haas)

Dilithium, Li_2 $[\sigma_g^2(2s)]$: This molecule has a bond order of one and is observed experimentally in the gas phase to have one Li-Li bond.

Diberylium, Be_2 $[\sigma_g^2\sigma_u^{*2}(2s)]$: This molecule has a bond order of zero due to the equal number of electrons in bonding and antibonding orbitals. Although Be_2 does not exist under ordinary conditions, it can be produced in a laboratory and its bond length measured (Figure 5.2.3.2). Although the bond is very weak, its bond length is surprisingly ordinary for a covalent bond of the second period elements.[2]

Diboron, B_2 $[\sigma_g^2\sigma_u^{*2}(2s)\pi_u^1\pi_u^1(2p)]$: The case of diboron is one that is much better described by molecular orbital theory than by Lewis structures or valence bond theory. This molecule has a bond order of one. The molecular orbital description of diboron also predicts, accurately, that diboron is paramagnetic. The paramagnetism is a consequence of orbital mixing, resulting in the σ_g orbital's being at a higher energy than the two degenerate π_u^* orbitals.

Dicarbon, C_2 $[\sigma_g^2\sigma_u^{*2}(2s)\pi_u^2\pi_u^2(2p)]$: This molecule has a bond order of two. Molecular orbital theory predicts two bonds with π symmetry, and no σ bonding. C_2 is rare in nature because its allotrope, diamond, is much more stable.

Dinitrogen, N_2 $[\sigma_g^2\sigma_u^{*2}(2s)\pi_u^2\pi_u^2\sigma_g^2(2p)]$: This molecule is predicted to have a triple bond. This prediction is consistent with its short bond length and bond dissociation energy. The energies of the $\sigma_g(2p)$ and $\pi_u(2p)$ orbitals are very close, and their relative energy levels have been a subject of some debate (see next section for discussion).

Dioxygen, O_2 $[\sigma_g^2\sigma_u^{*2}(2s)\sigma_g^2\pi_u^2\pi_u^2\pi_g^{*1}\pi_g^{*1}(2p)]$: This is another case where valence bond theory fails to predict actual properties. Molecular orbital theory correctly predicts that dioxygen is paramagnetic, with a bond order of two. Here, the molecular orbital diagram returns to its "normal" order of orbitals where orbital mixing could be somewhat ignored, and where $\sigma_g(2p)$ is lower in energy than $\pi_u(2p)$.

Difluorine, F_2 $[\sigma_g^2\sigma_u^{*2}(2s)\sigma_g^2\pi_u^2\pi_u^2\pi_g^{*2}\pi_g^{*2}(2p)]$: This molecule has a bond order of one and like oxygen, the $\sigma_g(2p)$ is lower in energy than $\pi_u(2p)$.

Dineon, Ne_2 $[\sigma_g^2\sigma_u^{*2}(2s)\sigma_g^2\pi_u^2\pi_u^2\pi_g^{*2}\pi_g^{*2}\sigma_u^{*2}(2p)]$: Like other noble gases, Ne exists in the atomic form and does not form bonds at ordinary temperatures and pressures. Like Be_2, Ne_2 is an unstable species that has been created in extreme laboratory conditions and its bond length has been measured (Figure **5.2.3.2**)

? Exercise 5.2.3.2

Draw the complete molecular orbital diagram for O_2. Show calculation of its bond order and tell whether it is diamagnetic or paramagnetic.

Answer

O_2 is paramagnetic with a bond order of 2. Its $\sigma_g(2p)$ molecular orbital is lower in energy that the set of $\pi_u(2p)$ orbitals.

$$\text{Bond order} = \frac{1}{2}\left[\left(\begin{array}{c}\textbf{8 electrons in}\\ \textbf{valence bonding orbitals}\end{array}\right) - \left(\begin{array}{c}\textbf{4 electrons in}\\ \textbf{valence antibonding orbitals}\end{array}\right)\right]$$

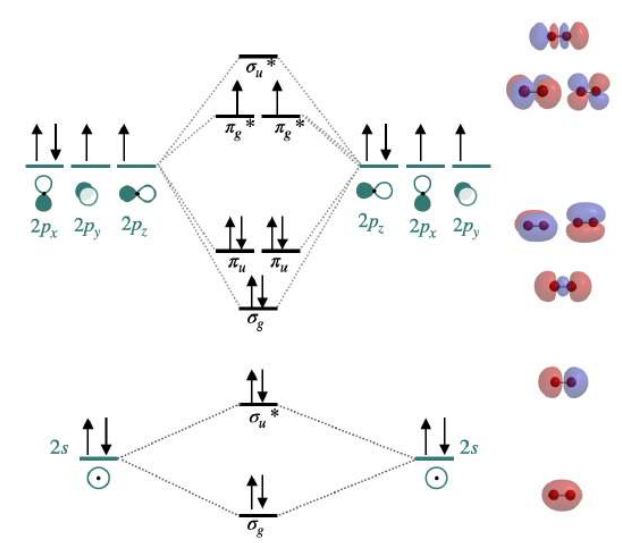


Figure for Exercise **5.2.3.2**. Molecular orbital diagram of O_2. (CC-BY-NC-SA, Kathryn Haas)

? Exercise 5.2.3.3: The Peroxide Ion

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

Answer

This diagram looks similar to that of $\mathbf{O_2}$, except that there are two additional electrons.
$(\sigma_g(2s))^2\,(\sigma_u^*(2s))^2\,(\sigma_g(2p))^2\,(\pi_u(2p))^4\,(\pi_g(2p))^4$; bond order of 1; no unpaired electrons.

Bond Lengths in Homonuclear Diatomic Molecules

The trends in experimental bond lengths are predicted by molecular orbital theory, specifically by the calculated bond order. The values of bond order and experimental bond lengths for the second period diatomic molecules are given in Figure **5.2.3.1**, and

shown in graphical format on the plot in Figure **5.2.3.2**. From the plot, we can see that bond length correlates well with bond order, with a minimum bond length occurring where the bond order is greatest ($\mathbf{N_2}$). The shortest bond distance is at $\mathbf{N_2}$ due to its high bond order of 3. From $\mathbf{N_2}$ to $\mathbf{F_2}$ the bond distance increases despite the fact that atomic radius decreases.

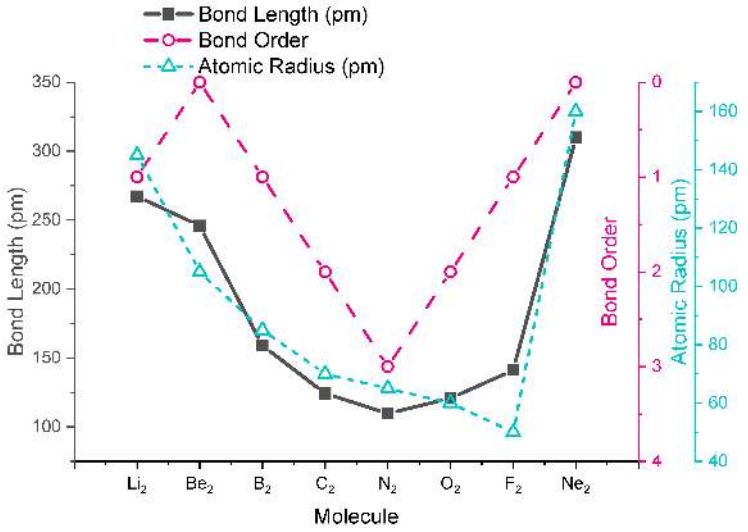


Figure **5.2.3.2**: Overlayed plots of bond length (black squares), bond order (pink circles), and atomic radius (teal triangles) versus atomic number for second period homonuclear diatomic molecules. (CC-BY-NC-SA; Kathryn Haas)

References

1. NIST, Calculated Geometries available for H_2^+ (Hydrogen cation) 2Σg+ D∞h, available at https://cccbdb.nist.gov/diatomicexpbondx.asp
2. Merritt, J. M.; Bondybey, V. E.; Heaven, M. C., Beryllium Dimer-Caught in the Act of Bonding. *Science* **2009,** *324* (5934), 1548-1551.

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5.2.4: Photoelectron Spectroscopy

A photoelectron spectrum can show the relative energies of occupied molecular orbitals by ionization. The *ionization energy* is a direct measure of the energy required to just remove the electron concerned from its initial level to the vacuum level (free electron). Photoelectron spectroscopy measures the relative energies of the ground and excited positive ion states that are obtained by removal of single electrons from the neutral molecule.

$$A + \text{photon} \rightarrow A^+ + e^-$$

The information obtained from photoelectron spectroscopy is typically discussed in terms of the electronic structure and bonding in the ground states of neutral molecules, with ionization of electrons occurring from bonding molecular orbitals, lone pairs, antibonding molecular orbitals, or atomic cores. These descriptions reflect the relationship of ionization energies to the molecular orbital model of electronic structure.

Ionization energies are directly related to the energies of molecular orbitals (by Koopmans' theorem).

Example: Photoelectron spectrum of dihydrogen

The molecular orbital description of dihydrogen involves two $1s$ atomic orbitals generating two molecular orbitals: a bonding σ_g and an antibonding σ_u^*. The two electrons occupy the σ_g bonding orbital, leaving the molecule with a bond order of one (Figure 5.2.4.1). The PES spectrum of dihydrogen (Figure 5.2.4.1) has a single band that corresponds to the ionization of one electron from the σ_g. The multiple peaks are due to electrons ejecting from a range of stimulated vibrational energy levels. When extensive vibrational structure is resolved in a PES molecular orbital, then the removal of an electron from that molecular orbital induces a significant change in the bonding (in this case an increase in the bond length due to decrease in bond order).

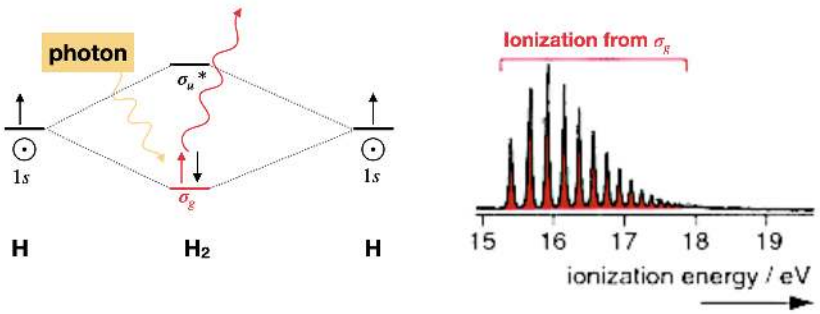


Figure 5.2.4.1: The molecular orbital diagram and photoelectron spectrum of dihydrogen. (CC-BY-NC-SA; Libretexts)

Example: Photoelectron spectrum of dinitrogen

Diatomic nitrogen is more complex than hydrogen since multiple molecular orbitals are occupied. Five molecular orbitals are occupied; two of them are degenerate. Three bands in the photoelectron spectrum correspond to ionization of an electron in $\sigma_g(2p)$, $\pi_u(2p)$ and $\sigma_u^*(2s)$ molecular orbitals. Ionization of the fourth type of orbital, $\sigma_g(2s)$, does not appear in Figure 5.2.4.2 because it is either off scale or because the incident light $h\nu$ used did not have sufficient energy to ionize electrons in that deeply stabilized molecular orbital. Note that extensive vibrational structure for the $\pi_u(2p)$ band indicates that the removal of an electron from this molecular orbital causes a significant change in the bonding.

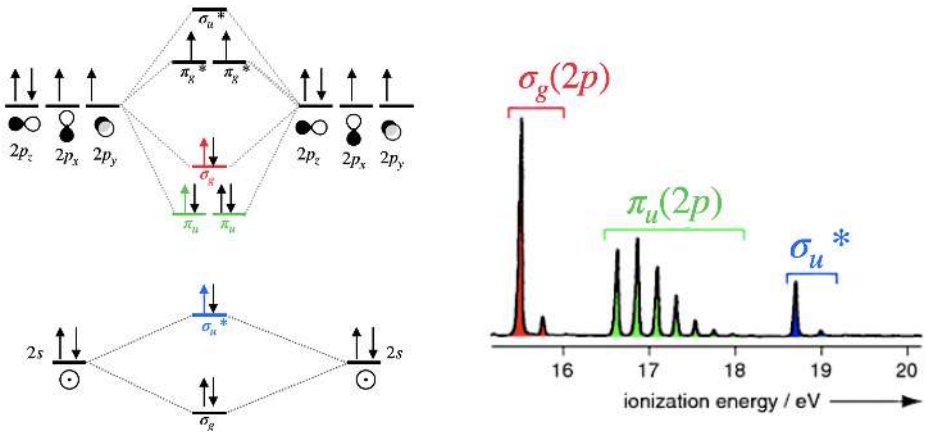


Figure **5.2.4.2**: The molecular orbital diagram and photoelectron spectrum of dinitrogen. (CC-BY-NC-SA; Libretexts)

From the photoelectron spectrum of dinitrogen, we can see that the electrons in the $\sigma_g(2p)$ orbital can be ionized using less energy than required to ionize electrons in the $\pi_u(2p)$ orbital. This is evidence for $\sigma_g(2p)$ existing at a higher energy than the $\pi_u(2p)$ orbitals.

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SECTION OVERVIEW

5.3: Heteronuclear Diatomic Molecules

Diatomic molecules with two non-identical atoms are called **heteronuclear** diatomic molecules. When atoms are not identical, the molecule forms by combining atomic orbitals of unequal energies. *The result is a polar bond in which atomic orbitals contribute unevenly to each molecular orbital*.

The application of molecular orbital theory to heteronuclear diatomic molecules is similar to the case of homonuclear diatomics, except that the atomic orbitals from each atom have different energies and contribute unequally to molecular orbitals. Recall that atomic orbitals must have compatible symmetry and similar energy to combine into molecular orbitals. In the case where atomic orbitals of like symmetry have different energies, they combine less favorably than orbitals that are closer to one another in energy. As a general rule, orbitals that have energy differences of greater than 10-14 eV do not combine favorably. In the molecular orbital diagram, the closer a molecular orbital is to an atomic orbital, the more that atomic orbital contributes to the molecular orbital. This last point is helpful for back-of-the napkin estimations of what the molecular orbitals "look" like.

In this section, you should learn how to generate molecular orbital diagrams of heteronuclear diatomic molecules. To approach such a problem, we must start with a knowledge of the relative energies of electrons in different atomic orbitals. In other words, we need knowledge of the orbital potential energies (or orbital ionization energies).

5.3.1: Orbital ionization energies

5.3.2: Polar bonds

5.3.3: Ionic Compounds and Molecular Orbitals

Sources:

- Gray, Harry. *Electrons and Chemical Bonding*, Benjamin, 1964.
- Miessler, Gary L, and Donald A. Tarr. *Inorganic Chemistry*. Upper Saddle River, N.J: Pearson Education, 2014. Print.

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5.3.1: Orbital ionization energies

To generate molecular orbital diagrams of heteronuclear diatomic molecules, we must start with a knowledge of the relative energies of electrons in different atomic orbitals. In other words, we need knowledge of the orbital potential energies (or orbital ionization energies).

Orbital Ionization Energies

There are two approaches you can use to "know" or estimate the atomic orbital energy levels.

1. Use a table of atomic orbital ionization energies, like those found in Table **5.3.1.1**.
2. When you do not have access to a table of values like the one below, use periodic trends in electronegativity and/or ionization energies as your guide to approximate relative values for different atoms.

Table **5.3.1.1**: These are one-electron ionization energies of the valence orbitals calculated by average energies of both the ground-state and ionized-state configurations. (From Harry Gray, "Electrons and Chemical Bonding," Benjamin, 1964, Appendix) Values are expressed in eV.

Atom	1*s*	2*s*	2*p*	3*s*	3*p*	4*s*	4*p*	*Atom*	3*d*	4*s*	4*p*
H	−13.64							*Sc*	−4.71	−5.70	−3.22
He	−24.55							*Ti*	−5.58	−6.08	−3.35
Li		−5.46						*V*	−6.32	−6.32	−3.47
Be		−9.30						*Cr*	−7.19	−6.57	−3.47
B		−14.01	−8.31					*Mn*	−7.93	−6.82	−3.60
C		−19.47	−10.66					*Fe*	−8.68	−7.07	−3.72
N		−25.54	−13.14					*Ni*	−10.04	−7.56	−3.84
O		−32.36	−15.87					*Cu*	−10.66	−7.69	−3.97
F		−46.37	−18.72								
Ne		−48.48	−21.57								
Na				−5.21							
Mg				−7.69							
Al				−11.28	−5.95						
Si				−15.00	−7.81						
P				−18.72	−10.17						
S				−20.71	−11.65						
Cl				−25.29	−13.76						
Ar				−29.26	−15.87						
K						−4.34					
Ca						−6.08					
Zn						−9.42					
Ga						−12.65	−5.95				
Ge						−15.62	−7.56				
As						−17.61	−9.05				
Se						−20.83	−10.79				
Br						−24.05	−12.52				
Kr						−27.52	−14.26				

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5.3.2: Polar bonds

Molecular orbital diagrams for heteronuclear diatomic molecules

The molecular orbital diagram of a heteronuclear diatomic molecule is approached in a way similar to that of a homonuclear diatomic molecule. The orbital diagrams may also look similar. A major difference is that the more electronegative atom will have orbitals at a lower energy level. Two examples of heteronuclear diatomic molecules will be explored below as illustrative examples.

Carbon monoxide MO diagram

Carbon monoxide is an example of a heteronuclear diatomic molecule where both atoms are second-row elements. The valence molecular orbitals in both atoms are the $2s$ and $2p$ orbitals. The molecular orbital diagram for carbon monoxide (Figure **5.3.2.1**) is constructed in a way similar to how you would construct dicarbon or dioxygen, except that the oxygen orbitals have a lower potential energy than analogous carbon orbitals. The labeling of molecular orbitals in this diagram follows a convention by which orbitals are given serial labels according to type of orbital (σ, π, etc.). The lowest energy orbitals of any type are assigned a value of 1 and higher energy orbitals of the same type are assigned by increasing intervals (..2, 3, 4...). The orbital labeling system described previously is inappropriate for heteronuclear diatomic molecules that cannot be assigned g and u subscripts.

A consequence of unequal atomic orbital energy levels is that orbital mixing is significant. Notice the order of the molecular orbitals labeled 1π and 3σ in Figure **5.3.2.1**. This is a similar order of π and σ orbitals to the one we saw in the case of the σ_g and π_u orbitals of N_2 and lighter diatomics of the second period. Because the oxygen $2p_z$ orbital is close in energy to both the carbon $2p_z$ and carbon $2s$, these three orbitals will have significant interaction (mixing). The result is an increase in the energy of the 3σ orbital and a decrease in energy of the $2\sigma^*$ orbital, resulting in the diagram shown in Figure **5.3.2.1**.

In the case of carbon monoxide (Figure **5.3.2.1**), atomic orbitals contribute unequally to each molecular orbital. For example, because the $2s$ orbital of oxygen is very close in energy to the 2σ moelcular orbital, it contributes to that molecular orbital more than the $2s$ orbital from carbon. Notice the shape of this 2σ orbital and how it is unevenly distributed over the two atoms; it is more heavily distributed on the oxygen because it is most like the oxygen $2s$. This is in line with the assumption that electron density is distributed more on oxygen because it is more electronegative than carbon. Likewise, the 1π orbitals are unevenly distributed, with more distribution close to the oxygen.

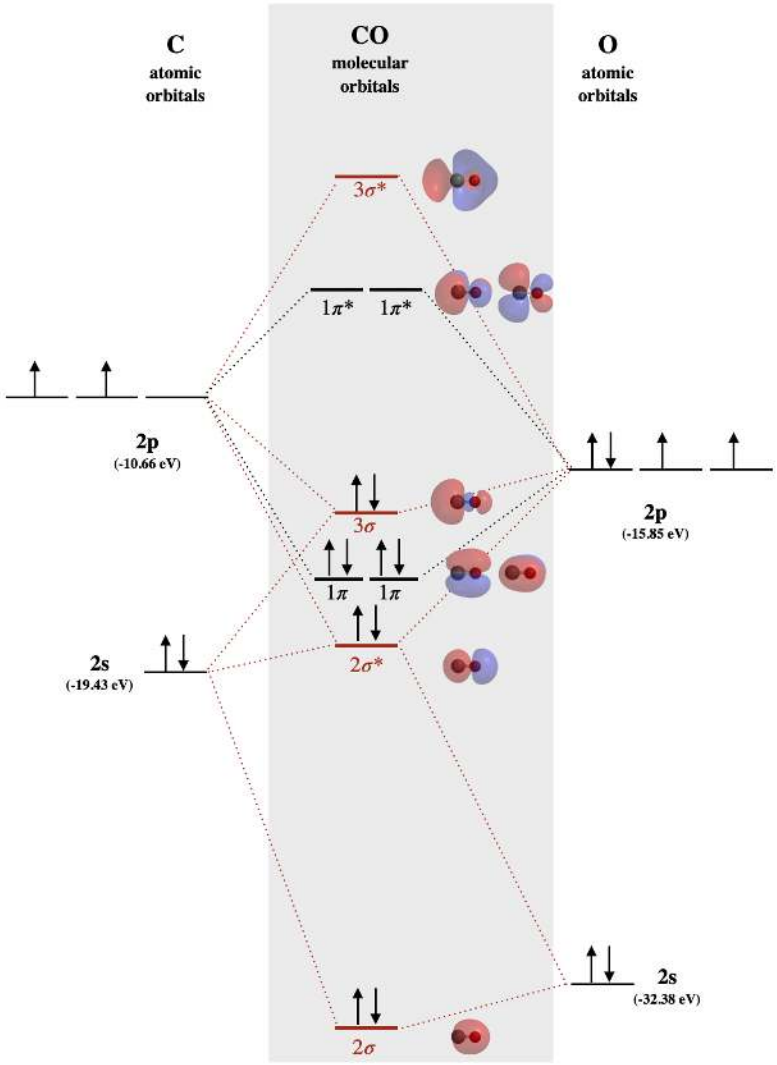


Figure 5.3.2.1: Molecular orbital diagram of carbon monoxide. The labeling of molecular orbitals in this diagram follows a convention by which orbitals are given serial names according to the type of orbital (σ, π, etc.). The lowest energy orbitals of any type are assigned a value of 1 and higher energy orbitals of the same type are assigned by increasing intervals (..2, 3, 4...). The orbital labeling system described previously is inappropriate for heteronuclear diatomic molecules that cannot be assigned g and u subscripts. Molecular orbital surfaces were calculated using Spartan software. (Kathryn Haas, CC-BY-NC-SA)

? Exercise 5.3.2.1

Examine the shape of the 3σ orbital of carbon monoxide in Figure 5.3.2.1. Describe what ways this shape is different from the shape of the σ_g orbitals from second period homonuclear diatomic molecules (see Fig. 5.2.1.1). Rationalize these differences. Both orbitals are re-created below for convenience.



σ_g of homonuclear diatomic

3σ of CO

Answer

The 3σ orbital is like the σ_g in that it has three lobes and two nodes distributed along the internuclear bond. They are different in their distribution. The two external lobes of σ_g are evenly distributed because they are an equal combination of two p_z orbitals (one from each atom). The 3σ orbital is more heavily distributed toward the carbon atom, the less electronegative atom, than toward the oxygen. The unequal distribution of 3σ is apparent in the unequal sizes of its exterior lobes and the uneven shape of the interior lobe. The heavier distribution within the exterior lobe on carbon is caused by the mixing of the carbon $2s$ orbital with carbon and oxygen $2p_z$ orbitals. The uneven shape of the interior lobe, where it leans toward oxygen, is best explained by the fact that the 3σ orbital is closer in energy to the oxygen $2p_z$ than the carbon $2p_z$.

Hydrogen fluoride MO diagram

Hydrogen fluoride is an example of a heteronuclear diatomic molecule in which the two atoms are from different periods. In this case, the valence orbital of H is $1s$ while those of F are $2s$ and $2p$. The molecular orbital diagram for HF is shown in Figure 5.3.2.2.

Three of these orbitals have compatible symmetry for mixing; these are the hydrogen $1s$, fluorine $2s$, and fluorine $2p$. However, the extent to which they will interact depends on their relative energies. Fluorine is more electronegative than H, and the fluorine atom has a higher first ionization energy than does hydrogen. From these trends, we can expect that the fluorine valence orbitals are lower in energy than that of hydrogen. From Table 5.3.1, we find that the 1s orbital of H (-13.6 eV) is higher in energy than both fluorine orbitals (-18.7 and -40.2 eV, respectively for $2p$ and $2s$). The energies of hydrogen $1s$ and fluorine $2p$ are a good match for combination; however, the fluorine $2s$ orbital is much too different to create a productive interaction. Therefore, we expect that the fluorine $2s$ will create a non-bonding molecular orbital, while the $1s$ and $2p_z$ orbitals combine to make σ bonding and σ^* antibonding molecular orbitals. The remaining $2p_x$ and $2p_y$ orbitals do not have compatible symmetry for bonding with hydrogen, and they will form non-bonding π molecular orbitals. The non-bonding orbitals will have similar energy and character as their component atomic orbitals.

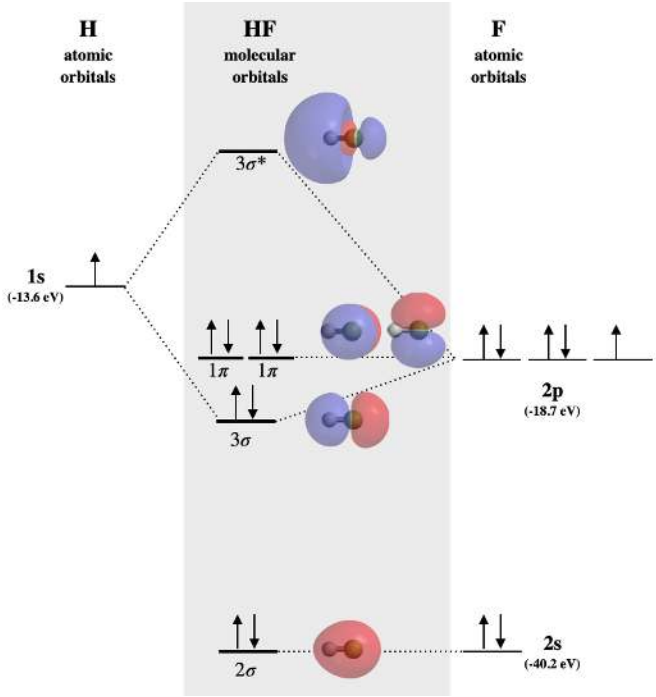


Figure 5.3.2.2: Molecular Orbital diagram of hydrogen fluoride. Molecular orbitals calculated using Spartan software. (Kathryn Haas, CC-BY-NC-SA)

Chemical reactions take place at the HOMO and LUMO orbitals

Knowledge of molecular orbital diagrams, and the shapes of molecular orbitals, can be used to accurately explain and predict chemical reactivity. Chemical reactions take place using the highest occupied molecular orbitals (HOMO) of a nucleophile or Lewis base, and the lowest unoccupied molecular orbital (LUMO) of an electrophile or Lewis acid.

> *Lewis bases react using electrons in the HOMO, while Lewis acids react using the empty LUMO.*

Example: Reactivity of CO with metal ions

CO is an excellent ligand for many metal ions. In fact, the strong affinity between CO and the heme iron (Fe) ions in hemoglobin can explain the mechanism of carbon monoxide poisoning. When CO binds in place of O_2 to hemoglobin, that hemoglobin can no longer carry O_2 to tissue cells. CO binding to hemoglobin is strong and practically irreversible. When CO binds to metal ions, it does so through the carbon atom. This is contrary to expectations based on the Lewis structure and the known bond polarity, where electron density is polarized toward oxygen. The distribution of the electron density of the HOMO of CO can explain this observation!

? Exercise 5.3.2.2

Refer to the MO diagram for CO. Identify the HOMO and explain why CO bonds to metal ions through the carbon atom rather than through the oxygen atom.

Answer

In the interaction between CO and a metal ion, CO would act as a Lewis base; thus it will react using electrons in its HOMO. The MO diagram for CO is shown in Figure 5.3.2.1: the HOMO is the 3σ orbital (also discussed in ? Exercise 5.3.2.1). The electron density of that MO is centered around the carbon atom, thus the carbon atom will be a better Lewis base than the O atom.

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5.3.3: Ionic Compounds and Molecular Orbitals

Ionic interactions lie at one extreme on a spectrum of bonding. On the opposite end of the spectrum are the non-polar covalent bonds (e.g., homonuclear diatomics). In these molecules, molecular orbitals are formed by equal-energy atomic orbitals, resulting in electron density evenly distributed over the molecule. In the middle of the spectrum are the cases of polar covalent bonds (e.g., heteronuclear diatomics), in which atomic orbitals of unequal energies contribute unequally to molecular orbitals, resulting in uneven distribution of electron density across the molecule. In the case of polar bonds, the electron density is shifted toward the more electronegative atom since that atom contributes more to the lowest energy bonding molecular orbitals. Molecular orbital diagrams can be drawn for ionic compounds as if they are extremely polar bonds in which electrons are not only shifted toward, but are transferred completely to the more electronegative atom.

Example: NaCl

In **NaCl**, the sodium **3*s*** orbital (-5.2 eV) is significantly higher in energy than the chlorine valence orbitals. The chlorine **3*s*** and **3p_z** orbitals have compatible symmetry, yet only the **3p_z** orbital (-13.8 eV) is close enough in energy to interact with the Na **3*s***; still, the energy difference is large enough to make bonding weak. The Na **3*s*** orbital combines with Cl **3p_z** to form the molecular orbitals labeled **4σ** and **4σ*** in Figure **5.3.3.1**. The **4σ** orbital is weakly bonding, but is very close in energy to the Cl **3p_z** orbital, and is mostly Cl-like in character. Notice that all **σ** orbitals look very much like either **s** or **p** orbitals centered on the **Cl** atom, while the **4σ*** orbital is centered almost entirely on Na. The lack of molecular orbitals that are distributed over both atoms at once is consistent with a lack of significant covalent bond character in **NaCl**. The bonding here is characterized by transfer of one electron from **Na** to **Cl** and is almost entirely electrostatic. Bonding that is mostly electrostatic in character is non-directional, unlike true covalent bonding.

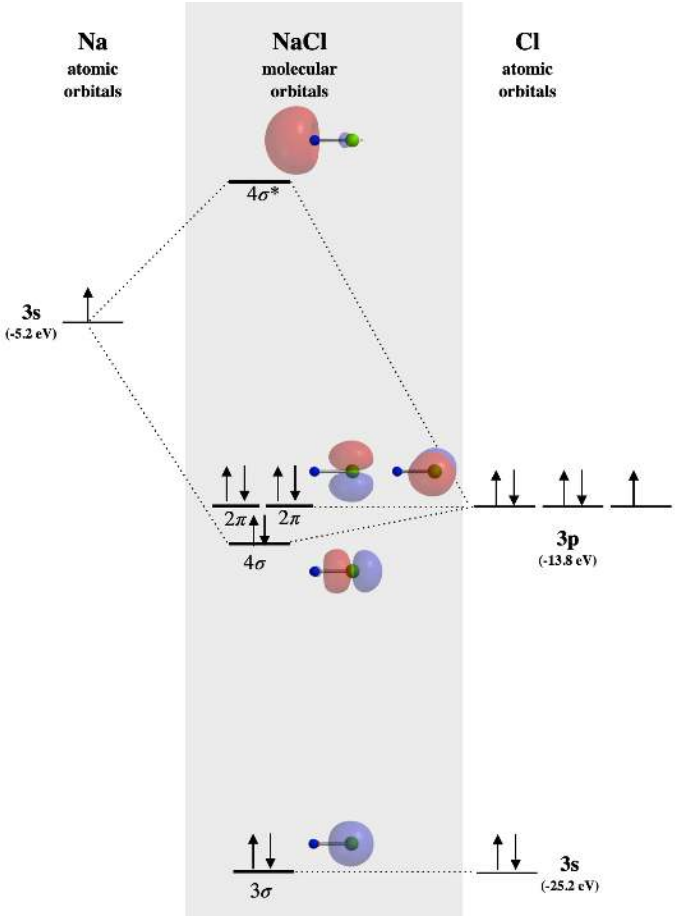


Figure **5.3.3.1**: The molecular orbital diagram for sodium chloride. Molecular orbital surfaces calculated using Spartan software indicate almost no covalent nature of bonding. (CC-BY-NC-SA, Kathryn Haas)

Exercise 5.3.3.1

Draw the molecular orbital diagram for **LiF**. Make sure to label all molecular orbitals appropriately, and specify whether they are mostly bonding, non-bonding, or antibonding. Identify the HOMO and LUMO. Sketch the approximate shapes of all orbitals.

Answer

We expect **LiF** to be an ionic compound because the energy difference in valence orbitals is at least 10-14 eV. (See Table 5.3.1) There are a variety of ways used to label molecular orbitals. In the figure below, we are using the convention of labeling each type of orbital with numbers starting from the lowest-energy orbitals. The 1σ orbital would be mostly F $1s$ in character and is not shown. The 2σ orbital is mostly non-bonding in nature, although it has a very small contribution from $2s$ of Li due to compatible symmetry. The 3σ orbital is slightly bonding but it is mostly F$2p$ in character. The two 1π orbitals are completely non-bonding. The $3\sigma^*$ orbital is antibonding.

- HOMO is 1π
- LUMO is $3\sigma^*$

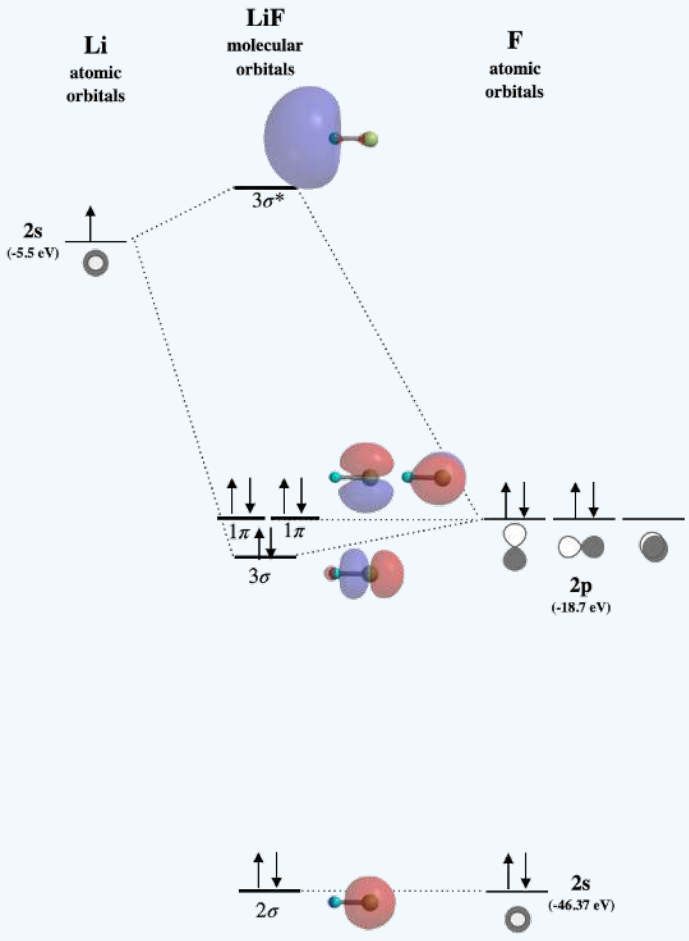


Figure for Exercise 5.3.3.1: Molecular orbital diagram for the ionic compund, LiF. (CC-BY-NC-SA, Kathryn Haas)

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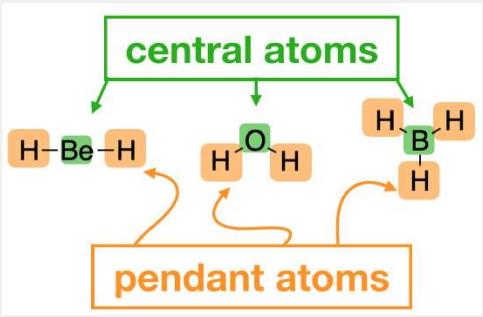
SECTION OVERVIEW

5.4: Larger (Polyatomic) Molecules

We can extend the method we used for diatomic molecules to draw the molecular orbitals of more complicated, polyatomic molecules (molecules with more than two atoms). To combine several different atoms in a molecular orbital diagram, we will group orbitals from different atoms into sets that match the symmetry of a central atom. These **group orbitals** are also referred to as **symmetry adapted linear combinations (SALCs)**. We'll use a stepwise approach to do this as summarized below.

Symmetry adapted linear combinations (SALCs)

We need SALCs (aka group orbitals) to draw molecular orbital (MO) diagrams of *polyatomic* molecules. SALCs are groups of orbitals on **pendant atoms**. These groups of orbitals much match the symmetry of valence orbitals on the **central atom** in order to create a productive interaction. When we combine SALCs with the atomic orbitals on the central atom, we can generate an MO diagram that gives us information about the molecule's bonding and electronic states.



Below is a set of steps you can follow to find SALCs and draw an MO Diagram. Each step will be illustrated in detail through the examples in the subsections that follow this page.

1. Find the **point group** of the molecule and assign Cartesian coordinates so that z is the principal axis.
   Sometimes we can simplify things by looking only at the point group of the relevant orbitals. Only simplify when instructed to do so.*
2. Identify and count the pendant atoms' valence orbitals.
   Is there more than 1 type for each atom (ex. just s, or s and p?) We expect 1 SALC for each ligand orbital.
3. Generate a **reducible representation (Γ)** for the group of pendant atom orbitals using the appropriate character table.
   You have to do this for each set of orbital types. If you only have s orbitals for each ligand, you only need to generate 1 reducible representation. If you have p orbitals, you would generate additional Γ*'s for p_x, p_y, and p_z.*
4. Break the Γ into its component **irreducible representations** from the character table. Note the symmetry of each irreducible representation, its associated orbitals, and their degeneracy.
5. If you are asked to sketch the shapes of SALCs, determine what they "look like" using one of the following strategies.
   (a) Shortcut: if the reducible representations are listed with s, p, or d orbitals in the character table, just draw them (… and skip steps b-c)
   (b) Systematic (Projection Operator) method: Draw an expanded character table and draw your molecule with each ligand identified by letters or numbers (*a,b,c...* or *i,j,k...* or *1,2,3...*) Determine where each pendant atom/orbital ends up under each of the operations of your expanded table. Project the values for each irreducible representation onto the chart you created and then add up the values. Positive and negative values are opposite signed orbitals.
6. Draw the MO diagram by combining SALCs with AO's of like symmetry. When drawing SALC energy levels, remember that the more nodal planes in your SALC orbital drawing, the higher the energy for that SALC orbital.

** When we are focused on orbitals, as in the case for finding group orbitals and drawing molecular orbital diagrams, the symmetry of the orbitals is what we are interested in. In the case of high-symmetry point groups, like $D_{\infty h}$ and $C_{\infty v}$, even though the molecule may have a C_∞ axis, the orbitals do not necessarily retain this symmetry element. For example, the p_x orbital would not have a C_∞ axis, but rather a C_2 axis. It is sufficient and useful to substitute D_{2h} for $D_{\infty h}$ and C_{2v} for $C_{\infty v}$ to simplify the problem.*

5.4.1: Bifluoride anion

5.4.2: Carbon Dioxide

5.4.3: H_2O

5.4.4: NH_3

5.4.5: CO_2 (Revisted with Projection Operators)

5.4.6: BF_3

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5.4.1: Bifluoride anion

Finding SALCs and drawing the MO diagram for [F-H-F]⁻

The linear anion [F-H-F]⁻ is a good place to start as an example to illustrate the process of generating pendant atom SALCs and then constructing a molecular orbital diagram for a polyatomic molecule. We will proceed using the steps outlined on the previous page for generating SALCs and a molecular orbital diagram.

Step 1. Find the point group of the molecule and assign Cartesian coordinates so that z is the principal axis.

We begin by assigning the appropriate point group for this molecule: $D_{\infty h}$ (Figure 5.4.1.1). As mentioned in the previous page, it is useful to substitute D_{2h} for $D_{\infty h}$ when generating SALCs and molecular orbital diagrams. The z axis is assigned to be colinear with the principal axis, and in this case is the same as the C_∞ axis (Figure 5.4.1.1).

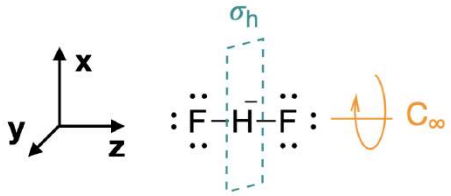


Figure 5.4.1.1: The [FHF]⁻ anion belongs to the $D\infty_h$ point group. (CC-BY-NC-SA; Kathryn Haas)

Step 2. Identify and count the pendant atoms' valence orbitals.

The next step is to identify the valence orbitals on the pendant F atoms that will form SALCs. In most cases, you should consider all of the valence orbitals. In this case, each of the fluorine atoms has four valence orbitals ($2s$, $2p_x$, $2p_y$, and $2p_z$). From these eight fluorine valence orbitals, we should expect eight group orbitals (SALCs).

3. - 5. Generate SALCS (shortcut)

To draw these SALCs for this molecule is rather simple, and we don't need to follow all the steps of finding the Γ's and reducing them. Rather, you can proceed as if you are creating bonding and antibonding molecular orbitals between the two F atoms, except that the F orbitals are separated by the H atom. Approximate sketches of the eight SALCs from F valence orbitals are shown in Figure 5.4.1.2.

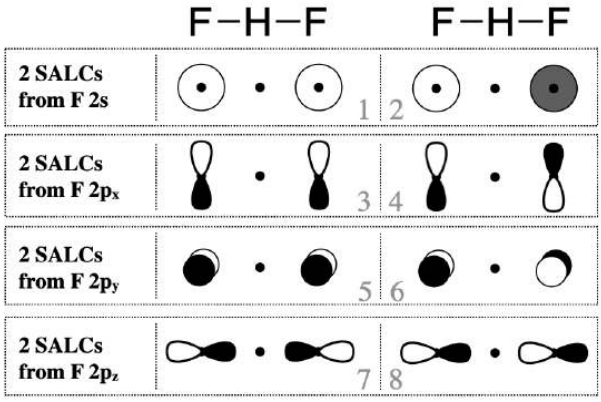


Figure 5.4.1.2: Eight SALCs from the valence orbitals of two fluorine atoms. (CC-BY-NC-SA; Kathryn Haas)

6. Draw the MO diagram by combining SALCs with AO's of like symmetry.

SALCs can productively interact with the central atom only when symmetry is compatible. Just some of the groups of orbitals in Figure 5.4.1.2 possess appropriate symmetry to combine with the hydrogen atom valence orbital (the H $1s$). In this simple case, you can decide whether orbitals have compatible symmetry by visually inspecting the shapes of the group orbitals. The F $2p_y$ and $2p_x$ orbitals do not have appropriate symmetry to bond to the H $1s$ orbital because the nodes of these orbitals run through the center of the H $1s$ orbital, thus we can eliminate all SALCs composed from F $2p_x$ and $2p_y$ (*these are SALCs numbered 3-6 in Figure* 5.4.1.2). On the other hand, the F $2s$ and $2p_z$ orbitals individually do have appropriate shape and direction in space for productive interaction

with an H $1s$ orbital. However only SALCs where the *entire group* has appropriate symmetry will combine with H $1s$ to produce bonding or antibonding molecular orbitals. Only the SALCs labeled with numbers 1 and 7 can combine with an s orbital in the center of the group. The ways in which these SALCs are able to combine with H $1s$ are illustrated in Figure 5.4.1.3.

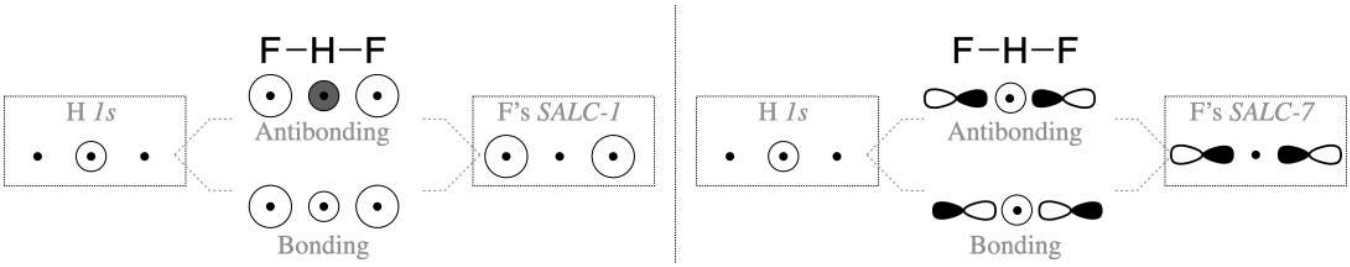
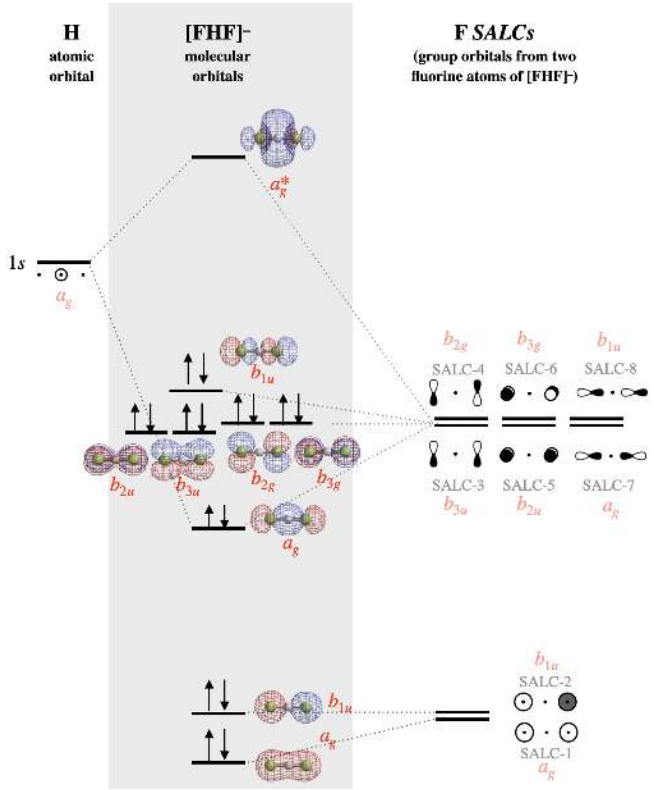


Figure 5.4.1.3: Combinations of a central H $1s$ orbital with the group orbitals, SALC-1 and SALC-7 from Figure 5.4.1.2, to create bonding and antibonding interactions. (CC-BY-NC-SA; Kathryn Haas)

Before we assume that both SALC-1 and SALC-7 will combine with the H $1s$ orbital, we must consider the energies of all atomic orbitals. The F $2p_z$ orbital has a potential energy of -18.7 eV (see Table 5.3.1). This is a good match for the H $1s$ orbital (-13.6 eV). However, the F $2s$ orbital has a much lower energy of -46.37 eV and would have weak interaction with the H $1s$.

The molecular orbital diagram for $[F\text{-}H\text{-}F]^-$ is shown in Figure 5.4.1.4. Notice that all atomic orbitals, group orbitals (SALCs), and molecular orbitals in Figure 5.4.1.4 are assigned a symmetry label that corresponds to each element's symmetry under the D_{2h} point group. The molecular orbital labels correspond to **lower-case Mulliken Labels** of individual reducible representations from the D_{2h} character table. Upper-case symbols are used to indicate symmetry and irreducible representations, while lower-case symbols are used to indicate the identity of an orbital with that symmetry. The labeling methods described for simple diatomic linear molecules (σ, π) are not sufficient to indicate the more complex symmetries of the molecular orbitals in polyatomic molecules. The use of lower-case Mulliken symbols is the most rigorous way to label the orbitals. Refer to your instructor for how you should label orbitals for any graded work.

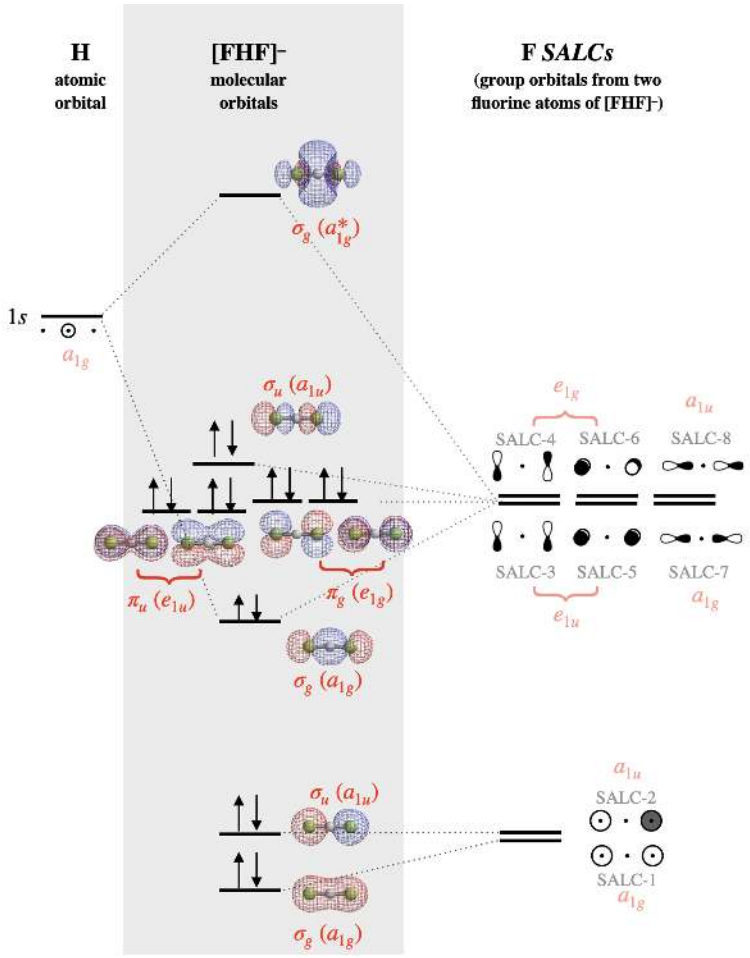


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Figure **5.4.1.4**:The molecular orbital diagram for [F-H-F]⁻. The molecular orbital surfaces and relative energy levels were calculated using Spartan software. SALCs are labeled according to numbers assigned in Figure **5.4.1.2**. The symmetry of each SALC and orbital under the D_{2h} **point group** is shown in red font. (CC-BY-NC-SA; Kathryn Haas)

Click here for a version of Figure 5.4.1.4 using $D_{\infty h}$ labeling:

For high-symmetry groups, a shortcut is to use a lower-symmetry group that maintains the critical symmetry elements. In the case of the $D_{\infty h}$ point group, it is often sufficient to use the approximation of the D_{2h} point group and character table. This is the same MO diagram as shown above, but using the symmetry labels appropriate for the D_{2h} approximation.



Alternate Figure **5.4.1.4**: The molecular orbital diagram for [F-H-F]⁻. The molecular orbital surfaces and relative energy levels were calculated using Spartan software. SALCs are labeled according to numbers assigned in Figure **5.4.1.2**. The symmetry of each SALC and orbital under the D_{2h} **point group** is shown in red font. (CC-BY-NC-SA; Kathryn Haas)

Constructing the MO diagram

After identifying the atomic orbitals and constructing SALCs, place the atomic orbitals of H on one side of the diagram and all SALCs from F on the other side. Molecular orbitals are in the center.

The lowest-energy fluorine SALCs will be those composed of the lowest-energy atomic orbitals of fluorine; these would be SALC-1 (a_{1g}) and SALC-2 (a_{1u}) that are constructed from fluorine s atomic orbitals. Of these two orbitals, the one with zero nodes would be slightly lower in energy than the one with one node. When these two orbitals form molecular orbitals, the completely symmetric SALC-1 will be mostly non-bonding with slight bonding character from minor combination with the hydrogen $1s$ orbital. SALC-2, however is symmetrically incompatible with hydrogen $1s$ and will be a truly non-bonding orbital distributed over both F atoms.

The six SALCs constructed of fluorine p orbitals will have higher energy since the fluorine p atomic orbitals are higher in energy than the s orbitals (SALC-3 through SALC-8). Again, we expect SALCs with more nodes (SALC-4, -6, -8) to have slightly higher

energy than those with fewer nodes (SALC-3, -5, -7). SALC-7 will form a bonding and antibonding interaction with the hydrogen **1*s*** orbital. All other SALCS are truly non-bonding, but are non-degenerate non-bonding orbitals.

In bifluoride, there is an important distinction between the Lewis structure and molecular orbital description of lone pairs. In Lewis theory, the lone pairs are localized to individual fluorine atoms, while in the molecular orbital description each lone pair is distributed over both fluorine atoms at once (see surface depiction of each molecular orbital in Figure **5.4.1.4**).

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5.4.2: Carbon Dioxide

Construct SALCs and the molecular orbital diagram for CO_2

Carbon dioxide is another linear molecule. This example is slightly more complex than the previous example of the bifluoride anion. While bifluoride had only one valence orbital to consider in its central H atom (the $1s$ orbital), carbon dioxide has a larger central atom, and thus more valence orbitals that will interact with SALCs.

Preliminary Steps

Step 1. Find the point group of the molecule and assign Cartesian coordinates so that z is the principal axis.

The CO_2 molecule is linear and its point group is $D_{\infty h}$. The z axis is collinear with the C_∞ axis. We will use the D_{2h} point group as a substitute since the orbital symmetries are retained in the D_{2h} point group.

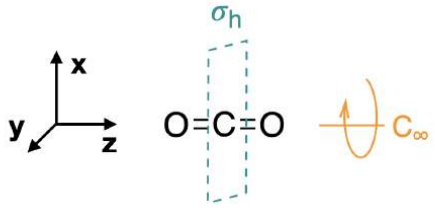


Figure 5.4.2.1: CO_2 belongs to the $D_{\infty h}$ point group. (CC_BY-NC-SA; Kathryn Haas)

Step 2. Identify and count the pendant atoms' valence orbitals.

Each of the two pendant oxygen atoms has four valence orbitals; $2s$, $2p_x$, $2p_y$, and $2p_z$. Thus, we can expect a total of eight SALCs.

Generate SALCs

The SALCs for CO_2 are identical in shape and symmetry to those described in the previous example for the bifluoride anion. But instead of cutting to the shortcut, we will systematically derive the SALCs here to demonstrate the process.

Step 3. Generate the Γ's

Use the D_{2h} character table to generate four reducible representations ($\Gamma's$); one for each of the four types of pendant atom orbitals (s, p_x, p_y, p_z). For each s orbital, assign a value of 1 if it remains in place during the operation or zero if it moves out of its original place. For each p orbital, assign 1 if there is no change, -1 if it remains in place but is inverted, and 0 if it moves out of its original position. The four Γ's are given below:

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Γ_{2s}	2	2	0	0	0	0	2	2
Γ_{2p_x}	2	−2	0	0	0	0	2	−2
Γ_{2p_y}	2	−2	0	0	0	0	−2	2
Γ_{2p_z}	2	2	0	0	0	0	2	2

Step 4. Break Γ's into irreducible representations for individual SALCs

Reduce each Γ into its component irreducible representations. There are two strategies that can be used to do this. The quick and easy way is to do it "by inspection", but this only works well for simple cases. The other is by using the systematic approach for breaking a Γ into reducible representations described previously in section 4.4.2 using the following formula:

$$\text{number of } i = \frac{1}{h}\sum(\text{number of operations in class}) \times (\chi_\Gamma) \times (\chi_i) \tag{5.4.2.1}$$

In other words, the number of irreducible representations of type i is equal to the sum of the number of operations in the class × the character of the Γ_{modes} × the character of i, and that sum is divided by the order of the group (h).

Using either approach results in the following eight irreducible representations ($2A_g + 2B_{1u} + B_{2g} + B_{3u} + B_{3g} + B_{2u}$):

$\mathbf{D_{2h}}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
$\mathbf{\Gamma_{2s} = A_g + B_{1u}}$	$\mathbf{\Gamma_{2s}}$	**2**	**2**	**0**	**0**	**0**	**0**	**2**	**2**
	A_g	1	1	1	1	1	1	1	1
	B_{1u}	1	1	−1	−1	−1	−1	1	1
$\mathbf{\Gamma_{2p_x} = B_{2g} + B_{3u}}$	$\mathbf{\Gamma_{2p_x}}$	**2**	**−2**	**0**	**0**	**0**	**0**	**2**	**−2**
	B_{2g}	1	−1	1	−1	1	−1	1	−1
	B_{3u}	1	−1	−1	1	−1	1	1	−1
$\mathbf{\Gamma_{2p_y} = B_{3g} + B_{2u}}$	$\mathbf{\Gamma_{2p_y}}$	**2**	**−2**	**0**	**0**	**0**	**0**	**−2**	**2**
	B_{3g}	1	−1	−1	1	1	−1	−1	1
	B_{2u}	1	−1	1	−1	−1	1	−1	1
$\mathbf{\Gamma_{2p_z} = A_g + B_{1u}}$	$\mathbf{\Gamma_{2p_z}}$	**2**	**2**	**0**	**0**	**0**	**0**	**2**	**2**
	A_g	1	1	1	1	1	1	1	1
	B_{1u}	1	1	−1	−1	−1	−1	1	1

Step 5. Sketch the SALCs

From the systematic process above, you have found the symmetries (the irreducible representations) of all eight SALCs under the D_{2h} point group. To sketch the SALC that corresponds to each irreducible representation, again we use the D_{2h} character table, and specifically the functions listed on the right side columns of the table.

Two A_g SALCs (one from s and one from p_z): The A_g SALCs are each singly degenerate and symmetric with respect to both the principal axis (z) and the inversion center (i) (based on its Mulliken Label). We can look at the functions in the D_{2h} character table that correspond to A_g and see that it is completely symmetric under the group (because the combination of x^2, y^2, z^2 shows that it is totally symmetric). This would be the same symmetry as an s orbital on the central atom. From this information, we know that these SALCs must have symmetry compatible with an s orbital on the central atom, and we can draw the two A_g SALCs shown in Figure 5.4.2.2.

Two B_{1u} SALCs (one from s and one from p_z): The Mulliken Label tells us that the B_{1u} SALCs are each antisymmetric with respect to both the principal axis and the inversion center. The function, z, appearing with B_{1u} in the character table tells us that these SALCs have the same symmetry as the z axis, or a p_z orbital on the central atom. From this information, we know that these two SALCs should be compatible with a p_z orbital on the central atom, and we can draw the two B_{1u} SALCs shown in Figure 5.4.2.2.

All other SALCs shown below are derived using a strategy similar to the one in the two cases described above.

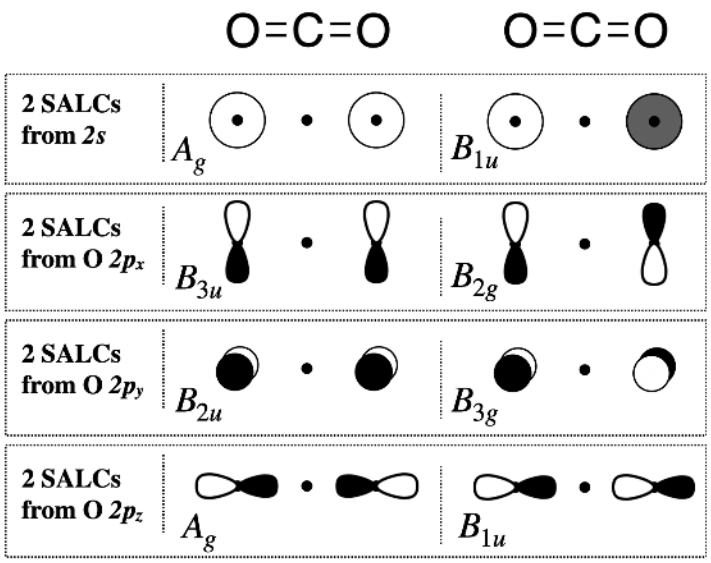


Figure 5.4.2.2: SALCs from the valence orbitals of oxygen atoms in CO_2. (CC-BY-NC-SA; Kathryn Haas)

Draw the MO diagram for CO_2

Step 6. Combine SALCs with AO's of like symmetry.

First we identify the valence orbitals on carbon: there are four including $2s$, $2p_x$, $2p_y$, and $2p_z$. Now we identify the symmetry of each using the D_{2h} character table. The symmetry of a central s orbital corresponds to the combination of functions x^2, y^2, and z^2 in the character table; this is A_g. The p_z orbital corresponds to the symmetry of the linear function z in the character table; this is B_{1u}. And so on... The symmetries of the C valence orbitals are listed below.

$$2s = A_g$$
$$2p_x = B_{3u}$$
$$2p_y = B_{2u}$$
$$2p_z = B_{1u}$$

Now that we have identified the symmetries of the eight oxygen SALCs and the four valence orbitals on carbon, we know which atomic orbitals and SALCs may combine based on compatible symmetries. We also need to know the relative orbital energy levels so that we can predict the relative strength of orbital interactions. The orbital ionization energies are listed in Section 5.3.

With knowledge of both orbital symmetries and energies, we can construct the molecular orbital diagram. The carbon atom goes on one side of the diagram while the oxygen SALCs are drawn on the opposite side. Molecular orbitals are drawn in the center column of the diagram:

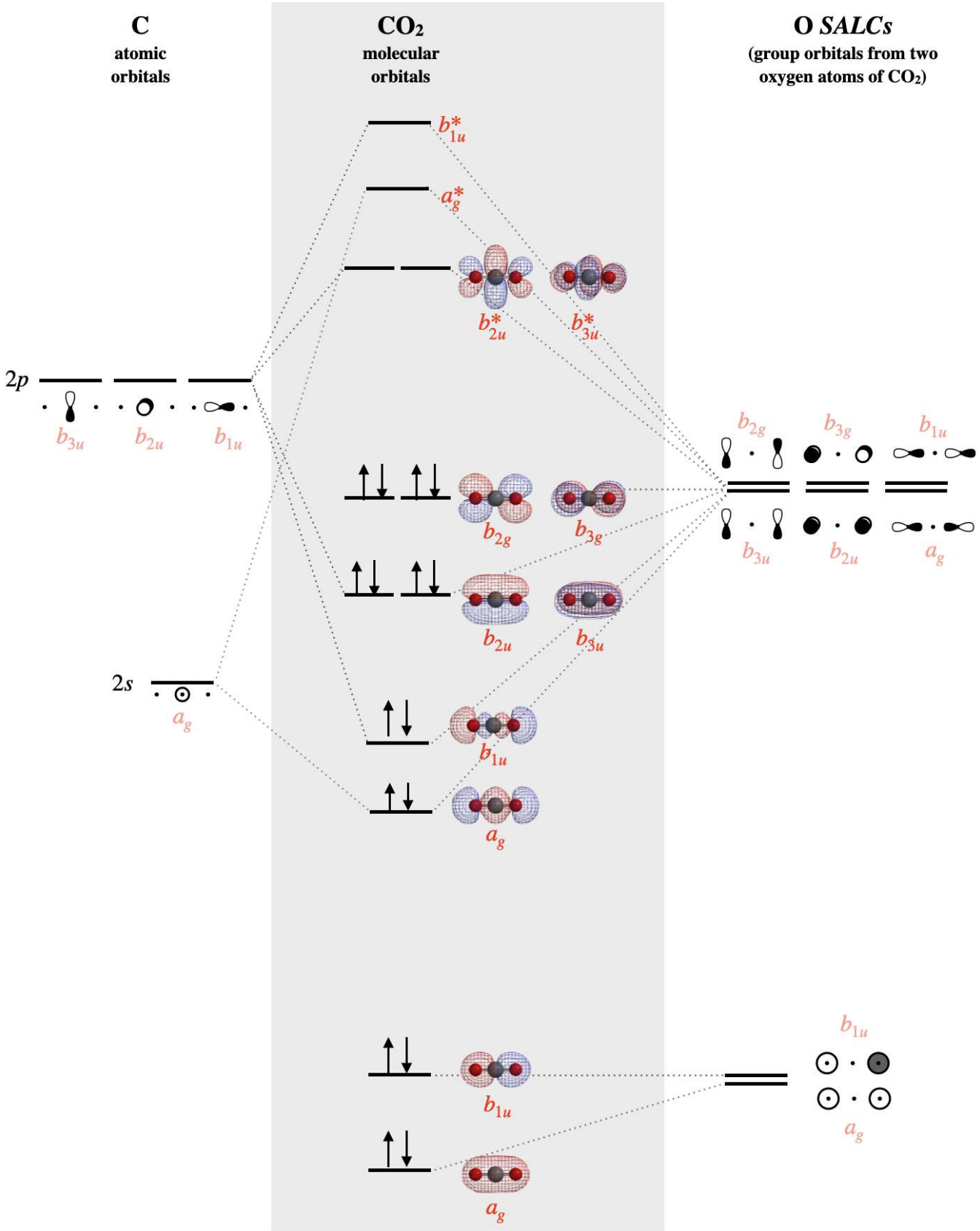


Figure 5.4.2.3: Molecular orbital diagram for carbon dioxide. (CC-BY-NC-SA; Kathryn Haas)

The SALCs on the right side of the diagram above are constructed from groups of either the $2s$ atomic orbitals of oxygen, or the $2p$ atomic orbitals of oxygen. Each SALC will combine with the atomic orbitals of carbon that have compatible symmetry; but the strength of the interaction depends on their relative energies. The individual valence atomic orbitals of oxygen have energies of $-32.36eV$ ($2s$) and $-15.87eV$ ($2p$), while the valence orbitals of carbon have energies of $-19.47eV$ ($2s$) and $-10.66eV$ ($2p$). The $2s$ orbitals of the oxygen are far lower in energy ($-32.36eV$) than all other valence orbitals, and so we should expect that molecular orbitals that are constructed from these oxygen $2s$ will be mostly non-bonding. These mostly non-bonding orbitals are the a_{1g} and b_{1g} orbitals shown at the bottom of Figure 5.4.2.3. The a_g orbital is lower in energy than the b_{1u} due to slight mixing with other orbitals of a_g symmetry.

The bonding orbitals of CO_2 include two $sigma$ molecular orbitals of a_g and b_{1u} symmetry and two π molecular orbitals of b_{2u} and b_{3u} symmetry. Each of these bonding molecular orbitals possesses a higher-energy antibonding partner. The b_{2g} and b_{3g} SALCs that are formed from oxygen $2p_x$ and $2p_y$ orbitals have no compatible match with carbon valence orbitals; thus they form two b_{2g} and b_{3g} molecular orbitals, which are truly non-bonding and mostly oxygen in character. Still, notice that each orbital is spread across both oxygen atoms at once, and again we see that each non-bonding electron pair in the HOMO is very different in molecular orbital theory compared to Lewis theory. Each non-bonding pair is distributed over both oxygen atoms at once in molecular orbital theory, while in Lewis theory each lone pair is isolated to one atom or to localized bonds attached to that atom.

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5.4.3: H_2O

Construct SALCs and the molecular orbital diagram for H_2O.

This is the first example so far that is not a linear molecule. Water is a bent molecule, and so it is important to remember that interactions of pendant ligands are dependent on their positions in space. You should consider the positions of the three atoms in water to be essentially fixed in relation to each other. The process for constructing the molecular orbital diagram *for a non-linear molecule*, like water, is similar to the process for linear molecules. We will walk through the steps below to construct the molecular orbital diagram of water.

Preliminary Steps

Step 1. Find the point group of the molecule and assign Cartesian coordinates so that z is the principal axis.

The H_2O molecule is bent and its point group is C_{2v}. The z axis is collinear with the principal axis, the C_2 axis. There is no need to simplify this problem, as we had done for previous examples. The C_{2v} point group is simple enough.

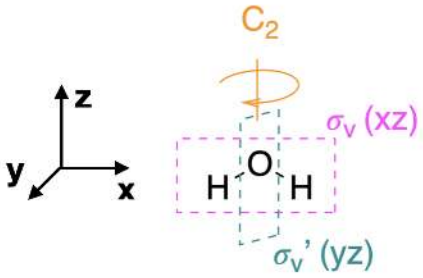


Figure 5.4.3.1: The water molecular is in the C_{2v} point group. (CC-BY-NC-SA; Kathryn Haas)

Step 2. Identify and count the pendant atoms' valence orbitals.

Each of the two pendant hydrogen atoms has one valence orbital, the $1s$. Thus, we can expect a total of two SALCs from these two atoms.

Generate SALCs

The SALCs for H_2O are quite simple, yet we will systematically derive the SALCs here to demonstrate the process.

Step 3. Generate the Γ's

Use the C_{2v} character table to generate one reducible representation (Γ); in this case we need only one Γ because there is only one type of valence orbital (the $1s$). For each s orbital, assign a value of 1 if it remains in place during the operation or zero if it moves out of its original place. The Γ is given below:

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
Γ_{1s}	2	0	2	0

Step 4. Break Γ's into irreducible representations for individual SALCs

Reduce each Γ into its component irreducible representations. Using either of the processes described previously, we find that the Γ reduces to the two irreducible representations A_1 and B_1 under the C_{2v} point group.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
Γ_{1s}	**2**	**0**	**2**	**0**
A_1	1	1	1	1
B_1	1	−1	1	−1

Step 5. Sketch the SALCs

From the systematic process above, you have found the symmetries (the irreducible representations) of both SALCs under the C_{2v} point group. To sketch the SALC that corresponds to each irreducible representation, again we use the C_{2v} character table, and

specifically the functions listed on the right side columns of the table.

One A_1 SALC: The A_1 SALC is singly degenerate and symmetric with respect to both the principle axis (z) and the inversion center (i) (based on its Mulliken Label). We can look at the functions in the C_{2v} character table that correspond to A_1 and see that it is completely symmetric under the group (because the combination of x^2, y^2, z^2 shows that it is totally symmetric). This would be the same symmetry as an s orbital on the central oxygen atom. From this information, we know that this SALC must have symmetry compatible with an s orbital on the central atom. We can also see from the character table that the z axis, and thus a p_z orbital on oxygen, also possesses A_1 symmetry. This tells us that in addition to being compatible with the oxygen s orbital, it should also be compatible with the oxygen p_z orbital. From this information we can draw the A_1 SALC shown in Figure 5.4.3.2. *If it is not obvious how the A_1 sketch in Fig. 5.4.3.2 is compatible with the s and p_z orbitals of oxygen, inspect the drawings corresponding to molecular orbitals $2a_1$ and $3a_1$ in Fig. 5.4.3.3.*

One B_1 SALC: The Mulliken Label tells us that the B_1 SALC is singly degenerate and antisymmetric with respect to both the principal axis and the inversion center. The function, x, appearing with B_1 in the character table tells us that this SALC has the same symmetry as the x axis, or a p_x orbital on the central oxygen atom. From this information, we know that this SALC should be compatible with a p_x orbital on the central atom, and we can draw the B_1 SALCs shown in Figure 5.4.3.2. *If it is not obvious how the B_1 sketch in Fig. 5.4.3.2 is compatible with the p_x orbital of oxygen, inspect the drawing corresponding to molecular orbital $1b_1$ in Fig. 5.4.3.3.*

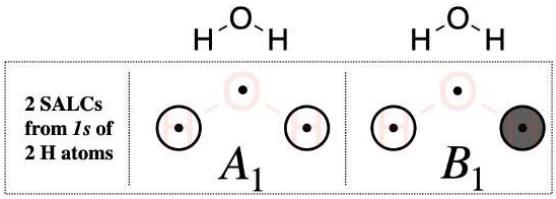


Figure 5.4.3.2: Sketch of the A_1 and B_1 hydrogen SALCs of water. (CC-BY-NC-SA; Kathryn Haas)

Not convinced about the sketches of these SALCs? You can convince yourself by putting them to the test. Try the exercise below.

? Exercise 5.4.3.1

Perform all operations of the C_{2v} point group on the two sketches of H SALCs shown in Figure 5.4.3.2, and convince yourself that each sketch does possess the A_1 and B_1 symmetries assigned to them, respectively, under the C_{2v} point group.

Answer

Add texts here. Do not delete this text first.

Draw the MO diagram for H_2O

Step 6. Combine SALCs with AO's of like symmetry.

First we must identify the valence orbitals on the central oxygen: there are four including $2s$, $2p_x$, $2p_y$, and $2p_z$. Now we identify the symmetry of each using the C_{2v} character table. The symmetry of a central $2s$ orbital corresponds to the combination of functions x^2, y^2, and z^2 in the character table; this is A_1. The p_z orbital also corresponds to A_1. And so on... The symmetries of oxygen valence orbitals are listed below.

$$2s = A_1$$
$$2p_x = B_1$$
$$2p_y = B_2$$
$$2p_z = A_1$$

Now that we have identified the symmetries of the two hydrogen SALCs and the four valence orbitals on oxygen, we know which atomic orbitals and SALCs may combine based on compatible symmetries. We also need to know the relative orbital energy levels so that we can predict the relative strength of orbital interactions. The orbital ionization energies are listed in Section 5.3.1.

With knowledge of both orbital symmetries and energies, we can construct the molecular orbital diagram. The valence orbitals of oxygen go on one side of the diagram while the hydrogen group orbitals are drawn on the opposite side. Molecular orbitals are

drawn in the center column of the diagram, as shown in Figure **5.4.3.3**:

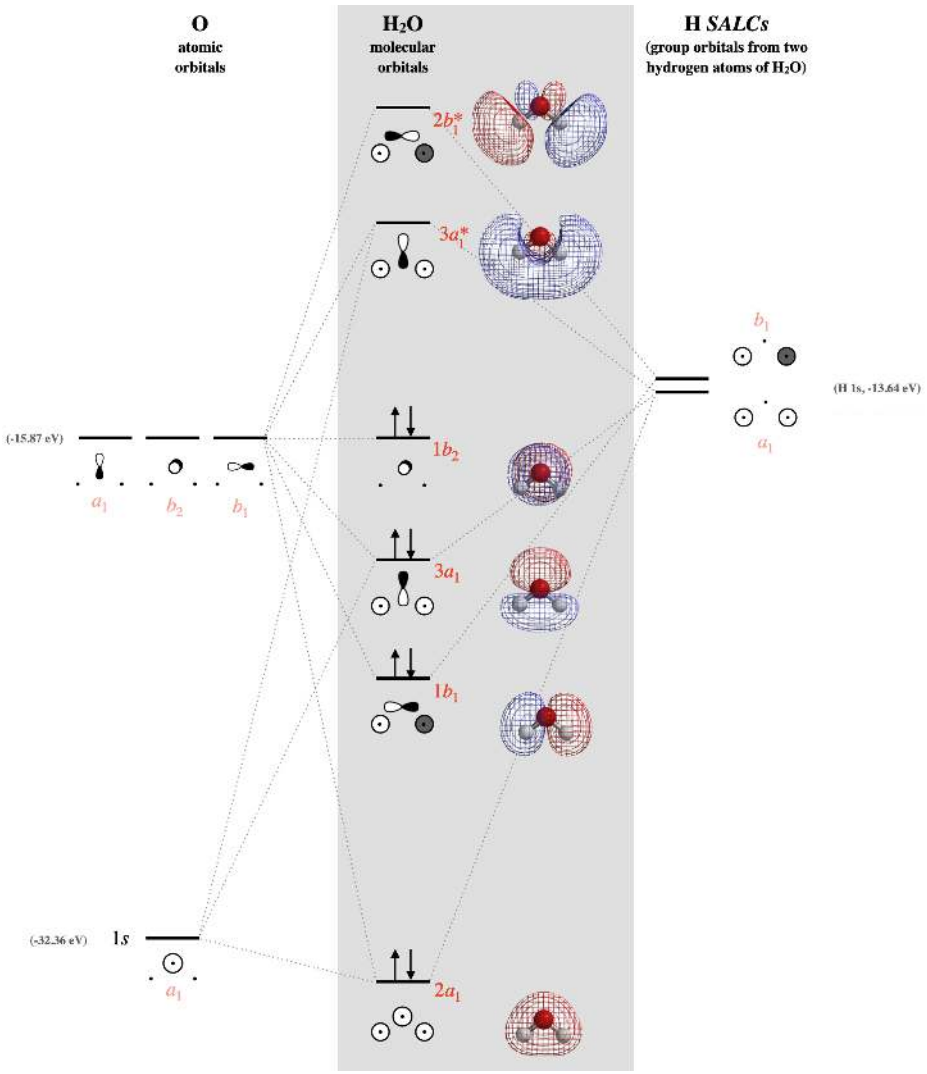


Figure **5.4.3.3**: The molecular orbital diagram of water. Molecular orbital surfaces calculated using Spartan software. The surface of the $3a_1^*$ orbital has been trimmed. (CC-BY-NC-SA; Kathryn Haas)

Example 5.4.3.1

In the previous examples shown for the molecular orbital diagrams of the bifluoride anion and carbon dioxide, we discussed differences in the understanding of those molecules from molecular orbital theory compared to Lewis structures. Water contains two lone pairs in its Lewis structure. Compare the predictions about water's lone pairs of electrons and its reactivity based on (1) the combination of elementary models (Lewis, Valence Bond, and Hybridized Orbital theories) and (2) Molecular Orbital theory. Specifically address and explain how the elementary models differ from molecular orbital theory in the following respects:

a. Where are the lone pairs in water?
b. Are the two lone pairs equivalent or are they different?
c. Where are sites on the molecule that will undergo reaction with electrophiles and nucleophiles?

Solution

1) Elementary models: The Lewis structure predicts that two lone pairs are (a) localized on the oxygen atom of water and that (b) both lone pairs are equivalent. The Lewis structure, combined with Valence Bond Theory, would predict that lone pairs occupy two equivalent hybridized sp^3 atomic orbitals on oxygen. (c) Lewis theory would predict that the oxygen lone pairs are

nucleophiles; thus an electrophile would react with the oxygen atom lone pairs. The polarized O-H bond leaves the H atoms as the most electrophilic locations on the water molecule; thus nucleophiles would react at the H atoms of water.

2) Molecular orbital theory: The molecular orbitals predict that (a) the two lone pairs of water are not equivalent, and that (b) each is distributed over the entire molecule. One lone pair is in the truly non-bonding $1b_2$ orbital (Figure **5.4.3.3**), which is also the HOMO. There is not another truly non-bonding orbital in the molecule, but the lowest-energy $2a_1$ orbital could be considered mostly non-bonding due to the large energy difference between it and other valence orbitals. (c) Although the $2a_1$ orbital can be considered mostly non-bonding, we cannot expect the electrons in $2a_1$ to react readily, as they are in the lowest-energy molecular orbital. Molecular orbital theory predicts that reactions occur at the HOMO and LUMO orbitals. The HOMO reacts with electrophiles, and in this case, the HOMO is distributed over the top and bottom faces of the molecule, and is centered on the oxygen atom. The LUMO would react with nucleophiles. The LUMO is the orbital labeled $3a_1^*$ in Figure **5.4.3.3**, and has a major lobe that is distributed more heavily over the H atoms, and from this we should predict H atoms to be the preferred site of reaction for nucleophiles.

Expressing molecular orbitals in terms of Ψ

The general expression for a molecular orbital, or the linear combination of atomic orbitals (LCAO), was given previously as $\Psi = c_a\psi_a + c_b\psi_b$. In this expression, the wavefunction of two atoms (ψ_a and ψ_b) is combined to form the wavefunction of the molecular orbital. The coefficients c_a and c_b quantify the contribution of each atomic ψ to the molecular Ψ.

$$\Psi = c_a\psi_a + c_b\psi_b$$

In the case of polyatomic orbitals, each LCAO is constructed of atomic orbitals from a central atom and group orbitals (SALCs) from the pendent atoms. In the case of water, the expression above could be modified to give the expression below.

$$\Psi = c_{oxygen}\,(\psi_{oxygen}) + c_{SALCs}\,(N(\psi_{H_a} \pm \psi_{H_b}))$$

N represents the normalizing requirement that was mentioned previously in reference to the requirements for electron wavefunctions and probability functions. The normalizing requirement simply stated is the requirement that the probability of finding the electron in any orbital, including group orbitals, is 1. In general, the value of N for a group orbital is...

$$N = \frac{1}{\sum c_i^2}$$

...where c_i is the coefficient of each unique atomic orbital that contributes to the group. For the hydrogen SALCs of water, there are two atomic orbitals that contribute to equally to each SALC, and so the coefficient on each of the two orbitals is 1. This gives $N = \left(\frac{1}{\sqrt{1^2+1^2}}\right) = \frac{1}{\sqrt{2}}$ for the H SALCs of water.

There are only two hydrogen SALCs: the one in which the hydrogen wavefunctions are added ($N(\psi_{H_a} + \psi_{H_b})$) has A_1 symmetry, and the one in which the hydrogen wavefunctions are subtracted ($N(\psi_{H_a} - \psi_{H_b})$) has B_1 symmetry.

The molecular orbitals from Figure **5.4.3.3** are expressed below in terms of their LCAO of individual wavefunctions. Yet, note that these expressions are simplifications that ignore orbital mixing. For example, as expressed below, they ignore contributions of oxygen $2s$ to the higher energy moelcular orbitals with A_1 symmetry (the $3a_1$ and $3a_1^*$ in Figure **5.4.3.3**).

MO		*OxygenAO*		*HydrogenSALC*	*Description*
Ψ_{2a_1}	=	$c_{(ox1)}\psi_{(2s)}$	+	$c_{(hy1)}[N(\psi_{H_a} + \psi_{H_b})]$	$c_{(hy1)}$ is positive; bonding, slightly nonbonding
Ψ_{1b_1}	=	$c_{(ox2)}\psi_{(2p_x)}$	+	$c_{(hy2)}[N(\psi_{H_a} - \psi_{H_b})]$	$c_{(hy2)}$ is positive; bonding
Ψ_{3a_1}	=	$c_{(ox3)}\psi_{(2p_z)}$	+	$c_{(hy3)}[N(\psi_{H_a} + \psi_{H_b})]$	$c_{(hy3)}$ is positive; bonding
Ψ_{1b_2}	=	$\psi_{(2p_y)}$			nonbonding
$\Psi^*_{3a_1}$	=	$c_{(ox4)}\psi_{(2p_z)}$	+	$c_{(hy4)}[N(\psi_{H_a} + \psi_{H_b})]$	$c_{(hy4)}$ is negative; antibonding
$\Psi^*_{1b_1}$	=	$c_{(ox5)}\psi_{(2p_x)}$	+	$c_{(hy5)}[N(\psi_{H_a} - \psi_{H_b})]$	$c_{(hy5)}$ is negative; antibonding

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5.4.4: NH_3

Construct SALCs and the molecular orbital diagram for NH_3

This is the first example so far that has more than two pendant atoms and the first example in which the molecule has atoms that lie in three dimensions (i.e., it is not flat). Ammonia is a trigonal pyramidal molecule, with three pendant hydrogen atoms. The three-dimensional shape and the odd number of pendant atoms makes this example more complicated than the previous cases of water, carbon dioxide, and bifluoride. In this case, sketching the shapes (step 5) of pendant atom SALCs is less straightforward; rather, an alternative method, the **projection operator method**, is preferred for generating pictorial representations of the SALCs.

As in previous examples, it is important to remember that interactions of pendant ligands are dependent on their positions in three-dimensional space. You should consider the positions of the four atoms in ammonia to be essentially fixed in relation to each other. We will walk through the steps used to construct the molecular orbital diagram of ammonia. The first few steps are the same as you've seen before:

Step 1. Find the point group of the molecule and assign Cartesian coordinates so that z is the principal axis.

The NH_3 molecule is trigonal pyramidal and its point group is C_{3v}. The z axis is collinear with the principal axis, the C_3 axis.

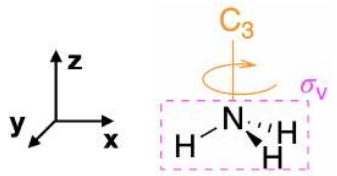


Figure 5.4.4.1: The ammonia molecule is in the C_{3v} point group. (CC-BY-NC-SA; Kathryn Haas)

Step 2. Identify and count the pendant atoms' valence orbitals.

Each of the three pendant hydrogen atoms has one valence orbital; the $1s$. Thus, we can expect a total of three SALCs from these three atoms.

Step 3. Generate the Γ's

Use the C_{3v} character table to generate one reducible representation (Γ); in this case we need only one Γ because there is only one type of valence orbital (the $1s$). For each s orbital, assign a value of 1 if it remains in place during the operation or zero if it moves out of its original place. The Γ is given below:

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_{1s}	3	0	1

Step 4. Break Γ's into irreducible representations for individual SALCs

Reduce each Γ into its component irreducible representations. Using either of the processes described previously, we find that the Γ reduces to the two irreducible representations A_1 and E under the C_{3v} point group.

C_{3v}	E	$2C_3$	$3\sigma_v$
Γ_{1s}	3	0	2
A_1	1	1	1
E	2	−1	0

Notice that we only found TWO irreducible representations. But, in fact we have THREE different SALCs. The E irreducible representation is doubly degenerate, which in this context means that it corresponds to two degenerate SALCs. Thus, we have already found the symmetries of the three SALCs for ammonia: Two of the SALCs are degenerate with E symmetry under the C_{3v} point group, while the third SALC has A_1 symmetry.

Step 5. Sketch the SALCs using the PROJECTION OPERATOR METHOD

From the first four steps (described above), you have found the symmetries (the irreducible representations) of all three SALCs under the C_{3v} point group. To sketch the SALC that corresponds to each irreducible representation, again we use the C_{3v} character

table. But now we will introduce the **projection operator method** to derive the surface representation of each SALC.

Step 5.1: Label the pendent atoms

In the projection operator method, first **label each of the pendant atoms so that we can distinguish identical atoms from one another**; for example, identify the three hydrogen atoms on ammonia as H_a, H_b, and H_c (Figure 5.4.4.2).

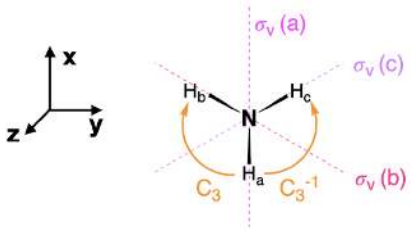


Figure 5.4.4.2: The three H's in NH_3 are chemically identical, but we can distinguish them using labels for the purpose of applying the projection operator method. In this figure, we have placed the z axis along the principal C_3 axis and placed the x axis colinear with one H. Each of the three H atoms has been labeled as H_a, H_b, or H_c. The σ_v that is coplanar with each H is labeled similarly (a, b, c) to keep account of each individual plane of symmetry. (CC-BY-NC-SA; Kathryn Haas)

Step 5.2: Create an expanded character table with one pendant atom's projected position after each operation

We will **perform each operation of the C_{3v} point group on this labeled molecule** and follow where one of the atoms is projected after the operation is complete. We will arbitrarily choose H_a. For example, upon performing the identity operation, E, the H_a atom is projected onto itself. On the other hand, H_a is projected onto H_b upon a clockwise C_3 rotation (as drawn in Figure 5.4.4.2). We take into account the result of each operation using an expanded character table (refer to the table below, 5.4.4.1). In the expanded character table, each operation within each class is written separately (i.e., $2C_3$ is accounted for separately as C_3 and C_3^{-1}).

Table 5.4.4.1: The expanded character table, and the projection of H_a by each operation is shown below.

C_{3v}	E	C_3	C_3^{-1}	$\sigma_v(a)$	$\sigma_v(b)$	$\sigma_v(c)$
Projection of H_a	H_a	H_b	H_c	H_a	H_c	H_b

(5.4.4.1)

Step 5.3: Find the contribution of each pendant atom to each SALC

Next, **create a linear combination of the projections for each of the SALCs** (the irreducible representations found in step 4). For each of the irreducible representations, multiply the projection by the respective character of the operation.

$$\text{Contribution of each atom to the SALC } = \sum(\text{Projection of } H_a \times \chi)$$

The linear combination for all irreducible representations of C_3v is shown below.

Table 5.4.4.2: The symmetry adapted linear combination (SALC) for each irreducible representation of C_3v is shown.

C_{3v}	E	C_3	C_3^{-1}	$\sigma_v(a)$	$\sigma_v(b)$	$\sigma_v(c)$	Linear Combination
Projection of H_a	H_a	H_b	H_c	H_a	H_c	H_b	
A_1	1	1	1	1	1	1	$= 2H_a + 2H_b + 2H_c$
A_2	1	1	1	−1	−1	−1	$= 0$
E	2	−1	−1	0	0	0	$= 2H_a - H_b - H_c$

(5.4.4.2)

Notice that there are only two irreducible representations that produce SALCs, and these are the same that were found in Step 4, above. This illustrates the fact that only the irreducible representations found through the reduction of the Γ will produce SALCs. We can ignore any irreducible representations that were not found in Step 4. Or, you can check your work in Step 4 by applying the projection operator to any irreducible representations not found in Step 4, and finding that they produce a sum of zero.

Step 5.4: Sketch the SALCs

The meaning of the linear combinations found in Table 5.4.4.2 is as follows:

- **Sketch the SALC with A_1 symmetry:** The linear combination $2H_a + 2H_b + 2H_c$ indicates all contributions to this SALC are of the same sign (of the wavefunction). Qualitatively, this means there is no node in this SALC. We can take this SALC almost literally to assume that all three H 1s wavefunctions contribute equally to the SALC. We can also use the fact that the A_1 representation possesses the full symmetry of the C_3v point group, is compatible with an s orbital on N, and thus is a totally symmetric SALC.

  Quantitatively, we can apply the normalizing factor, N, for this SALC. The linear combination for the A_1 SALC in Table 5.4.4.2 shows us that the coefficient for each orbital is 1. Thus, the normalizing factor for the A_1 SALC is $N = \left(\frac{1}{\sqrt{1^2+1^2+1^2}}\right) = \frac{1}{\sqrt{3}}$. This tells us that H_a, H_b, and H_c each contribute $\frac{1}{\sqrt{3}}$ to the normalized A_1 group orbital:

  $$A_1 \text{ group orbital } = \frac{1}{\sqrt{3}}\left[\psi_{H_a} + \psi_{H_b} + \psi_{H_c}\right]$$

  This is shown visually in Figure 5.4.4.3.
- **Sketch two SALCs with E symmetry:** The linear combination $2H_a - H_b - H_c$ indicates that there are contributions with both positive and negative sign to the wavefunction for each of the E group orbitals. Qualitatively, this tells us that there is a node within each of these two SALCs, and that the total contribution of the positive portion of the wavefunction is equal to the contribution of the negative portion.
  - **Finding the first E SALC:**
    For one of the SALCs, we can take the linear combination from Table 5.4.4.2 almost literally: The contribution from H_a is equal and opposite to the sum of the contributions from $H_b + H_c$. This would result in a SALC as shown in Figure 5.4.4.3 (E, left), that would have symmetry of the x axis and that would be compatible with the p_x orbital on N. The node exists in the yz plane and there is an equal contribution of positive and negative parts of the total wavefunction.

    We can also apply the normalizing factor, N, to find this SALC. The linear combination for the E SALC in Table 5.4.4.2 shows us that the coefficients for orbital contributions are 2, -1, and -1. Thus, the normalizing factor for the first E SALC is $N = \left(\frac{1}{\sqrt{2^2+(-1)^2+(-1)^2}}\right) = \frac{1}{\sqrt{6}}$. This normalized E group orbital is:

    $$\text{First } E \text{ group orbital } = \frac{1}{\sqrt{6}}\left[2\psi_{H_a} - \psi_{H_b} - \psi_{H_c}\right]$$

    This is shown visually in Figure 5.4.4.3 (E, left).
  - **Finding the second E SALC:**
    The second SALC is less obvious at first glance. We must use clues from the character table to help us determine what it should "look like". Since the E representation transforms as the group, (x, y), we know that one of the SALCs will have the symmetry of the x axis and p_x orbital on the central nitrogen atom, while the other should possess the symmetry of the y axis and be compatible with the p_y orbital on nitrogen. This alone could lead you to the sketch of the second SALC with E symmetry shown in Figure 5.4.4.3 (E, right). This second E SALC must have a node in the xz plane, and because H_a lies in this node, H_a cannot contribute to this group orbital. Retaining the fact that the positive and negative contributions of the linear combination must be equal, we can arrive at a SALC that has equal but opposite contributions of H_b and H_c, and no contribution by H_c (Figure 5.4.4.3, right).

    We can also apply the normalizing factor, N, to find this SALC. But we must apply the fact that H_a cannot contribute to the SALC with "y" symmetry. We remove the contribution of H_a, leaving us with coefficients of 0 for H_a and 1 for H_b and H_c. Thus, the normalizing factor for the second E SALC is $N = \left(\frac{1}{\sqrt{0^2+1^2+1^2}}\right) = \frac{1}{\sqrt{2}}$. To this, we must add positive and negative coefficients so that the entire wavefunction of this SALC is normalized. The result for this normalized E group orbital is:

    $$\text{Second } E \text{ group orbital } = \frac{1}{\sqrt{2}}\left[\psi_{H_b} - \psi_{H_c}\right]$$

    This is shown visually in Figure 5.4.4.3.

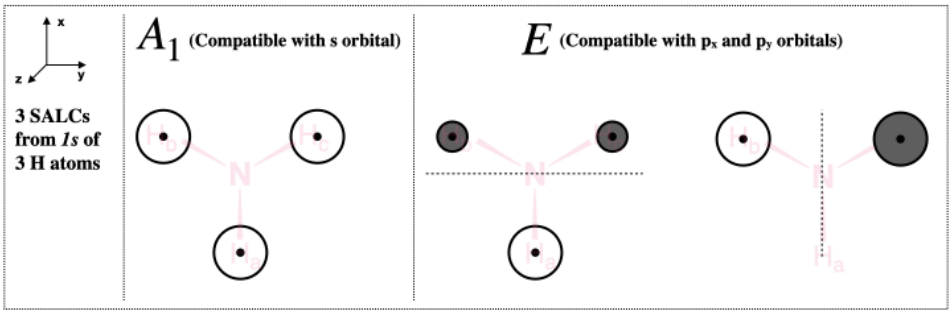


Figure 5.4.4.3: Sketches of H SALCs of ammonia from the perspective of the C_3 axiz (z axis). The A_1 SALC is shown at the left, while two degenerate SALCs with E symmetry are shown on the right. Nodes for E group orbitals are shown as dashed lines. (CC-BY-NC-SA; Kathryn Haas)

Step 6. Combine SALCs with AO's of like symmetry to draw the MO diagram for NH_3

First we must identify the valence orbitals on the central nitrogen: there are four including $2s$, $2p_x$, $2p_y$, and $2p_z$. Now we identify the symmetry of each using the C_{3v} character table. The symmetry of a central $2s$ orbital corresponds to the combination of functions x^2, y^2, and z^2 in the character table; this is A_1. The p_z orbital also corresponds to A_1. And so on... The symmetries of nitrogen valence orbitals are listed below.

$$2s = A_1$$
$$(2p_x,\ 2p_y) = E$$
$$2p_z = A_1$$

The next step is to get a sense of the relative energies of valence atomic orbitals for nitrogen and hydrogen, and then construct the molecular orbital diagram. The nitrogen $2s$ orbital is about 12 eV lower in energy than a H $1s$. This difference is an acceptable energy-match for the H orbitals to interact, but would not usually result in a strong interaction. On the other hand, the nitrogen 2p orbitals have an energy very close to the hydrogen 1s, different by only 0.5 eV. Knowledge of the relative energies of the atomic orbitals tells us that, when constructing a diagram, we can place the H SALCs at an energy similar to that of the N $2p$ orbitals, while the N $2s$ is much lower (Figure 5.4.4.4).

The $2s$ and $2p_z$ orbitals have A_1 symmetry and can combine with the A_1 SALC. These orbitals will give three molecular orbitals. The $2s$ orbital will not have strong interactions with the other orbitals of A_1 symmetry due to the large energy difference. The $2p_z$ orbital will not have good overlap with the wavefunctions for the three hydrogen orbitals due to their positions in space: The $2p_z$ orbital has half of its angular distribution pointed away from the hydrogen orbitals, and half pointed toward the center of a triangle formed by the three hydrogen atoms. The nitrogen $2s$ and $2p_z$ will combine with the hydrogen SALC of A_1 symmetry to give three molecular orbitals; one low-energy bonding orbital, one mid-energy non-bonding orbital, and one high-energy antibonding orbital. The mid-level non-bonding a_1 molecular orbital is close in energy to, and resembles, the nitrogen $2p_z$ orbital. The lowest energy a_1 molecular orbital will be lower in energy, but be similar to the nitrogen $2s$.

The remaining two $2p$ orbitals are degenerate and possess E symmetry under the C_{3v} point group. Although these orbitals are a good energy match, again, their orientation and positions in space do not allow for good orbital overlap, and their bonding and antibonding interactions are relatively weak compared to what we might otherwise expect from such a good energy match. The e atomic orbitals of nitrogen will combine with the e SALCs to give a set of two degenerate bonding molecular orbitals and a set of two degenerate antibonding orbitals (four total molecular orbitals of e symmetry). The MO diagram for NH_3 is shown in Figure 5.4.4.4, with calculated electron density surfaces of each MO shown.

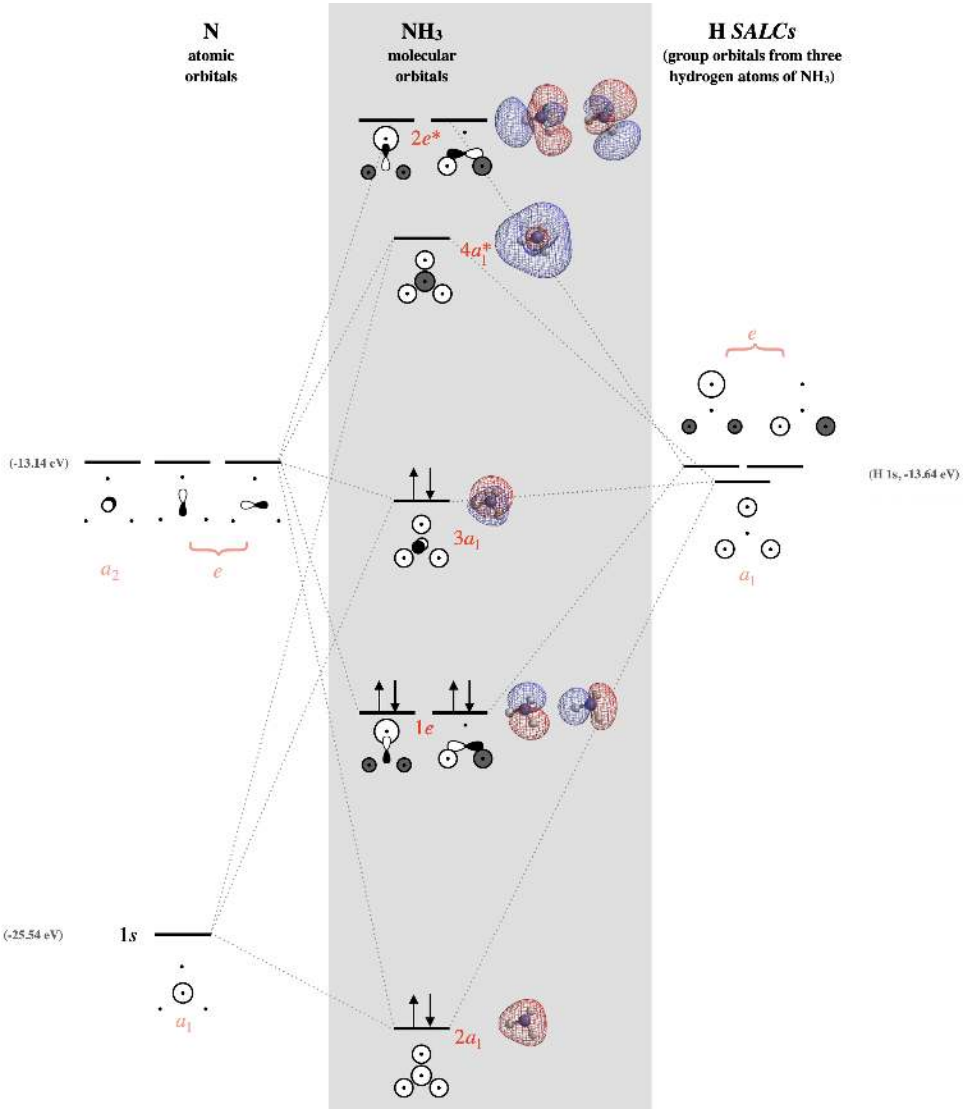


Figure **5.4.4.4**: The molecular orbital diagram of ammonia. Molecular orbitals surfaces calculated using Spartan software. (CC-BY-NC-SA; Kathryn Haas)

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5.4.5: CO_2 (Revisted with Projection Operators)

The process for finding SALCs and constructing the molecular orbital diagram for carbon dioxide was described in a previous section (Section 5.4.2). However, we also just presented an alternative strategy, the projection operator method, to finding the shapes of SALCs in Section 5.4.4. Let's revisit carbon dioxide and demonstrate how you can use the projection operator method to find SALCs for carbon dioxide.

Just as before, we can simplify the problem by approximating the $D_{\infty h}$point group using D_{2h}. The first four steps for constructing the MO diagram would be the same as described in Section 5.4.2. and we will pick up from that point (with Step 5) to find what the SALCs look like using the projection operator method.

The projection operator method applied to CO_2

Step 5.1: Label the pendent atoms.

We can label the pendant atoms as O_a and O_b, as in Figure 5.4.5.1.

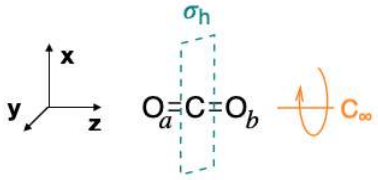


Figure 5.4.5.1: The structure of carbon dioxide with pendant oxygen atoms distinguished with labels a and b. Note that we will approximate the C_∞ axis as a C_2 axis to simplify the process of finding the SALCs. (CC-BY-SA; Kathryn Haas)

Step 5.2: Create an expanded character table with one pendant atom's projected position for each operation

The D_{2h} character table needs no expansion because each operation is in its own class. We will arbitrarily choose to determine the new position of O_a after each operation.

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
Projection of O_a	O_a	O_a	O_b	O_b	O_b	O_b	O_a	O_a

Step 5.3: Find the contribution of each pendant atom to each SALC

Create a linear combination of the projections for each or the SALCs. The irreducible representations were found in step 4 in Section 5.4.2. Eight irreducible representations were found to be: $2A_g + 2B_{1u} + B_{2g} + B_{3u} + B_{3g} + B_{2u}$. For each of the irreducible representations, multiply the projection by the respective character of the operation.

$$\text{Contribution of each atom to the SALC } = \sum(\text{Projection of } H_a \times \chi)$$

The linear combination for all irreducible representations of D_{2h} are shown below.

Table 5.4.5.1: The symmetry adapted linear combination (SALC) for each irreducible representations of C_3v are shown.

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	Linear Combination
Projection of O_a	O_a	O_a	O_b	O_b	O_b	O_b	O_a	O_a	
A_g	1	1	1	1	1	1	1	1	$= 4O_a + 4O_b$
B_{1u}	1	1	−1	−1	−1	−1	1	1	$= 4O_a - 4O_b$
B_{2g}	1	−1	1	−1	1	−1	1	−1	$= 0$
B_{3u}	1	−1	−1	1	−1	1	1	−1	$= 0$
B_{3g}	1	−1	−1	1	1	−1	−1	1	$= 0$
B_{2u}	1	−1	1	−1	−1	1	−1	1	$= 0$

(5.4.5.1)

Notice that there are only two irreducible representations that produce SALCs, the A_g and the B_{1u}. Since we found two of each ($2A_g + 2B_{1u}$) when we found the irreducible representations, we know that there will be two SALCs of A_g symmetry and two of B_{1u}

symmetry; that is four total SALCs from the pendant oxygens. This is the same as what we found in Section 5.4.2 using a different method.

Step 5.4: Sketch the SALCs

The SALCs with A_g symmetry: Quantitatively, we can apply the normalizing factor, N, for these SALCs. Each atom contributes equally to the SALCs, thus the normalizing factor for the A_g SALC is $N = \left(\frac{1}{\sqrt{1^2+1^2}}\right) = \frac{1}{\sqrt{2}}$. This tells us that each oxygen contributes $\frac{1}{\sqrt{2}}$ to each of the normalized A_g group orbitals:

$$A_g \text{ group orbital } = \frac{1}{\sqrt{2}}\left[\psi_{O_a} + \psi_{O_b}\right]$$

The linear combination $\mathbf{4O_a + 4O_b}$ indicates that wavefunctions from each oxygen atom contribute equally to each of the two SALCs, with the same sign of the wavefunction for each. Because we know that A_g is totally symmetric (all 1's in the characters), we can assume that the SALC's will look like a symmetric arrangement of oxygen orbitals. But which orbitals contribute? We could peek at the character table to get a hint. But we'll treat this problem systematically.

The SALCs with B_{1u} symmetry: The linear combination $\mathbf{4O_a - 4O_b}$ indicates that each oxygen atom contributes equally, but that they have opposite wavefunctions. Application of the normalizing factor would give us:

$$B_{1u} \text{ group orbital } = \frac{1}{\sqrt{2}}\left[\psi_{O_a} + \psi_{O_b}\right]$$

But how do we know what the SALCs look like? Again, the character table can give us some hints, but we'll use a systematic process, below.

What do the SALCs look like? One way to systematically derive the SALC shapes is to perform the projection (Step 5.3) on specific groups of orbitals on the oxygen atom. For example, if we replicate Table 5.4.5.1 using just the group of oxygen 2s orbitals and the A_g and B_{1u} representations, we get the following:

$\mathbf{D_{2h}}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	Linear Combination
Projection of 2s orbital of O_a	$\mathbf{O1s_a}$	$\mathbf{O1s_a}$	$\mathbf{O1s_b}$	$\mathbf{O1s_b}$	$\mathbf{O1s_b}$	$\mathbf{O1s_b}$	$\mathbf{O1s_a}$	$\mathbf{O1s_a}$	
A_g	1	1	1	1	1	1	1	1	$\mathbf{= 4O1s_a + 4O1s_b}$
B_{1u}	1	1	−1	−1	−1	−1	1	1	$\mathbf{= 4O1s_a - 4O1s_b}$

(5.4.5.2)

This tells us that one of the A_g SALCs looks like two oxygen 1s orbitals with equal signs and contributions. It also tells us that one of the B_{1u} SALCs looks like two s orbitals with opposite signs and equal magnitudes. These two SALCs are shown in Figure 5.4.5.2.

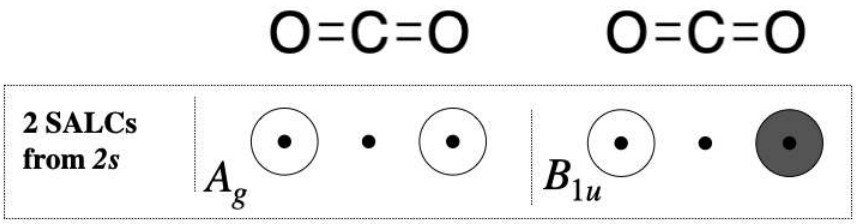


Figure 5.4.5.2: SALCs derived from two oxygen $2s$ orbitals from carbon dioxide. Compare to Section 5.4.2. (CC-BY-SA; Kathryn Haas)

If we do the same for the $2p_z$ orbitals, we need to pay attention to the orientation of the p orbital lobes. If the orbital is moved into the opposite orientation, it would get a negative sign in the projection (see below).

$\mathbf{D_{2h}}$	E	C_2 (z)	C_2 (y)	C_2 (x)	i	$\sigma(x$ $y)$	$\sigma(x$ $z)$	$\sigma(yz)$	Linear Combination
Projection of 2px orbital of O_a	$+O2$ pz_a	$+O2$ pz_a	$-O2$ pz_b	$+O2$ pz_b	$-O2$ pz_b	$-O2$ pz_b	$+O2$ pz_a	$+O2$ pz_a	
A_g	1	1	1	1	1	1	1	1	$= 4O2pz_a$ $- 4O2pz_b$
B_{1u}	1	1	−1	−1	−1	−1	1	1	$= 4O2pz_a$ $+ 4O2pz_b$

(5.4.5.3)

This tells us that one of the A_g SALCs is derived from two $2p_z$ orbitals of opposite sign but equal magnitude. In other words, the two p orbitals are pointing in opposite directions, but the lobes that are facing one another are of the same sign (see Figure 5.4.5.3, left). This also tells us that one of the B_{1u} orbitals is derived from two p_z orbitals of equal magnitude and equal sign (pointing in the same directions, with lobes facing one another of opposite sign!) (see Figure 5.4.5.3, right).

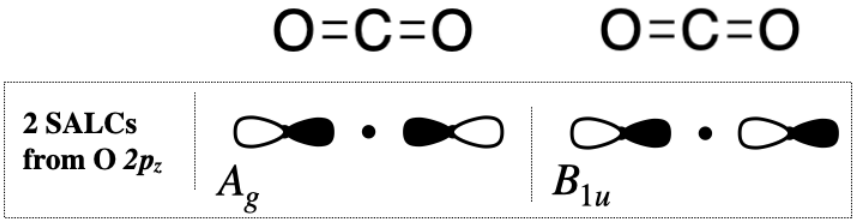


Figure 5.4.5.3: SALCs derived from two oxygen $2p_z$ orbitals from carbon dioxide. Compare to Section 5.4.2. (CC-BY-SA; Kathryn Haas)

Now we have reached the same SALCs that we found previously in Section 5.4.2, but by an alternate method.

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5.4.6: BF_3

The case of boron trifluoride (BF_3) is an example of a molecule with one more layer of complexity than the other examples we have seen in previous sections in this chapter. (BF_3) is more complex than previous examples because it is the first case in which there are multiple types of valence orbitals on the pendant atoms. (BF_3) possesses s and p orbitals on *both* the central atom and all of the pendant atoms. We can follow the same steps that we have previously to derive other molecular orbital diagrams; however, there is one important difference: we will treat each type of pendant orbital as an individual set of SALCs.

Step 1. Find the point group of the molecule and assign Cartesian coordinates so that z is the principal axis.

The BH_3 molecule is trigonal planar, and its point group is D_{3h}. The z axis is colinear with the principle axis, the C_3 axis.

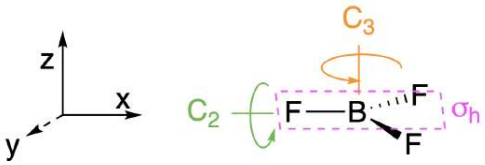


Figure 5.4.6.1: The molecule is in the D_{3h} point group. (CC-BY-NC-SA; Kathryn Haas)

Step 2. Identify and count the pendant atoms' valence orbitals.

Each of the three pendant fluorine atoms has four valence orbitals: one $2s$ and three $2p$ orbitals. Thus, we can expect a total of twelve SALCs from the three atoms. However, we will treat each type of orbital from the F atoms as its own set; each will have its own set of coordinates, with the y axis along the M-L bond. Thus we expect the following:

- One set of $2s$ SALCs: there is one 2s orbital on each of three atoms. This set will have three SALCs.
- One set of $2p_x$ SALCs: there is one $2p_x$ orbital on each of three atoms. Each of these individual orbitals is perpendicular to the M-L bond and coplanar with the molecule. This set will have three SALCs.
- One set of $2p_y$ SALCs: there is one $2p_y$ orbital on each of three atoms. Each of these individual orbitals is colinear with the M-L bond. This set will have three SALCs.
- One set of $2p_z$ SALCs: there is one $2p_z$ orbital on each of three atoms. Each of these individual orbitals is perpendicular to the M-L bond and parallel with the principal axis of the molecule. This set will have three SALCs.

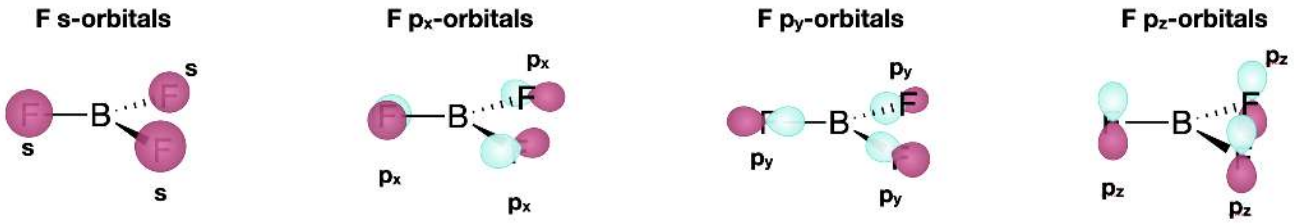


Figure 5.4.6.2: Individual sets of pendant fluorine atomic orbitals will create separate sets of SALCs. (CC-BY-SA; Kathryn Haas)

Step 3. Generate the Γ's for each set of SALCs

Use the D_{3h} character table to generate one reducible representation (Γ) for each of the four sets of pendant atomic orbitals shown in Figure 5.4.6.2; in this case we need four Γ because there are four types of valence orbital (the s, p_x, p_y, p_z).

- For the set of s orbitals: perform the operation for each class in the character table. Each s orbital is assigned a value depending on whether it moves or not: assign a value of 1 if it remains in place during the operation, or 0 (zero) if it moves out of its original place.
- for each set of p orbitals: Now there are phases (signs of the wavefunction), so a negative value is possible. Assign a value of 1 to each p orbital if it remains in place and in phase during the operation; assign a -1 if the atom's position remains, while the phase of the orbital is inverted (the positive lobe moves to the position of the negative lobe and vice versa); assign a 0 if it moves out of its original position.

The Γ for each type is given below:

$\mathbf{D_{3h}}$	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\mathbf{\Gamma_{2s}}$	3	0	1	3	0	1
$\mathbf{\Gamma_{2p_x}}$	3	0	−1	3	0	−1
$\mathbf{\Gamma_{2p_y}}$	3	0	1	3	0	1
$\mathbf{\Gamma_{2p_z}}$	3	0	−1	−3	0	1

Step 4. Break Γ's into irreducible representations for individual SALCs

Reduce each $\mathbf{\Gamma}$ into its component irreducible representations. Using either of the processes described previously, we find that each of the $\mathbf{\Gamma}$ reduces to two irreducible representations under the $\boldsymbol{D_{3h}}$ point group; in each case one is singly degenerate ($\boldsymbol{A}$) and the other doubly degenerate ($\boldsymbol{E}$). This equates to three SALCs for each $\mathbf{\Gamma}$ (orbital type) and a total of twelve SALCs. This should give us confidence! We were in fact expecting 12 SALCs because we found that there were twelve pendant atomic orbitals to start with.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\mathbf{\Gamma_{2s}}$	**3**	**0**	**1**	**3**	**0**	**1**
A_1'	1	1	1	1	1	1
E'	2	−1	0	2	−1	0

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\mathbf{\Gamma_{2p_x}}$	**3**	**0**	**−1**	**3**	**0**	**−1**
A_2'	1	1	−1	1	1	−1
E'	2	−1	0	2	−1	0

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\mathbf{\Gamma_{2p_y}}$	**3**	**0**	**1**	**3**	**0**	**1**
A_1'	1	1	1	1	1	1
E'	2	−1	0	2	−1	0

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
$\mathbf{\Gamma_{2p_z}}$	**3**	**0**	**−1**	**−3**	**0**	**1**
A_2''	1	1	−1	−1	−1	1
E''	2	−1	0	−2	1	0

Step 5: Sketch the SALCs

We'll skip this step for now to make this problem simpler.

Step 6: Draw the MO diagram by combining SALCs with AO's of like symmetry.

We now know the symmetries of different pendant orbital SALCs - and it is helpful if we also know their relative energies, and the energies of the valence orbitals on the central boron atom. We can make predictions based on periodic trends, or we can use a table of ionization energies as a guide. The symmetries of the boron $\boldsymbol{2s}$ and $\boldsymbol{2p}$ orbitals can be found from the $\boldsymbol{D_{3h}}$ character table.

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5.P: Problems

Concept Review Questions

1. What are the assumptions (axioms) of molecular orbital (MO) theory?

2. Explain qualitatively why the vectorial addition of atomic orbitals creates molecular orbitals (which underlying physical phenomenon is described by the vectorial addition?).

3. Explain qualitatively why molecular orbital theory is suitable to describe covalent bonding.

4. What are the three criteria that determine the degree of covalent interaction in MO theory?

5. Which three rules determine the degree of orbital overlap in MO theory?

6. Explain why the combination of a large, diffuse orbital and a small orbital produces only weak covalent interaction.

7. Explain why sigma interactions between atomic orbitals typically produce larger orbital overlaps than pi interactions.

8. Explain why the combination of orbitals of the same energy leads to the largest degree of covalent interaction.

9. What can be said about energy and location of a bonding and an anti-bonding molecular orbital that are made from atomic orbitals of large energy difference?

10. MO theory – even though designed for covalent bonding – can also make statements about ionic bonding. Explain why.

11. Explain the principles of SALC.

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Homework Problems

Section 1

Exercise 1

What will most likely lead to the smallest covalent interaction?

a) Overlap of a small and a large orbital.

b) Overlap of two small orbitals.

c) Overlap of two large orbitals.

Answer

a) Overlap of a small and a large orbital.

Exercise 2

What will most likely lead to the largest covalent interaction?

a) orbital overlap in sigma-fashion

b) orbital overlap in pi-fashion

c) orbital overlap in delta-fashion

Answer

a) orbital overlap in sigma-fashion

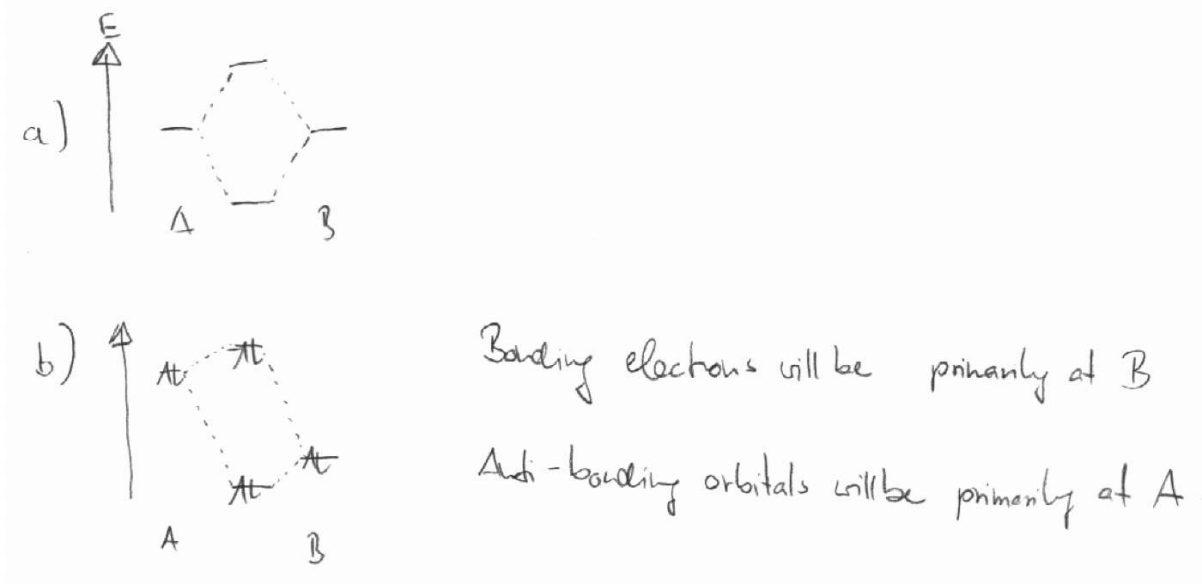
Exercise 3

Qualitatively construct the MO diagrams composed of

a) two 2s atom orbitals A and B of equal energy.

b) two 2s atom orbitals where the orbital energy of atom A is significantly higher than that of B. If both the bonding and the antibonding MO are filled with electrons, where will bonding and antibonding electrons primarily be located? Briefly explain your decision.

Answer



Exercise 4

Decide by "inspection" which of the following combinations of orbitals have the "right" symmetries to form molecular orbitals.

a) The $2p_x$ orbital of the first N atom and the $2p_y$ orbital of the second N atom in the molecule N_2. The z axis is defined as the bond axis in N_2.

b) The F $2p_x$ and the H 1s orbital in the HF molecule. The z axis is defined as the bond axis.

c) The $2p_z$ orbital of F and the 1s orbital in the HF molecule. The z axis is defined as the bond axis.

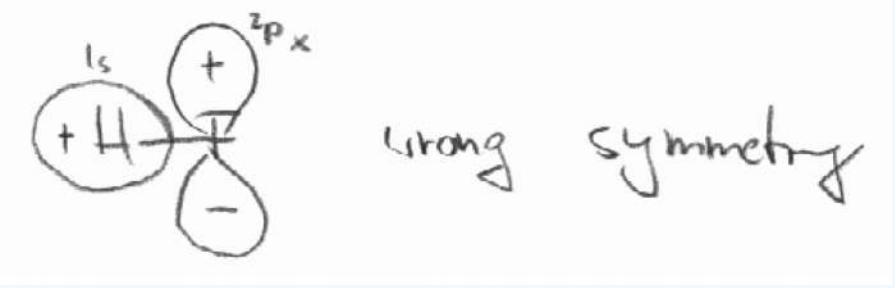
Answer

a)



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b)



c)



Exercise 5

The CH_4 molecule belongs to the point group T_d. You can find the character table of the point group in the internet.

a) Calculate the reducible representation for the ligand group orbitals (LGOs).

b) Calculate the irreducible representations of the ligand group orbitals (LGOs).

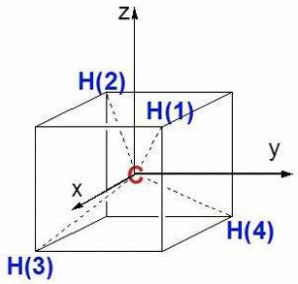
c) Draw a qualitative molecular orbital diagram for CH_4.

Answer

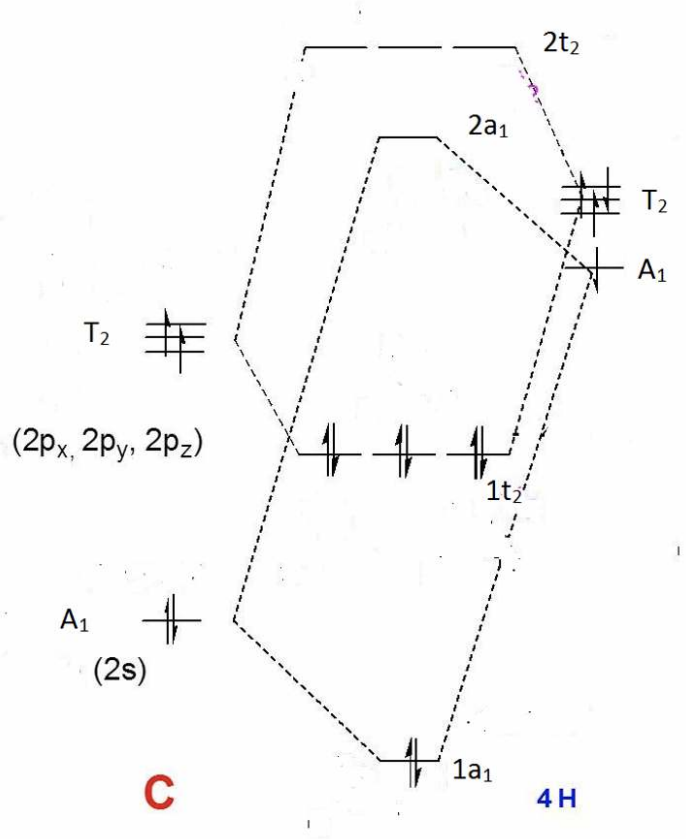
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The symmetry of 4H group orbitals:

$\Gamma_r = 4E+1C_3+0C_2+0S_4+2\sigma_d = A_1 + T_2$



T_d		
A_1		$x^2+y^2+z^2$
A_2		
E		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	(R_x,R_y,R_z)	
T_2	(x,y,z)	(xz, yz, xy)



Exercise 6

Which are the symmetry types of the central atom orbitals in the PCl_5 molecule?

Answer

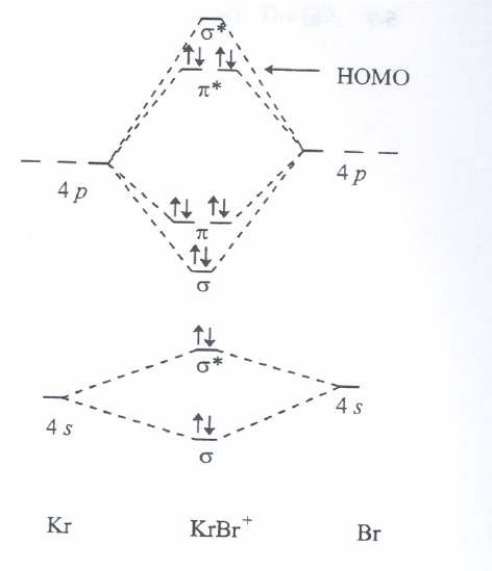
1. Determine point group of PCl_5. --> D_{3h}.
2. Decide what are the valence orbitals of the central atom: 3s, 3p
3. Look up the character table of D_{3h}, e.g., in the internet. You will find their symmetries to be: A_1' (3s), A_2'' ($3p_z$), E'($3p_x$, $3p_y$)

Exercise 7

For the hypothetical $BrKr^+$ molecule: Toward which atom is the HOMO polarized? Explain briefly why.

Answer

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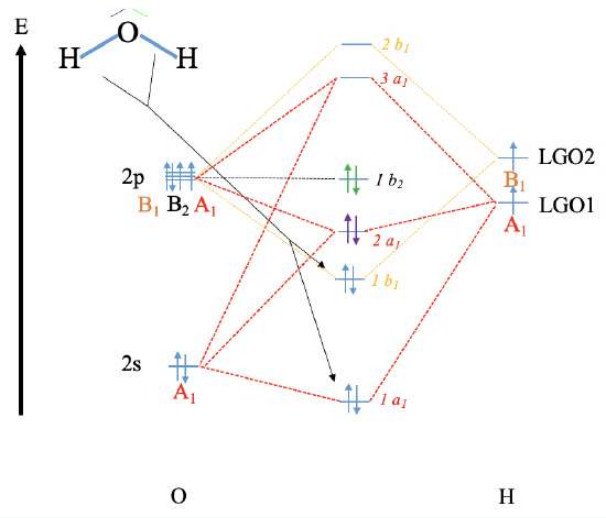
Orbital energies of Kr must be somewhat lower than the ones of Br because the electrons experience higher effective nuclear charge (Z_{eff} increases within a period). This means that the antibonding HOMO is polarized towards Br (HOMO energetically closer to 4p(Br) than 4p(Kr)).

Exercise 8

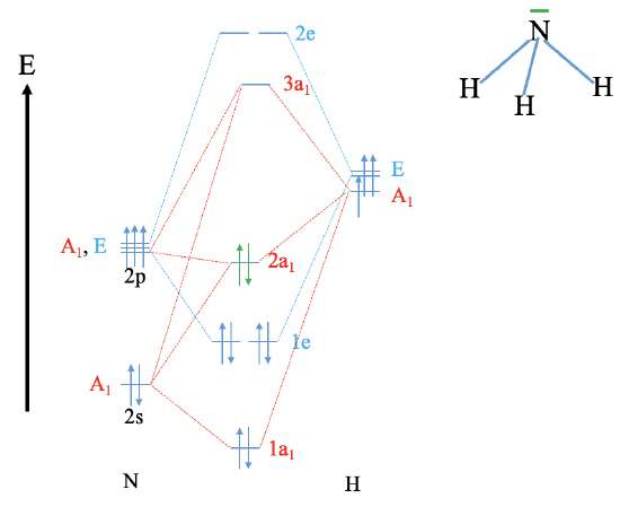
Reconstruct the MO diagram for water and NH_3 (repeat what we did in class without looking at your notes (only use the respective character tables).

Answer

Water



NH_3



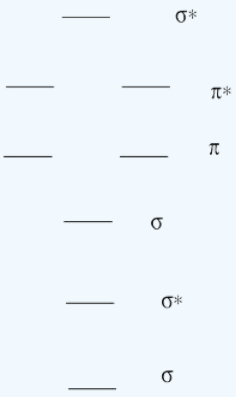
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Exercise 5.P.1

A Molecular Orbital Diagram for a diatomic molecule (two atoms) always has the same basic pattern.

- Draw a picture of the levels.
- Label each level with σ, σ*, π, π*

Answer



Exercise 5.P.2

A Molecular Orbital Diagram for a diatomic molecule (two atoms) varies in the number of electrons. How do you populate the electrons?

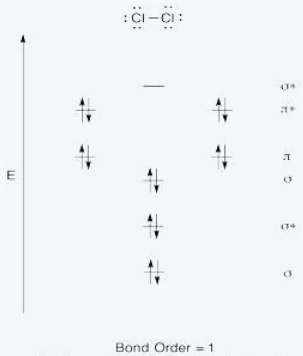
Answer

• Count the valence electrons on the molecule. That's the number of valence electrons on each atom, adjusted for any charge on the molecule. (eg C_2^{2-} has 10 valence electrons: 4 from each carbon -- that's 8 -- and two more for the 2- charge).
• Fill electrons into the lowest energy orbitals first.
• Pair electrons after all orbitals at the same energy level have one electron.

Exercise 5.P.3

Construct a qualitative molecular orbital diagram for chlorine, Cl_2. Compare the bond order to that seen in the Lewis structure (remember that an electron in an antibonding orbital cancels the stabilization due to bonding of an electron in a bonding orbital).

Answer

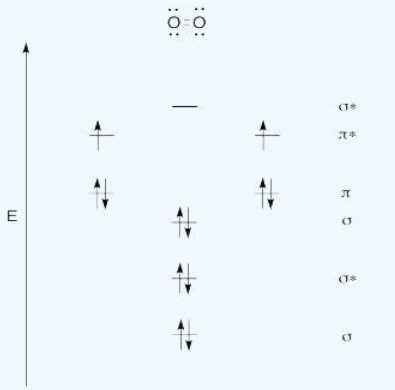


Bond Order = 1
MO diagram matches the Lewis structure

Exercise 5.P.4

a. Construct a qualitative molecular orbital diagram for oxygen, O_2.
b. Compare the bond order to that seen in the Lewis structure.
c. How else does this MO picture of oxygen compare to the Lewis structure? What do the two structures tell you about electron pairing?
d. Compounds that have all of their electrons paired are referred to as diamagnetic. Those with unpaired electrons are referred to as paramagnetic. Paramagnetic materials are attracted by a magnetic field, but diamagnetic things are not. How would you expect molecular oxygen to behave?

Answer



Bond Order = 2
MO diagram indicates two unpaired electrons and therefore does not match the Lewis structure. Based on the MO diagram oxygen would be paramagnetic and would be attracted to a magnetic field

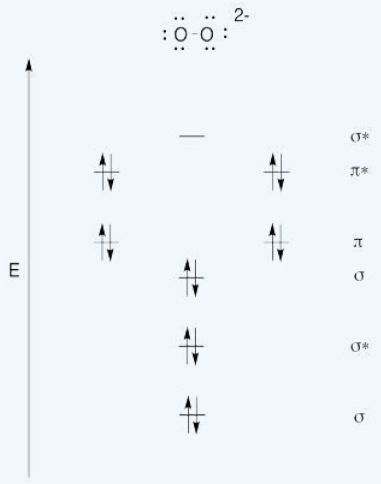
Exercise 5.P.5

a. Construct a qualitative molecular orbital diagram for peroxide anion, O_2^{2-}.
b. Compare the bond order to that seen in the Lewis structure.
c. How else does this MO picture of oxygen compare to the Lewis structure? What do the two structures tell you about electron pairing?

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d. Based on molecular orbital pictures, how easily do you think dioxygen could be reduced to peroxide (through the addition of two electrons)?

Answer

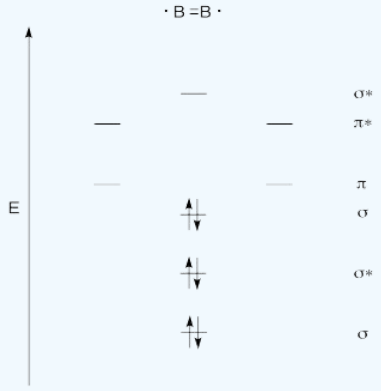


Bond Order = 1
MO diagram matches the Lewis structure. Both predict a Bond Order of 1 and 6 lone pairs of electrons. The addition of two electrons to O_2 to O_2^{2-} would be possible.

Exercise 5.P.6

Construct a qualitative molecular orbital diagram for diboron, B_2. Do you think boron-boron bonds could form easily, based on this picture?

Answer



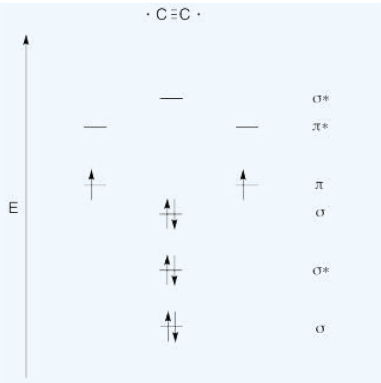
Bond Order = 1
Boron-Boron bonding should be possible

Exercise 5.P.7

a. Construct a qualitative molecular orbital diagram for dicarbon, C_2.
b. Compare the bond order to that seen in the Lewis structure.
c. How else does this MO picture of oxygen compare to the Lewis structure? What do the two structures tell you about electron pairing?

Answer

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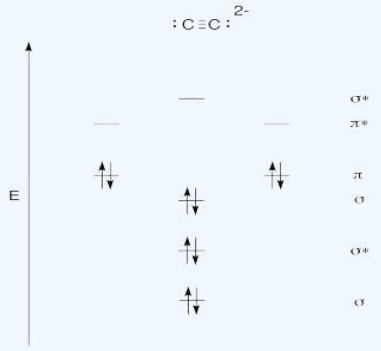


Bond Order = 2
MO diagram does not match the Lewis structure.
However, the MO diagram does concur about the
2 unpaired electrons.

Exercise 5.P.8

a. Construct a qualitative molecular orbital diagram for acetylide anion, C_2^{2-}.
b. Compare the bond order to that seen in the Lewis structure.
c. How else does this MO picture of oxygen compare to the Lewis structure? What do the two structures tell you about electron pairing?
d. Based on molecular orbital pictures, how easily do you think dicarbon could be reduced to acetylide (through the addition of two electrons)?

Answer

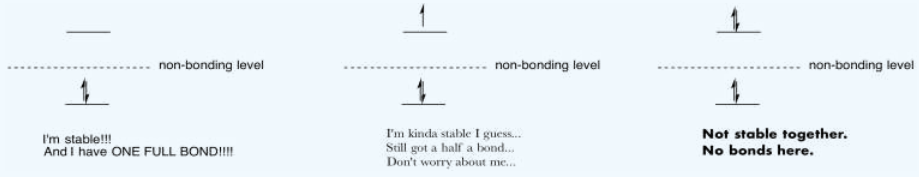


Bond Order = 3
MO diagram matches the Lewis structure.
Both predict a Bond Order of 3 and 2 lone
pairs of electrons. The addition of two
electrons to C_2 to C_2^{2-} would be possible.

Exercise 5.P.9

Make drawings and notes to summarize the effect of populating antibonding orbitals.

Answer



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Exercise 5.*P*.10

Researchers at Johns Hopkins recently reported the formation of Na_4Al_2 in a pulsed arc discharge (they put a lot of electric current through a sample of sodium and aluminum; Xinxing Zhang, Ivan A. Popov, Katie A. Lundell, Haopeng Wang, Chaonan Mu, Wei Wang, Hansgeorg Schnöckel, Alexander I. Boldyrev, Kit H. Bowen, *Angewandte Chemie International Edition*, **2018**, *57*(43), 14060-14064. Copyright 2018, John Wiley & Sons. Used with permission.).

a. The compound is ionic. Explain which atoms form the cations, based on periodic trends.
b. Therefore, what atoms form the anion?
c. The anion is one molecule. What is the charge on this molecule?
d. Show how to calculate the total valence electrons in this molecular anion.
e. Draw a Lewis structure for this molecular anion.
f. Construct a diatomic molecular orbital energy level diagram for this molecule. Label the energy levels (sigma, pi, etc.) and add in the correct number of electrons.
g. Show how to calculate the bond order in the molecule.

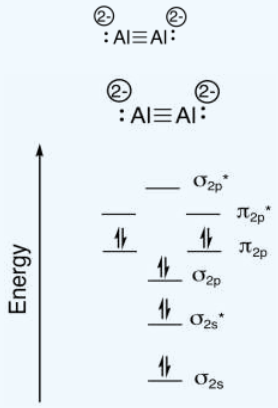
Answer

a) Na, because Na has a lower ionization potential (and a lower electronegativity) than Al.

b) Al

c) 4-, because there are four Na^+

d) total e^- = 2 x 3 e^- (per Al) + 4 e^- (for the negative charge) = 10 e-



g) bond order= $\frac{(\#bonding\ e^- - \#antibonding\ 3^-)}{2} = \frac{8-2}{2} = 3$

Exercise 5.*P*.1

Draw the molecular orbital diagram for (NO^-).

Answer

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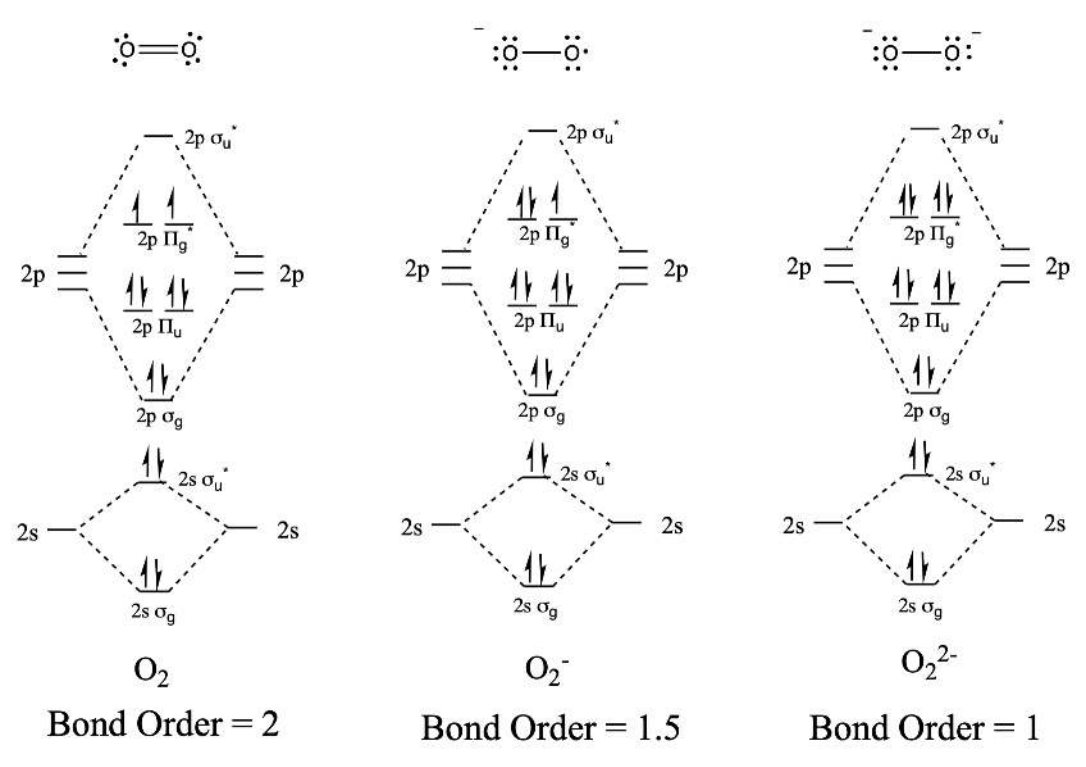
Exercise 5.*P*.1

Draw and compare the molecular orbital diagrams to the Lewis structure diagrams for O_2, O_2^-, and O_2^{2-}.

Answer

The Lewis structures and MO diagrams are shown below. In general, the bond order derived from the MO diagram agrees with the Lewis structure for each species. In the case of the two ions, the number of unpaired electrons from MO theory and the Lewis structure also agrees. In the case of dioxygen, however, there is an inconsistency between the Lewis

representation and the MO diagram. While the Lewis structure would lead us to believe that all electrons are paired, the MO diagram indicates paramagnetism, with two unpaired electrons. The MO diagram explains the magnetic behaviour of dioxygen.



Exercise 5.*P*.1

Draw the molecular orbital diagram for hydroxide ion (OH^-).

Answer

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Exercise 5.*P*.1

Draw the molecular orbital diagram for hydroxide fluoride (**HF**).

Answer

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Exercise 5.*P*.1

Draw the molecular orbital diagram for borane (**BN**).

Answer

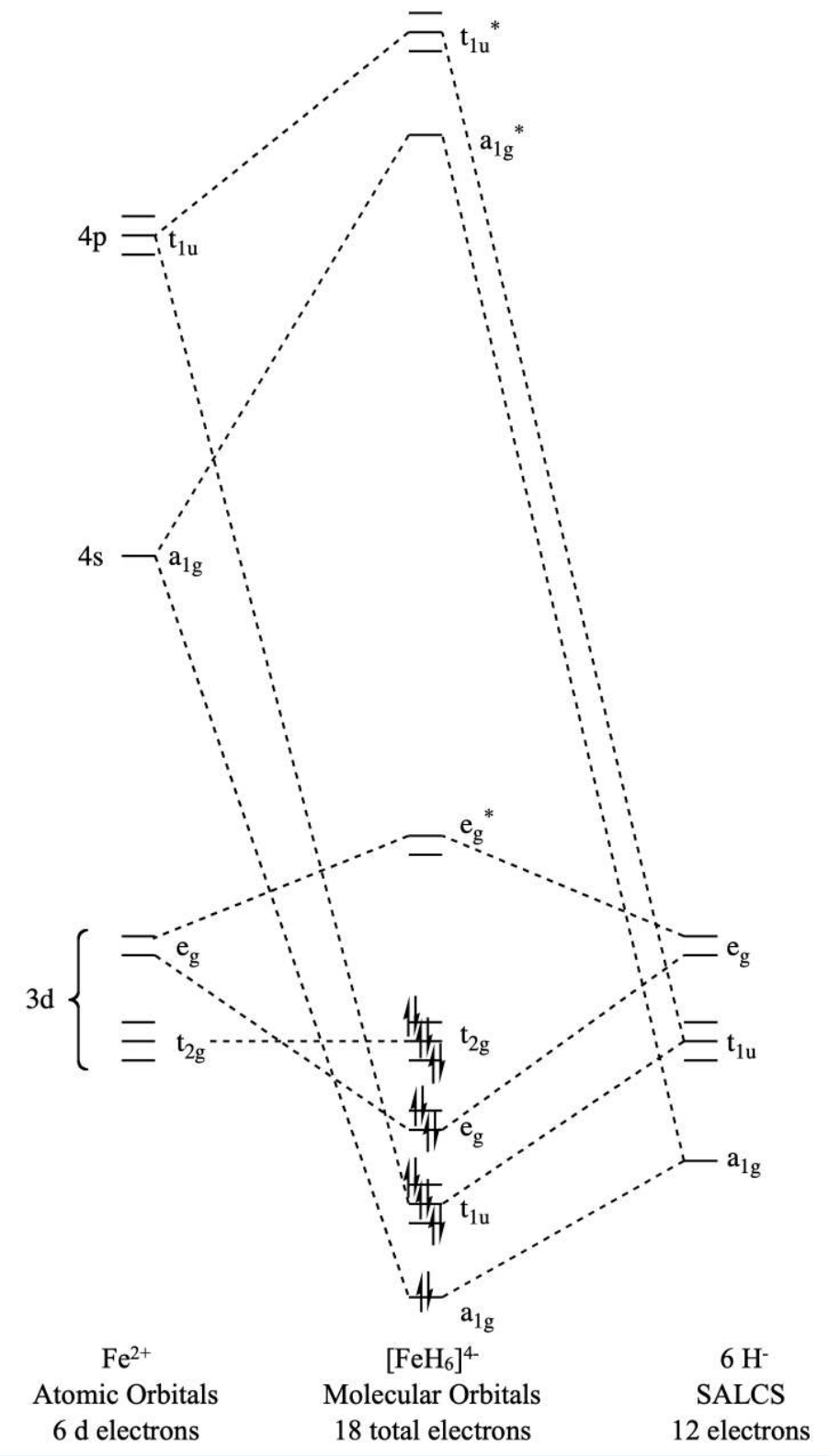
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BH3

Exercise 5.*P*.1

Draw the molecular orbital diagram for (FeH_6).

Answer



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Exercise 5.P.1

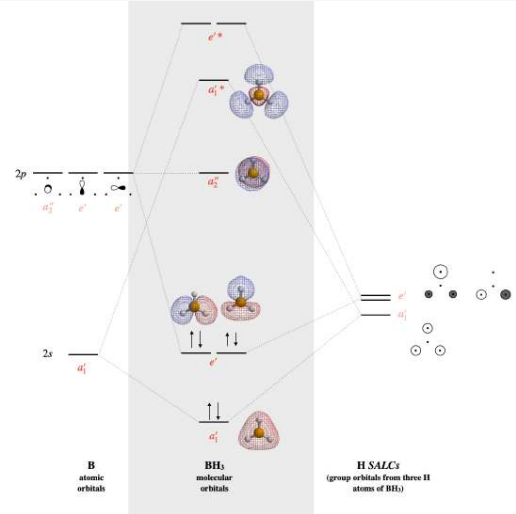
Draw the molecular orbital diagram for boron trifluoride (BF_3).

- What is the non-bonding orbital?
- What are the HOMO and LUMO orbitals?
- Why does e' have 2 lines of energy levels compared to a1', which has only a 1-line energy level?
- What is the bond order of BH_3 in this MO diagram?

Answer

The calculated MO diagram is shown below.

- a_2'' is the lone non-bonding orbital.
- The HOMO is the a_2'' nonbonding orbital, the LUMO is a bonding e' set of two degenerate orbitals/
- e' is doubly degenerate
- The bond order is 3



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CHAPTER OVERVIEW

6: Acid-Base and Donor-Acceptor Chemistry

6.1: Acid-Base Models as Organizing Concepts

6.2: Lewis Concept and Frontier Orbitals

6.2.1: The frontier orbital approach considers Lewis acid-base reactions in terms of the donation of electrons from the base's highest occupied orbital into the acid's lowest unoccupied orbital.

6.2.2: 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

6.2.3: The electronic spectra of charge transfer complexes illustrate the impact of frontier orbital interactions on the electronic structure of Lewis acid-base adducts

6.2.4: Bulky groups weaken the strength of Lewis acids and bases because they introduce steric strain into the resulting acid-base adduct.

6.2.5: Frustrated Lewis pair chemistry uses Lewis acid and base sites within a molecule that are sterically restricted from forming an adduct with each other.

6.3: Hard and Soft Acids and Bases

6.3.1: Hard-Hard and Soft-Soft preferences may be explained and quantified in terms of electrostatic and covalent and electronic stabilization on the stability of Lewis acid-base adducts

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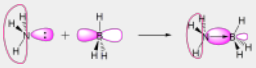
6.1: Acid-Base Models as Organizing Concepts

> *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. In particular it assesses proton donation to & removal from water using [H_3O^+] as a proxy. Readily accommodates the pH concept as a measure of the state of a solution.	Increases [H_3O^+]	Decreases [H_3O^+]	$\underset{acid}{HCl} + H_2O \rightarrow H_3O^+ + Cl^-$ $\underset{base}{NH_3} + H_2O \rightarrow NH_4^+ + OH^-$
Brønsted-Lowry (1923)	Envisions acid-base reactivity in terms of the transfer of an H^+ from one substance to another. Allows for conjugate acids and bases and solvent autoionization.	Donates H^+	Accepts H^+	$\underset{acid}{HCl} + \underset{base}{NH_3} \rightarrow \underset{conj.\ acid}{NH_4^+} + \underset{conj.\ base}{Cl^-}$ $\underset{acid}{HOAc} + \underset{base}{NH_3} \rightarrow \underset{conj.\ acid}{NH_4^+} + \underset{conj.\ base}{OAc^-}$ $\underset{amphoteric}{2\ H_2O} \rightarrow \underset{conj.\ acid}{H_3O^+} + \underset{conj.\ base}{OH^-}$
Lux-Flood (1939-~47)	Describes reactions involving oxides and oxyanions in terms of the transfer of oxide ion (O^{2-}). Mainly used in geochemistry, although it also can be used to describe some redox reactions.	Oxide acceptor	Oxide donor	$\underset{acid}{SiO_2} + \underset{base}{CaO} \rightarrow CaSiO_3$ $\underset{base}{H_2O} + \underset{acid}{CO} \rightarrow H_2 + CO_2$
Solvent System	Applies aspects of the Arrhenius , Brønsted-Lowry, and Lux-Flood acid base concepts to solvent cation & anion formation in a generalized reaction. Can be used to describe solution chemistry in nonaqueous solvent systems like BrF_3.	Is a solvent cation or increases the solvent cation concentration, often by receiving a lone pair- bearing group	Is a solvent anion or increases the solvent anion concentration, often by donating a lone pair- bearing group	$\underset{acid}{SbF_5} + \underset{base}{BrF_3} \rightarrow \underset{conj.\ base}{SbF_6^-} + \underset{conj.\ acid}{BrF_2^+}$ $\underset{amphoteric}{2\ BrF_3} \rightarrow \underset{conj.\ acid}{BrF_2^+} + \underset{conj.\ base}{BrF_4^-}$
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	Accepts an electron pair	Donates an electron pair	$\underset{base}{:NH_3} + \underset{acid}{BF_3} \rightarrow H_3N + BF_3$

Definition	Theoretical paradigm and notable features.	Acid	Base	Illustrative sample reactions
	integrates with molecular orbital descriptions of chemical reactivity in Frontier orbital theory.			
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	$\underset{base}{Br^-} + \underset{acid}{CH_3-Cl} \rightarrow Br-CH_3 + Cl^-$
Usanovich (1939)	Extends Lewis theory to include the donation and acceptance of any number of electrons, whether through the formation of an adduct or electron transfer.	Accepts electrons	Donates electrons	$\underset{base}{:NH_3} + \underset{acid}{BH_3} \rightarrow \underset{adduct}{H_3N-BH_3}$ $\underset{acid}{Fe^{2+}} + \underset{base}{Zn^0} \rightarrow Fe^0 + Zn^{2+}$
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 LUMO 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 Arrhenius and Brønsted acid 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, the solvent system acid-base concept defines acids and bases in terms of the transfer of a lone-pair bearing group and is particularly useful for conceptualizing the reactivity of main group halides, oxides, and related compounds. Some acid-base definitions seek to encompass an extremely wide range of chemical reactions. For instance, the Lewis acid-base definition encompasses the Arrhenius , Brønsted, and solvent system definitions and has also found wide use in inorganic chemistry owing to the ease with which 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.

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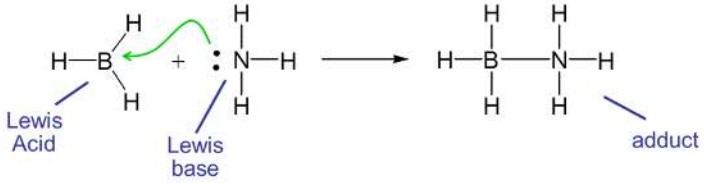
6.2: Lewis Concept and Frontier Orbitals

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.

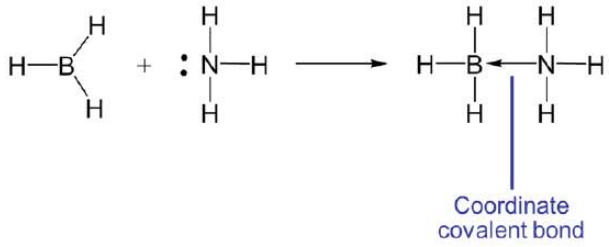
Under the Lewis definition

- **Lewis acids** are electron pair acceptors
- **Lewis bases** are electron pair donors

and 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:

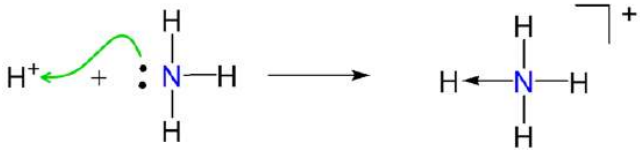


In this case the Lewis acid-base reaction results in the formation of a bond between BH_3, and NH_3. When the acid and base combine to form a larger unit, that unit is said to be an adduct, and the resulting bond is said to be a coordinate covalent or dative bond. Such coordinate covalent bonds are often 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

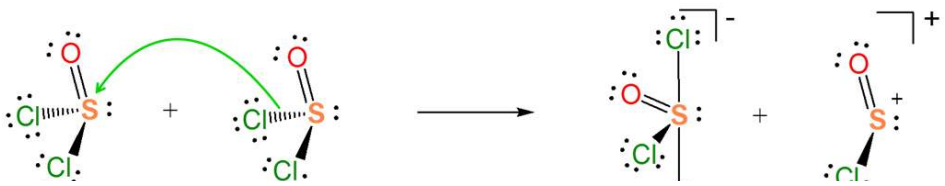


The arrow notation for the coordinate covalent bond is really just a convenient formalism - a bookkeeping tool to help keep track of where the electrons came from and where they might return if the reverse reaction occurs. In actuality a coordinate covalent bond is just an ordinary covalent bond like any other.

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, Brønsted acid-base reactions involve the formation of an adduct between H^+ and a base.



The Lewis acid-base concept nicely explains ionization reactions involving nonaqueous solvents. For instance, the autoionization of $SOCl_2$ is an acid-base reaction between two $SOCl_2$ molecules.



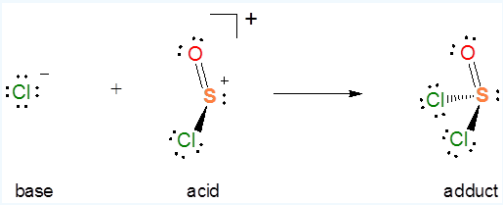


Example 6.2.1

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 a Cl^- base and an $SOCl^+$ 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:

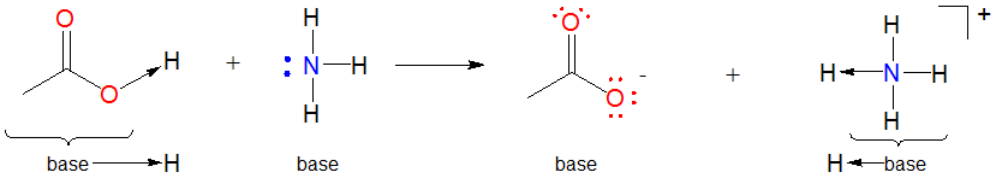


From the autoionization reaction it is also apparent that $SOCl_2$ itself acts as a Lewis acid towards the liberated Cl^-. So the autoionization reaction involves a transfer of the Cl^- base between the two Lewis acids - a Lewis acid-base displacement reaction.



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 to 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.

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:

$$Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-$$

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 Arrhenius 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.

$$Al(OH)_3 + 3H^+ + 3H_2O \rightarrow Al(H_2O)_6^{3+}$$

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
- Arrhenius 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

Substances that rapidly undergo Lewis acid-base reactions are called nucleophiles and electrophiles.

Two factors govern the course of chemical reactions - thermodynamics and kinetics. Thermodyamics determines what possible fates of the reaction can take place while kinetics determines which among those possible fates will take place quickly under a particular set of reaction conditions. Because of this, it can be helpful to distinguish Lewis acids and bases that tend to undergo reaction quickly with one another from those which do so more slowly. For this reason, synthetic chemists use the terms electrophile and nucleophile to refer to Lewis acids and bases that react quickly:

- electrophile - Lewis acids that rapidly react with a given Lewis base or class of Lewis bases are said to be good electrophiles
- nucleophile - Lewis bases that rapidly react with a given Lewis acid or class of Lewis acids are said to be good nucleophiles

The electrophile-nucleophile concept is sometimes referred to as the Ingold-Robinson acid-base concept after two organic chemists who did much to illustrate the utility of thinking about Lewis acid-base reactions in kinetic terms.

Several distinctions that should be kept in mind when using the electrophile-nucleophile/Ingold-Robinson concept to think about chemical reactivity:

1. Whether a given Lewis acid or base is able to react rapidly depends on the reaction conditions and the substrate (substance it is reacting with). This means that in principle, the terms nucleophile and electrophile should not be used without appropriately qualifying what the substances act as a nucleophile or electrophile towards and under what conditions. Unfortunately this is rarely done. In such cases, the conditions and substrate must be inferred from the context. For instance, when you learned that the chloride ion is a good nucleophile when studying organic chemistry, what was meant is that chloride is a good nucleophile towards electrophilic carbon atoms in organic molecules.

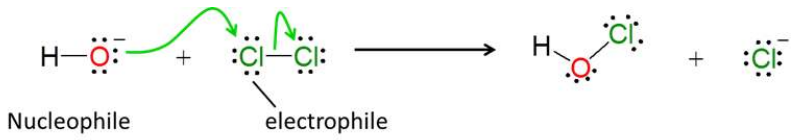
2. Acid and base strength and electrophilicity-nucleophilicity are not exactly the same thing. In many contexts where Lewis acids and bases are classified as electrophilic and nucleophilic substances, it is common to also refer to substances as being good acids or bases on the basis of their Brønsted acidity and basicity. In these contexts, the terms acid and base typically refer to the thermodynamic propensity of a substance to give and accept hydrogen ions while the terms nucleophile and electrophile refer to a substance's kinetic propensity to react with carbon-based Lewis acids and bases, respectively.

A substance may be both a good nucleophile and a strong Brønsted base. For instance, alkyllithium carbanion reagents and alkali metal hydrides are strong bases and good nucleophiles towards electrophilic carbon atoms in organic solvents at moderate temperatures. However, this is not always the case. Under such conditions iodide ion, I^-, is a good nucleophile towards electrophilic carbon atoms but is a poor Brønsted base (it is the conjugate of the strong acid HI). In fact, for the halide ions the order of Brønsted basicity is the opposite of the order of nucleophilicity towards electrophilic carbon:

stronger Brønsted base: F^-, Cl^-, Br^-, I^-: weaker Brønsted base

better nucleophlie: I^-, Br^-, Cl^-, F^-: poorer nucleophile

3. Although the nucleophile-electrophile concept is most often used to describe organic reactions, it is also useful for describing inorganic reactions as well. For instance, the formation of hypochlorite ion in chlorine water possibly involves nucleophilic attack of hydroxide on an electrophilic chlorine atom in an S_N2 type process:



The Usanovich Acid-base Concept

The Usanovich Acid-base concept encompasses a wider range of reactions than the Lewis acid-base concept but is perhaps too general to serve as a convenient framework for understanding reaction chemistry. The Usanovich acid-base concept was developed by the Russian chemist Mikhail Usanovich and extends the Lewis acid-base concept's definition of acids and bases as electron pair donors and acceptors even further. Within the Usanovich definition:

- Acids are anything that accepts electrons, increases cation concentrations, decreases anion concentrations, or reacts with bases
- Bases are anything that donates electrons, increases anion concentrations, decreases cation concentrations, or reacts with acids

These definitions essentially expand the Lewis definition by removing the requirement that the electrons donated or accepted be a pair and practically mean that Usanovich acid-base reactions include Lewis acid-base reactions plus oxidation-reduction reactions. In other words:

- Usanovich acids are Lewis acids plus oxidants
- Usanovich bases are Lewis bases plus reductants

Under this definition BF_3, Fe^{3+}, and $[Fe(CN)_6]^{3-}$ all act as acids, and : NH_3, CN^-, and Zn are all bases:

$$\underset{acid}{BF_3} + \underset{base}{NH_3} \rightarrow F_3B-NH_3$$

$$\underset{acid}{Fe^{3+}} + 6\underset{base}{CN:^-} \rightarrow [Fe(CN)_6]^{3-}$$

$$2\underset{acid}{[Fe(CN)_6]^{3-}} + \underset{base}{Zn} \rightarrow 2[Fe(CN)_6]^{3-} + Zn^{2+}$$

However, notice that while it is easy to think about how any acids might interchangeably react with a given base (and vice versa), under the other acid-base concepts chemists have found it more difficult to think about reactions between oxidants/reductants and Lewis acids and bases. For example, it is difficult to think about how a reaction between BF_3 and Zn metal might occur. Would two Zn donate a pair of electrons to the BF_3? For this reason, most chemists find it more convenient to think about Lewis acid-base and redox reactions under separate categories rather than unite them under the Usanovich definition.

$$2\underset{oxidant}{[Fe(CN)_6]^{3-}} + \underset{reductant}{Zn} \rightarrow 2[Fe(CN)_6]^{3-} + Zn^{2+}$$

Again, it can be helpful to remember Huheey's dictum that deciding between acid-base concepts is not a matter of which concept is the most correct but rather of which is more convenient for a given application.

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6.2.1: The frontier orbital approach considers Lewis acid-base reactions in terms of the donation of electrons from the base's highest occupied orbital into the acid's lowest unoccupied orbital.

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 conceptualizes chemical bonding and reactivity in terms of the interactions between frontier 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 highest energy occupied and lowest energy unoccupied 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 base's HOMO level into the acid's LUMO level. For example, in the frontier orbital approach, adduct formation between $\boldsymbol{NH_3}$ and $\boldsymbol{BH_3}$ involves the donation of electrons from ammonia's a_1 HOMO into BH_3's a_2'' LUMO level.

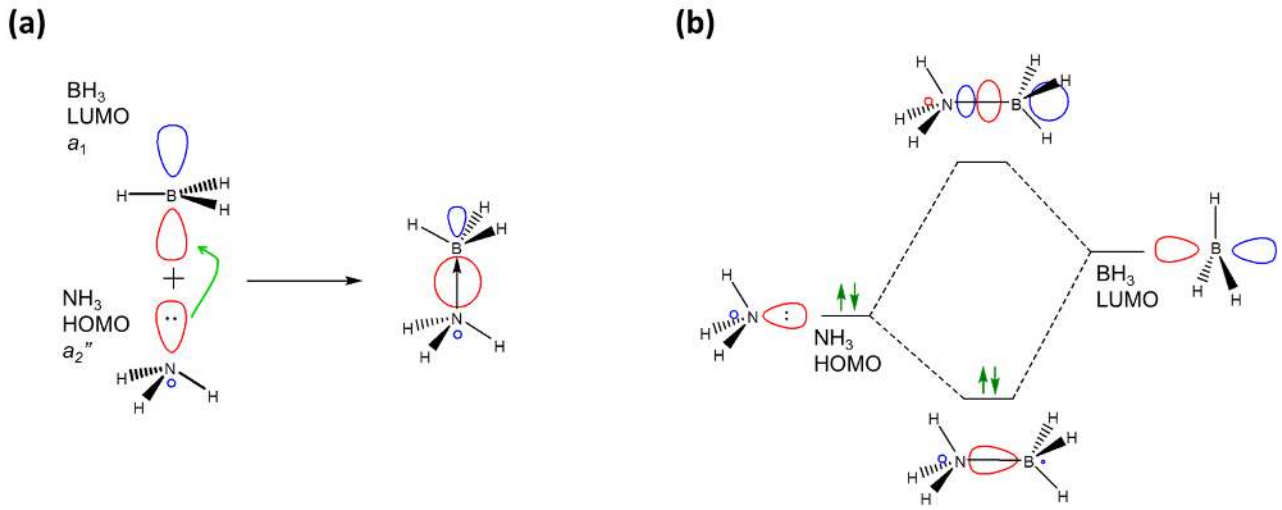


Figure **6.2.1.1**. Frontier orbital picture of adduct formation between ammonia and borane. (a) As $\boldsymbol{NH_3}$ and $\boldsymbol{BH_3}$ approach one another, interaction between the $\boldsymbol{NH_3}$ HOMO and $\boldsymbol{BH_3}$ LUMO gives a bonding MO. (b) Partial molecular orbital diagram for $\boldsymbol{NH_3 \rightarrow BH_3}$ showing the stabilization of the base ($\boldsymbol{NH_3}$) lone pair in a sigma bonding MO upon 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 **6.2.1.1**). Since it is occupied by an electron, the net result of the interaction is the lowering of the base's lone pair energy 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:

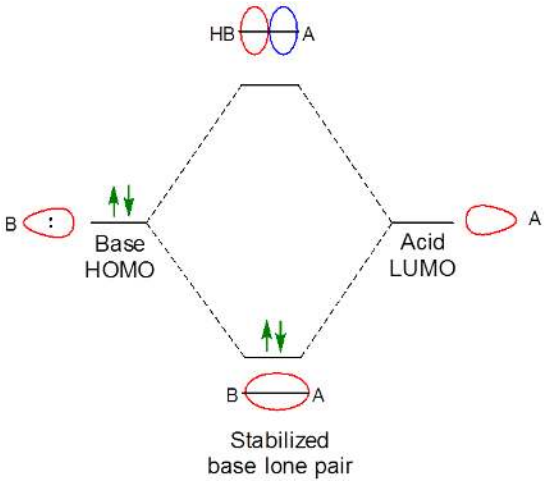
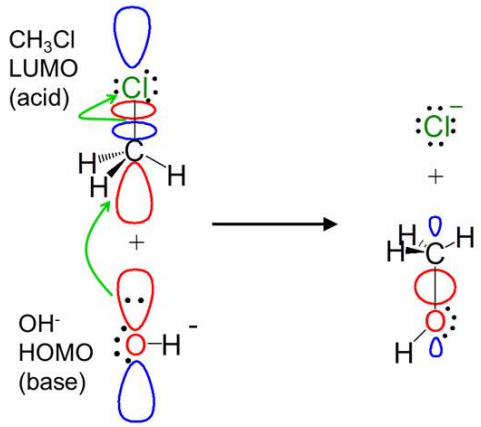


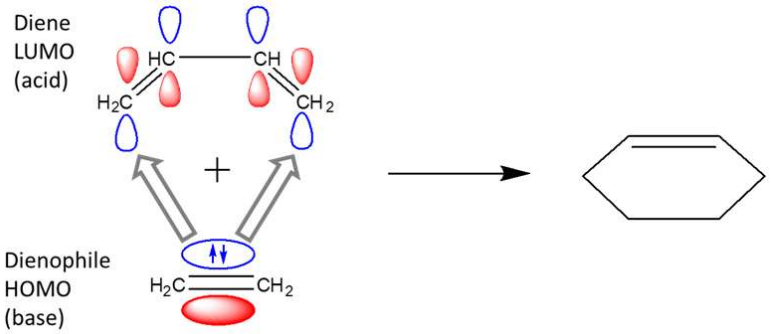
Figure **6.2.1.2**. Generalized frontier orbital picture for adduct formation between a Lewis base (B) and a Lewis acid (A) involving stabilization of the lone pair of the base HOMO by formation of a bonding orbital with the acid LUMO. The relative energies of the acid LUMO and base HOMO affect the character 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:

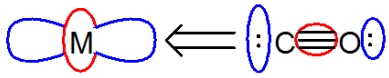


Notice how the frontier orbital approach even explains the displacement of the chloride leaving group. The donation of electrons from the hydroxide HOMO populates the antibonding CH_3Cl LUMO, breaking the C-Cl bond.

With 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.



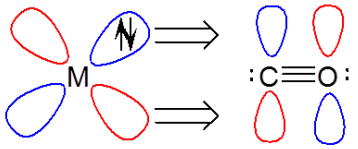
The orbital interactions involved in a given reaction can include both reactants acting as both an acid and base. In these cases the HOMO of each reactant interacts with the LUMO of the other. A good example of this involves **Π**-type interactions between a metal ion with occupied *d* orbitals and a 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

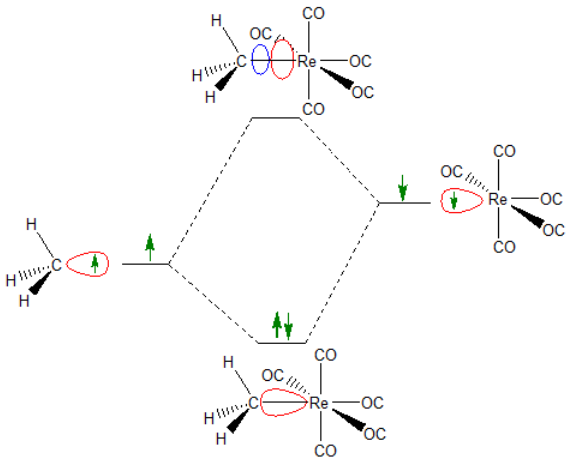
However, the metal can also act as a base towards the ligand LUMO (π^*) orbitals.



Metal HOMO (d_{xz}, d_{xz}) acts as a base

Carbon monoxide LUMO (π^*) acts as an acid

The frontier orbital concept can also be used to describe interactions between one or more singly occupied frontier orbitals. In fact, when approximate molecular orbital diagrams are being constructed, it can often be helpful to focus on one or two particularly instructive interactions. In these cases, it is sometimes convenient to think about a chemical bond as involving the formation of bonding and antibonding interactions between singly occupied frontier orbitals on different molecular fragments. For instance, when thinking about the chemistry of $CH_3Re(CO)_5$ it can sometimes be helpful to think about the C-Re bond as arising from the interaction between a singly-occupied sp^3 type orbital on a CH_3 group and a singly occupied d^2sp^3 orbital on the Re.



In introducing singly occupied orbitals, the frontier orbital concept formally handles interactions that the Lewis acid-base concept does not, since Lewis acid-base behavior is formally confined to the acceptance and donation of electron *pairs*.

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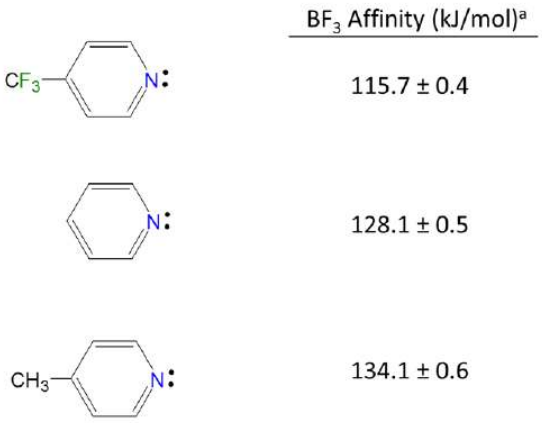
- **6.4.1: The frontier orbital approach considers Lewis acid-base reactions in terms of the donation of electrons from the base's highest occupied orbital into the acid's lowest unoccupied orbital.** by Stephen M. Contakes is licensed CC BY 4.0.

6.2.2: 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

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, substituent 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.



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 to decrease Lewis acidity by making sites less electron deficient.

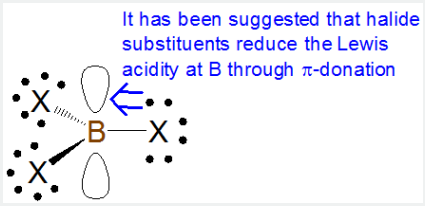
Nevertheless it can be difficult to predict substituent-based trends in Lewis acidity and basicity by inductive effects alone. This is because inductive effects are modest and often exists in competition with other substituent effects, such as

- Steric effects, discussed in section 6.4.7
- Hardness effects, discussed in section 6.6
- 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 upon adduct formation.

Avoid misconceptions about the impact of π donation and acceptance on Lewis acid-base affinity

As with σ-based induction effects, π-donation tends to increase Lewis basicity and decrease Lewis acidity 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:

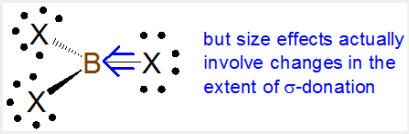


According to this explanation, the extent of this π-donation decreases down the halogen group as the boron-halogen bond distance decreases. This is consistent with the observed trend in Lewis acidity of the boron trihalides towards most bases, which runs counter to that suggested by inductive effects alone:

$$BI_3 > BBr_3 > BCl_3 >> BF_3$$

However, computational work suggests that this explanation is incorrect, since

- atomic size effects are important mainly for substituents in which the connected atom is in 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:

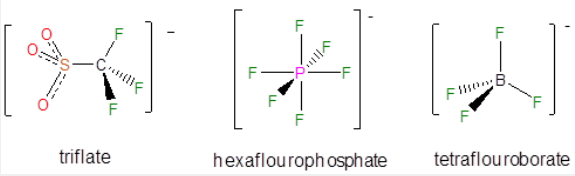
1. Plumley, J. A.; Evanseck, J. D., Periodic Trends and Index of Boron Lewis Acidity. *The Journal of Physical Chemistry A* 2009, 113 (20), 5985-5992.

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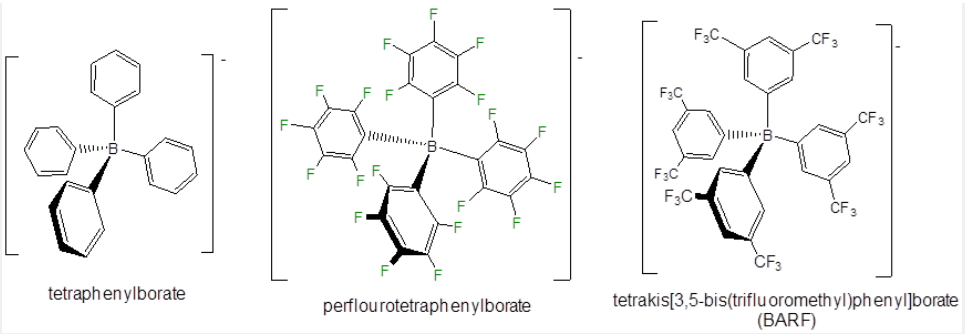
The conjugate bases of many Brønsted superacids have electron-withdrawing substituents that make them such poor Lewis bases that they are useful as noncoordinating anions.

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 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. In contrast, the conjugate bases of triflic acid, hexafluoroboric acid, and tetrafluoroboric acid are now more commonly used as counterions for isolating reactive cations.



Even less reactive noncoordination anions include derivatives of tetraphenylborate, particularly those with electron withdrawing substituents.



Other classes of noncoordinating ions include fluoroantimonate clusters, derivatives of the carborane anion ($CB_{11}H_{11}^-$), and fluorinated aluminum tetraalkoxides.

References

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.

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6.2.3: The electronic spectra of charge transfer complexes illustrate the impact of frontier orbital interactions on the electronic structure of Lewis acid-base adducts

When a Lewis acid-base adduct is formed, electron density and negative charge are transferred from the Lewis base to the acid.

The formation of a Lewis-acid base complex involves the transfer of electron density from the base to the acid.

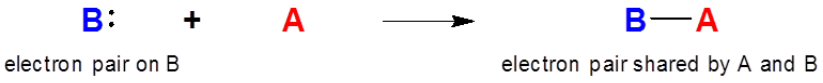


Figure 6.4.2.**6.2.3.1**.

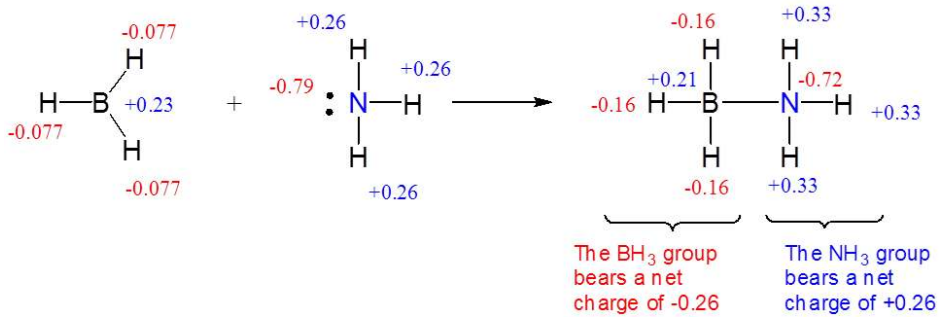


Figure 6.4.2.**6.2.3.1**. Calculated change in atomic charge distribution upon formation of an adduct between BH_3 and NH_3 in the gas phase. All partial charges were calculated for geometry-optimized molecules at the 6-31G** level.

Weakly bound Lewis acid-base adducts in which charge is incompletely transferred are called charge transfer complexes.

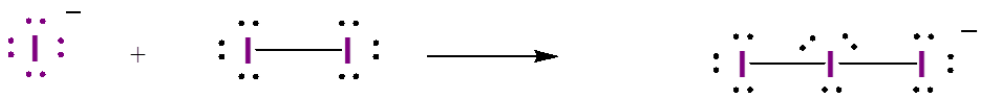
In many weakly bound Lewis acid-base complexes, the transfer of electron density and, consequently, charge from the base group to the acid group is only partial:

$$A + B \rightleftharpoons A^{\delta-}B^{\delta+}$$

Such Lewis acid-base adducts are commonly called **charge transfer complexes (CT complexes)** or **donor-acceptor complexes (DA complexes)**. In these

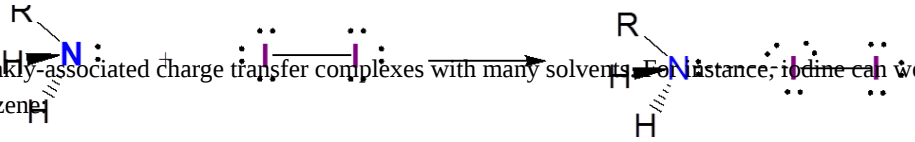
- the base is called the **donor (D)** since it is a net donor of electrons and, consequently, their negative charge
- the acid is called the **acceptor (A)** since it is a net acceptor of electrons and, consequently, their negative charge

A particularly well-known class of charge transfer complexes is 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.

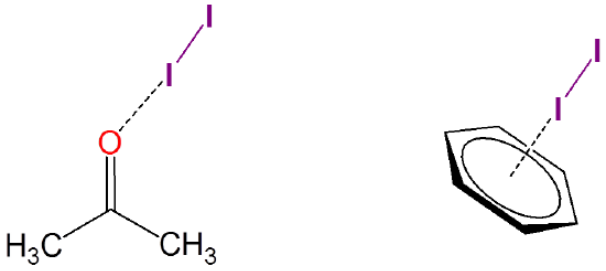


Triiodide is well-known from introductory chemistry from the bright blue color that appears when the triiodide complexes with starch to give the dark blue starch-iodide complex.

In contrast to the stable triiodide anion, iodine charge transfer complexes are only weakly associated. Complexes between iodine and amines are a well known example:

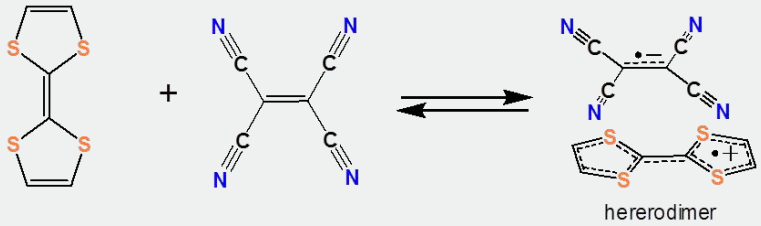


Iodine also forms weakly-associated charge transfer complexes with many solvents. For instance, iodine can weakly associate with both acetone and benzene:

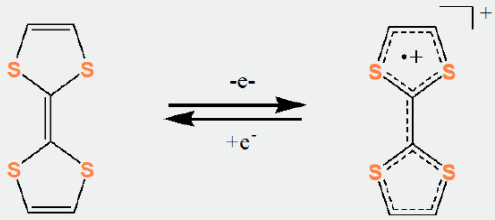


Organic Charge Transfer Complexes

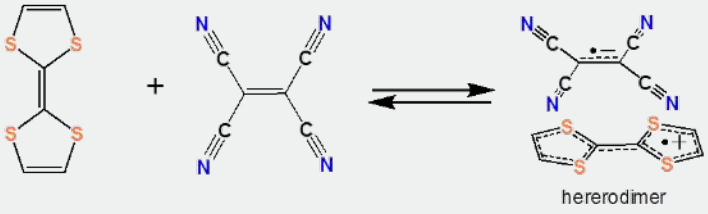
It is worth noting in passing that several organic charge transfer complex systems have been developed in which organic electron donors and acceptors weakly associate with each other. These are of considerable interest for use in molecular electronics applications, and as a result, a large variety of organic electron donors and acceptors have been developed. An example of an organic electron acceptor is tetracyanoethylene (TCNE):



and an example of an organic electron acceptor is tetrathiofulvalene (TTF).



Together they form a charge transfer complex:



Similar organic charge transfer systems have been investigated for use in organic photovoltaic cells. There is considerable interest in developing such organic photovoltaic devices owing to the ease with which organic materials may be fabricated from organic solutions and suspensions.

Charge transfer complexes exhibit charge transfer transitions in which absorption triggers the transfer of an electron from the donor to the acceptor.

When iodine is dissolved in solutions of donor solvents, the striking purple color of molecular iodine is replaced by a yellow-brown color. This is because charge transfer complexes like those formed by I_2 can absorb light in ways that neither the donor nor the

acceptor can on their own. Specifically, charge transfer complexes exhibit **charge transfer bands (CT bands)** in their absorption spectra. In the charge transfer transition the initial partial transfer of charge from the donor Lewis base to the acceptor Lewis acid in the charge transfer complex is pushed further by photoexcitation.

$$D^{\delta+} - A^{\delta-} \xrightarrow{h\nu_{CT}} D^{+} - A^{-}$$

The nature of these charge transfer transitions is seen from the orbital description of binding for iodine charge transfer complexes. When a donor-I_2 complex forms, the formation of donor-I_2 bonding and antibonding orbitals results in a shift in the $I2\sigma \rightarrow \sigma*$ transition to higher energy, as a new charge transfer band is formed, associated with the excitation of an electron from the largely amine-centered amine-I_2 σ orbital to the largely I_2-centered amine-I_2 $\sigma*$ orbital.

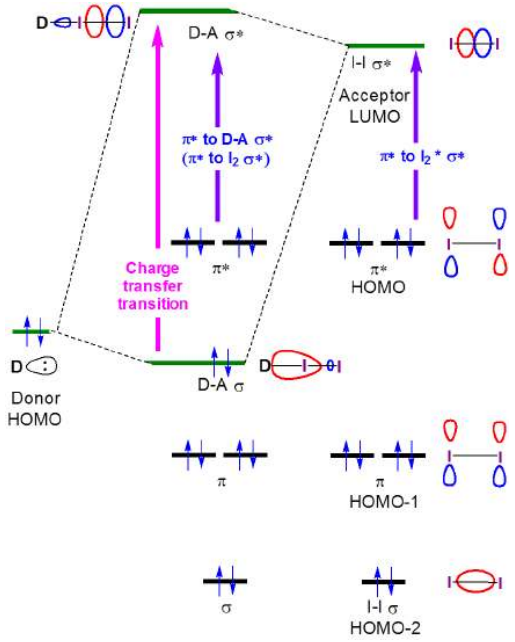


Figure 6.4.2.**6.2.3.2**. Frontier orbital interactions that give rise to changes in the absorption spectra of iodine when it forms a charge transfer complex with a Lewis base donor.

Solutions of I_2 as mixtures with Lewis bases such as amines and in donor solvents clearly have charge transfer bands in their absorption spectra. Several such spectra are given in Figure 6.4.2.3.

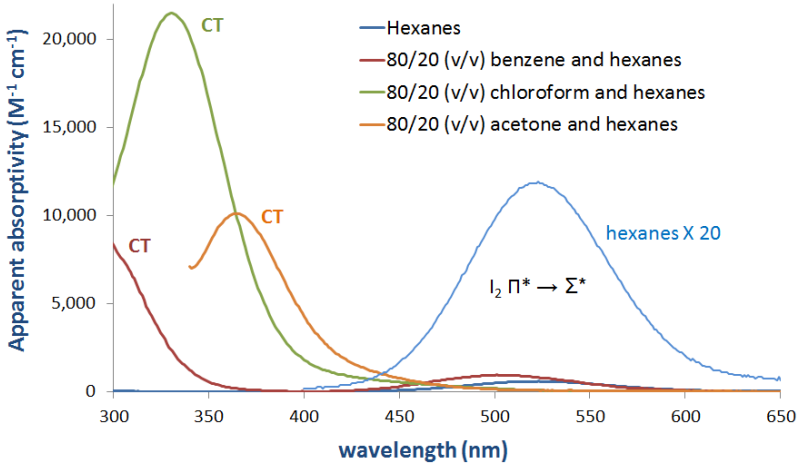


Figure **6.2.3.3**. Absorption spectrum of molecular iodine (I_2) in various solvents showing the appearance of a CT band in donor solvents.*

In principle, the energies of both the charge transfer and $I_2\ \pi* \rightarrow D-A\ \sigma*$ transitions both increase with donor strength, as shown in Figure 6.4.2.4.

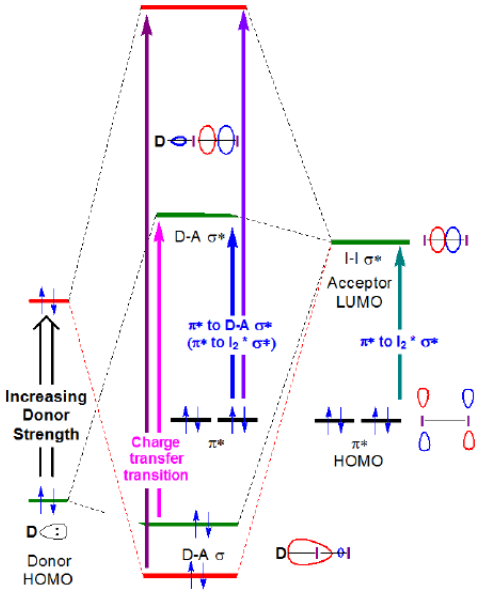


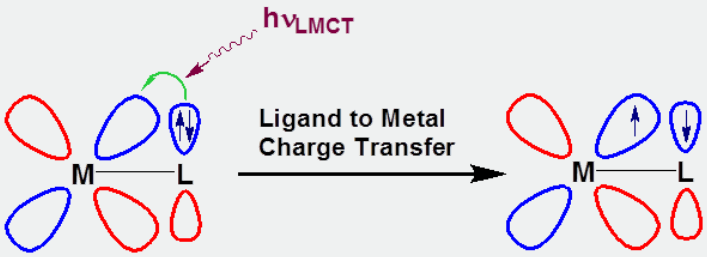
Figure **6.2.3.4**. Expected change in the frontier orbital energies associated with I_2 donor acceptor complex formation when the HOMO energy of the donor is increased.

As can be seen in Figure 6.4.2, the charge transfer band energy might be expected to increase as the donor HOMO increases in energy to become closer in energy to the acceptor LUMO. Although care should be taken when interpreting the solution phase spectra of I_2, this expectation is borne out by a cursory and qualitative analysis of the spectra in Figure 6.4.2.3. The CT transition energy shifts towards lower wavelengths (and thus higher energy) as the highest occupied atomic orbital energy for the donor atom increases on going from acetone (oxygen, -15.85 eV) to chloroform (chlorine, -13.67eV) and finally benzene (carbon, -10.66 eV).**

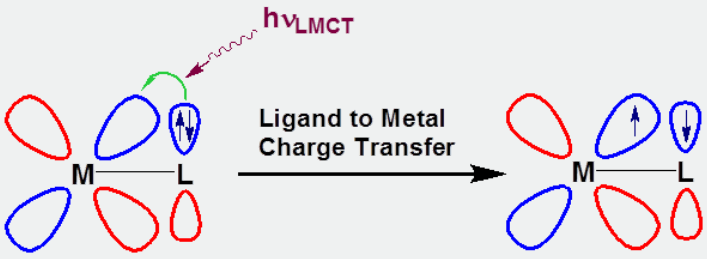
Charge Transfer Bands in Transition Metal Chemistry

Charge transfer transitions are responsible for the intense color of many transition metal complexes. In these cases, however, the weak Lewis acid-base interaction involves incomplete electron donation and acceptance in a $p\pi - d\pi$ (or $p\pi - d\pi*$)-bond between a metal and ligand. The charge transfer bands in the absorption spectra of these complexes involve the transfer of electrons between the metal and ligand. In particular,

- Metal to ligand charge transfer (MLCT or CTTL) bands involve the transfer of an electron from a filled or partly filled metal *d* orbital to a ligand $\pi*$-type orbital.



- Ligand to metal charge transfer (LMCT or CTTM) bands involve the transfer of an electron from a filled or partly filled ligand orbital to a metal *d*-orbital.



- Metal to metal charge transfer bands can be observed in some bimetallic complexes. However, these are usually thought of only as an electron transfer rather than as a shift in the status of a Lewis acid-base interaction.

Because metal-ligand charge transfer bands involve intermolecular electron transfer between the metal and ligand to generate a high energy redox state, the CT excited state is both a better oxidant and reductant than the ground state. Consequently there has been intense research into the development of metal complexes whose charge transfer excited states are powerful oxidants and reductants in the expectation that they will be able to drive the photocatalytic oxidation and reduction of substrates.

* The apparent absorptivity of I_2 in hexanes was calculated from the absorption spectrum of 215 μM I_2 in hexanes. All other apparent absorptivities were calculated from absorption spectra of solutions that were 44 μM in I_2.

** The band positions are not the CT band energies, and the HOMO energies given are atomic energy levels and do not necessarily correspond to the HOMO of the donor in solution. Because of this and other simplifications this analysis is not intended to replace a rigorous computational analysis of the factors that give rise to CT band positions.

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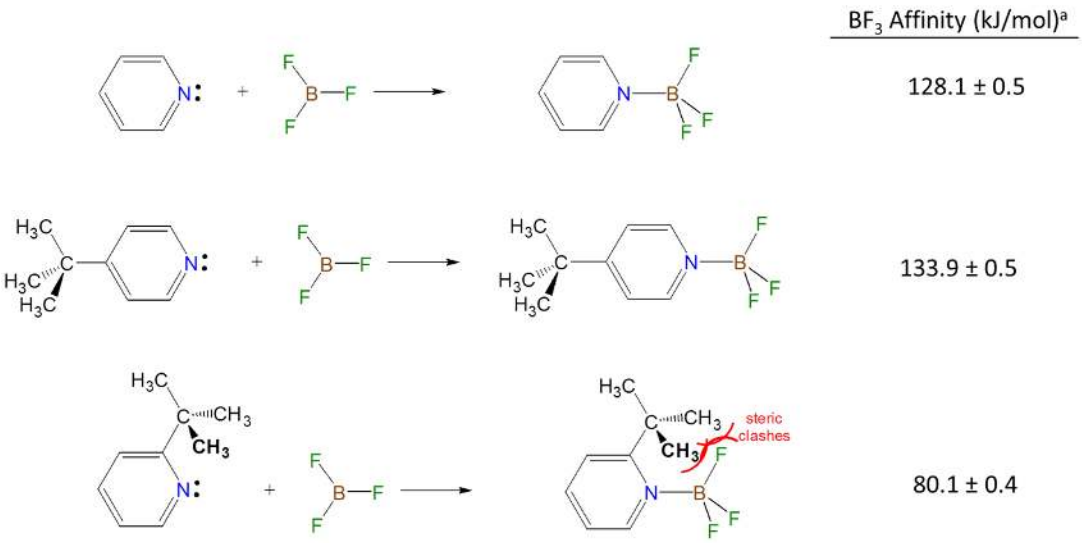
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6.2.4: Bulky groups weaken the strength of Lewis acids and bases because they introduce steric strain into the resulting acid-base adduct.

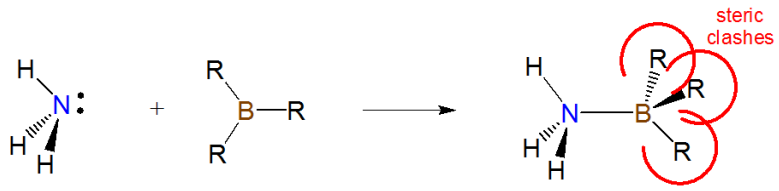
Steric effects can influence the ability of a Lewis acid or base to form adducts by introducing:

- **front strain (F-strain)** whereby bulky groups make it difficult for the Lewis acid and Lewis base centers to approach and interact.



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 upon adduct formation. For instance, when trivalent boron compounds form adducts with amines, the boron center changes from a more open trigonal 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

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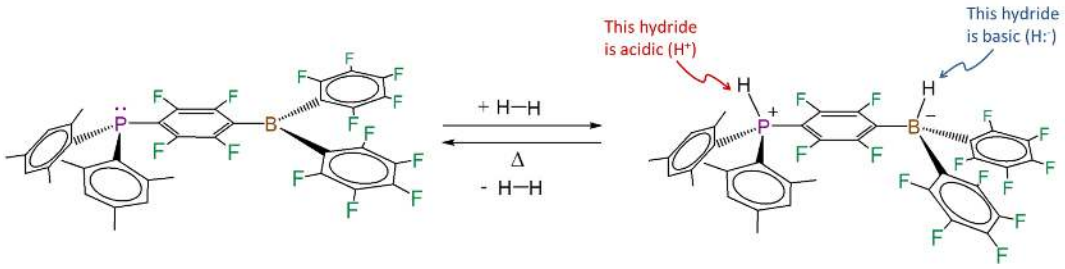
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- **6.4.7: Bulky groups weaken the strength of Lewis acids and bases because they introduce steric strain into the resulting acid-base adduct.** by Stephen M. Contakes is licensed CC BY 4.0.

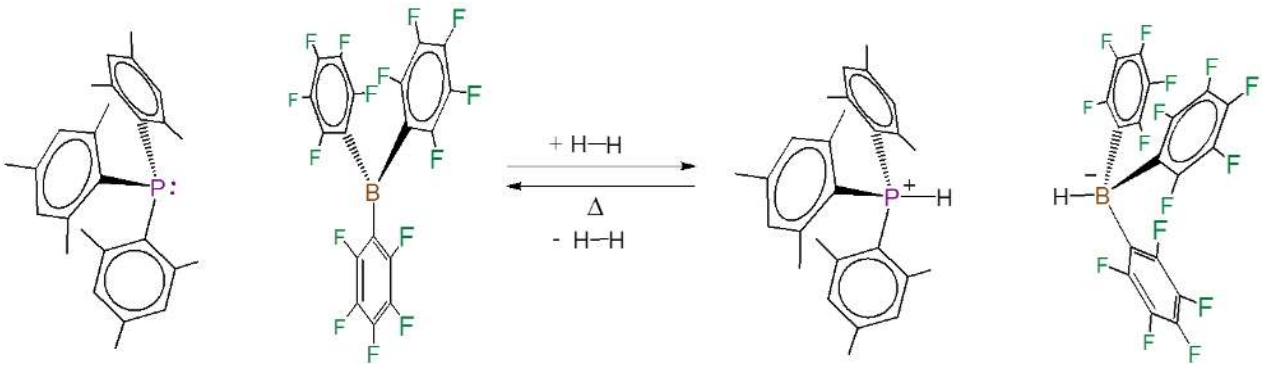
6.2.5: Frustrated Lewis pair chemistry uses Lewis acid and base sites within a molecule that are sterically restricted from forming an adduct with each other.

In certain cases when a Lewis acid-base adduct is sterically hindered from quantitatively forming an adduct (and perhaps even when they are so able), the Lewis acid and Lewis base can act together to heterolytically cleave chemical bonds. In such cases the pair of electrons that would otherwise be donated by the base is said to be a **frustrated Lewis pair (FLP)** and in performing the heterolytic cleavage the Lewis acid and base are said to exhibit **frustrated Lewis pair chemistry**.

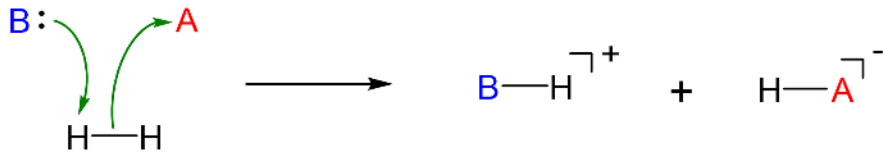
The **Stephan's phosphinoborane** illustrates how FLP chemistry works. It reversibly cleaves dihydrogen to give a zwitterionic species containing both acidic and basic element hydride bonds.



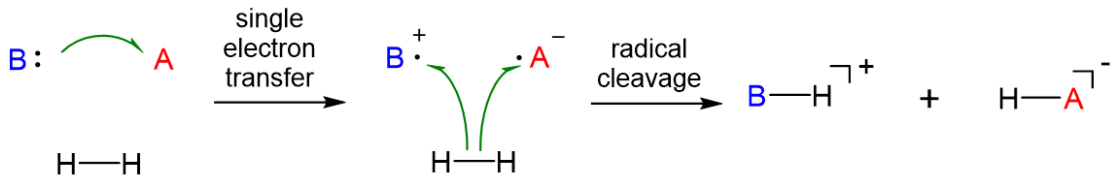
Note that the Lewis acid and base do not need to be part of the same molecule. Hydrogen is also heterolytically cleaved by mixtures of sterically encumbered triarylphosphines and triarylboranes. This time the reaction gives phosphonium and hydroborate ions:



Given the description of FLP systems as frustrated Lewis acid-base adducts, it is natural to think about the cleavage of substrates like H_2 as involving nucleophilic attack by the Lewis base while the Lewis acid acts like an electrophile in a heterolytic cleavage mechanism.



However, only some FLP systems cleave substrates through this mechanism. In others the mechanism involves homolytic cleavage by a diradical intermediate.



In either case, when substrates like H_2 are cleaved by FLPs, they are generally separated into more reactive fragments (e.g., in the case of H_2, H^+ and H^-). Because of this the substrates are said to be activated to undergo further reactions. Because FLP systems can cleave and activate substrates, there is considerable interest in the development of FLP systems that can facilitate reactions of economic or environmental interest. So far FLP systems have been developed that can catalyze various hydrogenations and activate numerous substrates, including CO, SO_2, and N_2.

References

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- **6.4.8: Frustrated Lewis pair chemistry uses Lewis acid and base sites within a molecule that are sterically restricted from forming an adduct with each other.** by Stephen M. Contakes is licensed CC BY 4.0.

6.3: Hard and Soft Acids and Bases

Origin of the Hard-Soft Acid-Base Principle

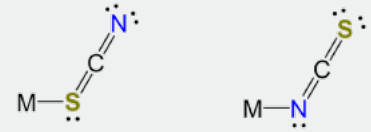
One of the strengths of the Lewis acid-base concept is the readiness with which it illuminates the role that covalent and electrostatic interactions in acid base behavior, specifically through its ability to explain chemical interactions in terms of frontier orbitals and the interactions between charged groups as electrons are donated from a base to an acid. However, simply acknowledging the presence of such interactions does little to illuminate the degree to which each mode of explanation best explains the bonding in a given system? To what extent is a given adduct better described as held together by covalent bonds as opposed to ionic ones - *e.g.* better described as a molecule rather than an ion pair? Moreover, does it even matter, given that the orbitals of quantum mechanics result from the combination of electrons' wavelike behavior with their electrostatic attraction to nuclei in either case?[1] These questions and more are addressed by one of the most important conceptual tools in contemporary inorganic chemistry, the Hard-Soft acid-base principle.

The **Hard-Soft acid-base principle (HSAB principle)** stems from the recognition that some Lewis acids and bases seem to have a natural affinity for one another.* Consider the following:

- Some metals are commonly found in nature as salts of chloride or as oxide ores while others are found in combination with sulfur. Geochemists even use the Goldschmidtt classification scheme to classify the halide and oxide formers as lithophiles and the sulfide formers as chalcophiles.
- In living systems small highly charged metals ions like Fe^{3+} are usually found bound to N and O atoms while larger metals with lower charges such as Zn^{2+} are often found attached to at least one S atom. Similarly, metals prefer to bind to one coordination site over the other when forming complexes with ambidentate ligands. The most well-known instances involve complexes of cyanate and thiocyanate, which can coordinate metals through either the N or chalcogen atom. For instance, Cu^{2+} and Zn^{2+} form *N*-thiocyanato complexes in species like $[Cu(NCS)_2(py)_2]$ and $[Zn(NCS)_4]^{2-}$ while their larger cogeners Au^{3+} and Hg^{2+} preferentially forms *S*-thiocyanato complexes, giving species like $[Hg(SCN)_4]^{2-}$.

Ambidentate ligands

Ambidentate ligands possess multiple coordination sites through which a metal may bind. For instance, thiocyanate may coordinate metals (M) at either the S or N to give *S*-thiocyanato or *N*-thiocyanato complexes.



S-thiocyanato *N*-thiocyanato

- The solubility trends for the alklai metal halides and silver halides are opposite, even though both involve salts of formula M^+X^- (salts can be thought of as involving Lewis acid-base adduct formation between the anions and cations). Specifically, although the silver halides are all relatively insoluble in water, the very modest solubility they possess follows the order:

$$X = F >> Cl > Br > I \text{ (for the solubility of AgX)}$$

In contrast, the much more ample solubility of the alkali metal halides** follows the opposite order. For example, the order for the lithium halides is

$$X = F << Cl < Br << I \text{ (for the solubility of LiX)}$$

Notes

1. Albeit suitably fudged through such niceties as the Aufbau principle and other approximations.

* Despite the fruitfulness of this observation, in general it is important to reduce the potential for observer bias by checking observations like these against compounds reported in the chemical literature and databases like the Inorganic Crystal Structure and Cambridge Crystallographic Databases.

** These are very soluble in water, to the point where some solutions are perhaps better described as solutions of water in the halide.

† This can be predicted based on the relative hardness of BF_3, BR_3, and BH_3 in the list of hard and soft acids. However, for those of you who may be confused as to why H is considered a better electron donor for the purposes of softening a Lewis acid center while alkyl groups are better electron donors for the purposes of stabilizing carbocations in organic chemistry, the dominant effect is the lower electronegativity of H relative to carbon (in CH_3). The effect of electron donation due to hyperconjugation isn't as great for thermodynamically stable bases like BX_3/BR_3.

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- **6.6: Hard and Soft Acids and Bases** by Stephen M. Contakes is licensed CC BY 4.0.

6.3.1: Hard-Hard and Soft-Soft preferences may be explained and quantified in terms of electrostatic and covalent and electronic stabilization on the stability of Lewis acid-base adducts

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 **6.3.1.1**). Pearson terms acids and bases which are relatively polarizable **soft** and those which are difficult to polarize **hard.**

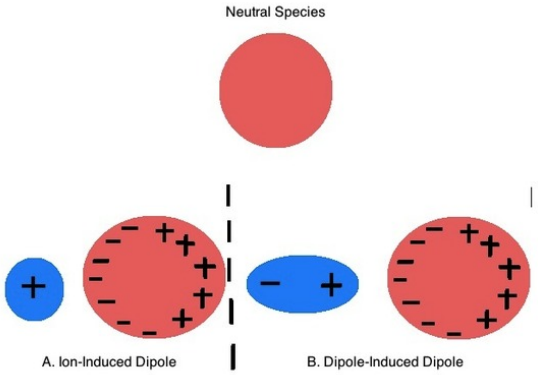


Figure **6.3.1.1**: Polarizability refers to the ease with which a substance's electron cloud may be distorted under the action of an electric field. A fragment's polarizability determines the degree to which its electron cloud is distorted by A.) an Ion and B.) a polar molecule to induce a dipole moment. The figure is taken from (and the caption expanded from) Cox, Kelly and Dana Reusser "Polarizability"

Recognizing Hard and Soft Acids and Bases

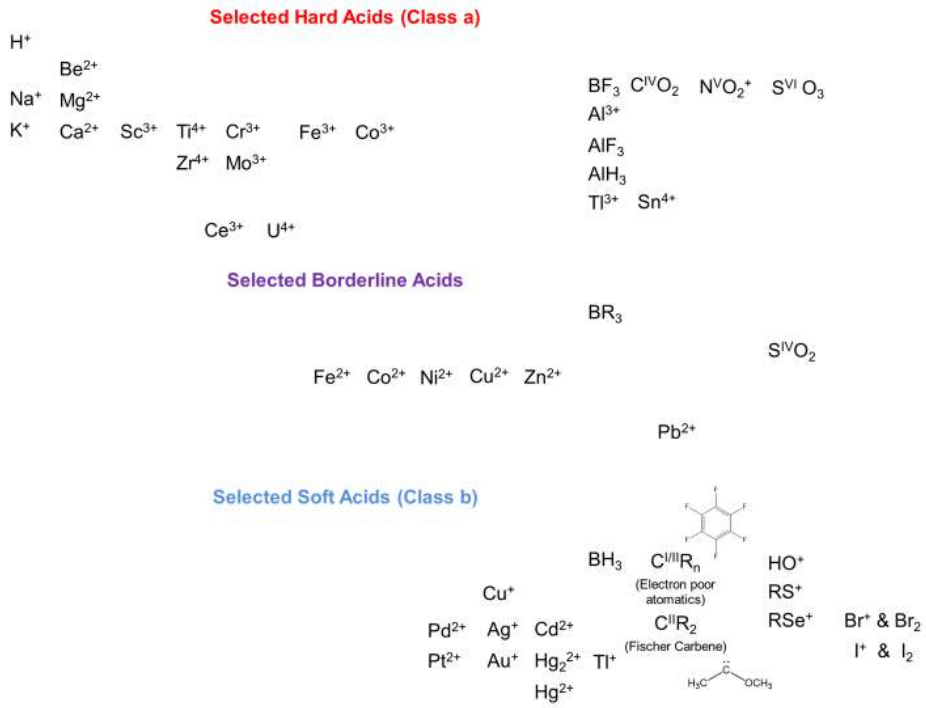
Hard acids and bases come in two varieties:

1. hard acid and base sites that possess few valence electrons and for which polarization therefore involves distorting core electrons, which are difficult to distort because they are close to the nucleus and experience a high nuclear charge. The most common examples of such substances are Lewis acid hard acids towards the left of the periodic table.
2. hard acid and base sites with a high charge density (highly charged relative to size) and/or which are electron deficient. In these cases polarization involves distorting electrons that already experience strong unshielded electrostatic interactions.

Soft acids and bases also come in two varieties

1. soft acids and bases which posses many valence electrons and so are more readily polarized. In consequence, all other things being equal, soft acids and bases are more likely to be found towards the middle or right of the periodic table.
2. soft acids and bases with little charge density and/or which are relatively electron rich.

Note that the hard-soft classification should not be thought of as if all hard acids and bases are equally hard and all soft acids and bases equally soft. There is a graduation in hardness and softness and a number of intermediate acids and bases which do not fit neatly in either category. With this caveat in mind, representative **hard, soft, and borderline acids** are given below. Notice how they illustrate the trends just outlined.



As expected, hard acids tend to be found towards the left side of the periodic table and involve higher oxidation states and/or electron donating substituents while soft acids are more common to the right of the periodic table and involve lower oxidation states and/or electron donating substituents.

Illustrative hard, soft, and borderline bases are given below. Again, notice how these substances illustrate the general trends.

Selected Hard Bases (Class a)

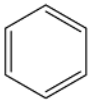
Nitrogen bases	Oxygen bases		small halides
NH_2^-	OH^-	CO_3^{2-}	F^-
NH_3	H_2O	RCO_2^-	Cl^-
RNH_2	ROH	NO_3^-	
NH_2NH_2	ROR	PO_4^{3-}	
		SO_4^{2-}	

Selected Borderline Bases

electron-poor Nitrogen bases		low oxidation state element oxyanions	intermediate halides
N_3^-		NO_2^-	
NO_2^-			Br^-
SCN^-		SO_3^{2-}	
N_2			

Selected Soft Bases (Class b)

Carbon bases	P and As bases	Sulfur bases	large halides & pseudohalides
R^-	PR_3	RS^-	H^-
CO	$P(OR)_3$	RSH	I^-
CN^-	AsR_3	RSR	
RNC		SCN^-	
$R_2C{=}CR_2$ (alkenes)			



(electron-rich aromatics)

Qualitative Estimation of the Relative Hardness and Softness of Lewis Acids and Bases

As can be seen from the examples above, **hard acids are relatively electron-poor and hard bases electron-rich** since they have comparatively

- small frontier orbitals, reflective of their relatively small atom/ion/fragment sizes
- high (for acids) or low (for bases) oxidation states on the base atom, reflected in a large positive formal charge (for acids) or negative formal charge (for bases)
- low polarizability, due to loss or gain of substantial numbers of electrons, or the localization of
  - positive charge on an electropositive element or an atom bearing electron-withdrawing substituents
  - negative charge on an electronegative element or an atom bearing electron-donating substituents

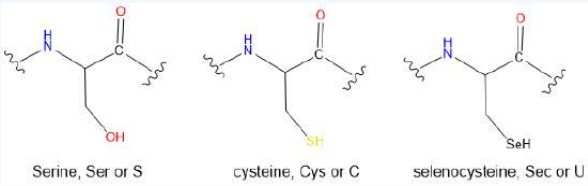
In contrast to hard acids and bases, **soft acids are relatively electron-rich and soft bases larger and more electron poor** since they have comparatively

- large frontier orbitals, reflective of their relatively large atom/ion/fragment sizes
- low oxidation states, often resulting in small or nonexistent atomic charges
- high polarizability, as might be expected of species in which electron-electron repulsions are lower and electrons are spread over a large volume. Sometimes this is indicated by
  - positive charge on an electronegative element or an atom bearing electron-donating substituents
  - negative charge on an electropositive element or an atom bearing electron-withdrawing substituents

Exercise 6.3.1.1

Rank the acids or bases in each set in increasing order of expected hardness.

a. Cr^{2+} and Cr^{3+}
b. H^+, Cs^+, and Tl^+
c. SCN^- (acting as a base at N) and SCN^- (acting as a base at S)
d. AlF_3, AlH_3, $AlMe_3$
e. The side chains of the following proteinogenic amino acids

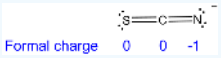


Answer

(a) $Cr^{2+} < Cr^{3+}$ All other things being equal, hardness increases with oxidation state.

(b) $Tl^+ < Cs^+ < H^+$ The order reflects Cs^+ and Tl^+'s larger size relative to H^+ (which doesn't possess any electrons that can be polarized anyway) and that Tl^+ still possesses two valence electrons while Cs^+ possesses none.

(c) SCN^- (acting as a base at S) < SCN^- (acting as a base at N). The order reflects the greater electronegativity of N than S and N's possession of a more negative formal charge of -1.



(d) $AlH_3 < AlMe_3 < AlF_3$. The hardness increases as the substituents on the Lewis acid Al center become less electron donating and more electron withdrawing (and, incidentally, harder bases) as their electronegativity increases in the order H^- < CH_3^- < F^-. Note that the order of electron donating ability for H^- and CH_3^- is the opposite observed for carbocations, for which hyperconjugation plays a larger role.

(e) Sec < Cys < Ser. The hardness increases as the electronegativity of the Lewis base chalcogen increases on going from a selenol to a thiol to an alcohol.

The Hard-Soft Acid-Base Principle (HSAB Principle)

The **Hard-Soft acid-base principle (HSAB Principle) explains patterns in Lewis acid-base reactivity in terms of a *like reacts with like preference***. Both thermodynamically and kinetically, hard acids prefer hard bases and soft acids soft bases. Specifically,

- Thermodynamically, hard acids form stronger acid-base complexes with hard bases while soft acids form stronger complexes with soft bases.
- Kinetically, hard acids/electrophiles react more quickly with hard bases/nucleophiles while soft acids/electrophiles react more quickly with soft bases/neucleophiles.

Applications of the HSAB principle include

1. Predicting the equilibrium or speed of *Lewis acid-base metathesis and displacement reactions.* In a Lewis acid-base **metathesis reaction** the acids and bases swap partners

$$\mathbf{A_1 : B_1 + A_2 : B_2 \overset{k_1,\, K_{eq_1}}{\rightleftharpoons} A_1 : B_2 + A_2 : B_1}$$

For example, the equilibrium position of the metathesis reaction between $\mathbf{TlF}$ and $\mathbf{K_2S}$ favors the products:

$$\mathbf{2\,TlF + H_2S \rightleftharpoons Tl_2S + 2\,KF}$$

consistent with the HSAB's hard-hard and soft-soft preference.



The HSAB principle also allows for prediction of the position of displacement reactions, in which a Lewis acid or base forms an adduct using a base or acid from an existing Lewis acid-base complex. In these reactions, the displacement of acid or base from the reactant complex may be thought of as a sort of metathesis reaction, one in which in the unbound acid or base switches places with one in the complex. For example, the reaction between **HI** and methylmercury cation

$$\mathbf{HI + HgSCH_3^+ \rightleftharpoons CH_3SHgI + H^+}$$

involves displacement of an iodide from **HI** to give $\mathbf{CH_3HgI}$. The position of the equilibrium favors $\mathbf{CH_3HgI}$ since both $\mathbf{CH_3Hg^+}$ and $\mathbf{I^-}$ are soft, while $\mathbf{H^+}$ is a hard acid.



? Exercise 6.3.1.2

Predict the position of equilibrium for the following reaction.

$$\mathbf{Fe_2O_3 + 3\,Ag_2S \rightleftharpoons Fe_2S_3 + 3\,Ag_2O}$$

Answer

The equilibrium will favor the reactants (K<1) since the hard-hard and soft-soft interactions in the reactants are more stable than the hard-soft interactions in the products.



? Exercise 6.3.1.3

Predict whether K for the following equilibria will be <<1, ~1, or >>1.

a. $\mathbf{2\,HF + (CH_3Hg)_2S \rightleftharpoons 2\,CH_3HgF + H_2S}$
b. $\mathbf{Ag(NH_3)_2^+ + 2\,PH_3 \rightleftharpoons Ag(PH_3)_2^+ + 2\,NH_3}$
c. $\mathbf{Ag(PH_3)_2^+ + 2\,H_3B{-}SH_2 \rightleftharpoons 2\,H_3B{-}PH_3 + Ag(SH_2)_2^+}$
d. $\mathbf{H_3B{-}NH_3 + F_3B{-}SH_2 \rightleftharpoons H_3B{-}SH_2 + F_3B{-}NH_3}$

Answer

a. K< < 1 since the reactant adducts are hard-hard and soft-soft while the products involve hard-soft interactions.

b. K>>1 since the reactant complex, diamine silver(I), is a complex of a hard base, NH_3, with the soft acid, Ag^+, while the product is a complex of the same soft acid with the soft base phosphine.

c. K~1 since all the adducts amongst the reactants and products involve soft acids and bases.

d. K>>1 since BH_3 is a softer acid than BF_3, so it will form a stronger complex with the softer base H_2S while the harder BF_3 forms a stronger complex with the harder base NH_3.

2. Predicting the relative strengths of a given set of *Lewis acids or bases towards a particular substrate*. Consider, for example, the relative strengths of a BH_3, BMe_3, and BF_3 towards group 15 hydrides like NH_3, PH_3, and AsH_3. Of the

boranes listed, the hardest acid BF_3 is the strongest acid towards the hard base NH_3 while BH_3 is the strongest towards AsH_3.[†]

? Exercise 6.3.1.4

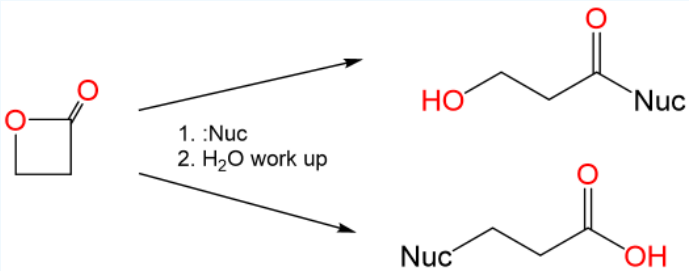
Which acid will form the most stable complex with **CO**: $\mathbf{BH_3}$, $\mathbf{BF_3}$, or $\mathbf{BMe_3}$?

Answer

$\mathbf{BH_3}$. Since **CO** forms complexes primarily through its carbon lone pair, it is a soft base and so will form the strongest complex with the softest Lewis acid.

? Exercise 6.3.1.5

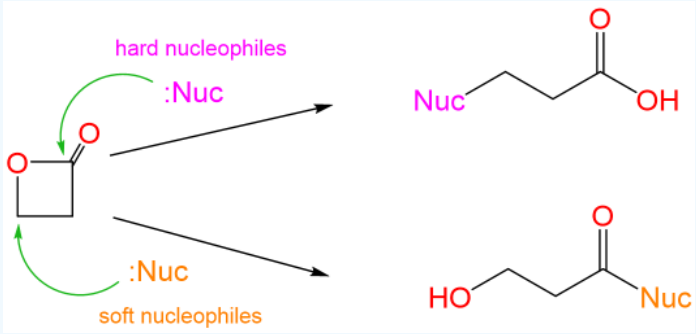
When lactones react with nucleophiles, they can undergo ring opening reactions to give either an alcohol or a carboxylic acid, as shown for propiolactone below:



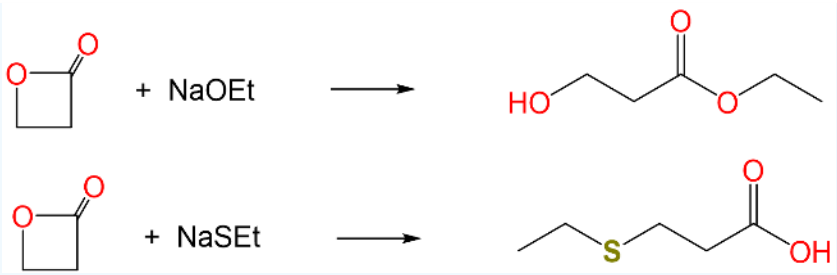
In the reaction above, sterically unhindered alkoxides give one product and sterically unhindered thioalkoxides the other. Explain why this is the case and predict the products of the reaction between propiolactone and the sodium salts of ethoxide and thioethoxide.

Answer

The two reaction products correspond to nucleophilic attack at the lactones' two electrophilic carbon centers. Specifically, the acid is produced by attack at the softer C^{I} center of the CH_2 directly attached to the ester oxygen and the alcohol by nucleophilic attack at the harder C^{III} center of the ester carbonyl.



Consequently, it is reasonable to expect that the harder base ethoxide will nucleophilically attack the harder carbonyl carbon while the softer thioethoxide will attack the softer methylene carbon.



The theoretical interpretation of the hard-soft acid-base principle is that hard-hard preferences reflect superior electrostatic stabilization while soft-soft preferences reflect superior covalent stabilization.

The hard-hard and soft-soft preferences in Lewis acid-base interactions reflect that

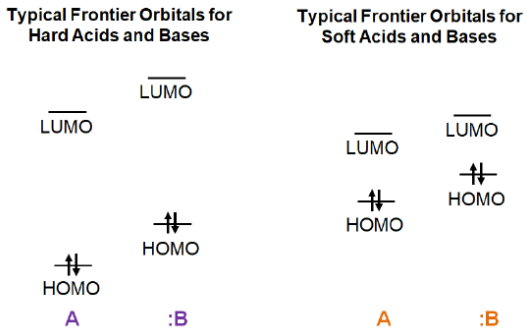
- The lone pair of a hard base is strongly stabilized electrostatically by a hard acid.
- The lone pair of a soft base is strongly stabilized by forming a covalent bond with a soft acid.
- The lone pair of a hard or soft base is comparatively weakly stabilized by an acid opposite to it in hardness or softness since the overall electrostatic and covalent stabilization of the adduct is comparatively weak.

To see why this is the case it is helpful to divide the contributions to the interaction energy between an acid and a base as follows:

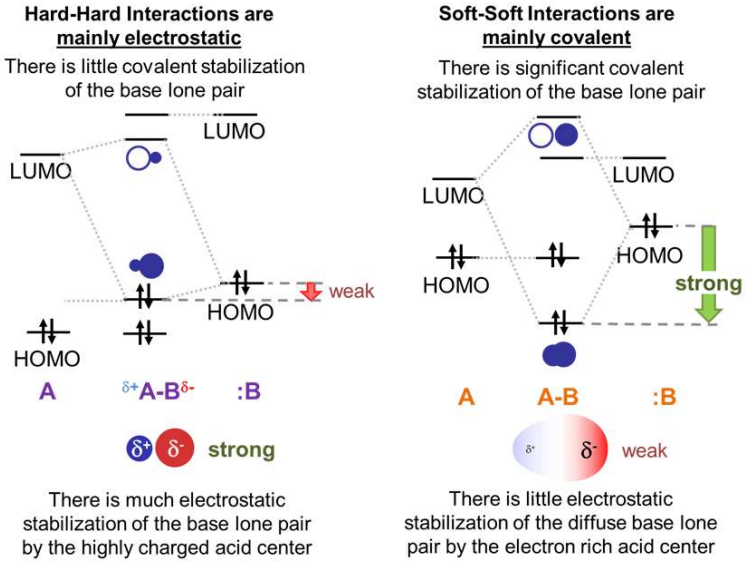
$$\text{Interaction Energy} = \underbrace{\text{Electrostatic attractions and repulsions of partial atomic charges}}_{\text{Ionic term}} + \underbrace{\text{Interactions between filled orbitals on one fragment and unfilled orbitals on the other}}_{\text{Covalent term}} + \underbrace{\text{Electrostatic repulsions between filled orbitals on the two fragments}}_{\text{Steric term}}$$

Of the three contributions to the interaction energy, only the ionic and covalent terms directly relate to the hardness of the interacting acid and base. One approach to thinking about how hardness influences the ionic and covalent contributions is to consider the frontier orbitals involved in the acid-base interaction. This is sometimes done through the use of the Salem-Klopman equation,[1,*] although in the treatment which follows a more qualitative approach will be employed.

Both hard acids and bases will have comparatively low energy HOMO levels and high energy LUMO levels, with a correspondingly high HOMO-LUMO gap. In contrast, soft acids and bases will have comparatively high-energy HOMO levels and low-energy LUMO levels, giving a comparatively smaller HOMO-LUMO gap.



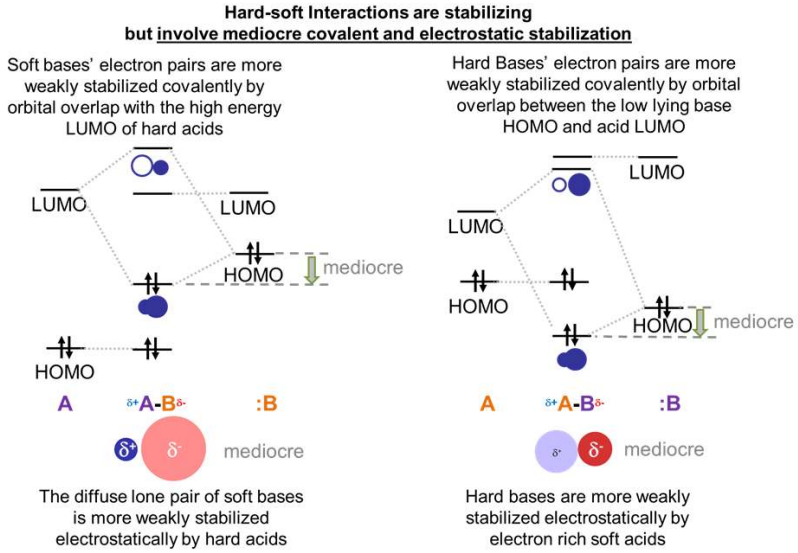
Given this, consider the frontier orbital interactions involved in the formation of an acid-base complex for the possible cases, as illustrated schematically below.



The large gap in energy between hard bases' highly stabilized HOMO lone pairs and the high energy LUMO of hard acids ensures that in **hard acid-hard base adducts the dominant stabilizing interaction will involve electrostatic attraction between the base lone pair and the electropositive Lewis acid center**. Fortunately, since the electron clouds in hard bases are relatively dense and electron rich while hard Lewis acids are highly charged and small, these electrostatic interactions are strong.

In contrast, in **soft acid-soft base adducts, the dominant stabilizing interaction will be covalent.** This is because the small gap in energy between a soft base HOMO and soft acid LUMO enables the formation of a well-stabilized bonding orbital with significant electron density between the acid and base.

The orbitals' interactions between hard acids and soft bases and soft acids and hard bases are intermediate between the hard acid-hard base and soft acid-soft base cases.



This means that the adducts are stable relative to free acid and base – just not as well stabilized as in the hard acid and hard base case. In the case of hard acids and soft bases the hard acids are less able to stabilize the soft bases' relatively diffuse electron pair electrostatically and there isn't as much covalent stabilization as in adducts of soft acids and bases due to the hard acid's high energy.

References

1. Ahrland, S.; Chatt, J.; Davies, N. R., The relative affinities of ligand atoms for acceptor molecules and ions. Quarterly Reviews, Chemical Society 1958, 12 (3), 265-276.

2. Pearson, R. G., Hard and Soft Acids and Bases. Journal of the American Chemical Society 1963, 85 (22), 3533-3539.

3. Fleming, I., Molecular orbitals and organic chemical reactions. Reference ed.; Wiley: Hoboken, N.J., 2010.

Notes

* Despite the fruitfulness of this observation, in general it is important to reduce the potential for observer bias by checking observations like these against compounds reported in the chemical literature and databases like the Inorganic Crystal Structure and Cambridge Crystallographic Databases.

** These are very soluble in water, to the point where some solutions are perhaps better described as solutions of water in the halide.

† This can be predicted based on the relative hardness of BF_3, BR_3, and BH_3 in the list of hard and soft acids. However, for those of you who may be confused as to why H is considered a better electron donor for the purposes of softening a Lewis acid center while alkyl groups are better electron donors for the purposes of stabilizing carbocations in organic chemistry, the dominant effect is the lower electronegativity of H relative to carbon (in CH_3). The effect of electron donation due to hyperconjugation isn't as great for thermodynamically stable bases like BX_3/BR_3.

†† For more on the Salem-Klopman equation see Fleming, I., Molecular orbitals and organic chemical reactions. Reference ed.; Wiley: Hoboken, N.J., 2010; pp. 138-143.

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7.1: General Trends in Main Group Chemistry

In addition to the Lewis, VSEPR, valence bond, molecular orbital, and various acid-base models that are important for understanding chemical structure and bonding, a number of general principles are useful for understanding trends in the properties of the main group elements. These include:

1. The **Periodic Law** and **Periodic Table**, most notably the ordering of elements with similar chemical properties by group, the **metal-nonmetal distinction**, and the **second row uniqueness principle**.
2. **Periodic trends** in atomic properties, most notably atomic radii, ionization energy, electron affinity, and electronegativity, on account of which there are **diagonal relationships** between elements in the periodic table.
3. **Periodic trends** in elements' redox properties, which can be helpfully illuminated with the aid of Latimer, Frost, and Pourbaix diagrams.

The remaining pages of this section will outline these principles.

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7.1.1: The Periodic Table is an Organizing Concept in Main Group Chemistry

The chemical and physical properties of the main group compounds result from the electronic properties of their constituent atoms and ions. These atomic electronic properties are determined by the number of electrons present and the ground state orbitals they occupy. Of these electrons the chemically most important are the **valence electrons** and the orbitals they occupy, called **valence orbitals**. These valence electron counts and orbital occupancies vary systematically in a way that is reflected in the organization of the periodic table. Specifically, the number of valence electrons and the types of atomic orbitals they occupy are determined by the element's group. This is reflected in the familiar block structure of the periodic table shown in Figure **7.1.1.1**.

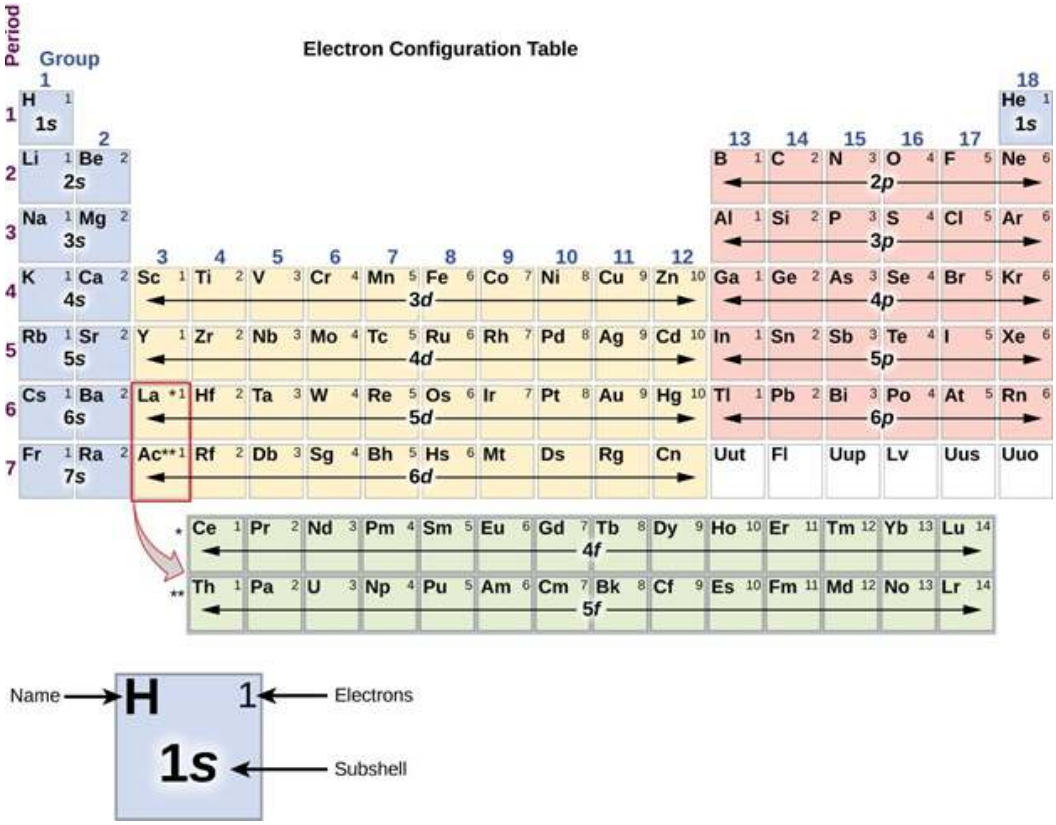


Figure **7.1.1.1**. Subshells of the outermost valence electrons of the elements. The image is taken from OpenStax College. **Located at:** http://openstaxcollege.org. **License:** *CC BY: Attribution*. **License Terms:** Download for free at https://openstaxcollege.org/textbooks/chemistry/get

From Figure **7.1.1.1** it can be seen that the main group elements are those with ns^x and $ns^2\ np^y$ type valence electron configurations – called *s* and *p* block elements. The exact occupancy of the *s* and *p* subshells increases with the total number of valence electrons from left to right across the periodic table as shown in Figure **7.1.1.2**.

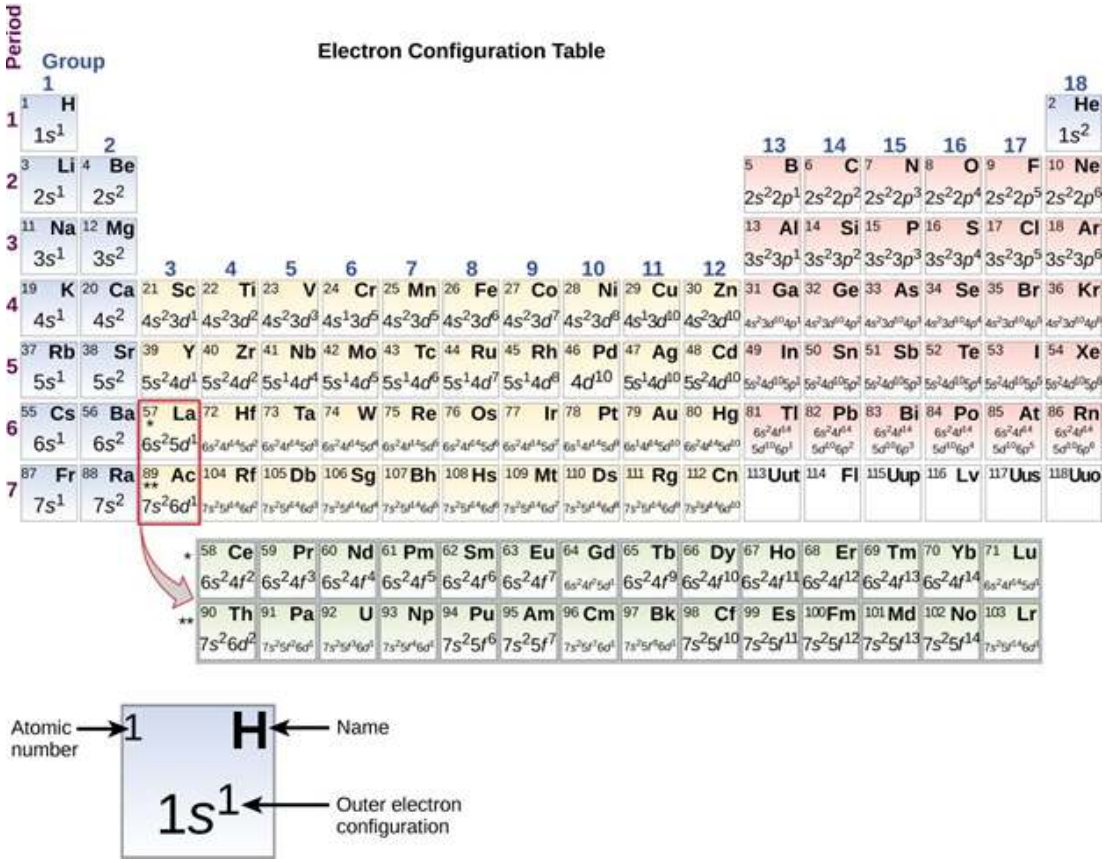


Figure **7.1.1.2**. Valence electron configurations of the elements. Note that for most purposes *d* and *f* electrons in lower shells do not contribute significantly to the bonding. The image is taken from OpenStax College. **Located at:** http://openstaxcollege.org. **License:** *CC BY: Attribution*. **License Terms:** Download for free at https://openstaxcollege.org/textbooks/chemistry/get

From Figure **7.1.1.2** it can be seen that elements within a group of the periodic table have the same configuration of *s* and *p* valence electrons. This is one reason why elements within the same group tend to have similar chemical properties.[1] Consequently, it is usually convenient to think and talk about the elements and their properties by group.

Groups may always be referred to by their group number or their first element. In addition, a number have common names that are widely used. These are given in Figure **7.1.1.3**.

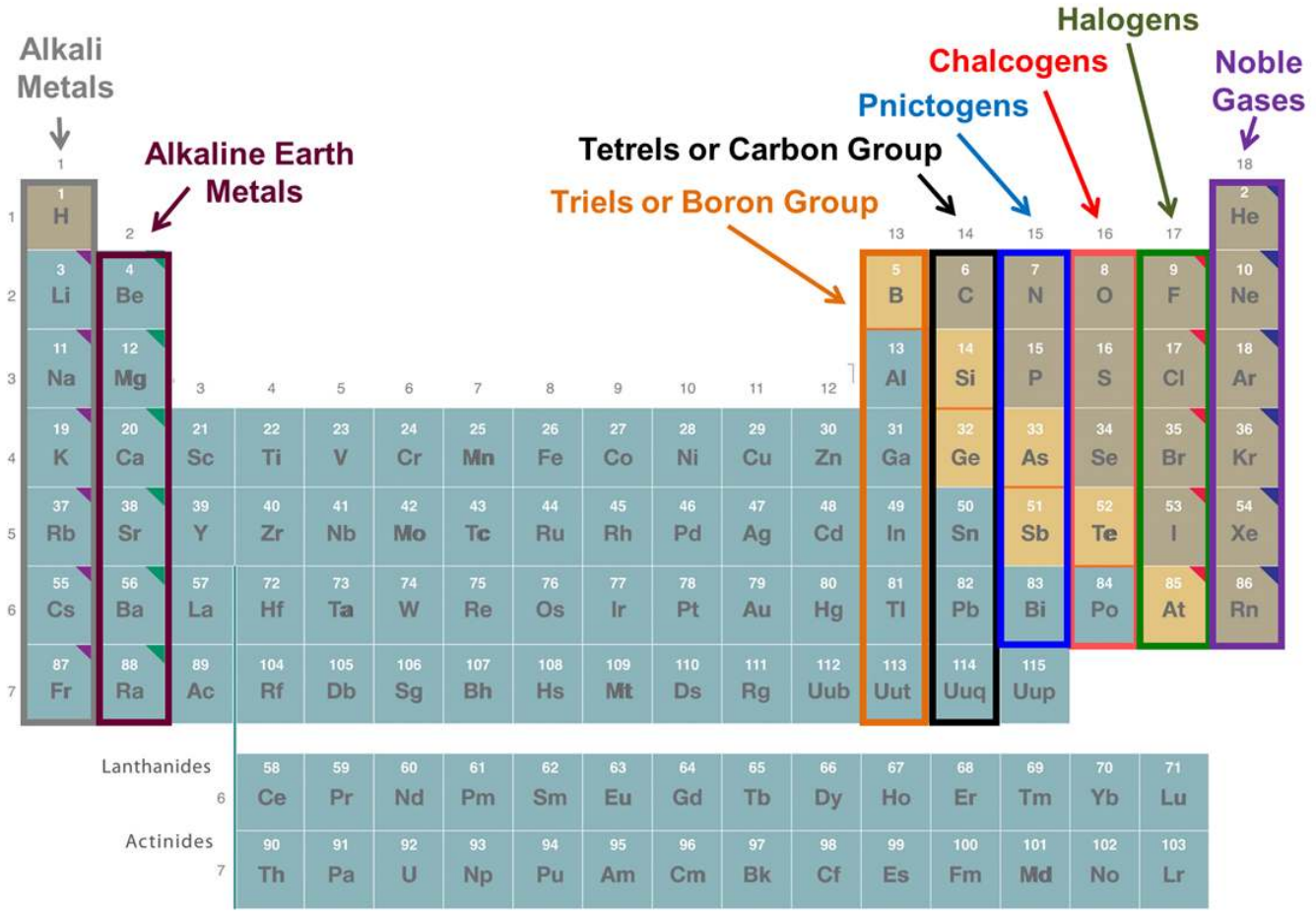


Figure 7.1.1.3. Commonly used group names. Note that hydrogen is not typically regarded as an alkali metal even though it is sometimes placed in the alkali metal goup. The image is adapted from https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/02._Atoms%2C_Molecules%2C_and_Ions/2.5%3A_The_Periodic_Table. Otherwise this work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Further insight into the properties of the elements may be gained by considering how the systematic variation in electron configuration that occurs across the periodic table's rows interacts with the systematic variations in atomic properties that occur across rows and down groups. A detailed understanding of these properties, how they vary throughout the periodic table, and why they vary in the way they do will be developed in later sections. For now, it is only necessary to know the trends in **valence orbital properties**, which are:

- The **valence orbital size tends to increase down a group** as the principle atomic number increases. This increase in orbital size corresponds to lengthening of the average electron-nuclear distance and consequently a weakening of the valence electron-nucleus attraction.
- The **valence orbital energy roughly decreases across a row as the effective nuclear charge, Z*, increases**. The major factor driving this decrease in energy is the increase in electron-nucleus attraction as Z* increases.
- The **valence orbital size roughly decreases across a row as the effective nuclear charge, Z*, increases**. This decrease in size corresponds to a shortening of the valence electron-nuclear distance and strengthening of the valence electron-nucleus attraction. This size effect reinforces the aforementioned lowering of valence orbital energies, effective nuclear charge, although in general the lowering of energy due to decreasing size is less important than the lowering of energy due to increasing charge. That is because size decreases gradually from left to right while the effective nuclear charge increases by about 2/3 of a charge unit when moving from group to group.

These trends are summarized in Figure 7.1.1.4.

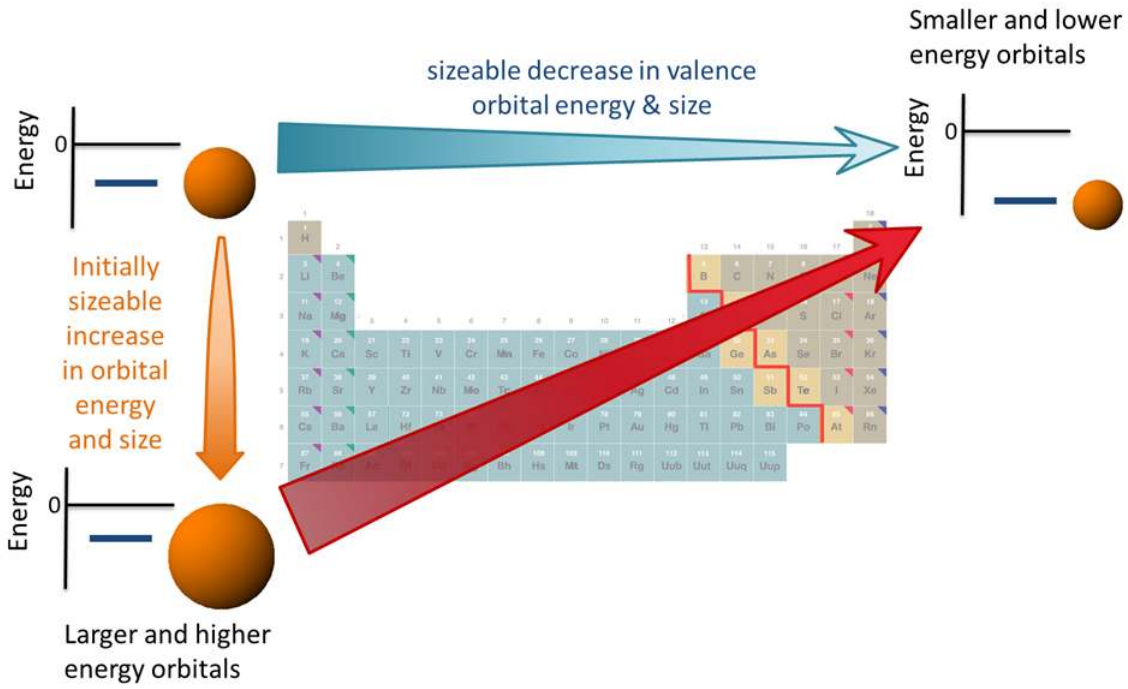


Figure **7.1.1.4**. Trends in valence orbital properties. The image is adapted from https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/02._Atoms%2C_Molecules%2C_and_Ions/2.5%3A_The_Periodic_Table. Otherwise this work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

These valence orbital property trends affect two different classes of atomic properties. The first class includes the valence orbital size-related properties such as atomic radii and the π-bonding interaction strength. The second class contains electron-nucleus attraction-related properties comprising ionization energy, electron affinity, and electronegativity.

The consequences of the valence orbital property trends for atomic properties are as follows

1. **Atomic size** *increases down a group* as the valence orbital becomes larger (n increases) and *roughly decreases across a row* as the effective nuclear charge increases.
2. **Ionization energy** *decreases down a group* as the valence orbital becomes larger and *roughly increases across a row* as the effective nuclear charge increases.
3. **Electron affinity** *decreases down a group* as the valence atomic orbital becomes larger and *roughly increases across a row* as the effective nuclear charge increases.
4. **Electronegativity** *decreases down a group* as the lowest incompletely occupied atomic orbital becomes larger and *roughly increases across a row* as the effective nuclear charge increases.

These consequences are summarized in Figure **7.1.1.5**.

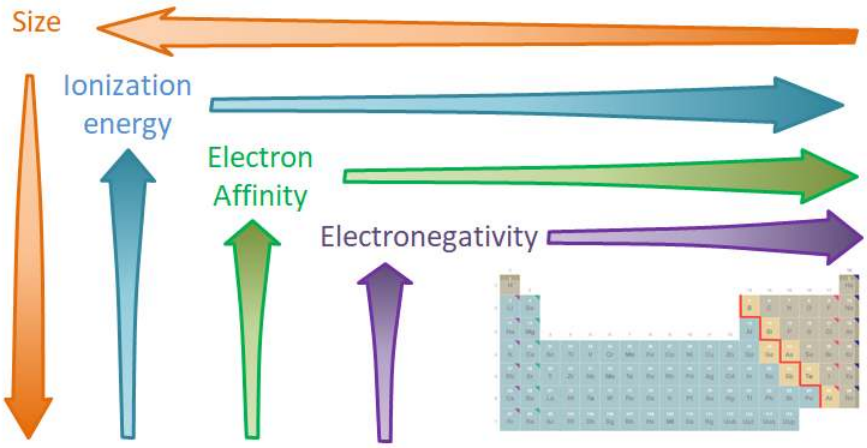


Figure 7.1.1.5. Periodic trends in atomic properties. The image is adapted from https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/02._Atoms%2C_Molecules%2C_and_Ions/2.5%3A_The_Periodic_Table. Otherwise this work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

These variations in turn explain the trends in main group element properties that are explored in the remainder of this chapter.

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[1] Another is that the valence orbital energies tend to vary relatively little down a group, especially as one moves from row three downward.

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7.1.1.1: The metal-nonmetal-metalloid distinction and the metal-nonmetal "line" are useful for thinking about trends in elements' physical properties

Two factors contribute to large-scale and rough variations in the sort of structure and bonding that main group elements engage in.

1. Decreasing valence orbital energy and size on moving from the lower left to the upper right of the periodic table
2. Increasing valence shell occupancy on moving from left to right across the main group

As summarized in Figure \(\PageIndex{1}\), the net effect of these trends is that

Elements in earlier groups with few valence electrons act as metals since they *tend to* either

- lose them to give cations with an empty valence shell

or

- share them by forming delocalized bonds in clusters and the solid state, although this tendency is less pronounced as one moves towards the top of the periodic table, since elements in earlier groups with more compact lower energy orbitals less readily ionize and more readily form strong covalent bonds (for example, consider the relative stability of alkyllithium and Mg-containing Gringard reagents compared to alkylsodium or calcium reagents)

Elements in later groups with many valence electrons act as nonmetals since they *tend to* either

- gain additional electrons to form anions with a stable filled valence shell

or

- form stable pairwise sigma bonds in molecular and network covalent solids, although this tendency is less pronounced as one moves down a group and the orbitals become more diffuse. As a result nonmetals exhibit an increased tendency to engage in delocalized and cluster bonding on moving down the periodic table.

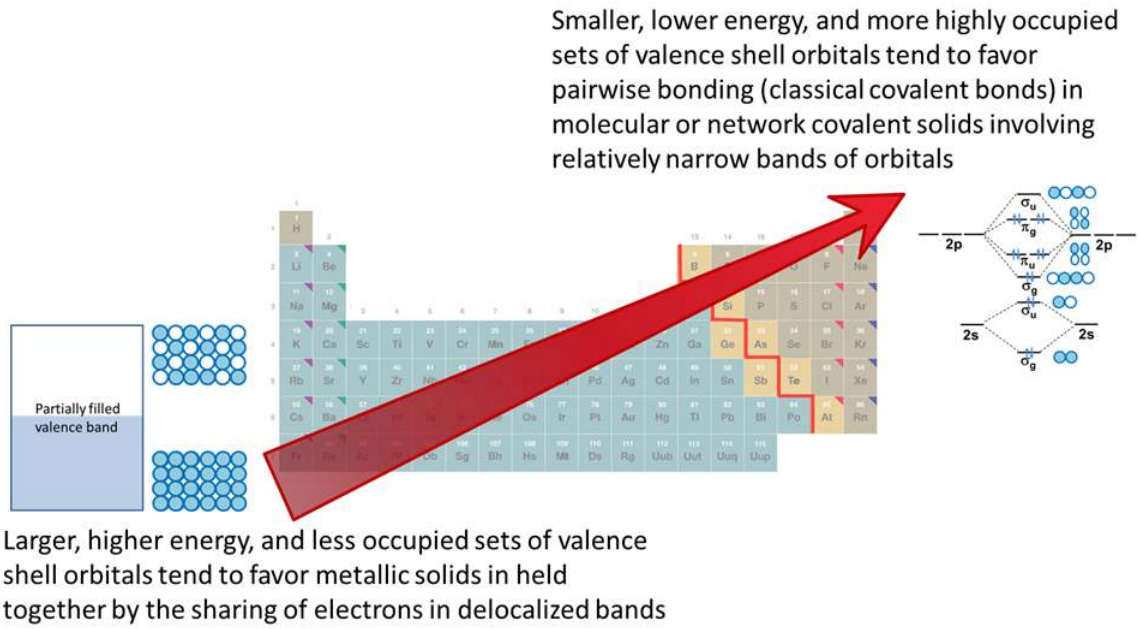


Figure \(\PageIndex{1}\). Trends in bonding across the periodic table. The image is adapted from https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/02._Atoms%2C_Molecules%2C_and_Ions/2.5%3A_The_Periodic_Table. Otherwise this work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

These periodic trends in bonding tendencies impact the sort of structures elements form and their physical properties. This is reflected in the classical division of the elements into metals, nonmentals, and metalloids depicted in Figure \(\PageIndex{2}\). As can be seen from Figure \(\PageIndex{2}\), the metals in the lower left of the periodic table are separated from the nonmetals in the

upper right by the **metal-nonmetal line**. Most of the elements adjacent to the line (which ones are chosen varies between periodic tables) exhibit properties intermediate between metals and nonmetals and are called **metalloids**.

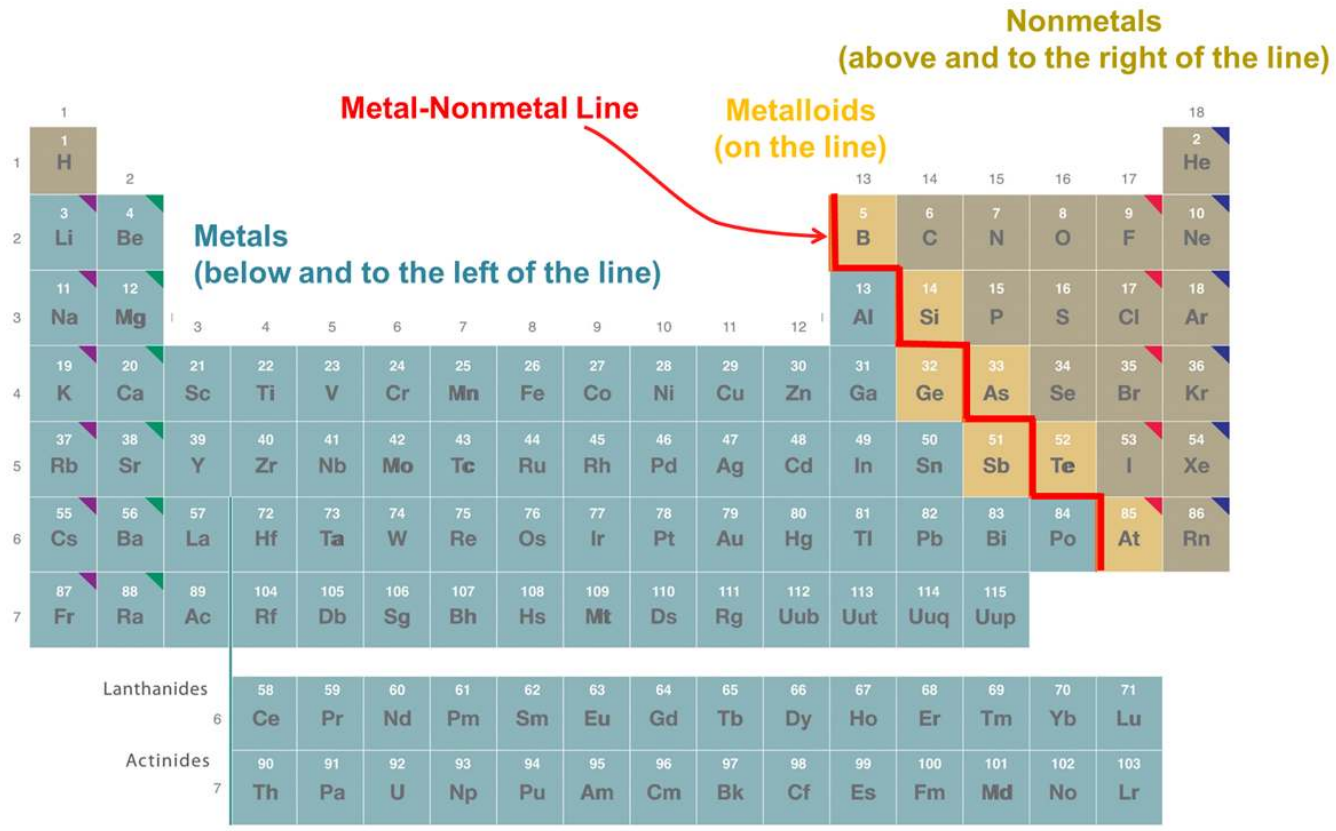


Figure \(\PageIndex{2}\). The metal-nonmetal-metalloid distinction and the metal-nonmetal "line". The image is adapted from https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/02._Atoms%2C_Molecules%2C_and_Ions/2.5%3A_The_Periodic_Table. Otherwise this work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

The **metals** towards lower left of the periodic table form metallic solids held together by delocalized bonding. As a result metals

- are *malleable* (able to be hammered into sheets) and *ductile* (able to be pulled into wires), since metals' solid state lattices may be deformed by dislocation movement (slip) without significantly disrupting the bonding.
- exhibit a *high thermal conductivity* and *high electrical conductivity*. Since they have an incompletely filled valence band delocalized throughout the structure, it is easy to transmit heat and charge by moving their electrons around.

In contrast, the **nonmentals** towards the upper right of the periodic table form molecular compounds and network covalent solids. In general these elements *tend to*

- be liquids, gases, or *brittle* solids. When present as solids, nonmetals tend to be brittle since deformation involves rupturing covalent bonds in the case of covalent solids or the rupture of intermolecular forces in the case of molecular solids.
- have *low thermal and electrical conductivity*, since for molecular solids the transfer of energy or electrons via collisions or through space is much much slower and, for network covalent solids held together by strong sigma bonds, involves excitation of electrons across a reasonably large band gap. Note that this is only a tendency. Network covalent solids held together by weaker covalent bonds or \(\pi\)-bonds sometimes have small or nonexistent band gaps. For example, the graphite allotrope of carbon is an outstanding electrical conductor because its \(\pi\)-valence band and \(\pi\)*-conduction band overlap, leaving no band gap.

The **metalloids** along the metal-nonmetal line form solids that exhibit bonding patterns and properties intermediate between those of metals and nonmetals. This is because is in reality there is a graduation in element properties as one moves from the lower left to the upper right of the periodic table. Consequently, although the distinction between metals, nonmetals, and metalloids can be a helpful one, these categories should not be understood too rigidly.

The same is true of the tendency of metals and nonmetals to form ionic compounds with one another, owing to the tendency of metals to lose electrons and nonmetals to gain them. In practice, there is a graduation in ionic character based on the difference in the elements' electronegativites and the size/polarizability of the atoms involved. As a result many compounds between metals and nonmetals may be profitably thought of as involving polar covalent bonds.

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7.1.1.2: There are qualitative differences between the chemistry of the elements in the first two rows and those in the rest of the periodic table

The bonding characteristics of the elements do not vary gradually down the groups in the main group of the periodic table. Instead, there are significant discontinuities on moving between the first and second row elements and the second row elements and the rest of the periodic table. These differences are outlined below and depicted schematically in Figure **7.1.1.2.1**.

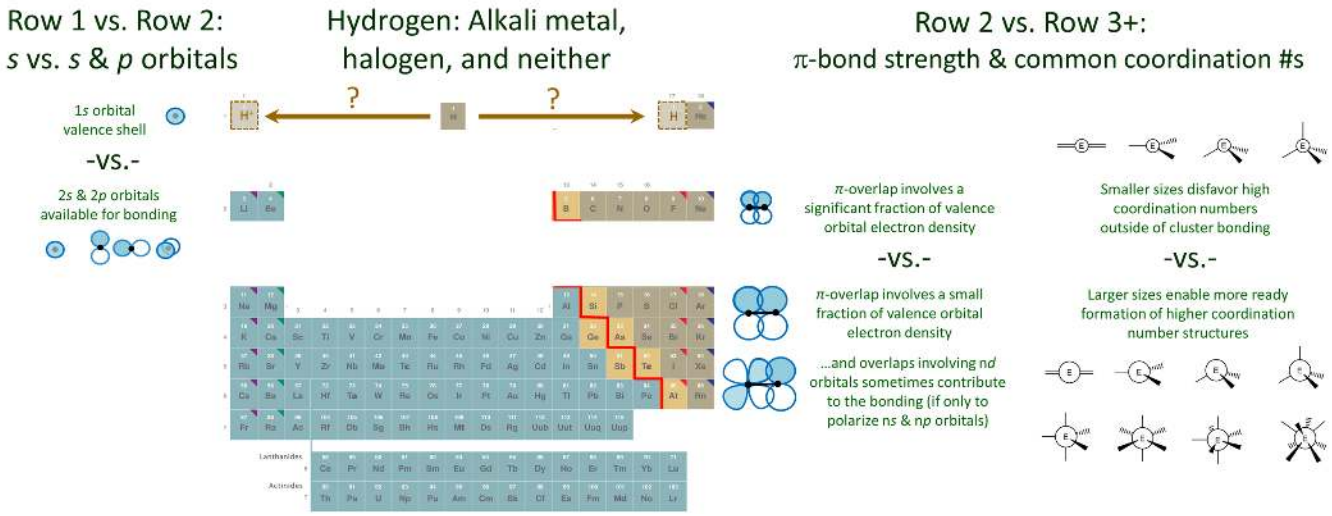


Figure **7.1.1.2.1**. Factors that contribute to major differences in the chemical properties between the elements of the first two rows and between the row 2 elements and those in the rest of the periodic table. The image is adapted from https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/02._Atoms%2C_Molecules%2C_and_Ions/2.5%3A_The_Periodic_Table. Otherwise this work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

The first row elements have a unique chemistry because their valence shell is only a 1*s* orbital.

In the case of He the 1*s* orbital is full, compact, and of low energy. Consequently He is extremely inert, to the point where no compounds of He are known.

Hydrogen's 1s orbital is comparatively higher in energy. As a result H is more reactive. It tends to lose or gain its single electron but can also contribute to multicenter bonding.

Because of its chemical versatility the location of H in the periodic table is ambiguous. Even though its electronegativity is much greater than that of lithium, it is usually placed at the head of the alkali metals. This placement is consistent with its possession of a singe valence electron and the consequent readiness with which it loses an electron, particularly in aqueous media. However, hydrogen is also just short a single electron and so in other contexts it readily forms hydrides. Thus it might be placed at the head of the halogens. Although it is rare to place H above the halogens, in some tables H is placed above the table to emphasize this chemical versatility.

According to the uniqueness principle the second row elements are unique in their ability to form strong multiple bonds and their resistance to serving as high coordination number centers.

There are three reasons why the second row elements differ significantly from their heavier cogeners.

1. Only the second row elements form strong π-bonds. As depicted schematically in Figure **7.1.1.2.1**, the second row elements are able to form strong π bonds since the fraction of electron density involved in the π-overlap is significant for the more compact orbitals and shorter bonds of the row 2 elements. In contrast, for row 3 and heavier elements, relatively little of the large and diffuse orbitals contributes to the overlap that stabilizes the π-bond. In consequence, π-bonds involving these elements are very weak and such bonds are *relatively* rare. This is because it is almost always more favorable for such elements to form multiple single bonds or engage in cluster bonding.

The tendency of Row 2 nonmetals to form strong π bonds in cases where their heavier cogeners form extended structures is apparent from the common allotropes formed by the *p*-block nonmetals. As shown in Figure **7.1.1.2.2**, Row 3+ elements have a greater tendency to form extended structures held together by single bonds than their Row 2 counterparts.

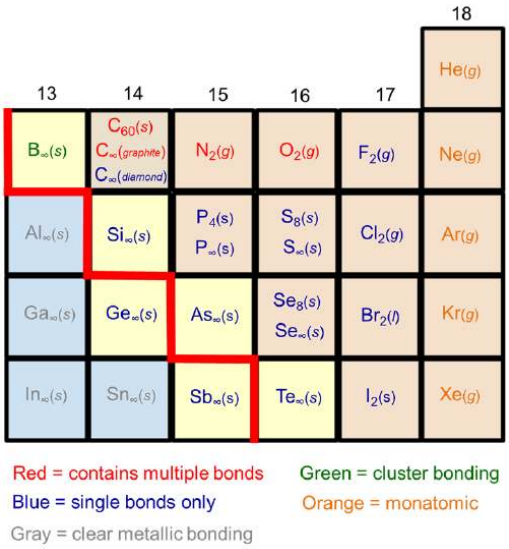


Figure **7.1.1.2.2**. Characteristics of the common allotropes of selected *p* block elements. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

As shown in Figure **7.1.1.2.3**, the Row 2 element carbon forms sheetlike structures involving multiple bonding (graphite, fullerenes, nanotubes) as well as 3D networks held together by single bonds (the diamond structure), while its heavier cogeners Si and Ge only form 3D networks. Similarly, nitrogen and oxygen form diatomic gases held together by multiple bonds, while their heavier cogeners form clusters (P), layers (As, Sb), or chains (S, Se, Te) held together by single covalent bonds.

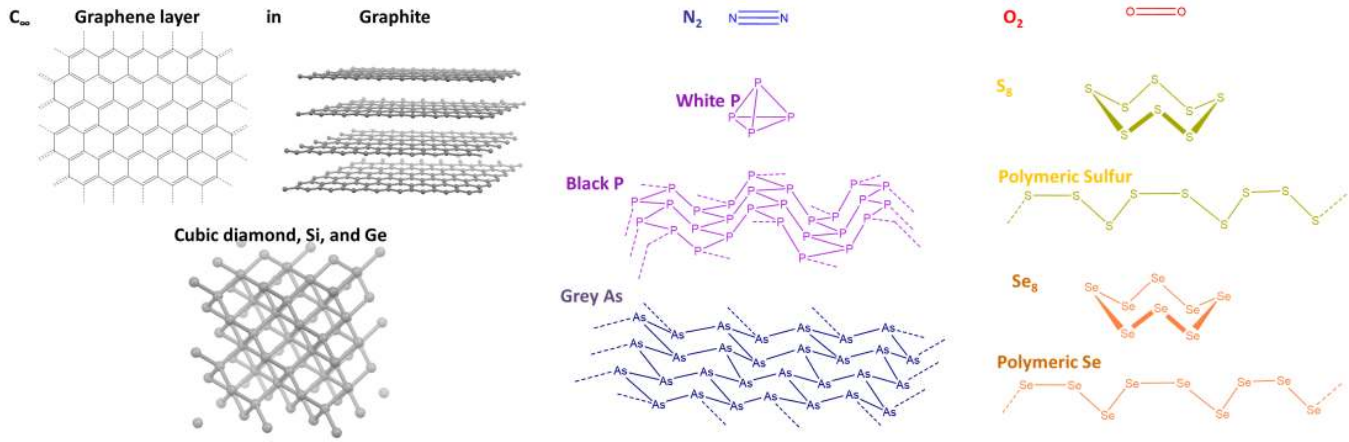


Figure **7.1.1.2.3**. While row 2 elements like C, N, and O form structures held together by multiple bonds, their heavier cogeners form singly bonded clusters, rings, chains, sheets, and networks. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

2. **The valence shell of the second row elements lacks low-lying n*d* orbitals.** As a result, only the 2*s* and 2*p* type orbitals of second row elements significantly contribute to the bonding in their compounds. In contrast, the main group elements of row 3 and higher possess low lying unoccupied n*d* orbitals, which enable them to act as a π acid towards a ligand atom by forming $d_\pi - p_\pi$ and $d_\pi - d_\pi$ overlaps.

3. As depicted in Figure **7.1.1.2.1**, **when second row elements serve as a central atom, they do not readily exhibit coordination numbers higher than four**. In contrast, the larger size of row 3 and heavier elements reduces the steric strain associated with the addition of multiple ligands about an element center. This makes it easier for these elements to form trigonal bipyramidal, octahedral, and other high coordination number structures.

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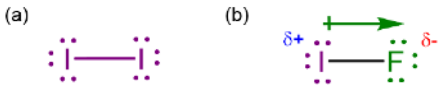
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7.1.2: Electronegativity increases and radius decreases towards the upper left of the periodic table, with electron withdrawing substituents, and with oxidation state

The physical and chemical properties of main group compounds depend in part on the electronegativity of the atoms involved.

Electronegativity is somewhat loosely defined as the ability of atoms to attract electrons towards themselves in covalent bonds. When atoms that differ in electronegativity form a covalent bond, the bonding electrons are not shared equally. Instead, the bonding electrons are more strongly attracted towards the more electronegative atom, resulting in a polar bond, as shown in Scheme **7.1.2.*I***.



Scheme **7.1.2.*I***. (a) The bonding electrons in molecular diiodine's homopolar bond are shared equally (b), while those in iodine monofluoride are more strongly attracted to the fluorine nucleus, polarizing the bond towards the fluorine.

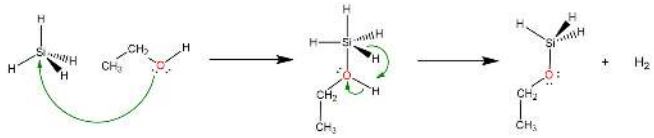
Because electronegativity determines the polarity of bonds and by extension molecules, it is one of the key determinants of the chemical and physical properties of main group compounds.

A classic example of the influence of bond polarity on reactivity involves the group IV/14 element hydrides. Carbon hydrides like methane and other alkanes do not react with water, alcohols, and other Brønsted acids, while silanes, germanes, and stannanes do. For example

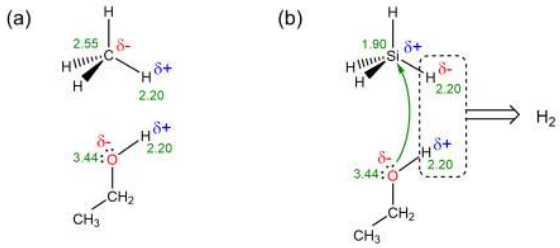
$$CH_4 + 4HOEt \rightarrow \text{No reaction}$$

$$SiH_4 + 4HOEt \rightarrow Si(OEt)_4 + 4H_2$$

This difference in reactivity reflects two factors. The first is a kinetic one. The ability of the larger Si atom to more readily add an additional ligand to give a relatively stable trigonal bipyramidal intermediate provides a relatively low energy pathway for the reaction, enabling it to take place quickly.



The second and much more important factor that determines the difference in reactivity is thermodynamic and has to do with the polarities of the C-H and Si-H bonds. These polarities depend on the electronegativities of carbon, silicon, hydrogen, and oxygen as depicted in Scheme **7.1.2.*I***. As can be seen in part a of Scheme **7.1.2.*I***, because carbon's electronegativity is greater than that of H, the hydrogens of C-H bonds are electrophilic and act as weak Brønsted acids, rendering them unreactive towards other Brønsted acids like alcohols. In contrast, as shown in part b, silicon's electronegativity is lower than that of H, so that the polarization of Si-H bonds facilitates both elimination of the Si-H and O-H as H_2 and nucleophilic attack of the ethanol O at the Si center.



Scheme **7.1.2.*II***. Structures of silane, methane, and ethanol showing the electronegativites of C, Si, H, and O in green. (a) In the case of methane the C-H bonds are polarized to disfavor nucleophilic addition of the ethanol oxygen and elimination of the C-H and O-H hydrogens. (b) In contrast, the polarity of silane's Si-H bonds facilitates both nucleophilic addition and elimination of the Si-H and O-H hydrogens as H_2.

The Pauling scale is the most commonly used scale to rate electronegativities.

Electronegativity is most commonly quantified using the Pauling scale. The Pauling scale is based on the observation that polar bonds are generally stronger than the average of their homopolar counterparts. This is well illustrated by the bond energies of H_2, Cl_2, and HCl given in Table **7.1.2.1**. As may be seen from the table, the average of the H-H and F-F bond energy of 295.5 kJ/mol is only 52% of the H-F bond energy of 567 kJ/mol.

Table 7.1.2.1. Bond energies of H_2, Cl_2, and HCl.

Bond	H-H	F-F	Average of HH & FF		H-F
Energy (kJ/mol)	436	155	295.5	<<	567

Figure **7.1.2.2**.

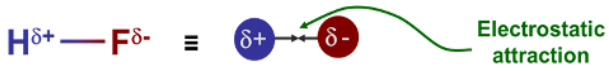


Figure **7.1.2.1**. Electrostatic attraction between partial atomic charges in HF.

In this model the greater the bond polarity (larger δ^+ and δ^-), the larger the "excess bond strength." Consequently the "excess bond strength"may be used as an empirical measure of the difference between the electronegativities χ of the elements involved. Pauling did this using equation **7.1.2.2**:

$$\left|\chi_A - \chi_B\right| = \sqrt{E_{A\ B}(\text{in eV}) - \frac{E_{A-A}(\text{in eV}) + E_{B-B}(\text{in eV})}{2}}$$

where A and B are a given pair of elements.

Equation **7.1.2.2** may only be used to determine differences in electronegativities. To determine absolute electronegativities, Pauling assigned the electronegativity of the most electronegative element in his scale, F, a value of 4.00, although to accomodate more accurate thermochemical data the Pauling electronegativity of F has since been adjusted to 3.98. Pauling electronegativities are given for the elements in Figure **7.1.2.2**.

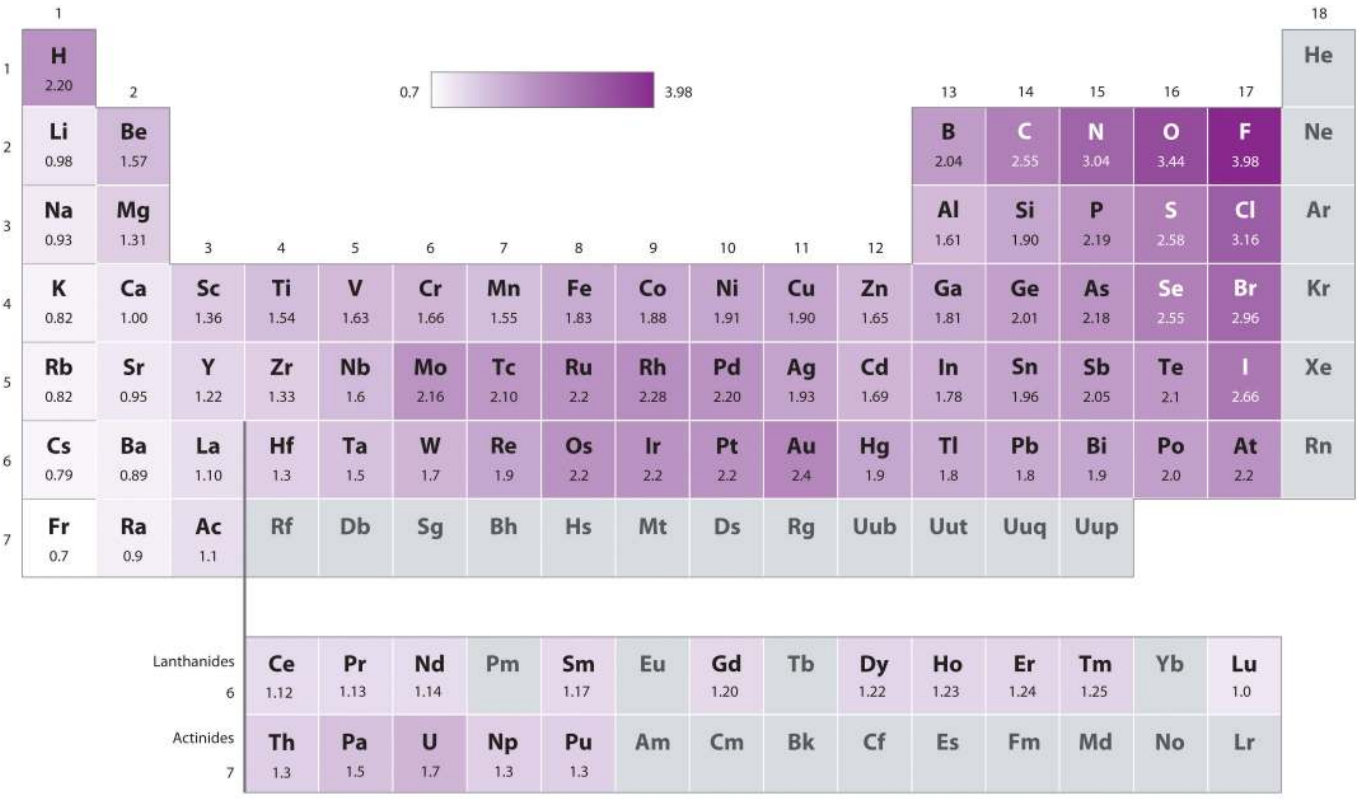


Figure **7.1.2.3**. Pauling electronegativities of the elements. Taken from https://chem.libretexts.org/Courses/Mount_Royal_University/Chem_1201/Unit_2._Periodic_Properties_of_the_Elements/2.12%3A_Electronegativity

Electronegativity generally increases across a row and decreases down a group

As can be seen from the Pauling electronegativity values in Figure **7.1.2.4**, within the main group electronegativity decreases down a group and roughly increases on moving from left to right across a group - *i.e.*, electronegativity roughly increases on moving from the lower left to the upper right of the periodic table.

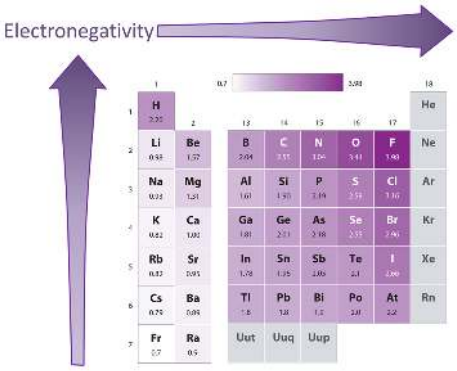


Figure **7.1.2.4**. Pauling electronegativities of the main group elements. Adapted from https://chem.libretexts.org/Courses/Mount_Royal_University/Chem_1201/Unit_2._Periodic_Properties_of_the_Elements/2.12%3A_Electronegativity

Two factors modify the overall pattern of increasing electronegativity on moving to the upper right of the periodic table.

The first is the aforementioned ambiguous position of hydrogen. The electronegativity of hydrogen does agree with this overall pattern if hydrogen is placed at the head of the alkali metal group. However, it is over a full unit higher than any other alkali metal and, if placed at the head of the halogen group, would be almost two units lower than that of F.

The second is the reversal of the expected decrease in electronegativity down a group for the pairs Al & Ga and Si & Ge. This is because the post transition metals have anomalously high electronegativities due to the increasing effective nuclear charge associated with the filling of the *d* block - *i.e.*, a sort of *d*-block contraction for electronegativity. The net effect is that the *post transition elements in the p block all have anomalously high electronegativities*. In the cases of Al & Ga and Si & Ge this results in an increase in electronegativity down the group as one moves from row 3 to row 4. In the case of the other post-transition elements it is seen that the movement between these two rows involves a modest decrease in electronegativity.

The electronegativity trends lead to diagonal relationships in which elements just to the left of and down a column to one another have similar chemical properties.

The increase in electronegativity across a row of the periodic table is sometimes compensated for by the decrease in electronegativity down a group, so that elements so diagonally related sometimes have similar electronegativities. Some such diagonally related elements have similar physical and chemical properties, although these similarities may not be due to the effect of electronegativity alone. Since atomic size also decreases across a row and increases down a group, some similarities reflect size effects as well. In any event, the result is that there are recognized **diagonal relationships** of chemical and physical similarity among elements diagonal to one another in the periodic table. Some of the more prominent diagonal relationships within the main group are shown in Figure **7.1.2.5**.

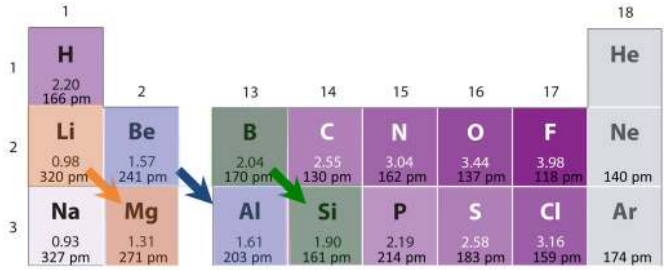


Figure **7.1.2.5**. Some commonly recognized diagonal relationships among the main group elements, which are listed along with their Pauling electronegativities and calculated Van der Waals radii. The radii are taken as the radii calculated at the CCSD(T) level using an ANO-RCC basis set as reported in Mantina, M.; Chamberlin, A. C.; Valero, R.; Cramer, C. J.; Truhlar, D. G., Consistent van der Waals Radii for the Whole Main Group. The Journal of Physical Chemistry A 2009, 113 (19), 5806-5812. The image is adapted from https://chem.libretexts.org/Courses/Mount_Royal_University/Chem_1201/Unit_2._Periodic_Properties_of_the_Elements/2.12%3A_Electronegativity

A few observations illustrate how these diagonal relationships work.

- **Li & Mg** – Lithium acts like Mg in that it is the only alkali metal to form stable nitride (Li_3N), oxide (Li_2O), and THF soluble alkyl carbanion salts as alkaline Earth metals do. This may be seen in the similar compounds formed by Li and Mg shown in Table **7.1.2.2**. In contrast, the larger alkali metals form insoluble polymeric carbanion reagents, superoxides or peroxides and not oxides, and extremely unstable nitrides.

Table 7.1.2.2. Similar compounds formed by the diagonally related elements Li and Mg.

Type of compound	Li	Mg
oxide	Li_2O	MgO
nitride	Li_3N	Mg_3N_2
alkyl carbanion reagent	alkyllithium (RLi)	Gringard Reagent (RMg^+)

- **Be & Al** – In contrast to the basic oxides and hydroxides of most alkali metals and the heavier group 13 elements, both Be and Al form amphoteric oxides and hydroxides (***Table*7.1.2.3**). Like Be and the remaining alkali metals, aluminum also forms a carbide (C^{4-}"salt") instead of an acetylide (C_2^{2-}) or allylide (C_3^{4-}).

Table 7.1.2.3. Amphoteric behavior of the oxides and hydroxides of beryllium and aluminum.

Reaction	Be	Al
Oxide hydrolysis to hydroxide	$BeO + H_2O \rightarrow Be(OH)_2$	$Al_2O_3 + 3H_2O \rightarrow 2Al(OH)_3$
Hydroxide as an Arrhenius and Brønsted Base	$Be(OH)_2 \rightarrow BeO(OH)^+ + OH^-$ or $Be(OH)_2 + 2H^+ \rightarrow Be^{2+} + 2H_2O$	$Al(OH)_3 \rightarrow 2AlO(OH)_2^+ + OH^-$ or $Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O$
Hydroxide as a Lewis Acid	$Be(OH)_2 + 2OH^- \rightarrow Be(OH)_4^{2-}$	$Al(OH)_3 + OH^- \rightarrow 2AlO(OH)_4^-$

- **B & Si** - Both of these elements act as semiconductors, form acidic complex polymeric covalent oxides containing interlinked EO_4 tetrahedra, and their halides (BCl_3 & $SiCl_4$) act as acid halides. In contrast, the oxides of carbon (CO and CO_2) are monomeric, while the oxides of the heavier cogeners of these elements (Al_2O_3, Ga_2O_3, In_2O_3, In_2O, Tl_2O and GeO_2, SnO_2, PbO_2, and PbO) are considered ionic oxides. The halides of the heavier cogeners of Si more readily act as ionic oxides, while the binary halides of carbon (*e.g.*, compounds like CCl_4) are usually not readily hydrolyzed.

The Mulliken and Allred-Rochow Electronegativity Scales connect Electronegativity to other Atomic Properties

While the Pauling scale considers electronegativity in terms of bonding, there are a number of other electronegativity scales that define electronegativity as a function of other atomic properties. Two of these will be considered here: the **Mulliken (or Mulliken-Jaffe)** scale, which defines electronegativity in terms of electron affinity and ionization energy (and by extension orbital energies), and the **Allred-Rochow** scale, which considers electronegativity in terms of effective nuclear charges.

The Mulliken Electronegativity Scale defines electronegativity in terms of Electron Affinity and Ionization Energy

The **Mulliken definition of electronegativity** was previously described in connection with absolute hardness and softness as the first derivative of a species energy with respect to changes in total number of electrons, N_{e^-}.

$$Mulliken\ electronegativity = \chi = \frac{dE}{dN_{e^-}}$$

where E is in eV

Since this derivative is difficult to evaluate experimentally, the Mulliken electronegativity is typically approximated as the average of the species' ionization energy and electronegativity.

$$Mulliken\ \ electronegativity = \chi \approx \frac{IE + EA}{2}$$

where IE and EA are in eV

which, if the IE is approximated by Koopman's theorem as the opposite of the energy of the lowest unoccupied atomic orbital (LUAO) $(IE = -E_{HOMO})$ and the EA as the opposite of the energy released on absorption of an electron, may be taken as an approximation of the LUMO energy.

$$E_{LUMO} \approx -EA$$

and the Mulliken electronegativity is just the average of the HOAO and LUAO energies (~Fermi energy):

$$Mulliken\ electronegativity, \chi \approx -\frac{E_{LUAO} + E_{HOAO}}{2}$$

where all values are for the gas phase atoms in units of eV

The Allred-Rochow Electronegativity Scale defines electronegativity in terms of the effective nuclear charge experienced by the valence electrons.

The Allred-Rochow electronegativity scale attempts to quantify electronegativity in terms of the electrostatic force attracting the bonding electrons to the atomic center. It does this by calculating the electronegativity as the associated electrostatic force.

$$\chi_{\text{Allred–Rochow, raw}} = -\frac{1}{4\pi\epsilon_0}\frac{e^2 Z*}{r_{\text{bond}}^2}$$

These raw values have units of force (N/electron or dyne/electron) and do not correspond closely to electronegativity values reported on the Pauling Scale. Consequently, an empirical correction factor is used to adjust the scale to give electronegativities that more closely correspond to their Pauling equivalents.

$$\chi_{\text{Allred–Rochow}} = 3590\frac{e^2 Z*}{r_{\text{bond}}^2}$$

+0.744

Mulliken electronegativities so calculated are given in Table **7.1.2.4**.

Table **7.1.2.4**: Allred-Rochow Electronegativity Values. Copied from https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Physical_Properties_of_Matter/Atomic_and_Molecular_Proper Rochow_Electronegativity

H **2.20**														
Li **0.97**	Be **1.47**											B **2.01**	C **2.50**	N **3.07**
Na **1.01**	Mg **1.23**											Al **1.47**	Si **1.74**	P **2.06**
K **0.91**	Ca **1.04**	Sc **1.20**	Ti **1.32**	V **1.45**	Cr **1.56**	Mn **1.60**	Fe **1.64**	Co **1.70**	Ni **1.75**	Cu **1.75**	Zn **1.66**	Ga **1.82**	Ge **2.02**	As **2.20**
Rb **0.89**	Sr **0.99**	Y **1.11**	Zr **1.22**	Nb **1.23**	Mo **1.30**	Te **1.36**	Ru **1.42**	Rh **1.45**	Pd **1.35**	Ag **1.42**	Cd **1.46**	In **1.49**	Sn **1.72**	Sb **1.82**
Cs **0.86**	Ba **0.97**	La **1.08**	Hf **1.23**	Ta **1.33**	W **1.40**	Re **1.46**	Os **1.52**	Ir **1.55**	Pt **1.44**	Au **1.42**	Hg **1.44**	Tl **1.44**	Pb **1.55**	Bi **1.67**

These values correlate reasonably well with Pauling electronegativities. One consequence of this good agreement is that both scales are useful for making qualitative predictions about a substance's chemical behavior. For this reason most chemists continue to use the Pauling scale. In this respect, perhaps the greatest value of the Mulliken and Allred-Rochow electronegativity scales for the bench chemist lies in how they connect electronegativity to parameters that may be used to tailor molecular structure and reactivity, namely, substituent effects and oxidation states.

The effective electronegativity of an atom varies increases with oxidation state and in the presence of electron withdrawing substituents

One of the advantages of the Allred-Rochow and Mulliken electronegativity systems over that of Pauling's is that they can consider electronegativity in the context of compounds, in which electron donating and withdrawing groups modify the ability of atomic centers to attract electrons in a bond. As was considered in the section on measures of hardness, the Mulliken scale can be used to define the electronegativity of Lewis acid centers simply by considering the HOMO and LUMO energy in place of the HOAO and LUAO energies.

$$\textit{Mulliken electronegativity of Lewis acid}, \chi \approx -\frac{E_{LUAO} + E_{HOAO}}{2}$$

$$\textbf{where all values are in units of eV}$$

The Allred-Rochow scale is not usually applied directly to molecules. However, its model of electronegativity as a measure of the electrostatic force experienced by the valence electrons may be applied to atoms in molecules, specifically by accounting for the influence of electron donating and withdrawing substituents on the effective nuclear charge an electron experiences. This is not usually done in any sort of rigorous way, and in the context of a typical advanced inorganic chemistry course, the influence of substituent groups on an atom's electronegativity may be estimated in one of two ways:

1. The **group electronegativity concept** may be used to *quantitatively estimate* an atom or functional group's electronegativity. A **group electronegativity** is the electronegativity of an atom that has been modified by attaching it to one or more substituents. These substituents modify the atom's base electronegativity by an amount equal to their empirically-determined substituent constants so that the group electronegativity, Missing open brace for subscript, may be calculated.[1]

Missing open brace for subscript

where Missing open brace for subscript and Missing open brace for subscript are the group's base electronegativity and the substituent constant, respectively. Because the substituent constant must be known in order to calculate group electronegativities, the group electronegativity concept has primarily been applied to organic compounds.

2. The effect of substituents on electronegativity may be *qualitatively rationalized* in terms of **inductive effects** and **oxidation state**. In this system

- electron donating groups decrease Z* and consequently a center's effective electronegativity; conversely, by increasing the Z* experienced by an atom's valence electrons, electron withdrawing groups increase its effective electronegativity.
- when an atomic center is oxidized, Z* and its effective electronegativity increase, while when it is reduced, Z* and its effective electronegativity decrease. This effect is commonly manifested as an increase in the acidity of polarized E-OH units as the oxidation state of the central element (E) increases, as illustrated for the inorganic oxyacids in Table **7.1.2.4**.

Table 7.1.2.4. pK_a vales for selected oxyacids illustrating the increase in Brønsted acidity with central atom oxidation state.[2]

Acid	Central atom oxidation state	pK_a (pK_{a1} unless otherwise noted)
H_2SO_3	S^{IV}	1.9
H_2SO_4	S^{VI}	<0
HNO_2	N^{III}	3.1
HNO_3	N^{V}	<0
H_3PO_3	P^{III}	3.1
H_3PO_4	P^{V}	1.3
HClO	Cl^{I}	7.40
$HClO_2$	Cl^{III}	1.94
$HClO_3$	Cl^{V}	-2.7 (predicted)
$HClO_4$	Cl^{VII}	~ -15[3]

References

1. Davis, M. A., Group electronegativity and polar substituent constants. The Journal of Organic Chemistry 1967, 32 (4), 1161-1163.

2. All pK_a values with the exception of that of $HClO_4$ and $HClO_3$ are taken from Perrin, D. D., *Ionization Constants of Inorganic Acids and Bases in Aqueous Solution*, *Second Edition*, Pergamon, Oxford, 1982.

3. The pK_a value of $HClO_4$ is taken from Trummal, A.; Lipping, L.; Kaljurand, I.; Koppel, I. A.; Leito, I., Acidity of Strong Acids in Water and Dimethyl Sulfoxide. The Journal of Physical Chemistry A 2016, 120 (20), 3663-3669.

Contributors and Attributions

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7.1.3: Ionization energy roughly increases towards the upper left of the periodic table but is also influenced by orbital energy and pairing energy effects

As with electronegativity, the ionization energy of the main group elements (Figure **7.1.3.1**) decreases down a group and increases from left to right across the periodic table.

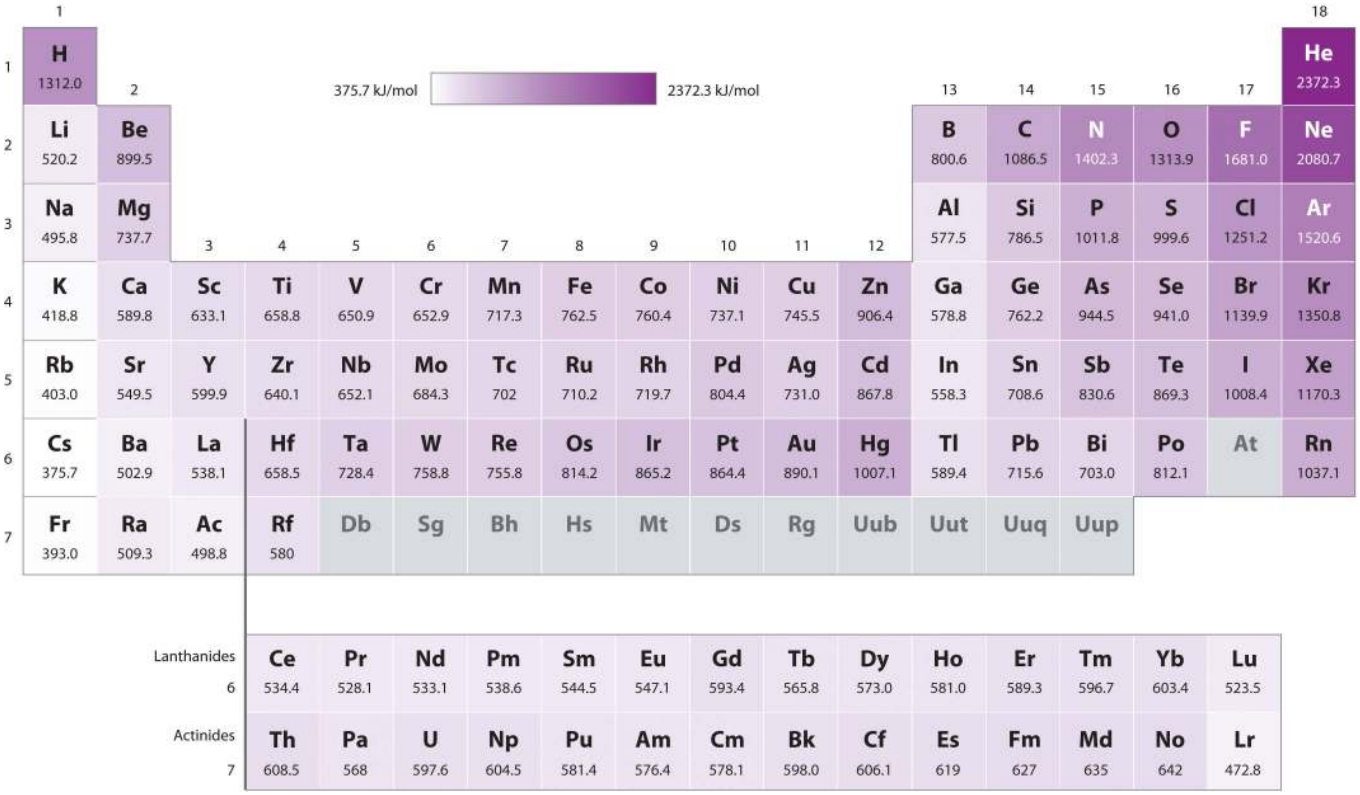


Figure **7.1.3.1**. Ionization energies of the elements in kJ/mol. (CC BY-SA-NC 3.0; anonymous)

As may be seen in Figure **7.1.3.1**, ionization energy does not increase steadily from left to right across a group. Instead, there are two discontinuities. These discontinuities are summarized in Figure **7.1.3.2**.

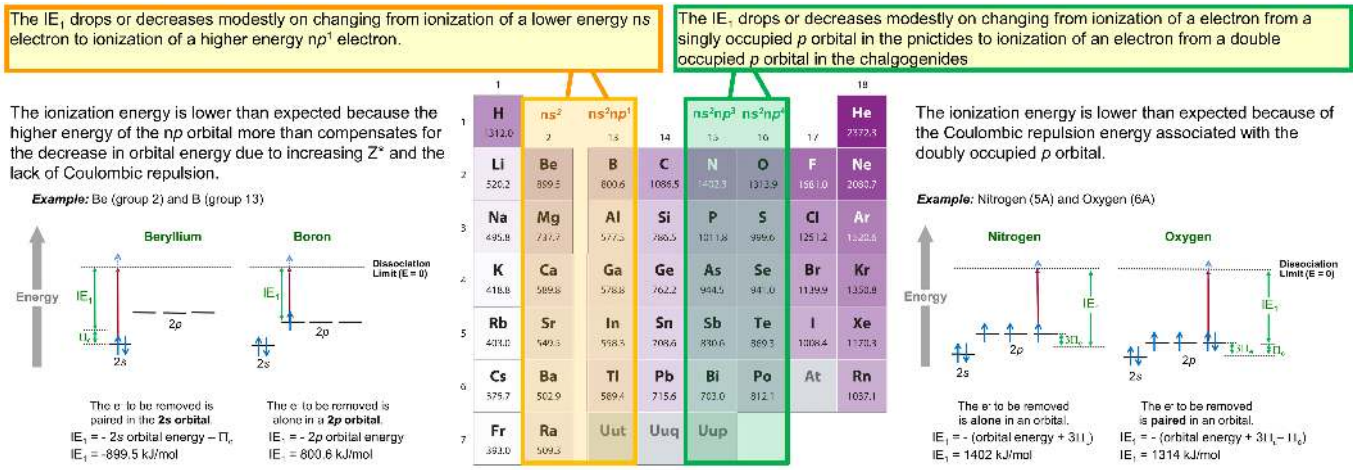


Figure **7.1.3.2**. Discontinuities in the expected increase in first ionization energy (IE_1) trends among the main group elements and their explanation in terms of changing valence subshells and their occupancy. The periodic table of ionization energies in this figure is adapted from https://chem.libretexts.org/Courses/Mount_Royal_University/Chem_1201/Unit_2._Periodic_Properties_of_the_Elements/2.09%3A_Ionization_Energy. Otherwise this work by Stephen Contakes is licensed under a Creative Commons Attribution 3.0 International License.

Briefly, the two discontinuities are as follows:

1. There is a decrease or meager increase in ionization energy that occurs on going from the alkaline earth metals to the boron group, which is caused by the change in the highest occupied orbital from a lower energy n*s* to a higher energy n*p* subshell.
2. There is a decrease or anomalously modest increase in ionization energy on going from the pnictides to the chalcogenides caused by the presence of Coulombic repulsion in the chalcogenide np^4 configuration that is not present in the pnictide np^3 configuration.

These discontinuities illustrate how orbital energy and electron configuration effects should be considered when considering the reactivity of the elements.

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- **8.1.3: Ionization energy roughly increases towards the upper left of the periodic table but is also influenced by orbital energy and pairing energy effects** by Stephen M. Contakes is licensed CC BY 4.0.

7.1.4: As may be seen from considering an element's redox diagrams, main group elements (aside from the noble gases) generally are more oxidizing towards the upper left of the periodic table and more reducing towards the lower right of the periodic table

The existence of diagonal relationships among elements in the periodic table and the unique properties of the first and second row elements have already been discussed. Thus before beginning a survey of the descriptive chemistry of the elements, it only remains to describe the general trends associated with the redox properties of the elements and to present several conceptual and graphical tools that make it possible to rapidly grasp the general features of the redox chemistry of each element. These are the subject of the present section.

Elements on the left of the periodic table tend to act as reductants; those on the right as oxidants

The ability of the elements to act as oxidants and reductants is usually described by citing the reduction potentials associated with the reactions they undergo in solution. Thus before considering trends in the redox properties of the main group elements, this section will begin by pointing out how redox potentials work and what they represent.

Substances' standard reduction potentials describe the *thermodynamic* propensity of a substance to undergo reduction.

Redox potentials represent the thermodynamic potential for the substance to undergo reduction relative to the ideal standard hydrogen electrode (SHE).

$$2H^+(aq) + 2e^- \rightarrow H_2(g) \quad E^\circ = 0.00V$$

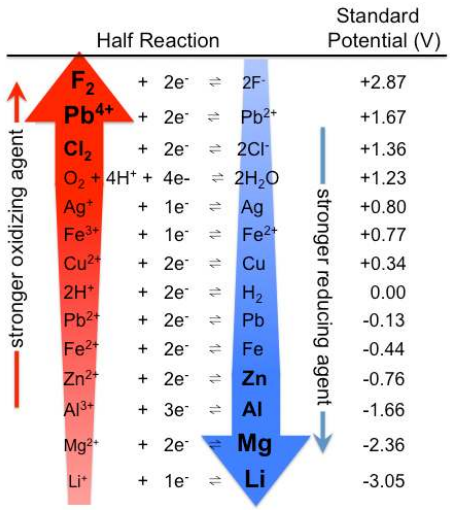
The ability of a substance to act as an oxidant or reductant is described by the relevant standard reduction potential. These correspond to reactions of the form

$$\underset{\text{reductant}}{\text{substance}_{ox}(solv)} + ne^- \rightarrow \underset{\text{oxidant}}{\text{substance}_{red}(solv)}$$

There are three things to notice about these standard reduction potentials.

1. Standard reduction potentials always corresponds to reduction of an oxidant to give a reductant. Consequently,

- thermodynamically better oxidants have more positive standard reduction potentials
- thermodynamically better reductants correspond to the products of standard reduction reactions with more negative standard reduction potentials (Figure \{\PageIndex{1}\}).



1. Substances with more positive reduction potentials are better oxidants while the reduction products of substances with more negative reduction potentials are better reductant
redox potentials are taken
libretexts.org/Bookshelves/Analytical_Chemistry/Supplemental_Modules_(Analytical_Chemistry)/Electrochemistry/Redox_Chemistry/Comparing_Strengths_of_Oxidants_and

2. Since $\Delta G^\circ = -nFE^\circ$, standard reduction potentials are a measure of the thermodynamic spontaneity of a reduction relative to the oxidation of H_2(g). As such, reduction potentials are useful for determining whether a reaction *can* occur but are not useful for determining whether a reaction actually will occur under a given set of conditions. The kinetics of the reduction should also be considered. For instance, thermodynamically nitrate is a powerful oxidant in aqueous solution:

$$2NO_3^-(aq) + 12H^+ + 10e^- \rightarrow N_2(g) + 6H_2O(l) \quad E^\circ = 6.229V!$$

However, in solution there is a large kinetic barrier for nitrate reduction, and nitrate usually functions as an inert spectator ion even when strong reductants are present.

3. Since reduction potentials are thermodynamic quantities, they depend on the stability of both their oxidized and reduced forms. For reactions involving soluble species in solution, these stabilities in turn depend on the energy of solvation of any solution phase species involved. For this reason, there is no

such thing as the potential of a given substance to act as an oxidant or reductant. They should always be specified relative to a given set of conditions.

Most tabulated redox potentials correspond to oxidations and reductions taking place in aqueous solutions. Moreover, for reactions involving the gain or loss of protons (or OH^-), they likely correspond to reactions taking place in 1.0 *M* H^+ solution (or, less commonly, 1.0 *M* OH^-). Such potentials may not correspond closely to those taking place in nonaqueous solvents or in water at other pH values. Nevertheless, with these caveats it is possible to recognize rough trends in the redox properties of the elements.

There are three trends in the redox properties of the elements

The redox properties of the elements very roughly follow three general trends:

1. The noble gases are inert and as elements tend not to act as good oxidants or reductants

Otherwise

2. As one moves towards the left of the periodic table, elements tend to act as good reductants, while those towards the right tend to act as increasingly good oxidants.

3. As one moves down a group of the periodic table, elements tend to act as either weaker oxidants or better reductants.

These trends are summarized in Figure **7.1.4.2**.

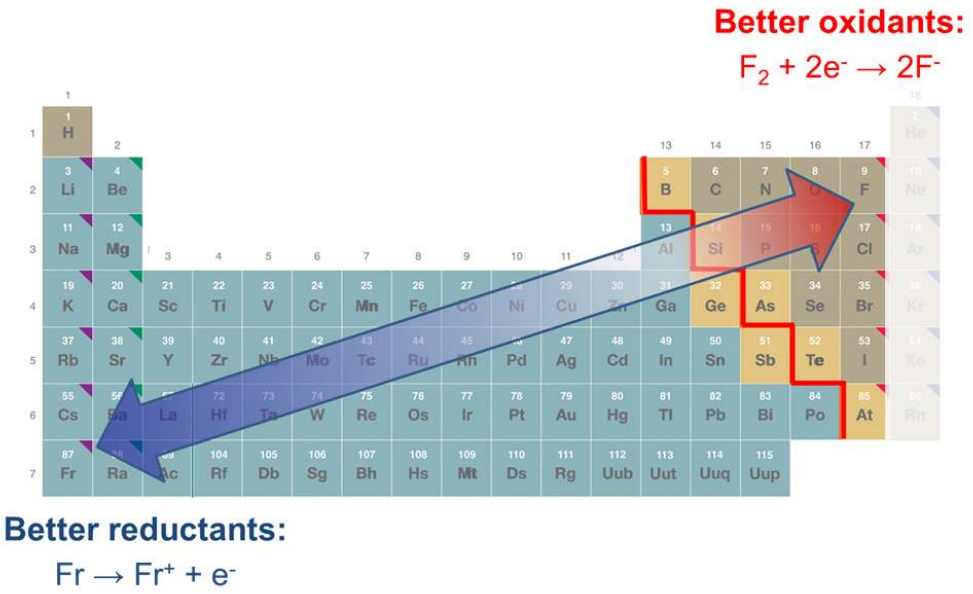


Figure **7.1.4.2**. Idealized scheme showing how elements' ability to act as reductants roughly increases towards the lower left of the periodic table while, noble gases excepted, their oxidizing power increases towards the upper left.

Since substances' ability to act as oxidants and reductants also depends on the stability of their oxidation and reduction products, these trends should be regarded as at best approximate. As can be seen from the data given in Table **7.1.4.1**, the alkali metals furnish an important exception to the general trend that substances become more reducing towards the lower left of the periodic table. Among the elements included,[2] lithium and not cesium is the most powerful reducing agent due to the high stability of the lithium cation in aqueous solution (anomalously high hydration energy). Further, from the potentials given in Table **7.1.4.1**, it can also be seen that on going from K^+ to Rb^+ and Cs^+ the reduction potentials do not decrease but instead remain approximately constant. In this case the decrease in ionization energy throughout this series is compensated for by a set of similar factors.[3]

Table 7.1.4.1 . Standard reduction potentials of aqueous alkali metal cations.

Reduction	***E°***
$Li^+(aq) + e^- \rightarrow Li(s)$	-3.040
$Na^+(aq) + e^- \rightarrow Na(s)$	-2.713
$K^+(aq) + e^- \rightarrow K(s)$	-2.924
$Rb^+(aq) + e^- \rightarrow Rb(s)$	-2.924
$Cs^+(aq) + e^- \rightarrow Cs(s)$	-2.923

Not only are there exceptions to the general trends in the redox properties of the free elements, but many elements also exhibit a rich and interesting redox chemistry involving the interconversion of multiple species possessing different oxidation states. In order to make sense of these it will be helpful to make

use of the schematic and graphical tools that will be developed in the next sections.

References and notes

Unless otherwise noted all reduction potentials are taken from reference 1.

1. Bard, A. J.; Parsons, R.; Jordan, J. Standard potentials in aqueous solution. M. Dekker: New York, 1985.

2. Francium is not included because it is an unstable element and its reduction potential is not known.

3. These factors are beyond the scope of the present section but involve changes in the difference between a metal's cohesion free energy and the hydration free energy of its monocation.

Contributors and Attributions

Stephen Contakes, Westmont College

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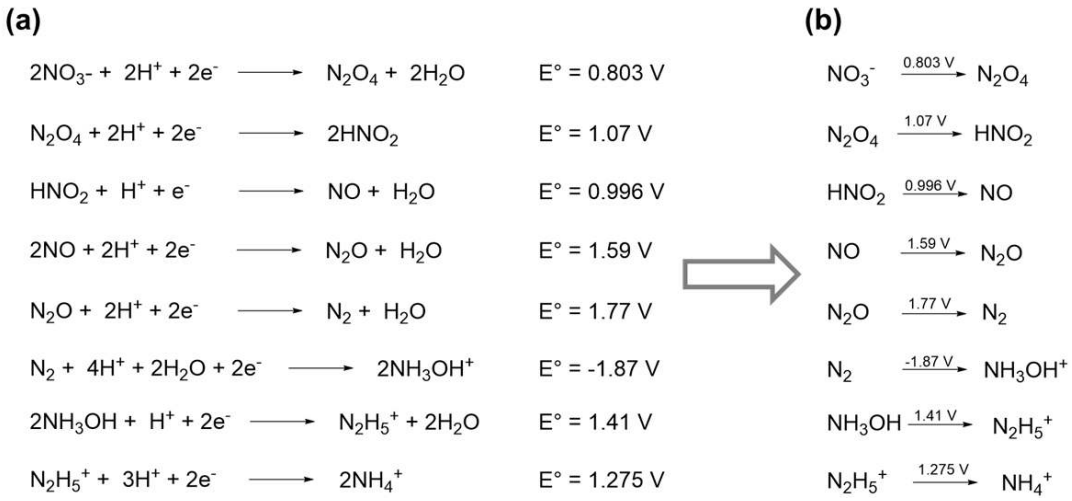
- **8.1.4: As may be seen from considering an element's redox diagrams, main group elements (aside from the noble gases) generally are more oxidizing towards the upper left of the periodic table and more reducing towards the lower right of the periodic table** is licensed CC BY 4.0.

7.1.4.1: Latimer Diagrams summarize elements' redox properties on a single line

Latimer diagrams helpfully summarize elements' redox chemistry in a compact format

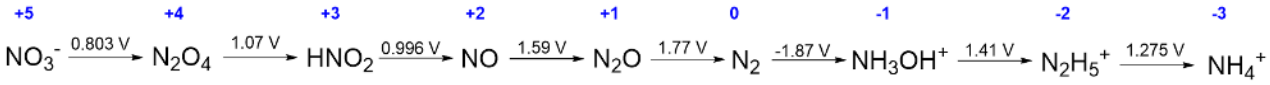
To see how Latimer diagrams work and why they are so useful, it is helpful to start with an example.

A selection of the redox reactions nitrogen is known to undergo in 1.0 *M* aqueous acid is given in Scheme **7.1.4.1.*Ia***.



Scheme **7.1.4.1.I**. (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 **7.1.4.1.*Ia*** is 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 from the stoichiometry of the reaction. Consequently, the information in scheme **7.1.4.1.*Ia*** 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 **7.1.4.1.*Ib***. Notice that in Scheme **7.1.4.1.*Ib***, 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 II.

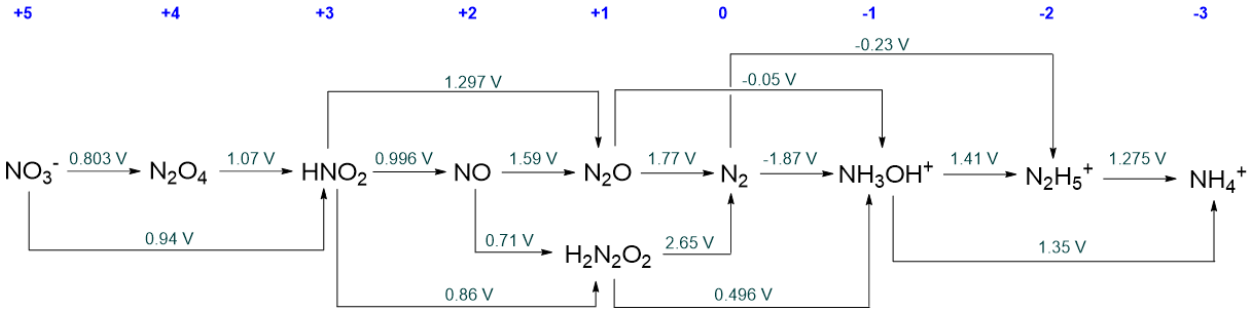


Scheme **7.1.4.1.II**. Acidic Latimer diagram for nitrogen.

The type of diagram shown in Scheme **7.1.4.1.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.
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 **7.1.4.1.*II***.

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 **7.1.4.1.*III***.



Scheme **7.1.4.1.III**. Latimer Diagram for Nitrogen at pH 0. Redrawn from reference 1.

The diagram in Scheme **7.1.4.1.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 fluorine,

$$F_2(g) \; + \; 2H^+ \; 2e^- \; \rightarrow \; 2HF \quad E^\circ \; = \; 3.053 \text{ V in acid}$$

This potential has not been experimentally measured since F_2 is unstable in aqueous solution, reacting rapidly to give HF and O_2.

$$2\,F_2 \; + \; 2\,H_2O \xrightarrow{\text{fast}} 4\,HF \; + O_2$$

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 **7.1.4.1.1** at the bottom of this page.

Latimer diagrams 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, but they also are useful for

1. Determining whether a species is thermodynamically unstable with respect to disproportionation.

Disproportionation occurs when a species reacts with itself to produce two or more stable products. For instance, in basic solution ReO_3 can undergo disproportionation to ReO_4^- and $ReO_2{\cdot}2H_2O$.

$$2Re^{VI}O_3 + 2H_2O \rightarrow Re^{VII}O_4^- + Re^{V}O_2 \cdot 2H_2O$$

As with all redox reactions, disproportionation 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 disproportionation reaction into its half reactions:

$$\text{Reduction}: Re^{VI}O_3 + H_2O + 2H^+ + e^- \rightarrow Re^{V}O_2 \cdot 2H_2O \qquad E^\circ = -0.446V$$

$$\text{Oxidation}: Re^{VI}O_3 + H_2O \rightarrow Re^{VII}O_4^- + 2H^+ + e^- \qquad E^\circ = +0.889V$$

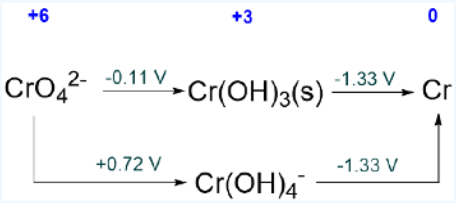
$$\text{Sum}: 2Re^{VI}O_3 + 2H_2O \rightarrow Re^{VII}O_4^- + Re^{V}O_2 \cdot 2H_2O \qquad E^\circ = -0.446V + 0.889V = +0.443V$$

Notice that the disproportionation of ReO_3 in basic solution is favored because the favorable reaction potential for ReO_3 oxidation is larger in magnitude than the 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 7.1.4.1.1

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 disproportionation?

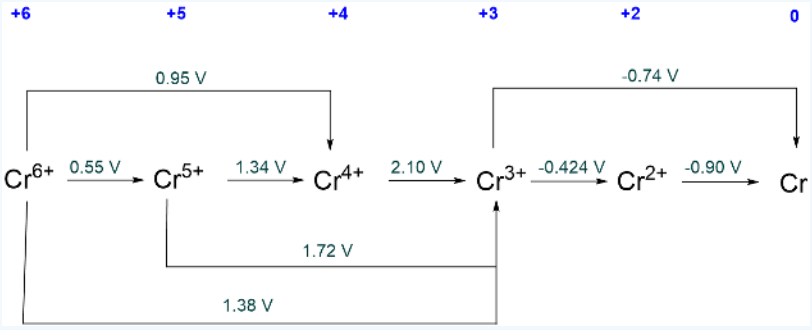


Solution

All of the species are stable with respect to disproportionation since all the potentials on the right of all the Cr^{3+} intermediates are less than those on their left.

Example 7.1.4.1.2

The Latimer diagram for Cr in pH 0 aqueous solution is given below. Which, if any, species are unstable with respect to disproportionation?

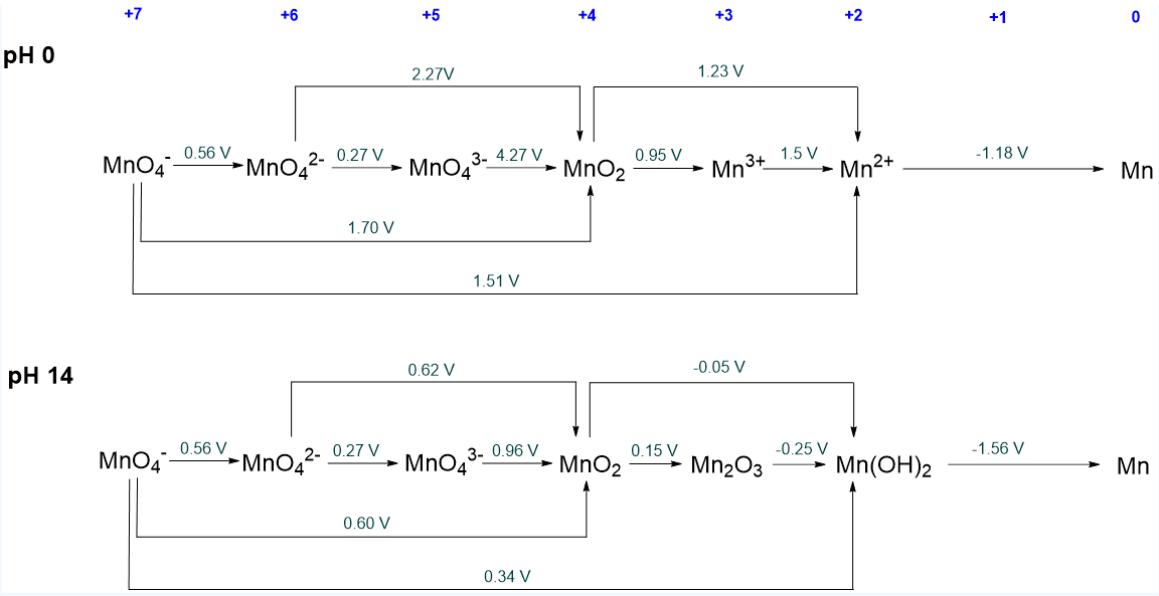


Solution

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 7.1.4.1.3

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 disproportionation? The Latimer diagrams for manganese are given below.



Solution

Under acidic conditions the following species are unstable with respect to disproportionation:

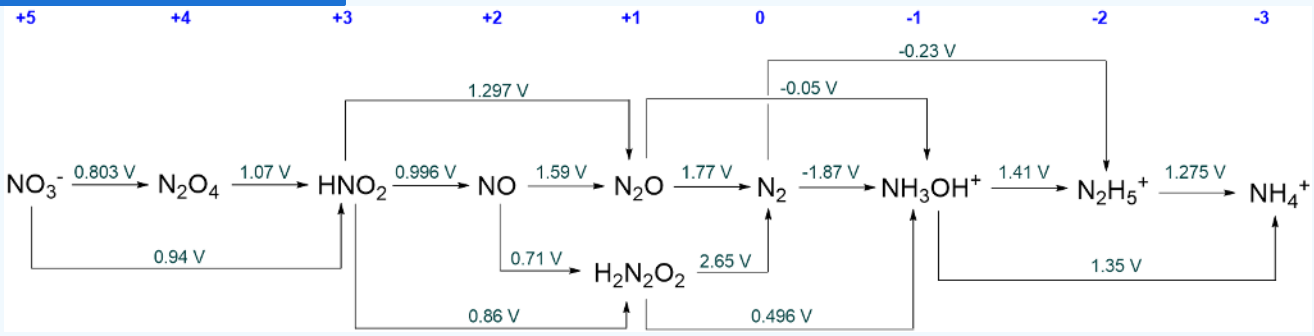
- MnO_4^{2-} is unstable with respect to disproportionation to MnO_4^- and MnO_2.
- MnO_4^{3-} is unstable with respect to MnO_4^{2-} and MnO_2. However, since MnO_4^{2-} is unstable with respect to disproportionation the ultimate products of the disproportionation will be MnO_4^- and MnO_2.
- Mn^{3+} is unstable towards disproportionation 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 disproportionation 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 disproportionation, the ultimate products of the disproportionation 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 7.1.4.1.1, part a



Which nitrogen species in Scheme **7.1.4.1.*III***, (which for convenience is reproduced above) are unstable with respect to disproportionation?

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^+.

? Exercise 7.1.4.1.1, part b

As far as you are able, determine what each metastable nitrogen species will disproportionate to at pH 0.

Answer

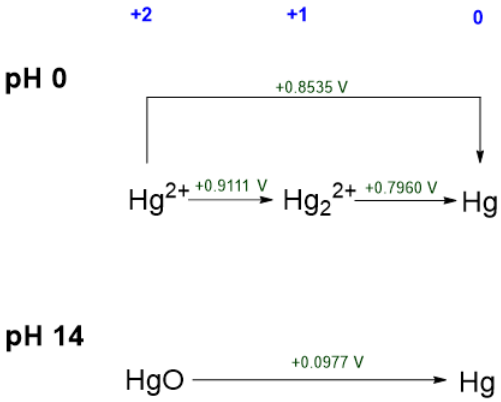
Initially the metastable species will disproportionate to give their immediate neighbors in the Latimer diagram.

However, many of these neighbors are themselves metastable with respect to disproportionation, and so ultimately disproportionation will only stop when species that are stable towards disproportionation are reached.

In the case of N_2O_4, HNO_2, NO, N_2O, and $H_2N_2O_2$, disproportionation will ultimately give NO_3^- and N_2.

For NH_3OH^+, disproportionation 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 **7.1.4.1.1** and **7.1.4.1.2**. A simple instance involves the acidic and basic Latimer diagrams of mercury shown in Scheme **7.1.4.1.*IV***.

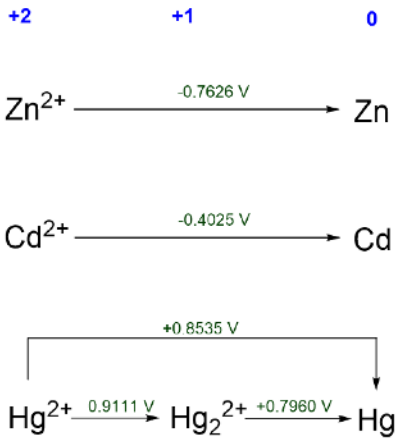


Scheme **7.1.4.1.*IV***: Latimer diagrams for mercury in aqueous solution.

From Scheme **7.1.4.1.*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 because 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 **E°** 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 disproportionation.

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 **7.1.4.1.*V***).



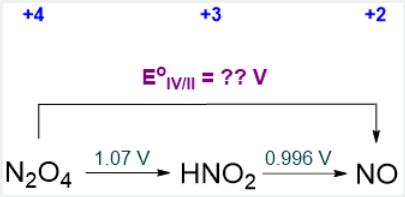
Scheme **7.1.4.1.*V***. Latimer diagrams for the group 12 elements in pH 0 aqueous solution.

From Scheme **7.1.4.1.*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 disproportionation 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.

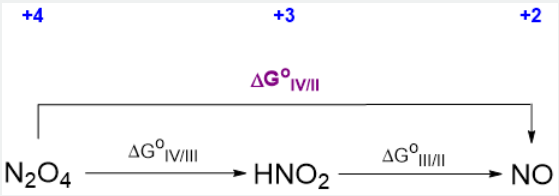
Note 7.1.4.1.1.

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 **7.1.4.1.*sfII***. Part of that diagram is reproduced as Scheme **7.1.4.1.VI** below.



Scheme **7.1.4.1.VI**. Partial Latimer diagram for nitrogen in acid.

The relevant thermodynamic cycle that may be used to calculate the unknown potential involves the free energies and is depicted in Scheme **7.1.4.1.VII**.

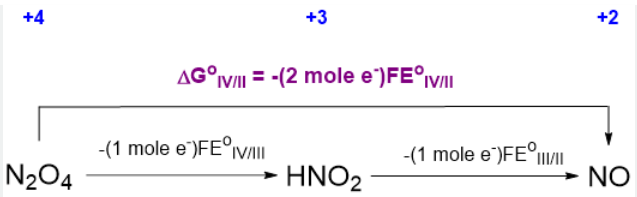


Scheme **7.1.4.1.VII**. Thermodynamic cycle that may be used to determine $E^\circ_{N_2O_4 \rightarrow NO}$.

The free energy for each conversion step in the cycle is related to the corresponding potential by the relationship

$$\Delta G^\circ = nFE^\circ$$

where n is the number of electrons involved in each step. With this substitution, the thermodynamic cycle above may be converted to the one shown in Scheme **7.1.4.1.VIII**.



Scheme **7.1.4.1.VIII**. Thermodynamic cycle expressed in terms of standard potentials.

From Scheme **7.1.4.1.VIII** it may be seen that

$$\Delta G^{\circ}_{IV/II} = -(2\ mol\ e^{-})FE^{\circ}_{IV/II} = -(1\ mol\ e^{-})FE^{\circ}_{IV/III} - (1\ mol\ e^{-})FE^{\circ}_{III/II}$$

Cancelling the constant F and replacing the unknown potentials with the values in Scheme **7.1.4.1.VI** gives

$$-(2\ mol\ e^{-})E^{\circ}_{IV/II} = -(1\ mol\ e^{-})(1.07\ V) - (1\ mol\ e^{-})(0.996\ V)$$

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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7.1.4.2: Frost Diagrams show how stable element's redox states are relative to the free element

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 $\boldsymbol{NE°}$, sometimes expressed as $\boldsymbol{nE°}$. On this page $\boldsymbol{N}$ will be used in place of $\boldsymbol{n}$ to avoid confusion with the common use of $\boldsymbol{n}$ in redox chemistry to denote the number of electrons involved in individual oxidation or reduction reaction steps.

In Frost diagrams the quantity $\boldsymbol{NE°}$ is used since it is proportional to the standard free energy change for conversion of the free element to that oxidation state.

In $\boldsymbol{NE°}$

- $\boldsymbol{N}$ is the oxidation state.
- $\mathbf{E°}$ is the standard *reduction potential* associated with *interconversion between the free element and that oxidation state*.

For a proof that $\boldsymbol{NE°}$ is proportional to the free energy of an element's oxidation state and more information on how $\boldsymbol{NE°}$ may be calculated, see Note **7.1.4.2.1** 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 $\boldsymbol{NE°}$ is a measure of thermodynamic stability, the lower its value the more stable the state. Moreover, since $\boldsymbol{NE°}$ measures stability relative to the free element, negative values of $\boldsymbol{NE°}$ 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 **7.1.4.2.1**.

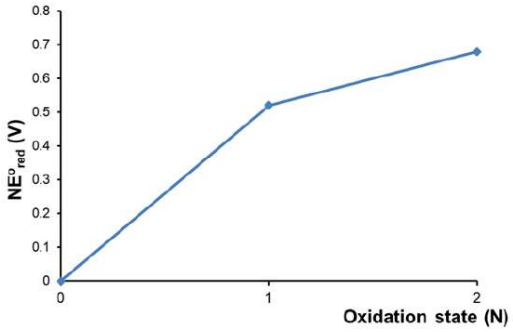


Figure **7.1.4.2.1**. Frost diagram for copper in aqueous acid. (CC BY-SA 4.0 International; Stephen Contakes)

As can be seen in Figure **7.1.4.2.1**, Cu^{+} and Cu^{2+} are both higher in free energy ($\propto \boldsymbol{NE°}$) 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 **7.1.4.2.2** 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).

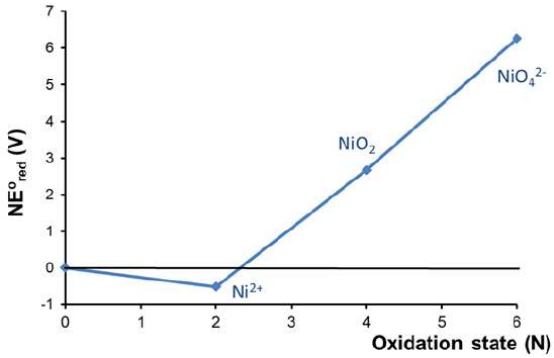


Figure **7.1.4.2.2**. Frost diagram for nickel in aqueous acid. (CC BY-SA 4.0 International; Stephen Contakes)

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 7.1.4.2.1. Interpreting a Frost Diagram

Consider the Frost diagram of Cr in acid shown in Figure **7.1.4.2.3**. What can be determined about the relative stability of chromium's oxidation states in acid?

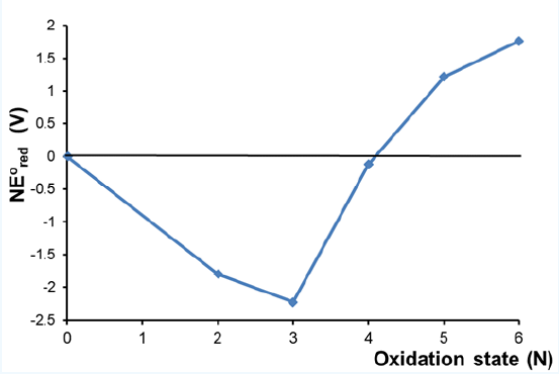


Figure **7.1.4.2.3**. Frost diagram for Cr in acidic solution. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

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 **7.1.4.2.4**.

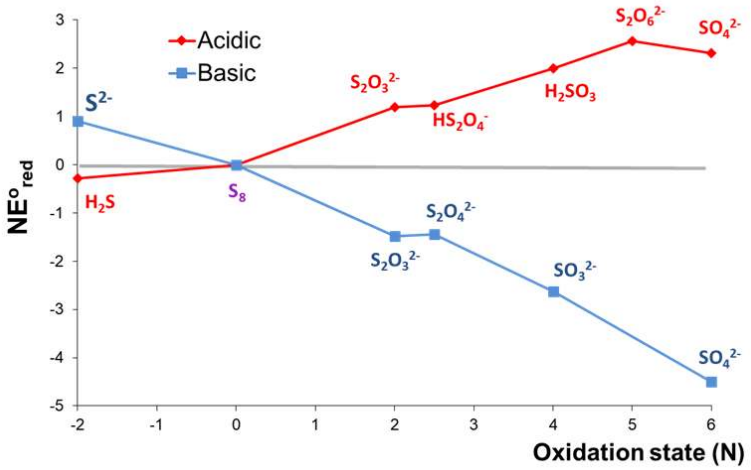


Figure **7.1.4.2.4**. Frost diagrams for sulfur at pH 0 and 14. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

As can be seen in Figure **7.1.4.2.4**, 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 **7.1.4.2.5**.

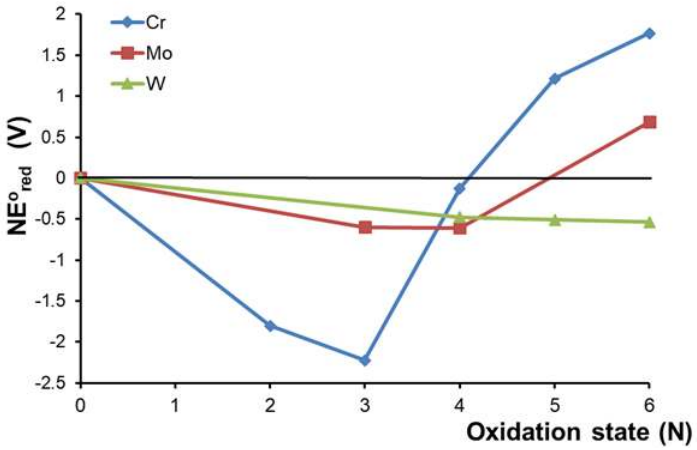


Figure **7.1.4.2.5**. Frost diagrams for the group 6 elements at pH 0. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Several trends may be noted from the data in Figure **7.1.4.2.5**. 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 **7.1.4.2.6**.[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).

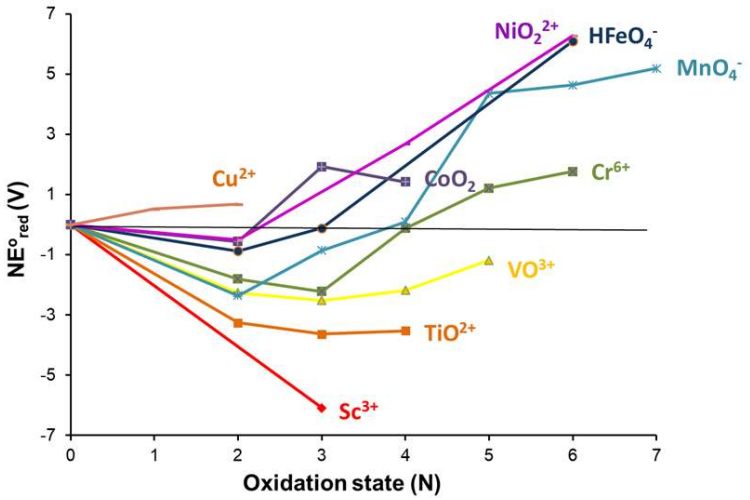


Figure **7.1.4.2.6**. Frost diagrams for the first transition series at pH 0. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

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 **7.1.4.2.7*a***.

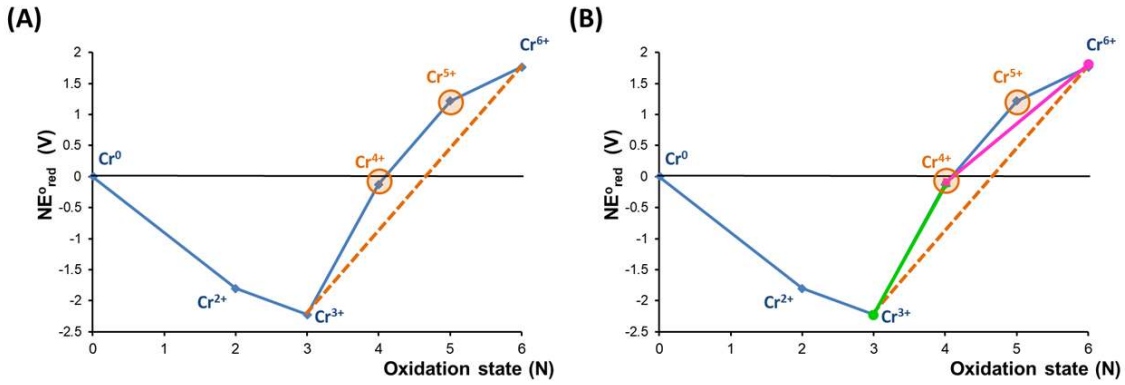


Figure **7.1.4.2.7**. (a) Frost diagram for Cr in acidic solution showing that the Cr^{4+} and Cr^{5+} states lie above a tie-line between the Cr^{3+} and Cr^{6+} states. (b) In the case of Cr^{4+}, disproportionation is favored because the $Cr^{4/3+}$ potential (slope of the green tie-line connecting 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 **7.1.4.2.7*a***, 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 **7.1.4.2.7*b***, 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 **7.1.4.2.2**.

✔ Example 7.1.4.2.2. Systematic identification of Mn redox states that are unstable towards disproportionation in acid.

Consider the Frost diagram of Mn in acid shown in Figure **7.1.4.2.8**. Which, if any, of manganese's oxidation states are unstable towards disproportionation at pH 0?

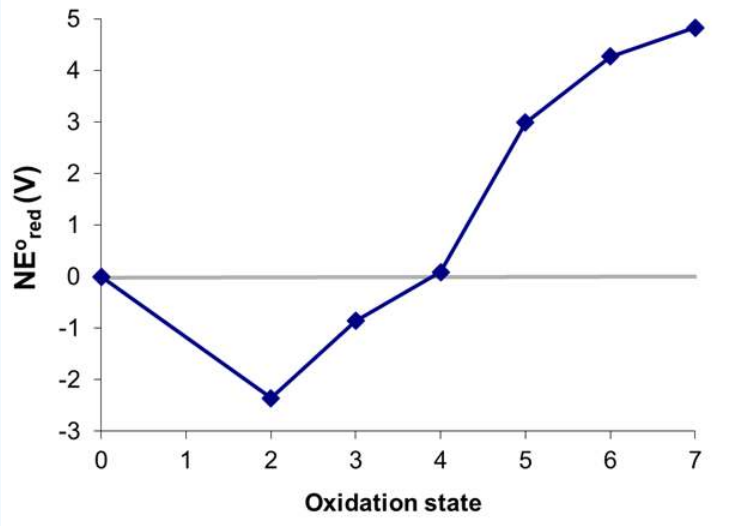
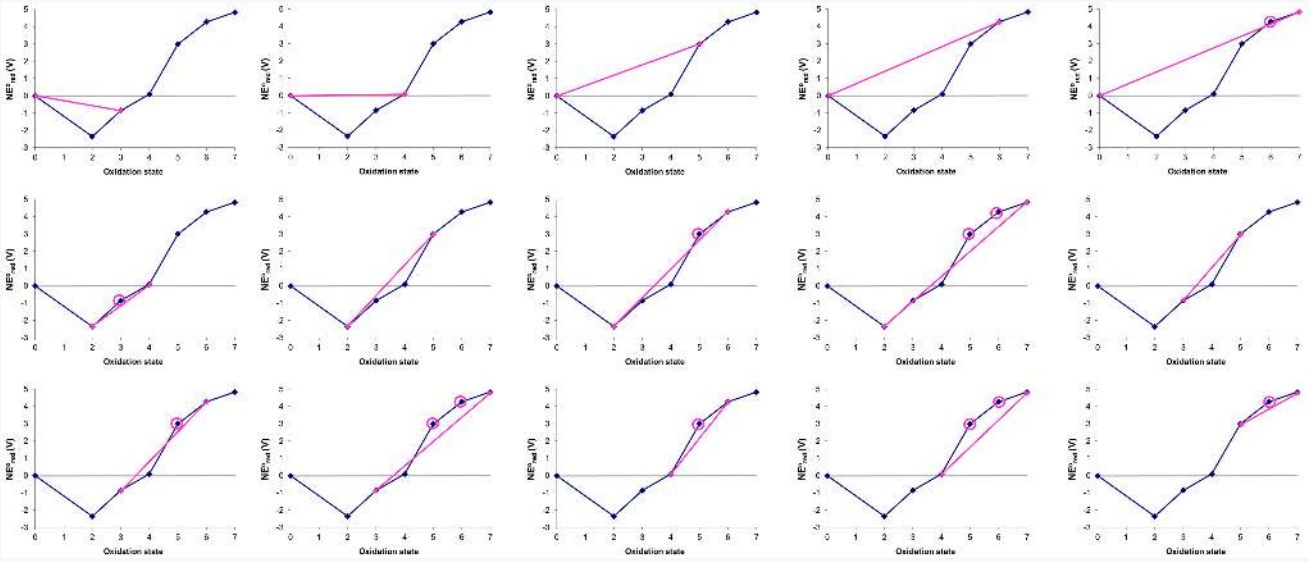


Figure **7.1.4.2.8**. Frost diagram for Mn at pH 0. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

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.

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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 **7.1.4.2.9*a***.

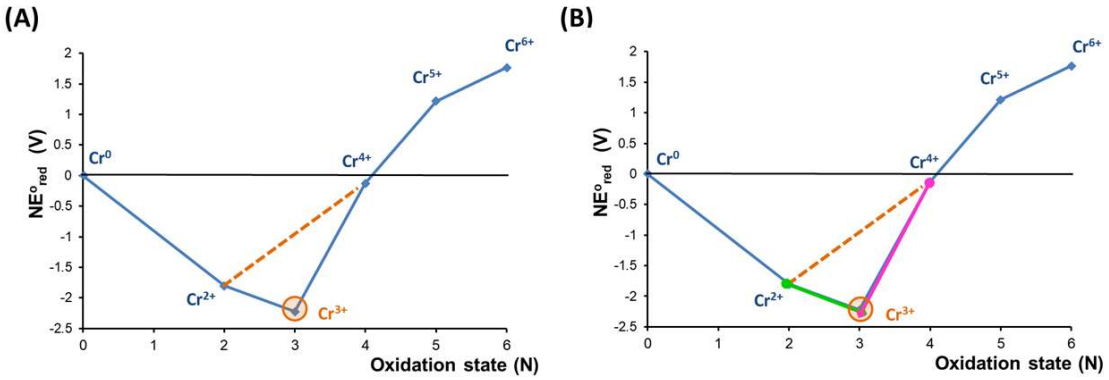


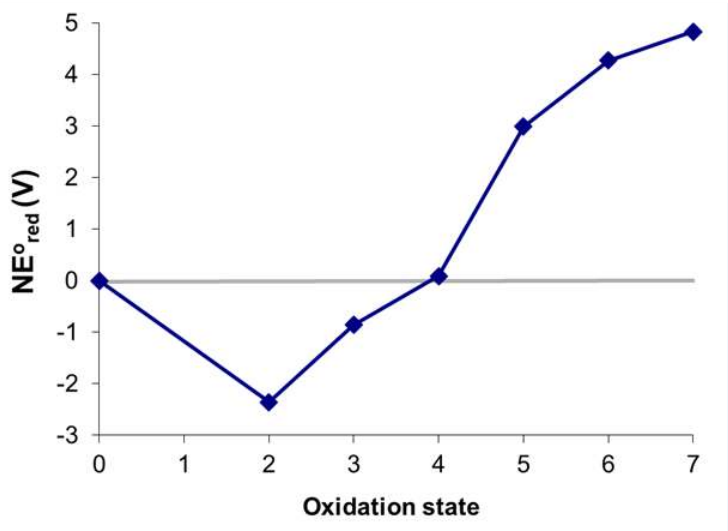
Figure **7.1.4.2.9**. (a) Frost diagram for Cr in acidic solution showing that the Cr^{3+} redox state lies below a tie-line between the Cr^{2+} and Cr^{4+} states. (b) The slope of the green line connecting the Cr^{2+} and Cr^{3+} states is less than that of the pink line connecting the Cr^{3+} and Cr^{4+} states. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

As shown in Figure **7.1.4.2.9*a***, 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 disproportionation. 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 **7.1.4.2.3**.

✔ Example **7.1.4.2.3**. 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 **7.1.4.2.8** of Example **7.1.4.2.2**, 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 7.1.4.2.2.

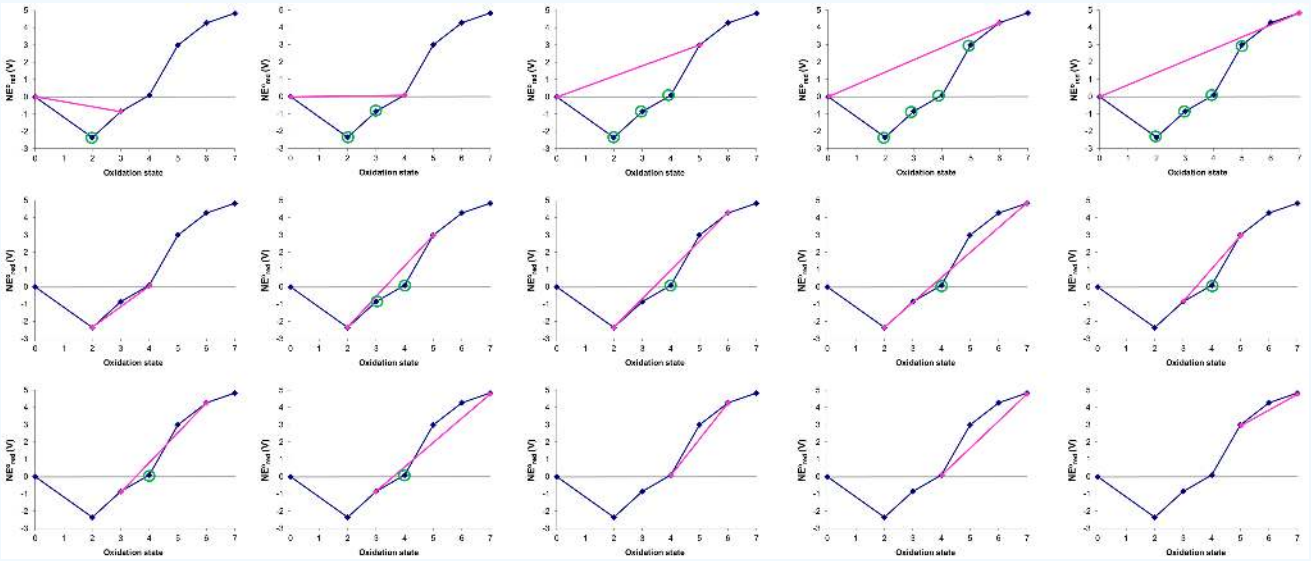


Figure above: the lower energy comproportionation products that species form are circled in green. The comproportionations identified involve the following pairs of oxidation states:

- 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 **7.1.4.2.3** 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 7.1.4.2.1

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.



Answer

The disproportionation of Cr^{4+} to Cr^{3+} and Cr^{6+} is the sum of two processes:

$$Cr^{4+}\text{reduction}: \quad Cr^{4+} + e^- \rightarrow Cr^{3+} \qquad E^\circ_{Cr^{4/3+}} = 2.10\ V$$

$$Cr^{4+}\text{oxidation}: \quad Cr^{4+} \rightarrow Cr^{6+} + 2e^- \qquad E^\circ = -E^\circ_{Cr^{6/4+}}$$

$$\text{Sum}: \quad 3Cr^{4+} + \rightarrow Cr^{6+} + 2Cr^{3+} \qquad E^\circ_{disproportionation} = E^\circ_{Cr^{4/3+}} - E^\circ_{Cr^{6/4+}}$$

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,

$$E^\circ_{disproportionation} = E^\circ_{Cr^{4/3+}} \qquad E^\circ_{Cr^{6/4+}} = 2.10\ V - 1.89\ V = +0.21\ V$$

which is spontaneous.

? Exercise 7.1.4.2.2

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.



Answer

The comproportionation of Cr^{2+} and Cr^{4+} to Cr^{3+} is the sum of two processes:

$$Cr^{4+}\text{reduction}: \quad Cr^{4+} + e^- \rightarrow Cr^{3+} \qquad E^\circ_{Cr^{4/3+}} = +2.10\ V$$

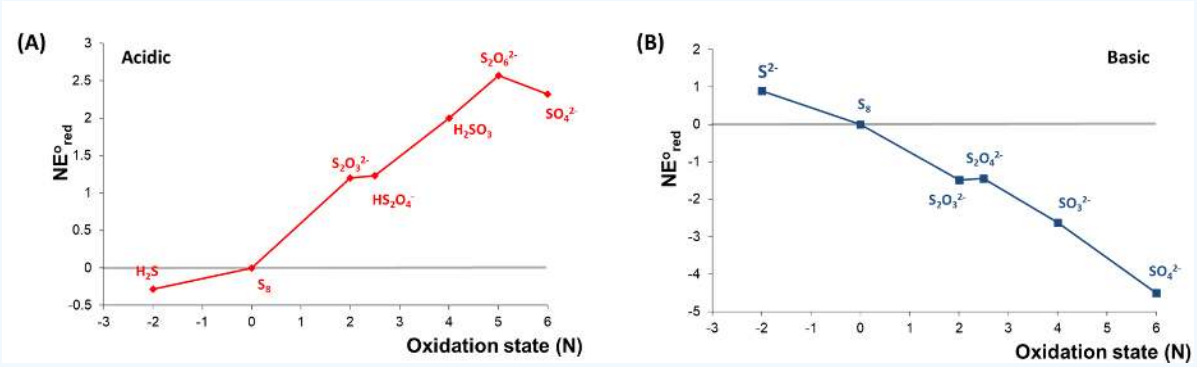
$$Cr^{2+}\text{oxidation}: \quad Cr^{2+} \rightarrow Cr^{3+} + e^- \qquad E^\circ = -E^\circ_{Cr^{3/2+}} = -(-0.424\ V) = +0.424\ V$$

$$\text{Sum}: \quad Cr^{2+} + Cr^{4+} \rightarrow 2Cr^{3+} \qquad E^\circ_{comproportionation} = +2.10\ V + 0.424\ V = +2.524\ V$$

Since $E^\circ_{comproportionation}$ is positive, the comproportionation is spontaneous.

? Exercise 7.1.4.2.3. Identifying thermodynamically favored comproportionation and disproportionation reactions.

The Frost diagrams for acidic and basic solutions of sulfur are given below.



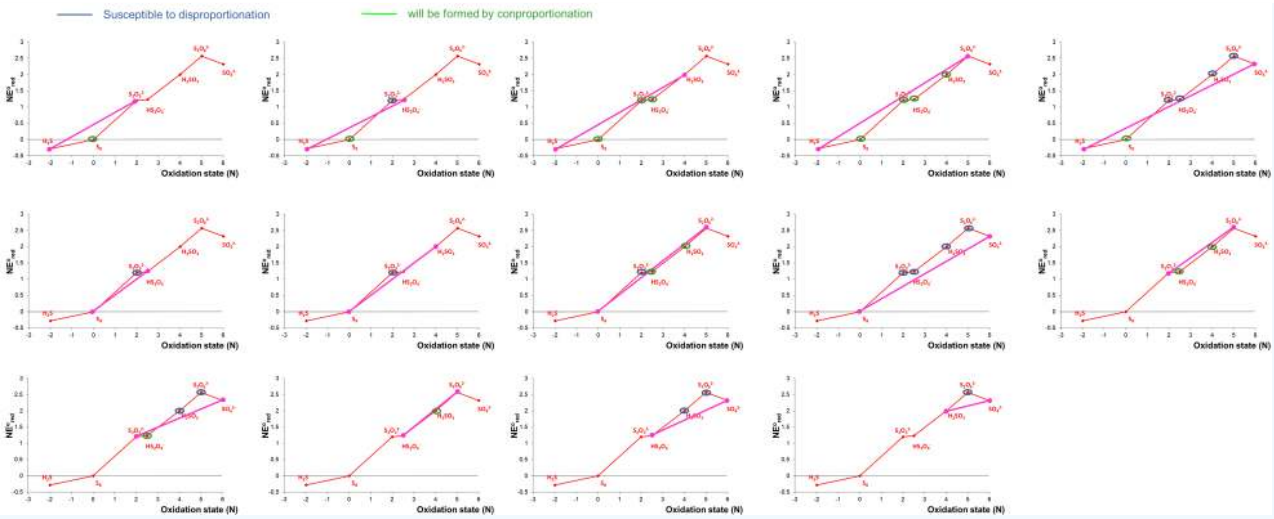
a. Identify any species that are unstable towards disproportionation under acidic or basic conditions.

b. Identify any species that can be formed by comproportionation under acidic or basic conditions.

Answer

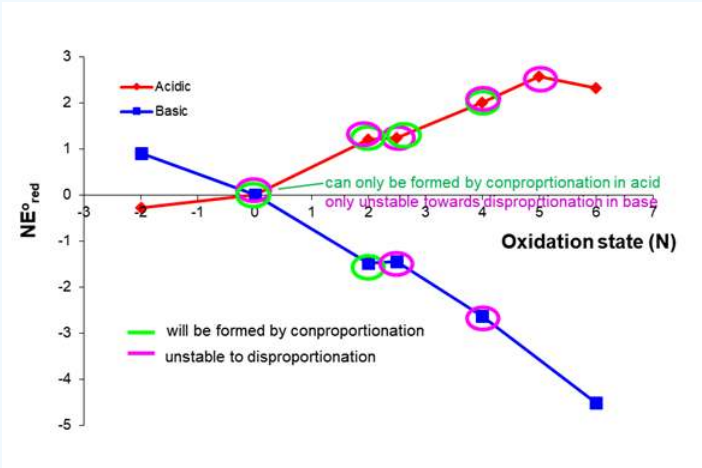
The species that are unstable towards *disproportionation* and *comproportionation* may be identified by constructing tie-lines between nonadjacent redox states and identifying any that fall above and below these lines. Species that are unstable to *disproportionation* will lie above a line; those that 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 7.1.4.2.1. 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

$$E^\circ_{ox} = E^\circ = -E^\circ_{red}$$

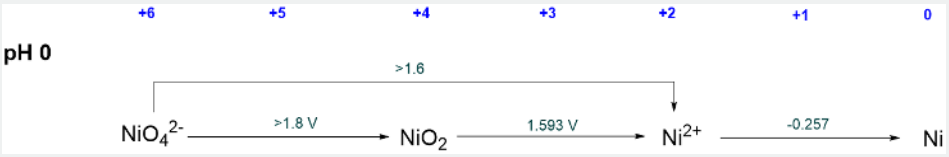
So that for positive oxidation states,

$$\Delta G^\circ_{ox} = -\Delta G^\circ_{red} = -(-nFE^\circ_{red}) = F(NE^\circ)$$

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:

$$\Delta G^\circ_{NiO_2 \rightarrow Ni} = \Delta G^\circ_{NiO_2 \rightarrow Ni^{2+}} + \Delta G^\circ_{Ni^{2+} \rightarrow Ni}$$

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

$$-n_{e^-,NiO_2 \rightarrow Ni} FE^\circ_{NiO_2 \rightarrow Ni} = -n_{e^-,NiO_2 \rightarrow Ni^{2+}} FE^\circ_{NiO_2 \rightarrow Ni^{2+}} + -n_{e^-,Ni^{2+} \rightarrow Ni} FE^\circ_{Ni^{2+} \rightarrow Ni}$$

which may be further simplified by cancelling the Faraday constant, F, from both sides, giving an expression for the desired value of NE°:

$$-n_{e^-,NiO_2 \rightarrow Ni} E^\circ_{NiO_2 \rightarrow Ni} = NE^\circ_{Ni \rightarrow NiO_2} = -n_{e^-,NiO_2 \rightarrow Ni^{2+}} E^\circ_{NiO_2 \rightarrow Ni^{2+}} + -n_{e^-,Ni^{2+} \rightarrow Ni} E^\circ_{Ni^{2+} \rightarrow Ni}$$

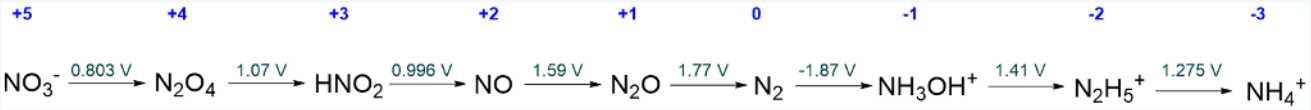
From this expression the value of $NE^\circ_{Ni \rightarrow NiO_2}$ may be calculated by inserting the relevant reduction potentials and number of electrons:

$$NE^{\circ}_{Ni \rightarrow NiO_2} = 2 \times (+1.593V) + 2 \times (-0.257V) = +2.672V$$

For complex cases it can be helpful to tabulate the calculations, as is done in the following example.

Example 7.1.4.2.1: 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 7.1.4.2.1. The calculations follow the procedure:

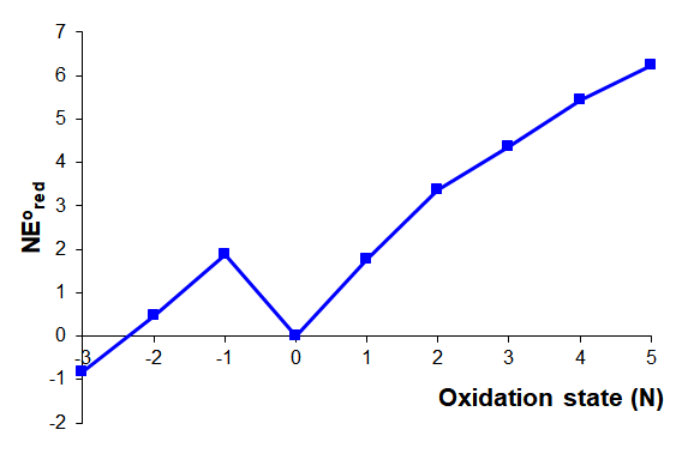
1. Set NE° = 0 for the free element.
2. Use NE° = O.S. × associated E° to calculate NE° for the lowest positive and negative oxidation states.
3. Iteratively use $NE^{\circ} = NE^{\circ}_{\text{last step}} + NE^{\circ}_{\text{one lower oxidation state}}$ to calculate NE° for all higher oxidation states.

Table 7.1.4.2.1: Calculation of NE° for each oxidation state of nitrogen.

Oxidation State	Step	$\mathbf{NE^\circ}$ =	Calculated as the sum of the steps	Notes
5	$N_2 \rightarrow NO_3^-$	$5 \times (E^\circ_{NO_3^- \rightarrow N_2})$	$N_2 \rightarrow N_2O_4 \rightarrow NO_3^-$ $NE^\circ = 1 \times E^\circ_{NO_3^- \rightarrow N_2O_4} + 4 \times E^\circ_{N_2O_4 \rightarrow N_2}$ $NE^\circ = 1 \times E^\circ_{NO_3^- \rightarrow N_2O_4} + NE^\circ_{+4\ O.S.}$ $NE^\circ = 1 \times 0.803V + 5.426V = 6.229V$	Calculate NE° for the +4 oxidation state, NO, first. Then use it in this calculation.
4	$N_2 \rightarrow N_2O_4$	$4 \times (E^\circ_{N_2O_4 \rightarrow N_2})$	$N_2 \rightarrow HNO_2 \rightarrow N_2O_4$ $NE^\circ = 1 \times E^\circ_{HNO_2 \rightarrow NO} + 3 \times E^\circ_{HNO_2 \rightarrow N_2}$ $NE^\circ = 1 \times E^\circ_{N_2O_4 \rightarrow HNO_2} + NE^\circ_{+3\ O.S.}$ $NE^\circ = 1 \times 1.07V + 4.356V = 5.426V$	Calculate NE° for the +3 oxidation state, NO, first. Then use it in this calculation.
3	$N_2 \rightarrow HNO_2$	$3 \times (E^\circ_{HNO_2 \rightarrow N_2})$	$N_2 \rightarrow NO \rightarrow HNO_2$ $NE^\circ = 1 \times E^\circ_{HNO_2 \rightarrow NO} + 2 \times E^\circ_{NO \rightarrow N_2}$ $NE^\circ = 1 \times E^\circ_{NO \rightarrow N_2O} + NE^\circ_{+2\ O.S.}$ $NE^\circ = 1 \times 0.996V + 3.36V = 4.356V$	Calculate NE° for the +2 oxidation state, NO, first. Then use it in this calculation.
2	$N_2 \rightarrow NO$	$2 \times (E^\circ_{NO \rightarrow N_2})$	$N_2 \rightarrow N_2O \rightarrow NO$ $NE^\circ = 1 \times E^\circ_{NO \rightarrow N_2O} + 1 \times E^\circ_{N_2O \rightarrow N_2}$ $NE^\circ = 1 \times E^\circ_{NO \rightarrow N_2O} + NE^\circ_{+1\ O.S.}$ $NE^\circ = 1 \times 1.59V + 1.77V = 3.36V$	Calculate NE° for the +1 oxidation state, NO, first. Then use it in this calculation.
1	$N_2 \rightarrow N_2O$	$1 \times E^\circ_{N_2O \rightarrow N_2}$	$N_2 \rightarrow N_2O$ $NE^\circ = 1 \times E^\circ_{N_2O \rightarrow N_2}$ $NE^\circ = 1 \times +1.77V = +1.77V$	
0	None	0 V	$NE^\circ = 0V$ by definition.	Defined as 0 V
-1	$N_2 \rightarrow NH_3OH^+$	$(-1) \times E^\circ_{N_2 \rightarrow NH_3OH^+}$	$N_2 \rightarrow NH_3OH^+$ $NE^\circ = (-1)E^\circ_{N_2 \rightarrow NH_3OH^+}$ $NE^\circ = (-1) \times (-1.87V) = +1.87V$	
-2	$N_2 \rightarrow N_2H_5^+$	$(-2) \times E^\circ_{N_2 \rightarrow N_2H_5^+}$	$N_2 \rightarrow NH_3OH^+ \rightarrow N_2H_5^+$ $NE^\circ = (-1) \times E^\circ_{N_2 \rightarrow NH_3OH^+} + (-1)E^\circ_{NH_3OH^+ \rightarrow N_2H_5^+}$ $NE^\circ = NE^\circ_{-1\ O.S.} + (-1)E^\circ_{NH_3OH^+ \rightarrow N_2H_5^+}$ $NE^\circ = +1.87V + (-1) \times 1.41V = 0.46V$	Calculate NE° for the -1 oxidation state, NO, first. Then use it in this calculation.

Oxidation State	Step	NE° =	Calculated as the sum of the steps	Notes
-3	$N_2 \rightarrow NH_4^+$	$(-3) \times E^\circ_{N_2 \rightarrow NH_4^+}$	$N_2 \rightarrow N_2H_5^+ \rightarrow NH_4^+$ $NE^\circ = (-1)E^\circ_{N_2 \rightarrow N_2H_5^+} + (-1)E^\circ_{N_2H_5^+ \rightarrow NH_4^+}$ $NE^\circ = NE^\circ_{-2\ O.S.} + (-1)E^\circ_{N_2H_5^+ \rightarrow NH_4^+}$ $NE^\circ = +0.46V + (-1) \times 1.275V = -0.815V$	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.



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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.

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7.1.4.3: Pourbaix Diagrams are Redox Phase Diagrams that Summarize the most stable form of an element at a given pH and solution potential

Pourbaix diagrams depict the most stable species or phase of an element as a function of potential and pH

Pourbaix or potential-pH/E-pH diagrams were developed and popularized by Marcel Pourbaix, who used them to study corrosion. Pourbaix diagrams depict the most stable species or phase of an element in aqueous solution as a function of potential (on the y-axis) and pH (on the x-axis). Pourbaix's *Atlas of Electrochemical Equilibria in Aqueous Solution* contains diagrams for many elements along with extensive notes on their construction.[1] An example of a Pourbaix diagram is that for Fe shown in Figure **7.1.4.3.1**.

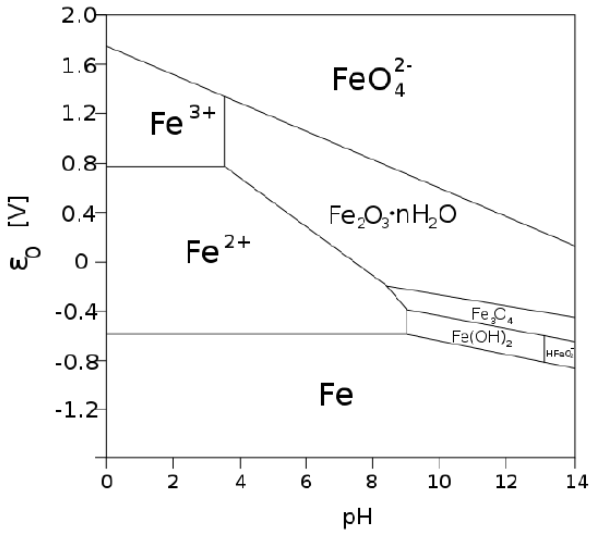


Figure **7.1.4.3.1**. Pourbaix diagram for Fe at an unknown Fe concentration. (CC BY-SA 2.5, Andel Früh via Wikipedia)

The species shown on Pourbaix diagrams include solution phase species (Fe^{2+}, Fe^{3+}, $HFeO_2^-$, and FeO_4^{2-}) and insoluble or poorly soluble solids (Fe, $Fe_2O_3{\cdot}nH_2O$, Fe_3O_4, and $Fe(OH)_3$). Thus on some diagrams the phase is also indicated using (s), (l), and (aq) designators. This is the case for the Fe Pourbaix diagram in Figure **7.1.4.3.2**.

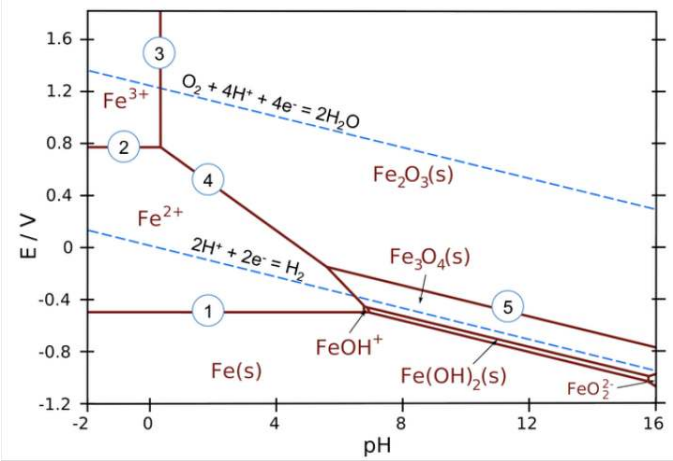


Figure **7.1.4.3.2**. Partial Pourbaix diagram for Fe, at a different Fe concentration than the diagram in Figure **7.1.4.3.1**. (CC BY-SA 3.0 Unported; Metallos via Wikipedia)

Pourbaix diagrams are similar to phase diagrams in that they show species as a function of potential and pH. Unlike a conventional phase diagram, the regions depict the dominant species instead of the only species present under a given set of conditions (for more detail see Note 1).[1] For solution phase species, the dominant chemical species will not only depend on potential and pH as depicted in the diagram; the formal concentration of the species is important too. For the sort of corrosion applications Pourbaix envisioned,

these concentrations are typically quite low, so for this reason the regions depicted in most Pourbaix diagrams correspond to 1 mM total concentration.

The way in which Pourbaix diagrams provide insight into corrosion chemistry may be seen by looking more carefully at the Pourbaix diagram for Fe in Figure **7.1.4.3.2**. Notice that the diagram also shows equilibrium lines for water reduction

$$2H^+ + 2e^- \rightarrow H_2$$

and oxidation

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O.$$

These lines are useful for several reasons.

- First, in cases where water oxidation and reduction are fast relative to the electrochemical phenomenon of interest, the water oxidation and reduction potentials limit the potential that the element can experience - *i.e.*, if a solution is exposed to a more extreme potential in the form of an electrode or a strong chemical or photochemical oxidant or reductant, then that substance will oxidize or reduce water instead of the element depicted in the diagram.
- Second, the oxygen reduction equilibrium is important for corrosion applications taking place in an oxygen-containing environment. In these environments, the pH-dependent standard potential of oxygen reduction depicted by the upper blue line in Figure **7.1.4.3.2** determines the potential of the system. As can be seen in Figure **7.1.4.3.2**, the potential of this equilibrium is above that of the region of stability of metallic iron. This indicates that metallic iron is not thermodynamically stable at the oxygen partial pressures of the diagram; Fe^{3+} species are instead. Moreover, the precise species that metallic iron will form when it is exposed to a higher potential varies with pH. At higher pH values, an oxide will be produced - either $Fe(OH)_2$(s), Fe_3O_4(s), or Fe_2O_3(s). If these solid phases coat the surface of the iron so as to insulate it from reaction with oxygen, they will effectively prevent iron's oxidation. Such layers are said to be **passivating**, and the resulting **anodic passivation** is a form of kinetic, not thermodynamic, stabilization of the metal.[2]

Straightforward applications of Pourbaix diagrams involve estimating how the potential of a system at equilibrium changes with conditions, as illustrated in Example **7.1.4.3.1**.

Example 7.1.4.3.1

Metal indicator electrodes are used to measure the potential of solutions. The potential is determined by the redox equilibria taking place therein. This potential may be measured by immersing the metal indicator electrode and a reference electrode in the solution to be tested.

Use the information in Figure **7.1.4.3.2** (Do not use the information in Figure **7.1.4.3.1** since it corresponds to a different Fe concentration) to:

1. Explain how you might construct a pH-sensitive electrode from a Pt wire metal indicator electrode, $FeSO_4$ (which is water soluble) and rust, which for the purposes of this problem you may take as equivalent to Fe_2O_3(s) and its hydrates.
2. What would be the pH range limits of the sensor?
3. What voltages would it read (vs. NHE) over this range?
4. Are there any limitations that should be observed when using this electrode to measure pH?

Solution

1. The electrode may be made by dissolving the $FeSO_4$ in the solution to be tested to give a solution that is ~1mM Fe^{2+}. Then enough rust would be added to give a cloudy solution, indicating that solid is present and the equilibrium between Fe^{2+} and $FeSO_4$ established. Finally, the Pt wire and a suitable reference electrode would be inserted into the solution and the potential measured.
2. The electrode would only work between pH values of ~0.5 and 7. Below pH 0.5 the Fe_2O_3 would dissolve, while above pH 7 the Fe^{2+} will precipitate.
3. The voltages should range from ~0.77 V (vs. SHE) at pH ~0.5 to ~-0.44V (vs. SHE) at pH~7.

4. There are several limitations and much would need to be done to validate this as a suitable method for the determination of pH. First, the potentials listed above assume that the iron concentration in the test solution is the same as that used to construct the diagram in Figure **7.1.4.3.1**. Thus they are at best rough estimates, and the electrode would need to be calibrated using solutions of known pH before use. Second, if the electrode is used in air, over time the Fe^{2+} will oxidize to Fe^{3+} species, shifting the response of the electrode. Because of this the electrode should either be used in an anoxic environment or prepared just before use.

What do the lines in a Pourbaix diagram mean?

The phase lines in Pourbaix diagrams correspond to switchpoints between the dominant species in solution for solution phase species or the points at which precipitation or phase change occurs for equilibria involving solid and/or pure liquid phases. To see how this works it helps to consider the three common cases:

- *Equilibria that involve electron transfer only* give rise to horizontal lines because the potential does not depend on pH. An example is the line between the Fe^{3+} and Fe^{2+} regions, marked 2 in Figure **7.1.4.3.2**. In this case the reaction potential when $\frac{Fe^{2+}}{Fe^{3+}}$=1 is $E^\circ_{Fe^{3/2+}}$:

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad E = E^\circ_{Fe^{3/2+}} - \frac{0.05916\ V}{1}\log\frac{[Fe^{2+}]}{[Fe^{3+}]}$$
$$= E^\circ_{Fe^{3/2+}} - (0.05916\ V)\log 1 = E^\circ_{Fe^{3/2+}}$$

- *Acid-base equilibria that do not involve changes in the redox state of the elements involved* give rise to vertical lines, the position of which depend on the stated concentration of the diagram. An example is the line between the Fe^{3+}(aq) and Fe_2O_3(s) regions, marked 3 in Figure **7.1.4.3.2**. This corresponds to the equilibrium:

$$2\ Fe^{3+} + 3\ H_2O \rightarrow Fe_2O_3(s) + 6\ H^+$$

  The equilibrium line in this case is determined by the reaction's equilibrium constant

$$K = \frac{[H^+]^6}{[Fe^{3+}]^2}$$

  From this it can be seen that the pH ($[H^+]$) is a function only of the value of $[Fe^{3+}]$ used to construct the diagram (since $[H^+] = (K[Fe^{3+}]^2)^{1/6} = \text{constant}$), so the line is vertical.

- *Equilibria that involve a combination of electron transfer and acid-base chemistry* give rise to slanted lines. An example is the equilibrium between Fe^{2+} and Fe_2O_3(s), marked 4 in Figure **7.1.4.3.2**. This corresponds to the equilibrium:

$$Fe_2O_3(s) + 6\ H^+ + 2\ e^- \rightarrow 2\ Fe^{2+} + 3\ H_2O$$

  for which

$$E = E^\circ_{Fe_2O_3/Fe^{2+}} - \frac{0.05916\ V}{2}\log\frac{[Fe^{2+}]^2}{[H^+]^6}$$

  from which it can be seen that the potential will be pH dependent.

References

1. Pourbaix, M., Atlas of electrochemical equilibria in aqueous solutions. 2nd ed. Houston: National Association of Corrosion Engineers, 1974.
2. The other common corrosion resistance strategy, cathodic protection, couples the metal to be protected to an even more reactive metal that is oxidized in place of the metal to be protected.

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7.2: What are the main group elements and why should anyone care about them?

What are the main group elements?

The main group elements are those in the *s* and *p* blocks of the periodic table, as shown in Figure **7.2.1**.

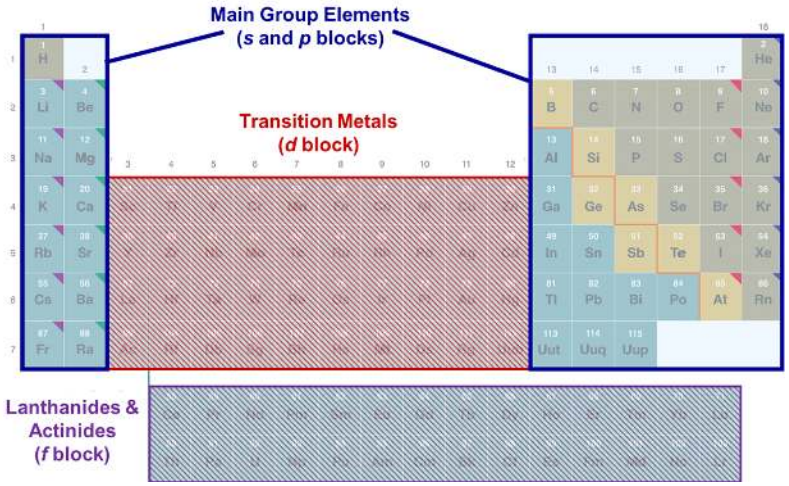
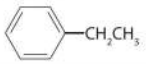
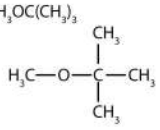
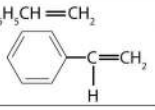
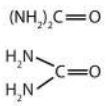
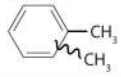


Figure **7.2.1**. Location of the main group elements in the periodic table.[1]

Why should anyone care about the main group elements?

In addition to being interesting in their own right as fundamental constituents of ordinary matter with a rich and interesting chemistry, the main group elements are of tremendous societal importance. As shown in Table **7.2.1**, thirteen of the top 25 chemicals produced in the United States are inorganic main group compounds.

Table 7.2.1. Top 25 industrial chemicals produced in the US in 2002.[2]

Rank	Name	Formula (Structure)	Billions of Pounds	Rank	Name	Formula (Structure)	Billions of Pounds
1	sulfuric acid	H_2SO_4	88.80	14	1,2-dichloroethane (ethylene dichloride)	$ClCH_2CH_2Cl$	15.94
2	nitrogen	N_2	58.70	15	ammonium nitrate	NH_4NO_3	15.33
3	oxygen	O_2	42.38	16	vinyl chloride	$CH_2{=}CHCl$	13.23
4	ethylene	$H_2C{=}CH_2$	40.41	17	benzene	C_6H_6	12.01
5	ammonia	NH_3	35.95	18	ethylbenzene	$C_6H_5CH_2CH_3$ 	10.99
6	calcium oxide (lime)	CaO	34.72	19	carbon dioxide	CO_2	10.91
7	phosphoric acid	H_3PO_4	25.36	20	methyl *t*-butyl ether	$CH_3OC(CH_3)_3$ 	10.86
8	sodium hydroxide	NaOH	24.02				
9	propylene (propene)	$CH_3CH{=}CH_2$	22.60	21	styrene	$C_6H_5CH{=}CH_2$ 	8.94
10	chlorine	Cl_2	22.28	22	methanol	CH_3OH	8.73
11	sodium carbonate	Na_2CO_3	20.89	23	formaldehyde		6.98
12	urea		16.84	24	xylenes (mixture)†	$(CH_3)_2C_6H_4$ 	6.38
13	nitric acid	HNO_3	16.08	25	toluene	$C_6H_5CH_3$	6.03

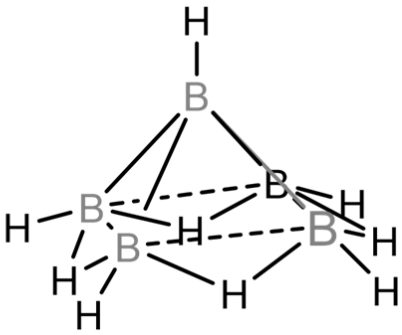
*Nonlinear structures not previously introduced are shown with their respective formulas.
†The squiggly line indicates that the second —CH_3 group can be attached to any of the other positions of the ring.

This chapter's approach to the descriptive chemistry of the main group elements

The aim of this chapter is to introduce you to the descriptive chemistry of the main group elements. In general descriptive chemistry involves presenting information about the chemistry of the elements, as opposed to describing more fundamental concepts, theories, and models. Nevertheless, in presenting this information no attempt will be made to be exhaustive; instead the focus will be on describing important or characteristic features of the chemistry. Moreover, as intimated by the structures shown in Scheme **7.2.I**, the bonds which hold main group compounds together do not always obey the rules developed in typical general and organic chemistry courses. Consequently, as opportunity presents itself, this description of the chemistry of the elements will also be used to enlarge your understanding of what types of chemical structures are possible or even common.

Scheme 7.2.I. Chlorine atoms bridge Al centers in aluminum chloride dimer at left while the structure of pentaborane nonahydride shown at right includes four B-H-B bridge bonds arranged around the open face of a cluster of five B atoms held together by cluster bonds.





The elements will be considered by group after an introductory section that reviews several concepts that help to make sense of periodic trends in the descriptive chemistry of these elements.

References

1. Adapted from the periodic table at https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/02._Atoms%2C_Molecules%2C_and_Ions/2.5%3A_The_Periodic_Table.

2. Taken from https://chem.libretexts.org/Bookshelves/General_Chemistry/Book%3A_Chemistry_(Averill_and_Eldredge)/02%3A_Molecules%2C_Ions%2C_and_Chemical_Formulas/2.6_Industrially_Important_Chemicals

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The unknown authors of Table **7.2.1** and the periodic table portion of Figure **7.2.1**.

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7.3: Group 1, The Alkali Metals

The Alkali Metals

The alkali metals comprise the elements lithium through francium in group 1 of the periodic table, as shown in Figure **7.3.1**.

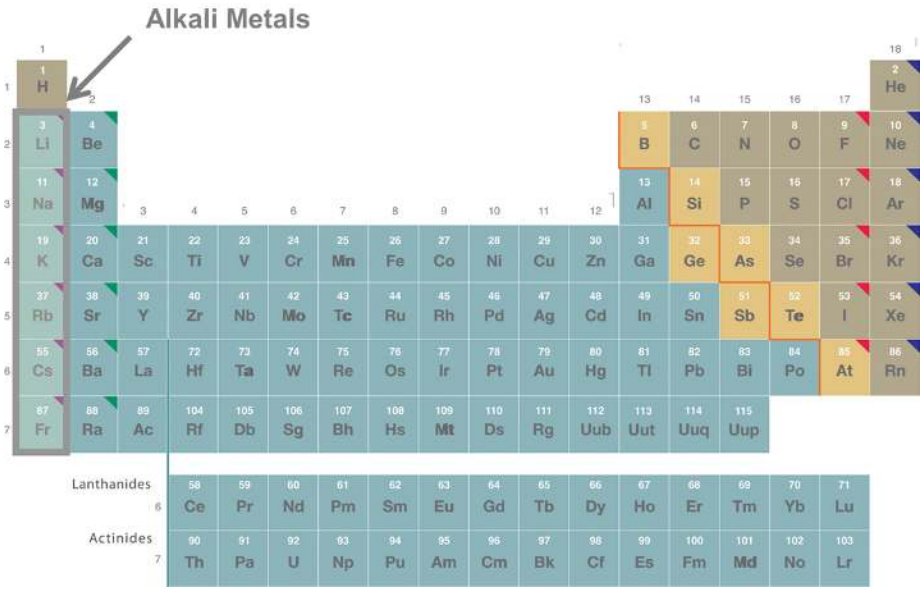


Figure **7.3.1**. Position of the alkali metals in the periodic table. (CC-BY-SA-NC 3.0; Anonymous via LibreTexts)

Alkali metals are powerful reductants and so do not exist as the free metal in the relatively oxidizing environment at the earth's surface. As a result they are commonly found as the +1 cations in a variety of minerals like rock salt (halite, NaCl) and natron ($Na_2CO_3 \cdot 10H_2O$).

Because they occur as minerals, free alkali metals are prepared by electrolytic reduction of their +1 cations. For example, in the Downs process for making sodium, NaCl is electrolyzed to Na(l) and Cl_2(g).

$$2\,NaCl\,(l) \rightarrow 2\,Na\,(l) + Cl_2\,(g)$$

In order for this process to occur rapidly, transport of cations to the cathode and anions to the anode must occur. To permit this, the salt to be electrolyzed is melted.[1] In addition, since the alkali metal is reactive the electrolysis must take place in a specialized cell that permits separation of the metal from both the salt and any oxidation products formed at the anode. For example, to prevent the explosively exothermic reaction between the chlorine gas and molten sodium products in the Downs process, specialized Downs cells in which the cathode and anode are carefully separated are employed. A typical way Downs cell is depicted in Figure **7.3.2**.

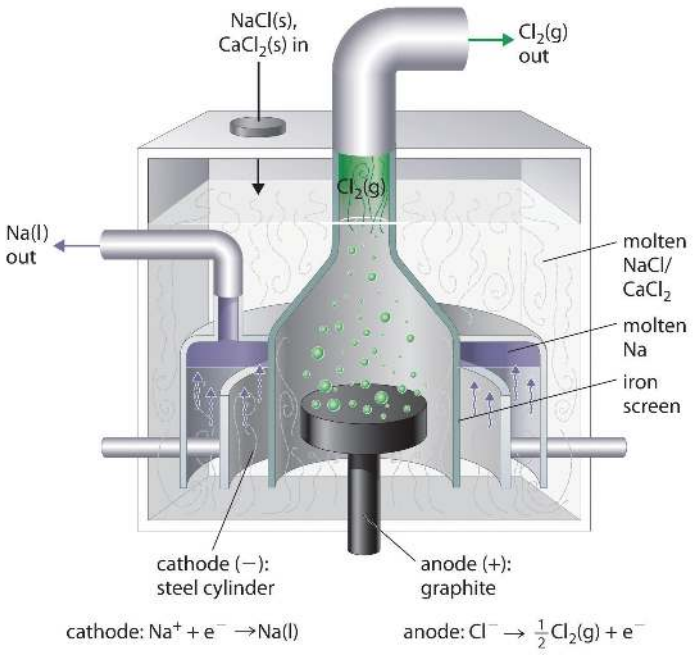


Figure **7.3.2**. Downs cell for the electrolysis of molten sodium. (CC-BY-SA-NC 3.0; Anonymous via LibreTexts)

As can be seen from the cell in Figure **7.3.2**, the chlorine gas formed at the anode and sodium metal formed at the cathode are kept separate by allowing Cl_2 gas to bubble out of the cell and the sodium metal to collect above the cathode (since sodium's density is lower than that of molten NaCl it floats to the top of the molten sodium chloride).

Alkali metals can also be formed by chemical reduction. For example, potassium can be made by reducing potassium salts with Na, carbide, or carbon according to the following reactions.

$$KCl + Na \longrightarrow K + NaCl$$

$$2\,KX + CaC_2 \rightarrow 2\,K + CaX_2 + C\ (X = F, Cl)$$

$$K_2CO_3 + 2\,C \rightarrow 2\,K + 3\,CO$$

Once formed, alkali metals are stored under an inert atmosphere or under hydrocarbon oil to prevent their reoxidation.

Properties

In metallic form, alkali metals possess a body centered cubic (BCC) structure and are silvery solids, as shown in Figure **7.3.3**.

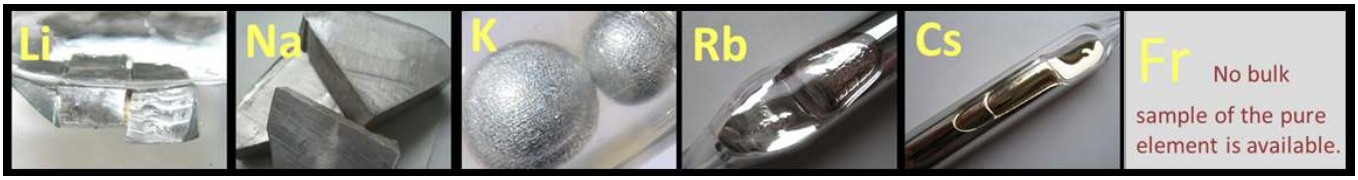


Figure **7.3.3**. The alkali metals. Notice that most of the samples are either stored in mineral oil or sealed in glass tubes to prevent ther reoxidation by atmospheric oxygen. The images of the alkali metals are adapted from those at en.Wikipedia.org/wiki/Alkali_metal. Individual image credits for the alkali metals are given in reference two at the end of this page.

Like other metals, alkali metals are good conductors of heat and electricity, malleable, and ductile. However, compared to other metals alkali metals have a small number of valence electrons and relatively low effective nuclear charges. As a result the metallic bonds which hold solid and liquid alkali metals together are weaker than those in other metals and they melt and boil at lower temperatures, as illustrated by the melting and boiling points listed in Table **7.3.1**. Further, as can be seen from the data in Table **7.3.1**, both the melting and boiling points decrease down the alkali metal group. This decrease in melting and boiling points reflects a decrease in metallic bonding strength as the atomic size (and consequently average electron-nucleus distance) increases down the group.

Table **7.3.1**. Melting and boiling points of the alkali metals and selected reference substances.[3]

Substance	Melting Point (° C)	Boiling Point (° C)
Alkali Metal		
Lithium, Li	181	1347
Sodium, Na	98	883
Potassium, K	64	774
Rubidium, Rb	39	688
Cesium, Cs	28	678
Francium	27	677
Non-alkali Metal		
Magnesium	649	1090
Barium	727	1845
Titanium	1660	3287
Iron, Fe	1538	2861
Copper	1083	2567
Water	0	100
benzene	6	80

The relatively low strength metallic bonding in the alkali metals is also reflected in their softness. The metals are so soft that they may be pressed into sheets and cut with an ordinary lab spatula. In fact, spatulas are commonly used to cut appropriate size portions of metal when they are used in the laboratory.

The atomic properties of alkali metals reflect the relatively high energy and large size of their ns valence orbitals. In consequence, they possess larger atomic radii and lower ionization energies than most metals, as may be seen from the data shown in Table **7.3.2**.

Table **7.3.2**. Selected atomic properties of the alkali metals and selected reference compounds.[3,4]

Substance	Atomic radius (Angstroms)	Ionization energy (kJ/mol)	Pauling Electronegativity
Alkali Metal			
Lithium, Li	1.45	513	0.98
Sodium, Na	1.80	496	0.93
Potassium, K	2.20	419	0.82
Rubidium, Rb	2.35	403	0.82
Cesium, Cs	2.60	376	0.79
Francium. Fr	not determined	400	0.7
Non-alkali Metal			
Magnesium, Mg	1.50	738	1.31
Barium, Ba	2.15	503	0.89
Titanium, Ti	1.40	658	1.54
Iron, Fe	1.40	759	1.83
Copper, Cu	1.35	745	1.90
Boron, B	0.85	801	2.04
Nitrogen, N	0.65	1402	3.04

As will be explained in the next section, the small ionization energies of the alkali metals is among the factors contributing to their extreme reactivity.

References

1. The mineral to be electrolyzed must be capable of melting at suitably low temperatures, either on its own or when mixed with an electrolytically inert salt to lower its melting point.
2. Alkali metal image credits: (a) Li: By Tomihahndorf at German Wikipedia - Transferred from de.Wikipedia to Commons., Public Domain, commons.wikimedia.org/w/inde...?curid=1744000; (b) Na: The original uploader was Dnn87 at English Wikipedia. / CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0); (c) K: Unknown author / CC BY (https://creativecommons.org/licenses/by/1.0); (d) Rb: Dnn87 / CC BY (https://creativecommons.org/licenses/by/3.0); and (e) Cs: Dnn87 Contact email: Dnn87yahoo.dk / CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0)
3. All physical and atomic property data for elements except atomic radii and the boiling and melting points of Ba and Fe are calculated from data in Emsley, J. *The elements 2nd ed.* Oxford University Press, 1991. The phase transition points for Ba and Fe were taken from https://www.rsc.org/periodic-table/element/56/barium and should be taken as tentative.
4. Atomic radii are the empirical radii determined by John C. Slater as reported in Slater, J. C. *J. Chem. Phys*. **1964**, *41*, 3199-3204.

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7.3.1: Alkali Metals' Chemical Properties

The chemistry of the alkali metals reflects their tendency to form +1 cations.

The alkali metals tend to form +1 cations. Cation formation is favored by the relatively low ionization energies of the free metal (which makes it easier to form the cation) and the high solvation energy of their cations (which indicates that the cation is thermodynamically stabilized in solution). The variations in ionization energy and solvation energies down the alkali metal group help explain why Li is more reducing than the other alkali metals.[1] The relevant ionization energies and hydration enthalpies are given in Table **7.3.1.1**. As can be seen from the data in Table **7.3.1.1**, the ionization energy of the metal decreases by ~20% on going from Li to Cs while the solvation energy of the cation decreases by ~75% over the same range (with ~2/3 of that decrease taking place on going from Li^+ to Na^+).

Table 7.3.1.1. Selected thermodynamic properties of alkali metals and their cations.[2,3]

Alkali Metal	Ionization Energy (kJ/mol)	Solvation Enthalpy of the +1 Cation (kJ/mol)
Lithium, Li	513	-1091
Sodium, Na	496	-515
Potassium, K	419	-405
Rubidium, Rb	403	-321
Cesium, Cs	376	-296
Francium. Fr	400	-263

One result of this greater stability of Li^+ in solution relative to that of other alkali metal cations is that Li tends to be the most reducing of the alkali metals, as illustrated by the reduction potentials of the metals given in Figure **7.3.1.1**. Nevertheless, as can be seen in Figure **7.3.1.1**, the reduction potentials of the other alkali metals do not monotonically increase on going from Na to Cs. Instead, Na is the least reducing metal, while the reduction potentials of K, Rb, and Cs are approximately equal.

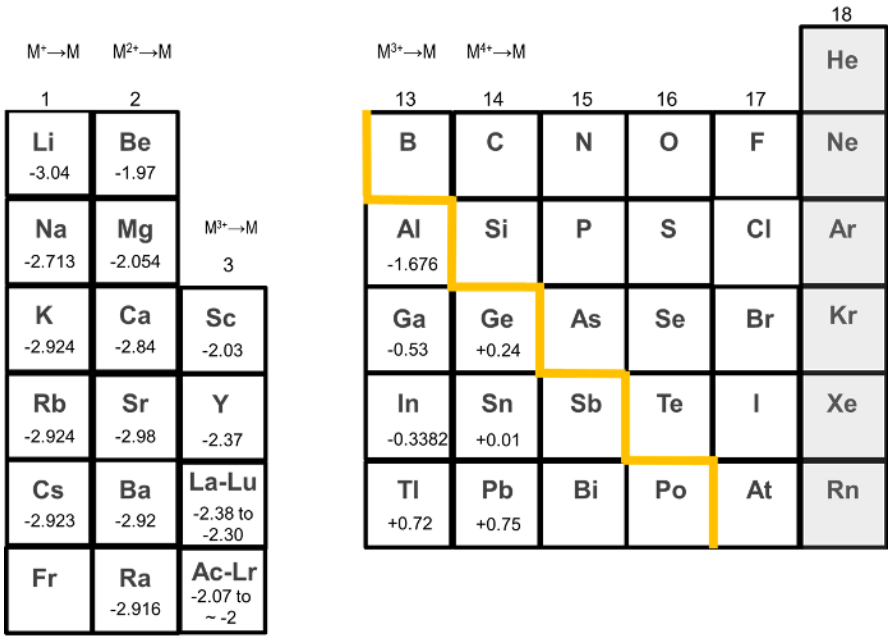


Figure **7.3.1.1**. Standard reduction potentials in volts for reduction of selected aqueous cations in acid solution.

Because of their tendency to form cations, alkali metals are effective reducing agents.

Because of their tendency to form cations, alkali metals are highly reducing. All react vigorously with water to give hydroxides.

$$2\ M(s)\ +\ 2\ H_2O(l)\ \rightarrow\ 2\ M^+\ +\ 2\ OH^-\ +\ H_2(g) \qquad (M\ =\ =Li,\ Na,\ K,\ Rb,\ Cs)$$

The reactions are all exothermic and often lead to combustion of the evolved H_2 gas. As a result, while Li usually just fizzes as it reacts, Na and K usually result in the formation of a colored flame, while the reactions of Rb and Cs result in an explosion.

More synthetically useful is the reduction of alkyl halides by Li metal to give organolithium reagents.

$$R-Cl\ +\ 2\ Li(s)\ \xrightarrow{THF}\ RLi\ +\ LiCl$$

Under conditions where the metal cation is stabilized in the absence of an oxidizing agent, it is even possible to form salts of free or solvated electrons. Small amounts of sodium may be dissolved in dry donor solvents (ammonia, tertiary amines, hexamethylphosphoramide) to give paramagnetic blue solutions containing solvated electrons.

$$Na(s)\ \xrightarrow{NH_3}\ Na(NH_3)_6^+\ +\ e^-(solv.) \quad (\text{at low } Na^+ \text{ concentrations})$$

At higher concentrations of sodium, bronze solutions containing sodide anions (*e.g.* M-) are formed.

$$2\ Na(s)\ \xrightarrow{NH_3}\ Na(NH_3)_6^+\ +\ Na^-(solv.) \quad (\text{at high } Na^+ \text{ concentrations})$$

As either electrides or sodides, the solutions are excellent reducing agents. In some cases, they can even be used to reduce metals to negative oxidation states.

$$Na(NH_3)_6^+\ +\ e^-(solv.)\ +\ Au(s)\ \longrightarrow\ Na(NH_3)_6^+\ +\ Au^-(solv.)$$

In the presence of a catalyst the solvated electron decomposes by reducing the ammonia.

$$2\ e^-(solv.)\ +\ 2\ NH_3\ \xrightarrow{catalyst}\ 2\ NH_2^-\ +\ H_2$$

Synthetically, sodium-ammonia solutions are useful for preparing acetylides and reduced organometallic complexes.

$$R-C\equiv C-H\ +\ Na^+(solv.)\ +\ e^-(solv.)\ \longrightarrow\ R-C\equiv C:^-\ Na^+\ +\ \tfrac{1}{2}\ H_2$$

$$Fe(CO)_5\ +\ 2\ Na^+(solv.)\ +\ 2\ e^-(solv.)\ \longrightarrow\ (Na^+)_2[Fe(CO)_5^{2-}]\ +\ \tfrac{1}{2}\ H_2$$

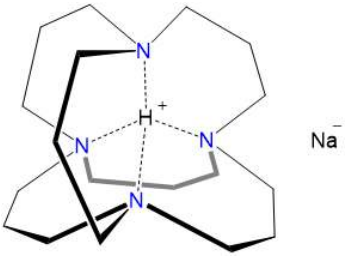
Solid electride salts - *i.e.*, in which the anion is a free electron - may even be prepared by adding a ligand that encapsulates and stabilizes the metal cation and then allowing the solvent to evaporate away from the solvated electron.

$$Na(NH_3)_6^+\ +\ e^-(solv.)\ +\ \text{encapsulating ligand}\ \xrightarrow[-6\ NH_3]{}\ Na(\text{encapsulating ligand})^+e^-(s)$$

Most of the resulting solid electride salts are only stable at low temperatures. The electron density of the free electron "counterions" in crystalline electrides is thought to be localized in cavities within the structure.

The anion of sodium, sodide, Na^-, can be formed by reducing the alkali metal under suitable conditions. Among the more remarkable alkali metal anion salts is "inverse sodium hydride." Inverse sodium hydride is formally an H^+ salt of Na^-, in which the H^+ ion is encapsulated in an adamanzane cage (Figure **7.3.1.2**). This encapsulation slows the thermodynamically favorable reduction of H^+ by the sodide anion, stabilizing the inverse sodium hydride long enough to permit its isolation.

Scheme 7.3.1.I. "Inverse sodium hydride" (*i.e.* H^+Na^-).



The chemistry of the alkali metals depends on the size of the alkali metal cations.

The stability of alkali metal compounds depends on the stabilization of their +1 cations. This stability in turn depends on the size of the cations. Alkali metal cation size helps determine the structure and in some cases the identity of the compound that a given alkali metal forms with a given nonmental. An example of this involves the structures formed by the alkali metal halides. The halides of smaller alkali metal cations -- Li^+, Na^+, K^+, and Rb^+ -- crystallize in the rock salt structure with six halide ions about each ion (Figure **7.3.1.2A**). In contrast, the chlorides, bromides, and iodides of the larger Cs^+ ion crystallize in the CsCl structure, in which there are eight halides about the larger Cs^+ ion (Figure **7.3.1.2B**).

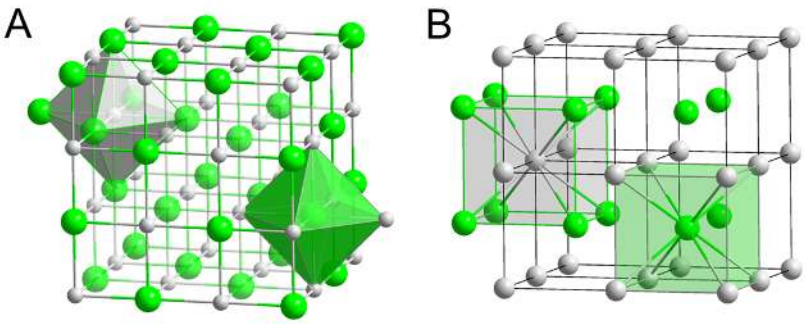


Figure **7.3.1.2**. (A) Rock salt structure formed by LiX, NaX, KX, and RbX (X = F, Cl, Br, and I) showing octahedral coordination of six halides about each metal ion. (B) CsCl structure formed by CsCl, CsBr, and CsI showing square coordination of eight halides about each Cs atom. The rock salt structure is by Solid State - Own work, Public Domain, commons.wikimedia.org/w/inde...?curid=3837309 ; the CsCl structure image by Solid State - Own work, Public Domain, commons.wikimedia.org/w/inde...?curid=3837330.

Size effects are also believed to be responsible for alkali metals' unusual tendency to form peroxides and superoxides when burned in an excess of oxygen. While most metals form oxides when burned in an excess of oxygen, Li and Na also form 2:1 salts of the larger peroxide ion (O_2^{2-}) and K, Rb, and Cs 1:1 salts of the similarly large superoxide ion (O_2^-) (Figure **7.3.1.3**).

Size

Alkali Metal	superoxide O_2^-	Peroxide O_2^{2-}	Oxide O^{2-}
Li	not formed	Li_2O_2 forms but is less stable than Li_2O	Li_2O
Na	not formed	Na_2O_2	Na_2O forms but is less stable than Na_2O_2
K	KO_2	not formed	not formed
Rb	RbO_2	not formed	not formed
Cs	CsO_2	not formed	not formed

Superoxide preference

Figure **7.3.1.3**. Products formed when metals are heated in an excess of dry O_2, showing the increasing preference of larger alkali metals to form peroxides and superoxides.

Perhaps the most striking examples of size effects in alkali metal chemistry involve alkali metal complexes with macrocyclic ligands, particularly crown ethers and cryptands like those shown in Figure **7.3.1.4**.

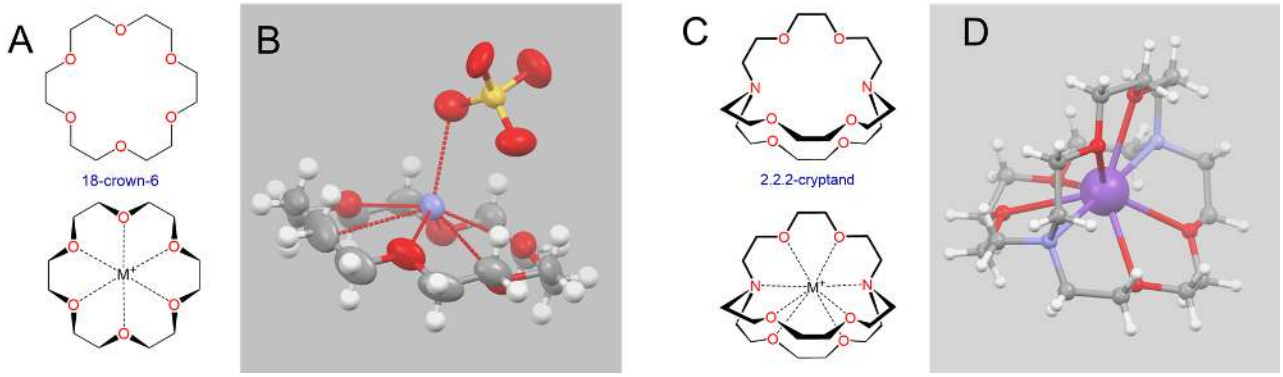
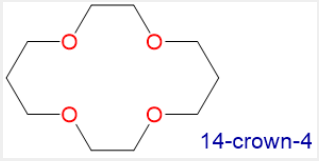
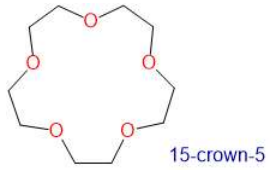
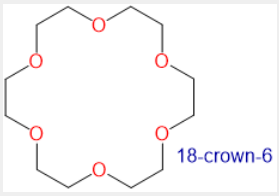
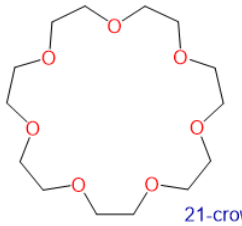


Figure 7.3.1.4. Structures of typical crown ether and cryptand complexes. (A) Cyclic ethers like 18-crown-6 can chelate metal ions through their oxygen lone pairs. They are called crown ethers[3] because they take on a crownlike puckered appearance when bound to the metal, as may be seen from (B) the coordination of 18-crown-6 and sulfate to Cs^+ in the structure of $Cs[H_2PO_4]_{0.5}[HSO_4]_{0.5}\cdot 3H_2O$ in which the crown ether "crowns" the Cs^+ ion by binding to one side of it. This leaves the Cs^+ free to bind additional ligands like SO_4^{2-}. (C) In contrast to crown ethers, cryptands like 2.2.2-cryptand[4] consist of two amines connected by three polyether chains. This allows them to completely encapsulate or "entomb" metals, (D) as may be seen by the coordination of 2.2.2.cryptand to K^+ in (2.2.2-Cryptand)potassium tetracarbonylcobaltate(−1). Key: grey = C; white = H; red = O; yellow = S; blue = Cs; and violet = K^+. The structures in B and C are drawn from the cif files reported in references 8 and 9, respectively.

Crown ethers and cryptands prefer to bind alkali metal cations with sizes that match that of their binding cavity. For instance, as shown in Table 7.3.1.2, 14-crown-4 preferentially binds to Li^+, 15-crown-5 preferentially binds to Na^+, 18-crown-6 preferentially binds to K^+, and 21-crown-7 preferentially binds to Cs^+.

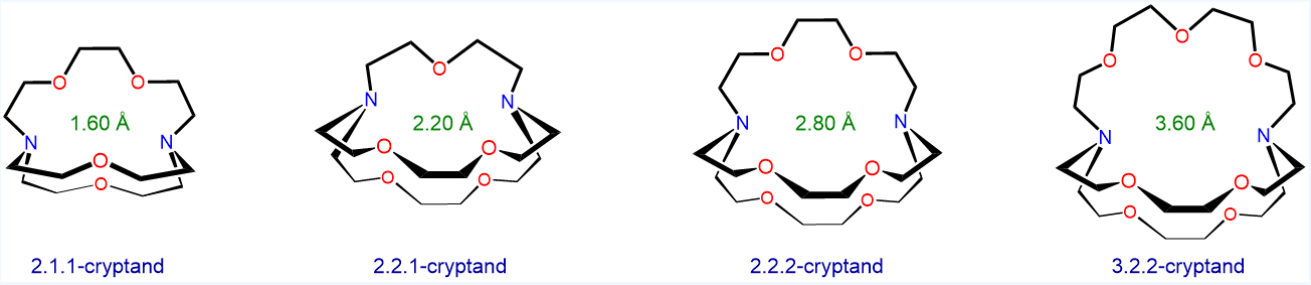
Table 7.3.1.2. Crown ethers preferentially bind cations with sizes that match the cavity size of their crown-shaped conformers. Cavity and cation diameters are taken from reference 10.

Crown ether	...with a cavity diameter of (in Å)	...preferentially binds	...which has a cation diameter of (in Å)
	1.2-1.5	Li^+	1.36
	1.7-2.2	Na^+	1.94
	2.6-3.2	K^+	2.66
	3.4-4.3	Cs^+	3.34

Exercise 7.3.1.1

Cryptand ligands also preferentially bind alkali metal ions with sizes that match the size of their binding cavities. The structure and approximate cavity sizes of several cryptands are given in Scheme **7.3.1.II**. Use the information in Scheme **7.3.1.II** and Table **7.3.1.2** along with a cation diameter of 2.98 Å for Rb^+ to predict which alkali metal ion each cryptand will preferentially bind.

Scheme 7.3.1.II. Structures and approximate binding cavity diameters for several cryptands.



Answer

The cryptands might be expected to selectively bind the largest ion which fits within the cavity. These predictions are summarized in Table **7.3.1.3**.

Table 7.3.1.3. Predicted selectivity of crown ethers for alkali metal cations based on the hypothesis that they will selectively bind the largest ion which fits their binding cavity.

Cryptand	...with a cavity diameter of (Å)	...will be selective for	...with a radius of (in Å)
2.1.1-cryptand	1.60	Li^+	1.36
2.1.1-cryptand	2.20	Na^+	1.96
2.1.1-cryptand	2.80	K^+	2.66
2.1.1-cryptand	3.60	Cs^+	3.34

These predicted selectivities match the experimental observations with one exception. It turns out that 2.1.1-cryptand preferentially binds the smaller Rb^+ ion over Cs^+, although the difference in binding constants is a small one (for more details see reference 12). One reason for this is the flexibility of the cryptand ring system, which allows the cryptand oxygen and nitrogen Lewis base sites to adjust position to accommodate the needs of each alkali metal. In fact, because of this flexibility, all four cryptands can bind all the alkali metals, even those that are nominally too large to fit the cryptand's optimal cavity diameter.

The ability of flexibile macrocycles like cryptands and crown ethers to change conformation when binding a Lewis acid means that the cavity size estimates given in Scheme**7.3.1.II** are of limited utility in predicting the relative binding strengths.

References

1. Since enthalpies of solution involve the dissolution of a solid and ionization energies the ionization of gas phase atoms, a rigorous analysis should also account for the energy associated with sublimation.

2. Ionization energies are taken from Emsley, J. *The elements 2nd ed.* Oxford University Press, 1991.

3. Hydration enthalpies are converted to kJ/mol from the values given in Burgess, J. *Metal ions in solution* Halsted Press: Chichester
New York, 1978; pp. 182-183.

4. Crown ethers are named x-crown-y after the total number of atoms in the ring, x, and the number of oxygen ligand sites, y. Thus the ring of 18-crown-six contains a total of 18 atoms, 6 O and 12 C.

5. Cryptands are named x.y.z.-crypt after the number of oxygen binding sites in each of the chains connecting the two amine groups. Thus 2.2.2-crypt consists of two amines connected by three diether chains.

6. Bard, A. J.; Parsons, R.; Jordan, J.; International Union of Pure and Applied Chemistry., Standard potentials in aqueous solution. 1st ed.; M. Dekker: New York, 1985.

7. Redko, M. Y.; Vlassa, M.; Jackson, J. E.; Misiolek, A. W.; Huang, R. H.; Dye, J. L., “Inverse Sodium Hydride”: A Crystalline Salt that Contains H+ and Na. Journal of the American Chemical Society 2002, 124 (21), 5928-5929.

8. Braga, D.; Modena, E.; Polito, M.; Rubini, K.; Grepioni, F., Crystal forms of highly “dynamic” 18-crown[6] complexes with M[HSO4] and M[H2PO4] (M+ = NH4+, Rb+, Cs+): thermal behaviour and solid-state preparation. New Journal of Chemistry 2008, 32 (10), 1718-1724.

9. Brennessel, W. W.; Ellis, J. E., (2.2.2-Cryptand)potassium tetra-carbonyl-cobaltate(-I). Acta Crystallogr Sect E Struct Rep Online 2014, 70 (Pt 5), m180-m180.

10. Pederson, C.J. "Synthetic Multidentate Macrocyclic Compounds" in Izatt, R. M.; Christensen, J. J., (eds.) Synthetic multidentate macrocyclic compounds. Academic Press: New York, 1978; pp. 24-25.

11. Wagner, M. J.; Dye, J. L., Alkalides, Electrides, and Expanded Metals. Annual Review of Materials Science 1993, 23 (1), 223-253.

12. Dye, J. L., Electrides, Negatively Charged Metal Ions, and Related Phenomena. In Progress in Inorganic Chemistry, Lippard, S. J., Ed. Wiley: 1984; pp 327-441.

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7.4: Hydrogen

Hydrogen Isotopes

Elemental hydrogen exists primarily as the hydrogen-1 isotope, although hydrogen-2 and hydrogen-3 are also known. Some properties of these isotopes are given in Table **7.4.1**.

Table 7.4.1. Atomic properties of hydrogen isotopes. Adapted slightly from https://chem.libretexts.org/Bookshelves/General_Chemistry/Book%3A_Chemistry_(Averill_and_Eldredge)/21%3A_Periodic_Trends_and_the_s-Block_Elements/21.2%3A_The_Chemistry_of_Hydrogen

	Protium	**Deuterium**	**Tritium**
symbol	$^{1}_{1}H$	$^{2}_{1}H$ or D	$^{3}_{1}H$ or T
neutrons	0	1	2
mass (amu)	1.00783	2.0140	3.01605
abundance (%)	99.9885	0.0115	$\sim 10^{-17}$
half-life (years)	—	—	12.32
boiling point of X_2 (K)	20.28	23.67	25
melting point/boiling point of X_2O (°C)	0.0/100.0	3.8/101.4	4.5/?
Notable features	NMR active with a spin of $1/2$	NMR active with a spin of 1	

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7.4.1: Hydrogen's Chemical Properties

Chemical Properties

As described in Section 8.1.1.2., hydrogen and helium are distinguished from all other elements in that their valence shell only consists of the 1*s* orbital. In the case of neutral atomic hydrogen, this orbital is occupied by one electron. Consequently, the chemistry of hydrogen is distinguished by stable bonding arrangements in which the 1*s* orbital is "filled" by one of the following:

- loss of an electron to give hydrogen ion, H^+. In condensed phases these H^+ ions are typically stabilized as Lewis base adducts (*e.g.*, in species like H_3O^+ and NH_4^+)
- gain of an electron to give hydride ion, H^-. This type of bonding adequately explains the behavior of many metal hydrides.
- pairwise sharing of electrons to give covalent E-H bonds that can adequately be described by Lewis theory.
- multicenter sharing of electrons in multicenter covalent bonds, such as those in hydrides that bridge two or more atoms.
- contributing electrons and orbitals to the band structure of a solid state lattice. This is common in interstitial/metallic hydrides.

The first four of these possibilities are summarized in Scheme **7.4.1.I**.

Scheme 7.4.1.I. Common bonding arrangements for hydrogen. The E-H and E---E bonds in the bridging hydride represent sharing of two or more electrons among the three atoms.

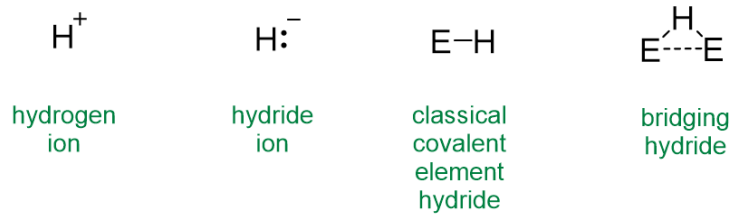


Figure **7.4.1.1**).

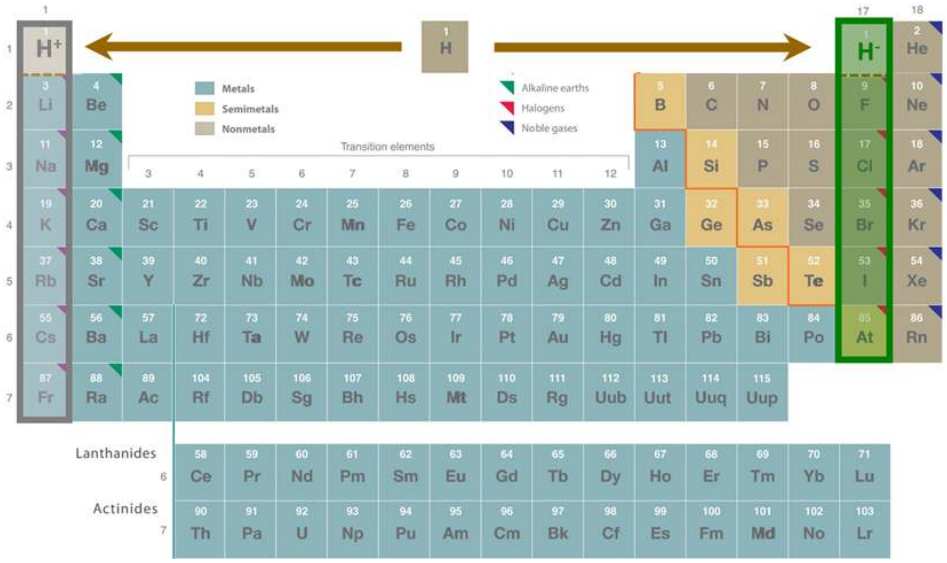


Figure **7.4.1.1**. Hydrogen has an ambiguous position in the periodic table. It is usually placed above the alkali metal group, although it could also be placed above the halogens.

Elemental Hydrogen

At room temperature and pressure, elemental hydrogen exists in the form of dihydrogen, H_2. Dihydrogen is a colorless, odorless gas that finds wide industrial application.

Preparation

In the laboratory H_2 may be prepared by the electrolytic or chemical reduction of water involving the half reaction.

$$2H_2O + 2e^- \rightarrow H_2 + OH^-$$

Such reductions are commonly carried out on acidic solutions since the potentials required are lower, as may be seen from the Pourbaix diagram for hydrogen given in Figure **7.4.1.2**.

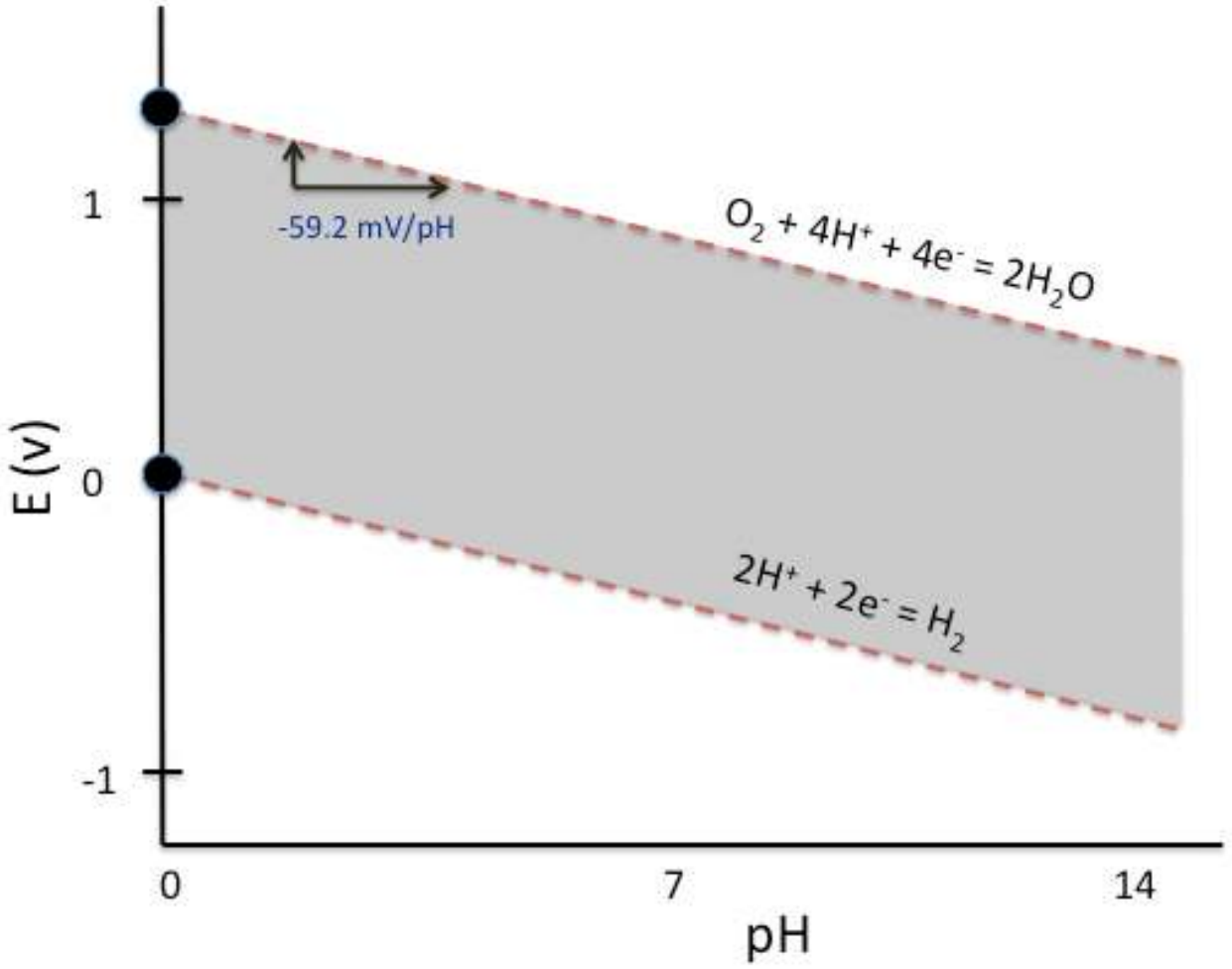


Figure **7.4.1.2**. Pourbaix diagram for hydrogen in water. By tem5psu - https://commons.wikimedia.org/wiki/F...2OPourbaix.png, CC BY-SA 3.0, https://commons.wikimedia.org/w/inde...curid=57288471

A common method is to add Zn to a solution of hydrochloric acid.

$$2\ H^+(aq)\ +\ Zn(s)\ \rightarrow H_2(g)\ +\ Zn^{2+}(aq)$$

In electrolysis the electrons come from the oxidation of water at the anode so that hydrogen production involves water splitting.

$$2\ H_2O(l)\ \rightarrow\ 2\ H_2(g)\ +\ O_2(g)$$

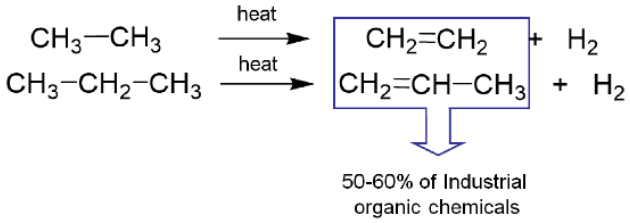
Industrially it is more common to produce hydrogen via **steam reforming** of methane and other hydrocarbons.

$$CH_4(g)\ +\ H_2O(g)\ \xrightarrow{Ni}\ CO(g)\ +\ 3\ H_2(g)\quad \text{(steam reforming)}$$

In this process the formally C^{4-} of methane acts as the reductant. The product of steam reforming is a mixture of CO and H_2. Similar mixtures can also be produced by the anaerobic thermal decomposition of organics and in coal gasification reactions. In all cases they are called **syngas (*i.e.*, synthesis gas)** since they can be used in other industrial syntheses. Its CO component is capable of acting as a reductant, so additional hydrogen can be produced from it via the **water-gas shift reaction**.

$$CO(g)\ +\ H_2O(g)\ \rightarrow\ CO_2(g)\ +\ H_2(g)\quad \text{(water gas shift)}$$

The "cracking" of hydrocarbons also serves as a source of industrially-produced hydrogen, although the alkenes so produced are perhaps even more important as the source of a majority of commodity organic chemicals.



Much of the hydrogen produced industrially is consumed in the Haber-Bosch synthesis of ammonia. The quantities involved are such that hydrogen production for this purpose has been variously estimated to account for 1-2% of global energy consumption.

$$N_2(g) + 3\,H_2(g) \rightarrow 2NH_3(g) \quad \text{(Haber – Bosch process)}$$

Dihydrogen has also been considered for use as a fuel since its combustion is both highly exothermic and green, giving rise only to water.

$$2\,H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

One of the major obstacles to the implementation of hydrogen as a fuel is that its production by steam reforming and the water-gas shift reaction generates CO and CO_2, and costs more energy than is gained from its combustion. For this reason, photocatalytic water splitting is considered one of the holy grails of energy research.

Compounds of hydrogen

Compounds of hydrogen are called hydrides whether or not they contain hydride anion. There are three main types of hydrides - ionic, covalent, and interstitial hydrides. As shown in the periodic table of hydrides given in Figure **7.4.1.3**, interstitial or metallic hydrides are formed by some transition metals, while ionic hydrides are mainly formed by more electropositive metals and covalent hydrides by the nonmetals. The hydrides of Be, some metalloids, and some post-transition metals are said to be intermediate hydrides since they form network covalent structures (sometimes in addition to molecular ones) and tend to function as bases and hydride donors like the ionic hydrides. Not all of the transition metals are known to form hydrides. No hydrides are known for the transition metals of groups 7-9, which are said to constitute **the hydride gap**.

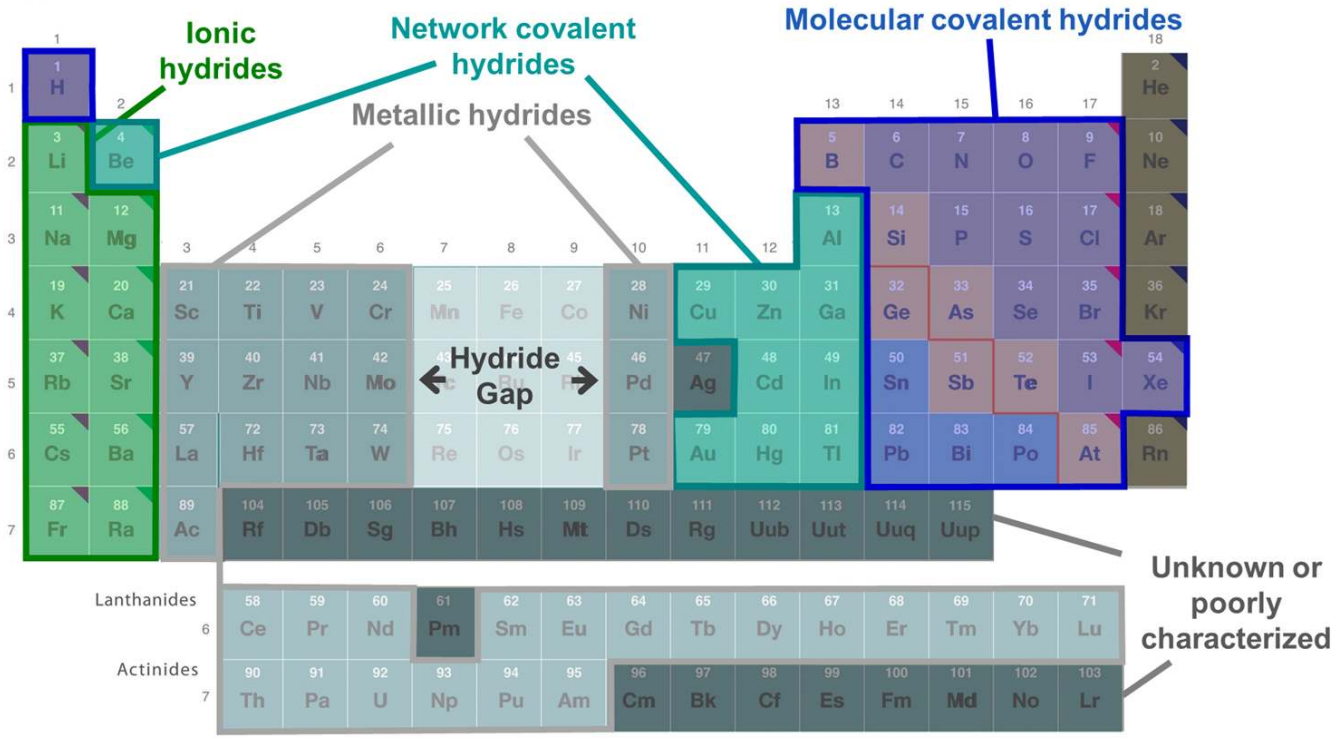


Figure **7.4.1.3**. Distribution of the different types of element hydrides across the periodic table. The figure is adapted from the Periodic Table at https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/02._Atoms%2C_Molecules%2C_and_Ions/2.5%3A_The_Periodic_Table

Ionic hydrides (a.k.a. saline hydrides)

Ionic hydrides are metal salts of the hydride anion, H^-. These are formed by the alkali metals and all the alkaline earth metals except Be. These are typically prepared by direct reaction of the metal and hydrogen.

$$2\,M(s) + H_2(g) \xrightarrow{\Delta} 2\,MH(s) \quad (M = Li, Na, K, Rb)$$

$$M(s) + H_2(g) \xrightarrow{\Delta} 2\,MH_2(s) \quad (M = Mg, Ca, Sr, Ba)$$

As salts of H^-, ionic hydrides form ionic lattices (the NaCl structure is common for MH, the Rutile and PbI_2 for MH_2).

Chemically ionic hydrides act as

- *reducing agents* towards metal oxides. For example

$$2CaH_2(s) + TiO_2(l) \rightarrow 2CaO(s) + Ti(s) + 2\,H_2(aq)$$

- *strong bases* towards protic E-H bonds. All react exothermically with water to liberate hydrogen gas.

$$MH(s) + H_2O(l) \rightarrow M^+(aq) + H_2(g) + OH^-(aq)$$

  For this reason CaH_2 is widely used as a drying agent for organic solvents.

  Reactive metal hydrides may also be used to deprotonate reactive C-H bonds:

$$NaH(s) + CH_3C \equiv C - H(g) \rightarrow CH_3C \equiv C :^- Na^+ + H_2(g)$$

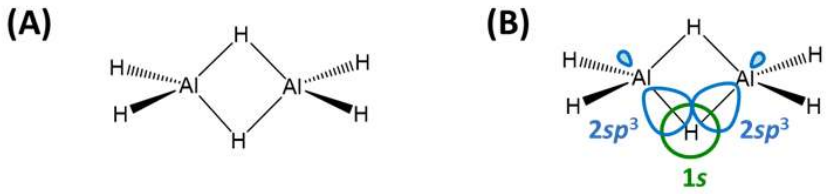
  The $H:^-$ ion in an ionic hydride may in principle act as a nucleophile. However, in practice this application is limited to the less reactive and consequently more selective hydrides of aluminum and boron, both of which are usually classified as intermediate hydrides on account of the covalent character of their E-H bonds.

Covalent and intermediate hydrides

Covalent molecular hydrides are formed by the nonmetals, metalloids, and many post-transition metals. The chemical and physical properties they possess vary across the main group and depend somewhat on the row and whether the element hydride is electron deficient, electron rich, or electron precise. Specifically,

Electron deficient hydrides are those of Be and the group 13 elements (B, Al, Ga, In, and Tl) for which the neutral monomeric element hydride (BeH_2, BH_3, AlH_3, GaH_3, InH_3, and TlH_3 does not possess enough electrons to satisfy the octet rule. Thus these hydrides commonly form dimers (B, Al, Ga, In, Tl) or polymers (Be) held together by bridging E-H-E bonds (Scheme **7.4.1.IIA**). These E-H-E bonds are explained as three-center two-electron bonds in valence bond theory)Scheme **7.4.1.IIB**), but may also be described in terms of molecular orbitals (Note **7.4.1.1**).

Scheme 7.4.1.II. (A) Bridging E-H-E bonds in Al_2H_6 and (B) their valence bond description in terms of overlap between the H 1*s* and Al sp^3 orbitals.

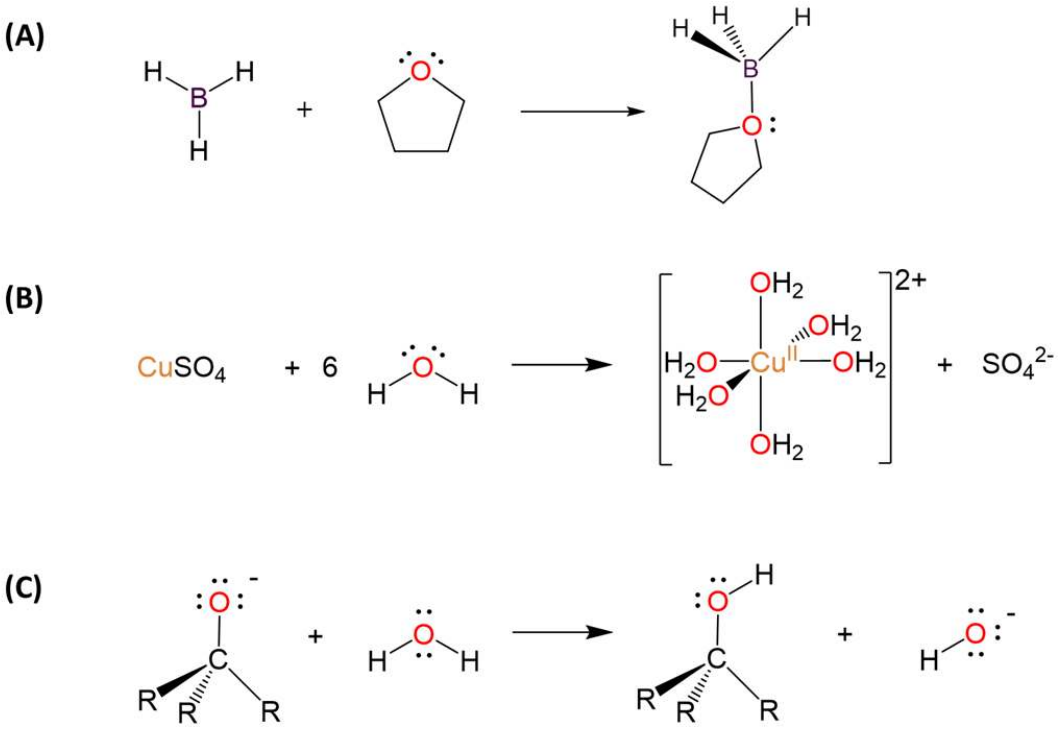


Electron precise and electron rich hydrides are formed by C, N, O, F, and their heavier cogeners. The E-H bonds in these may be described as classical two-center two-electron E-H bonds of Lewis Theory. The electron precise and electron rich hydrides are distinguished in that the electron rich hydrides possess lone pair electrons, while electron precise hydrides do not. In other words,

- electron precise hydrides are those of the group 14 elements, and include the alkanes, alkenes, and alkynes of carbon along with SiH_4, GeH_4, SnH_4, and PbH_4, of which the hydride adducts of group 13 EH_3 compounds like BH_4^- and AlH_4^- are analogues.
- electron rich hydrides are NH_3, H_2O,, HF and their heavier analogues (PH_3, H_2S, HCl, etc.). Regardless of the hydride's classification, the stability of element hydrides decreases down a group. For example, among the group 14 elements, it follows the order $CH_4 > SiH_4 > GeH_4 > SnH_4 > PbH_4$. The same is true of compounds possessing E-E bonds so that while a vast number of alkanes are known, there are relatively few silanes, fewer germanes, and only the organic analogs of stannane are known (such as $(CH_3)_3Sn\text{-}Sn(CH_3)_3$).

The distinction between electron precise and electron rich hydrides is important mainly in thinking about the Lewis acid-base properties of the element hydrides. As illustrated in Scheme **7.4.1.III**, electron deficient hydrides tend to function as Lewis acids and electron rich hydrides as Lewis bases and Brønsted acids.

Scheme 7.4.1.III. In the absence of extremely strong acids or bases, electron-deficient hydrides like BH_3 tend to act as (A) Lewis acids in forming adducts with bases like THF, while electron rich hydrides can act as (B) Lewis bases through their lone pairs, as water does with Cu^{2+} when anhydrous $CuSO_4$ is dissolved in water, or as (C) Brønsted acids, as water does when it is used to quench the alkoxide product of a nucleophilic addition reaction.



The reactivity of electron precise hydrides depends on the characteristics of E. For example, while most alkanes do not act as Lewis acids at the carbon atom, row 3 and heavier electron precise hydrides can form trigonal bipyramidal adducts.

Moreover, all element hydrides - whether electron deficient, precise, or rich - can function as a weak Brønsted acids or hydride donors depending on the polarity of the E-H bond. Hydrides in which hydrogen is bound to an electron rich and electronegative element tend to act as Brønsted acids, while those involving more electropositive elements tend to function as hydride donors, as illustrated in Scheme **7.4.1.IV**.

Scheme 7.4.1.IV. (A) The electron rich hydride of chlorine acts as a Brønsted acid in forming a pyridinium complex while (B) the relatively electropositive hydride in tetrahydroaluminate is widely used as a hydride donor in organic chemistry, as illustrated by the use of lithium aluminum hydride to form alcohols from ketones.

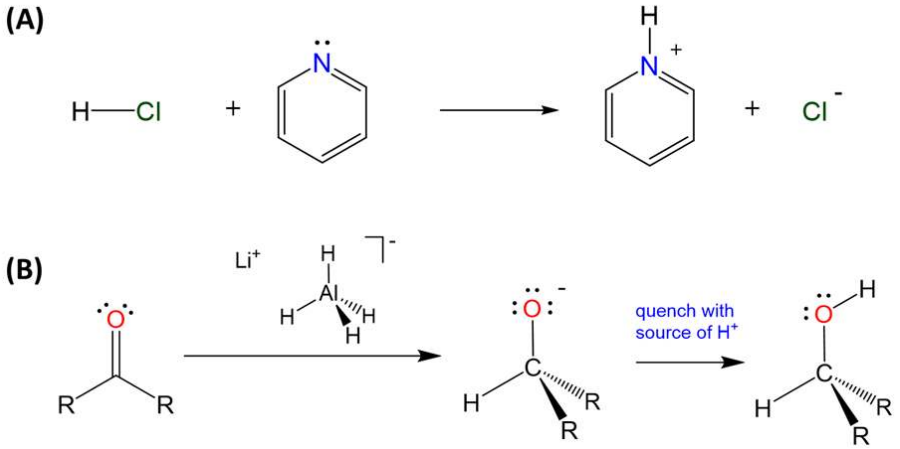


Figure **7.4.1.4**, the metals give hydrides of $E^{\delta-}-H^{\delta+}$ bonds, the metalloids (including B) weakly polarized $E^{\delta-}-H^{\delta+}$ bonds and most nonmetals $E^{\delta-}-H^{\delta+}$ bonds.

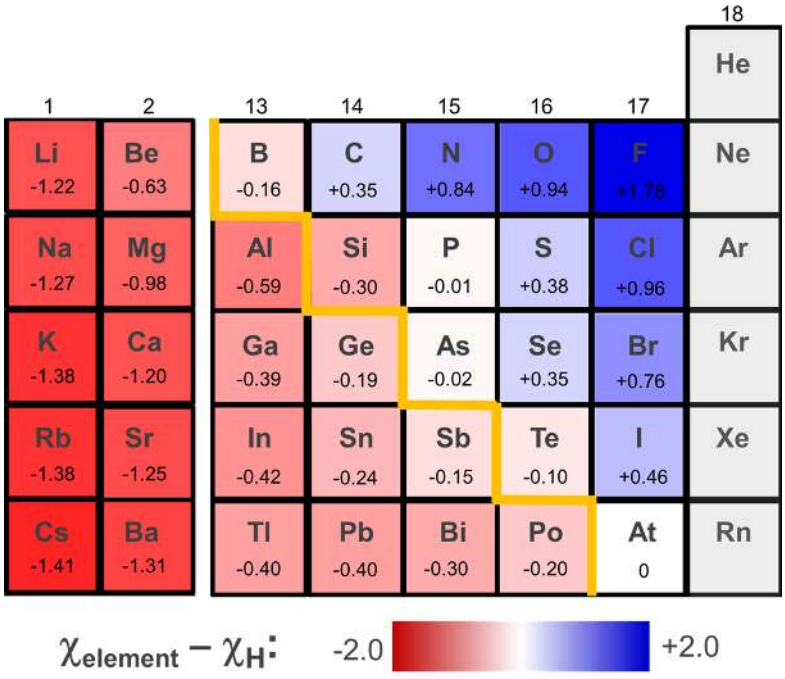


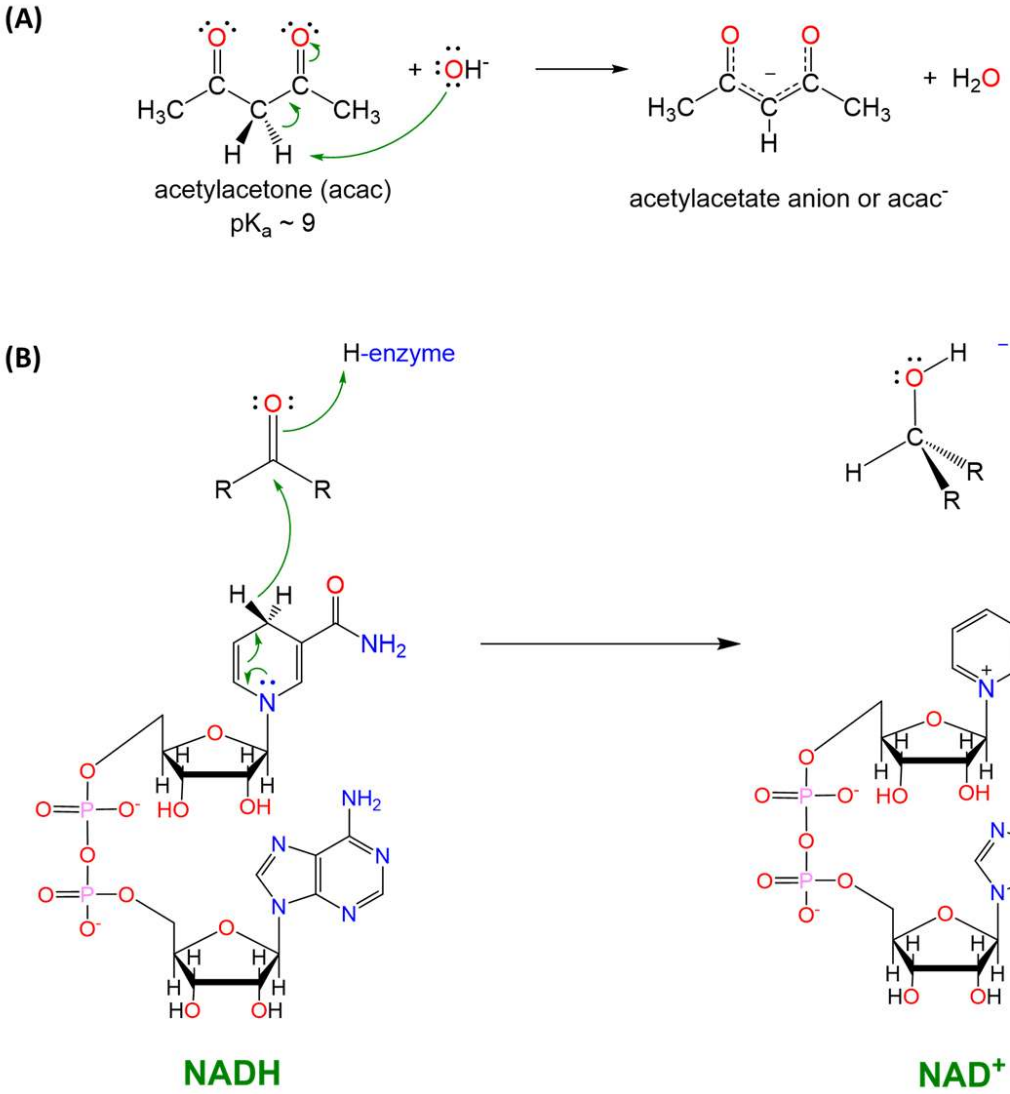
Figure **7.4.1.4**. Difference between element and hydrogen Pauling electronegativities. More positive values correspond to positively polarized hydrogen while more negative ones have a larger partial negative charge on hydrogen.

The ability of a given element hydride to function as an acid or hydride donor may be modified by a number of factors. One of these is the solvation energy of the species formed. According to Figure **7.4.1.4**, Germane (GeH_4) might be expected to function as a hydride donor. However, it can be deprotonated in liquid ammonia, likely because of the large solvation energy of the resulting H^+ ion.

$$GeH_4 \xrightarrow{NH_3(l)} H^+(solv.) + GeH_3^-(solv.)$$

Electronic factors that affect the stability of the element hydride's conjugate acid or base forms also play a role. For example, carbon-hydrogen bonds are normally very weakly acidic but can act as strong Brønsted acids when the resulting anion is highly stabilized or as a hydride donor when the resulting cation is highly stabilized. This is illustrated by the well-known ability of C-H bonds to function as Brønsted acids, hydride donors, or neither depending on the electron-richness of the carbon center and the stability of the resulting structure (Scheme **7.4.1.V**).

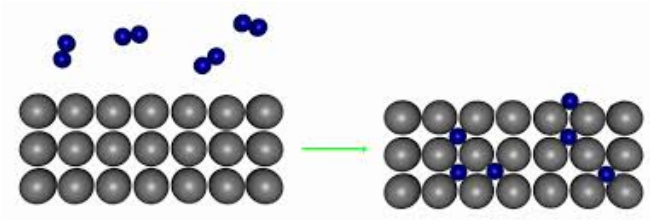
Scheme 7.4.1.V. (A) enolate chemistry such as that used in the formation of acetylacetate (acac) ligands is based on the ability of C-H bonds α to a carbonyl to act as acids, and (B) a C-H bond of NADH functions as a hydride donor in biochemical systems. Notice the similarity in reactivity of the C-H hydride in NADH and the Al-H in $LiAlH_4$ shown in Scheme **7.4.1.IV**.



Additional aspects of the acid-base chemistry of the element hydrides are described in 6: Acid-Base and Donor-Acceptor Chemistry, as is hydrogen's ability to form hydrogen bonds.

Interstitial hydrides (a.k.a. metallic hydrides)

In **interstitial or metallic hydrides,** hydrogen dissolves in a metal to form nonstoichiometric compounds (solid solutions) of formula MH_n. They are called metallic hydrides since they possess the typical metallic properties of luster, hardness, and conductivity and are called interstitial hydrides because the H occupies interstices in an FCC, HCP, or BCC metal lattice, as illustrated schematically in Figure **7.4.1.5**.



gure **7.4.1.5**. Schematic illustration of the process of formation of an interstitial hydride showing breakup of dihydrogen and its uptake into the metal lattic he metal lattice expands 10-20% during this process.[1] Taken fro tps://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Map%3A_Inorganic_Chemistry_(Housecroft)/10%3A_Hydrogen/10.7%3A_Binary_Hydrides_Classification_and_General_Properties/10.7D%3A_Molecular_Hydrides_and_Complexes_Derived_from_them

The process of interstitial hydride formation is reversible, and metals can dissolve varying amounts of hydrogen depending on the number of interstices available. Because of this, interstitial hydrides have been considered as storage materials for hydrogen.

Note

7.4.1.1. A Qualitative Molecular Orbital Description of the Bonding in Diborane

The B-H-B bonds in diborane may also be explained using a molecular orbital description, as illustrated by the qualitative MO diagram in Figure **7.4.1.6**.

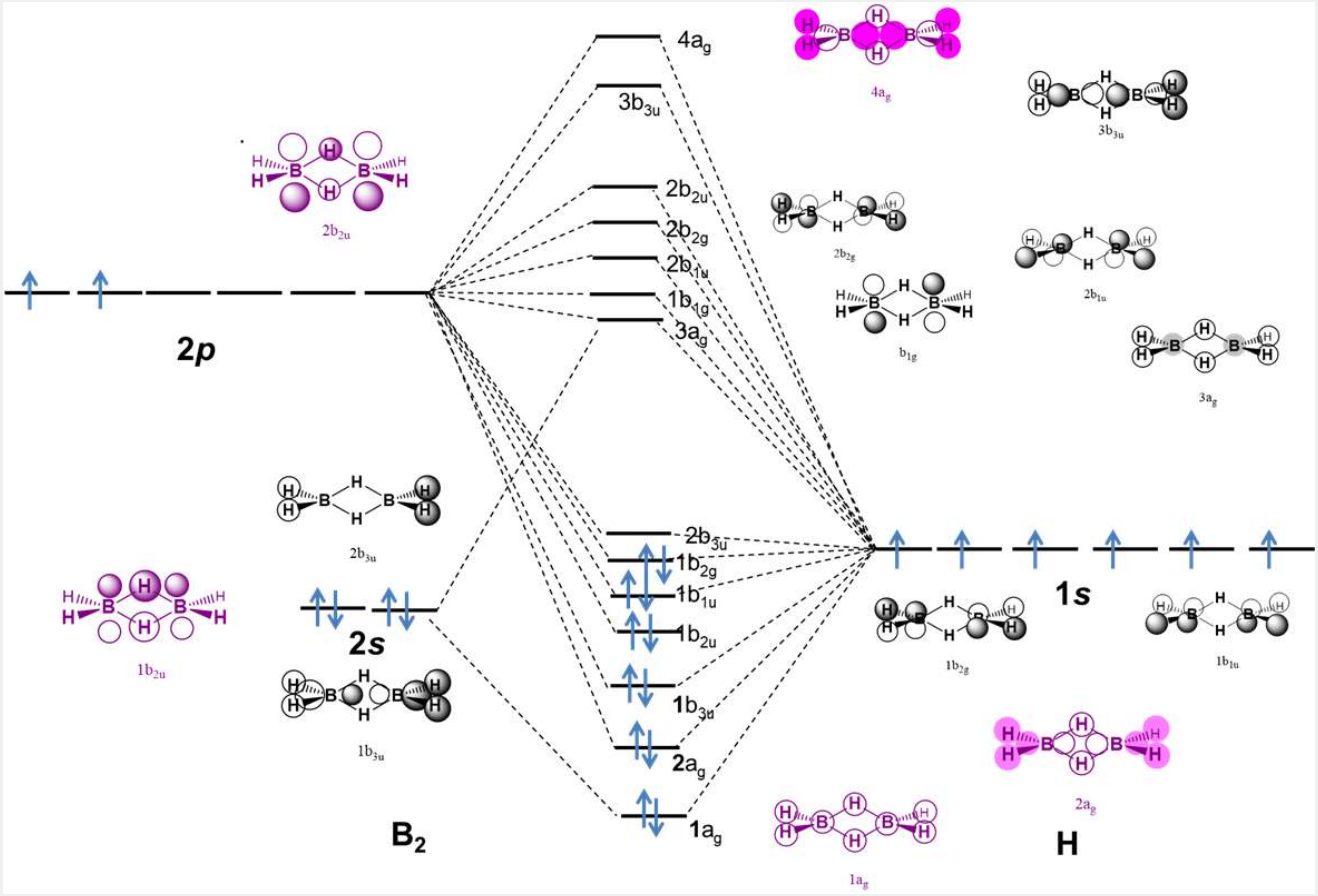


Figure **7.4.1.6**. Qualitative MO diagram for diborane. The symmetry adapted bonding and antibonding MOs involved in bridge bonding are shown in violet. The derivation of this diagram is presented in 8.5.1. Properties of the Group 13 Elements and Boron Chemistry.

References

1. Møller, K. T.; Jensen, T. R.; Akiba, E.; Li, H.-w., Hydrogen - A sustainable energy carrier. Progress in Natural Science: Materials International 2017, 27 (1), 34-40.

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7.5: Group 2, The Alkaline Earth Metals

The alkaline earth metals

The alkaline earth metals comprise the elements Be through Ra in group 2 of the periodic table, as show in Figure **7.5.1**.

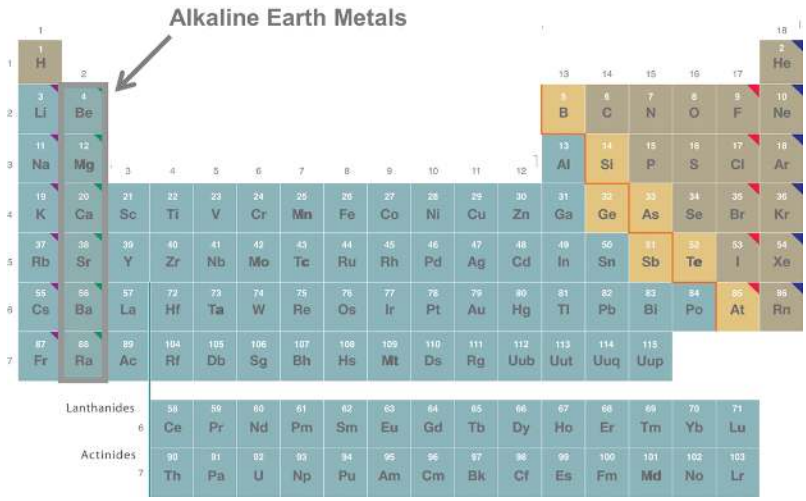


Figure **7.5.1**. Position of the alkaline earth metals in the periodic table. Adapted from the periodic table at https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/02._Atoms%2C_Molecules%2C_and_Ions/2.5%3A_The_Periodic_Table.

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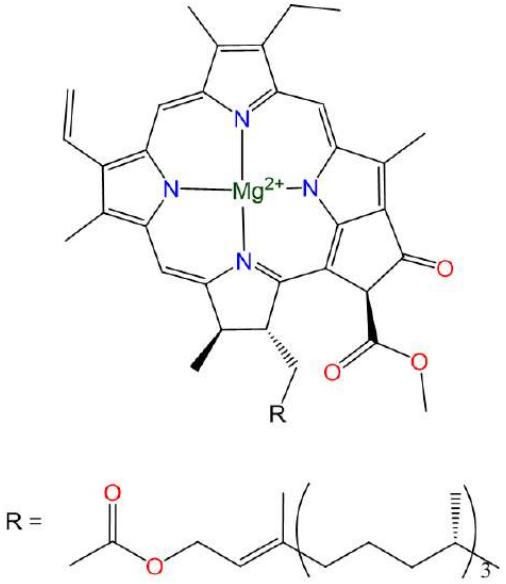
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7.5.1: Preparation and General Properties of the Alkaline Earth Elements

Like the alkali metals, the alkaline earth metals are good reductants that are only found on Earth in their +2 oxidation states. Magnesium and calcium are particularly common. Magnesium-containing chlorophylls are the photosynthetic pigments of green plants and photosynthetic algae (Scheme **7.5.1.1**).

Scheme 7.5.1.1. Structure of chlorophyll a, one of the principle green pigments of plants.



Seawater is about 0.05 *M* in Mg^{2+} and 0.01 *M* in Ca^{2+}, and beryllium and calcium are components of many important minerals. Examples of alkaline earth metal-bearing minerals that were known and used since antiquity include beryl, $Be_3Al_2Si_6O_{18}$; gypsum, $CaSO_4{\cdot}2H_2O$; limestone, $CaCO_3$; and lime, CaO, the latter of which were more recently replaced in construction by calcium silicate-based sand lime bricks and Portland cement containing concrete.

Despite calcium and magnesium's widespread environmental distribution and importance, the metals were only isolated in the late 18th and early 19th century after the development of electrolysis. Humphrey Davy's isolation of Mg and Ca is illustrative.

$$2\ MO \xrightarrow{\text{electrolysis}} 2\ M(s) + O_2 \quad \text{Davy, } (M = Mg,\ Ca,\ 1808)$$

Today Ca, Mg, and the other alkaline earth metals are produced either by electrolysis of their chlorides or chemical reduction by carbon or aluminum.

$$2\ MCl_2 \xrightarrow{\text{electrolysis}} 2\ M(s) + Cl_2 \quad (M = Be,\ Mg,\ Ca,\ Sr)$$

$$MgO + C \xrightarrow{\text{electrolysis}} Mg(s) + CO$$

$$3\ MO + 2\ Al \xrightarrow{\text{electrolysis}} M(s) + Al_2O_3 \quad (M = Ca,\ Sr,\ Ra)$$

$$4\ BaO + 2\ Al \xrightarrow{\text{electrolysis}} Ba(s) + BaAl_2O_4$$

Once formed, the metals are reactive towards atmospheric oxygen. Nevertheless, Be and Mg may be stored and used in air since their initial oxidation gives a thin passivating layer of the oxide that seals off the bulk metal from further oxidation. The other alkaline earth metals need to be stored under an inert atomosphere to prevent their degradation to the oxide.

Physical Properties

Like the alkali metals, the alkaline earth metals are all grey or silvery solids that crystallize in a cubic lattice, HCP for Be and Mg, FCC/CCP for Ca and Sr, and BCC for Ba and Ra. All possess the typical metallic properties of high heat and thermal conductivity.

Aside from the lightest member of the group, they are comparatively low melting and soft on account of their large atomic radii, low effective nuclear charges, and just two valence electrons that contribute to metallic bonding. Thus they melt and boil at higher temperatures than the alkali metals but lower temperatures than most transition metals, as illustrated by the melting and boiling points listed in Table **7.5.1.1**. As with the alkali metals, the melting and boiling points decrease down the group as the atomic size increases.

Table 7.5.1.1. Melting and boiling points of the alkaline earth metals and selected reference substances.[3]

Substance	Melting Point (° C)	Boiling Point (° C)
Alkaline Earth Metal		
Beryllium, Be	1278	2468
Magnesium, Mg	649	1090
Calcium, Ca	839	1484
Strontium, Sr	769	1384
Barium, Ba	727	1845
Radium, Ra	700	1140
Non-alkaline Earth Metal		
Lithium, Li	181	1347
Sodium, Na	98	883
Cesium, Cs	28	678
Titanium, Ti	1660	3287
Iron, Fe	1538	2861
Copper, Cu	1083	2567
Water	0	100
Benzene	6	80

The atomic properties of alkaline earth metals reflect the

- relatively high energy and large size of their ns orbitals
- higher effective nuclear charge experienced by electrons in their ns valence orbitals when compared to those of the corresponding alkali metals

As may be seen from the atomic radii and ionization energies given in Table **7.5.1.2**, overall the radii and ionization energies of the alkaline earth metals follow the expected periodic trends. The radii increase down a group, and across a row they follow the trend

$$\text{alkali metal} > \text{alkaline earth metal} > \text{transition metals}$$

Because of their smaller size and larger atomic mass, alkaline earth metals are significantly more dense than the corresponding alkali metals (Table **7.5.1.2**).

Correspondingly, the ionization energies of the alkaline earth metals decrease down a group while across a row their ionization energies follow the trend

$$\text{alkali metal} < \text{alkaline earth metal} < \text{transition metals}$$

In consequence the alkaline earth metals are good reductants and prefer to form the +2 ion, although they are not as reactive as the alkali metals. Moreover, Be possesses an anomalously small radius, high ionization energy, and large electronegativity when

compared with heavier alkaline earth metals. Consequently, its chemical behavior is similar to that of boron and aluminum, as will be discussed in the next section.

Table 7.5.1.2. Selected atomic properties of the alkali metals and selected reference compounds.[3,4]

Substance	Atomic Radius (Angstroms)	First Ionization Energy (kJ/mol)	Pauling Electronegativity	Density of the Solid (g/mL)
Alkaline Earth Metal				
Beryllium, Be	1.05	899	1.57	1.85
Magnesium, Mg	1.50	738	1.31	1.74
Calcium, Ca	1.80	590	1.00	1.55
Strontium, Sr	2.00	550	0.95	2.54
Barium, Ba	2.15	503	0.89	3.59
Radium, Ra	2.15	509	0.89	5.0
Non-alkaline Earth Metal				
Lithium, Li (same row as Be)	1.45	513	0.98	0.53
Sodium, Na (same row as Mg)	1.80	496	0.93	0.97
Potassium, K (same row as Ca)	2.20	419	0.82	0.86
Rubidium, Rb (same row as Sr)	2.35	403	0.82	1.53
Cesium, Cs (same row as Ba)	2.60	376	0.79	1.87
Francium. Fr (same row as Ra)	not determined	400	0.7	not determined
Titanium, Ti	1.40	658	1.54	4.54
Iron, Fe	1.40	759	1.83	7.87
Copper, Cu	1.35	745	1.90	8.96
Boron, B	0.85	801	2.04	2.34
Aluminum, Al	1.25	577	1.61	2.70
Nitrogen, N	0.65	1402	3.04	1.03 (at 21 K)

As will be explained in the next section, one of the factors that contributes to the reactivity of the alkali metals is their small ionization energies.

References and Notes

1. All physical and atomic property data for elements except atomic radii and the boiling and melting points of Ba, Be, and Fe are calculated from data in Emsley, J. *The elements 2nd ed.* Oxford University Press, 1991. Since the phase transition points for Be, Ba

and Fe were either listed as correspoding to high pressure conditions or disagreed with values reported elsewhere they were taken from the data listed at https://www.rsc.org/periodic-table.

2. Atomic radii are the empirical radii determined by John C. Slater as reported in Slater, J. C. *J. Chem. Phys*. **1964**, *41*, 3199-3204. Values of these radii may be conveniently accessed at http://www.knowledgedoor.com/2/elements_handbook/slater_atomic-ionic_radius.html

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7.5.2: Alkaline Earth Metals' Chemical Properties

Alkaline earth metals are good reducing agents that tend to form the +2 oxidation state.

The alkaline earth metals tend to form +2 cations. As can be seen from Figure **7.5.2.2**, alkaline earth metals possess large negative $M^{2+/0}$ standard reduction potentials which strongly favor the +2 cation. The potentials for reduction of Ca^{2+}, Sr^{2+}, and Ba^{2+} to the metal of ~ -3 V are even similar to those of the alkali metals.

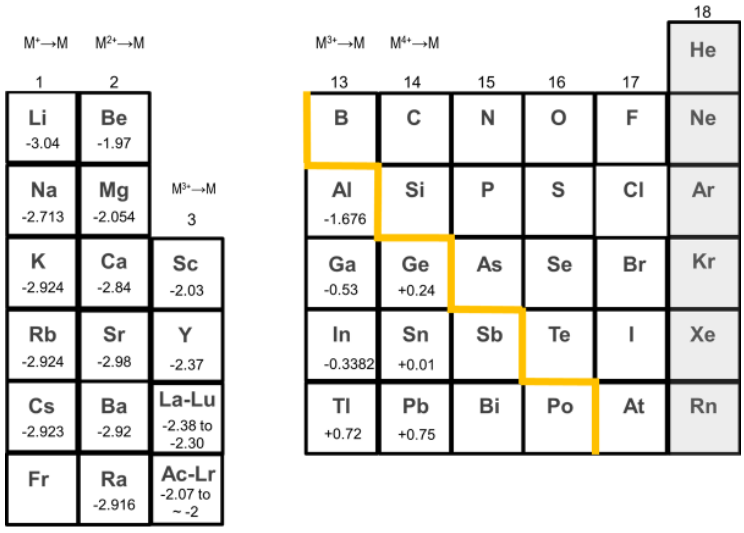


Figure **7.5.2.1**. Standard reduction potentials in volts for reduction of selected aqueous cations in acid solution. This figure is a copy of that used in section 8.3.2. Alkali Metals' Chemical Properties. Because of their tendency to form +2 cations, the alkaline earth metals are good reducing agents.

Like the alkali metals, Ca, Sr, and Ba dissolve in liquid ammonia to give solutions containing solvated electrons, although these have not been as heavily studied as those of the alkali metals.

Unlike the alkali metals, all the alkaline earth metals react with oxygen to give oxides of formula MO, although the peroxides of the heavier alkaline earths can be formed by solution phase precipitation of the metal cation with a source of peroxide anion (O_2^{2-}).

$$2\,M(s) + O_2 \longrightarrow 2\,MO(s) \qquad (M = Be, Mg, Ca, Sr, Ba, \text{and presumably Ra})$$

$$M(OH)_2(aq) + H_2O_2(aq) \longrightarrow MO_2(s) + 2\,H_2O \qquad (M = Mg, Ca, Sr, Ba, \text{and presumably Ra})$$

Calcium, strontium, barium (and presumably radium) react with water to liberate dihydrogen gas and form hydroxides.

$$M(s) + 2\,H_2O(l) \rightarrow M^{2+} + 2\,OH^- + H_2(g) \qquad (M = Ca, Sr, Ba, \text{and presumably Ra})$$

although unlike the alkali metals the reduction is slow and usually liberates hydrogen without fire or explosion.

Beryllium and magnesium do not react with water at room temperature, although they do dissolve in acid and react with steam at high temperatures and pressures to give the oxide (which can be thought of as a dehydrated hydroxide).

$$M(s) + 2\,H^+ \rightarrow M^{2+} + H_2(g) \qquad (M = Be \text{ and } Mg)$$

$$M(s) + H_2O(g) \xrightarrow{\text{high T, P}} MO(s) + H_2(g) \qquad (M = Be \text{ and } Mg)$$

Presumably Ca, Sr, Ba, and Ra would react this way as well, although due to their higher reactivity the reaction is likely to be violent.

Like other metal oxides containing low oxidation state metals, the alkaline earth oxides are basic. The oxides of the heavier alkaline earth metals react with water to give the hydroxides.

$$\text{MO} \quad (\text{M} = \text{Be, Mg, Ca, Sr, Ba, and presumably Ra}) \quad + \ \text{H}_2\text{O} \longrightarrow \text{M(OH)}_2$$

The hydrolysis of BeO and MgO usually requires high temperatures and pressures. Consequently their hydroxides are more commonly prepared by addition of base to a soluble salt.

$$\text{M}^{2+}\text{(aq)} \quad (\text{M} = \text{Be, Mg, Ca, Sr, Ba, and presumably Ra}) \quad + \ 2\ \text{OH}^- \rightarrow \text{M(OH)}_2$$

The alkaline earth metals react directly with halogens to give the dihalides, although given the exothermicity of reactions involving the powerfully reducing alkaline earth metals with oxidizing halogens in the laboratory, it is usually safer to react the hydroxides or oxides with the appropriate hydrohalic acid.

$$\text{M(s)} + \text{X}_2^- \quad (\text{M} = \text{Be, Mg, Ca, Sr, Ba, and presumably Ra; X} = \text{F, Cl, Br, I}) \quad \rightarrow \text{MX}_2$$

$$\text{M(OH)}_2 + 2\ \text{HX} \rightarrow \text{MX}_2 \quad (\text{M} = \text{Mg, Ca, Sr, Ba, and presumably Ra; X} = \text{F, Cl, Br, I}) \quad + \ 2\ \text{H}_2\text{O}$$

$$\text{MO} + 2\ \text{HX} \rightarrow \text{MX}_2 \quad (\text{M} = \text{Mg, Ca, Sr, Ba, and presumably Ra; X} = \text{F, Cl, Br, I}) \quad + \ \text{H}_2\text{O}$$

The heavier alkaline earth metals (Mg through Ba) also reduce hydrogen to give hydrides.

$$\text{M(s)} \quad (\text{M} = \text{Mg, Ca, Sr, Ba, and presumably Ra}) \quad + \ \text{H}_2\text{(g)} \rightarrow \text{MH}_2$$

As discussed in section 8.2.1. Hydrogen's Chemical Properties, these alkaline earth hydrides are ionic salts of hydride ion. Thus they react with water and other electrophiles.

$$\text{MH}_2\text{(s)} + \text{H}_2\text{O(l)} \rightarrow \text{M(OH)}_2 \quad (\text{M} = \text{Mg, Ca, Sr, Ba, and presumably Ra}) \quad + \ \text{H}_2\text{(g)}$$

The consumption of water in this reaction forms the basis for the use of calcium hydride as a drying agent for organic solvents.

Unlike the heavier alkaline earth metals, beryllium does not react directly with hydrogen, and the resulting hydride, though still nucleophilic, acts as a polar covalent hydride and hydrolyzes relatively slowly.

Divalent Alkaline Earth cations polarize anions

The classic example of alkaline earth cations' ability to polarize anions involves the decomposition of the metal carbonates. Alkali metal carbonates and nitrates thermally decompose to release CO_2 and a mixture of NO_2 and O_2, respectively.

$$\text{MCO}_3\text{(s)} \xrightarrow{\Delta} \text{MO(s)} + \text{CO}_2\text{(g)}$$

$$\text{M(NO}_3\text{)}_2\text{(s)} \xrightarrow{\Delta} \text{MO(s)} + 2\ \text{NO}_2\text{(g)} + \text{O}_2\text{(g)}$$

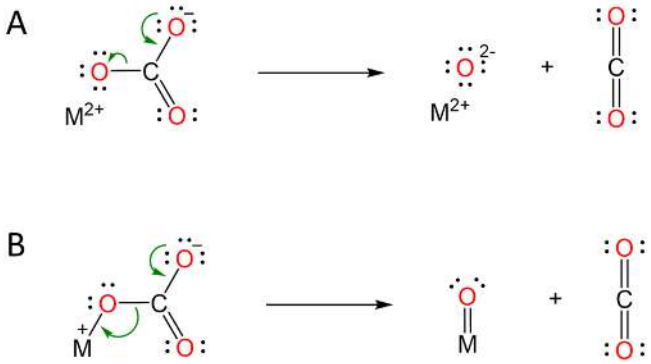
Complex factors govern decomposition of the nitrates but, as shown in Table **7.5.2.1**, the decomposition of the alkaline earth carbonates shows that on going down the group, carbonate decomposition requires increasingly higher temperatures.

Table 7.5.2.1. Decomposition temperatures of alkaline earth carbonates

Carbonate	**Midpoint of decomposition range[2] (K)**
$BeCO_3$	not reported; unstable at room temperature (298 K)
$MgCO_3$	903
$CaCO_3$	953
$SrCO_3$	1178
$BaCO_3$	1316

The typical explanation for this trend involves the mechanism of carbonate decomposition depicted in Scheme **7.5.2.II**. As the alkaline earth metal cation becomes larger on going from Be to Ba, its ability to polarize the carbonate anion is lessened, making it more difficult to form the oxide.

Scheme 7.5.2.I. Models explaining how alkaline earth metal cations facilitate carbonate decomposition. (A) Ionic model in which the negative charge buildup is stabilized by interaction between the dication and one of the carbonate oxygens. (B) Semi-covalent representation of the same interaction, now depicted as a M=O bond (which should not be taken to imply that such a bond actually exists).



Exercise 7.5.2.1

Alkaline earth metal sulfates undergo decomposition reactions similar to those of the carbonates and nitrates.

1. Write a decomposition reaction that involves the liberation of a single molecular gas from the sulfate to give an oxide.
2. Rank the alkaline earth metal sulfates in order of increasing decomposition temperature.

Answer

1. The sulfates decompose by liberating SO_3 according to the reaction

$$MSO_4(s) \xrightarrow{\Delta} MO(s) + SO_3(g)$$

Note that another possible decomposition mode is

$$MSO_4(s) \xrightarrow{\Delta} MO(s) + \tfrac{1}{2}\,O_2(g) + SO_2(g)$$

However, that reaction is not the one asked for by the prompt since it involves the liberation of two different molecular gases (O_2 and SO_2).

2. The expected decomposition order of the alkaline earth metal sulfates along with known decomposition temperatures is

$$\underset{580\ ^\circ C}{BeSO_4} < \underset{895\ ^\circ C}{MgSO_4} < \underset{1149\ ^\circ C}{CaSO_4} < \underset{1374\ ^\circ C}{SrSO_4} < BaSO_4 < RaSO_4$$

Beryllium, and to a lesser extent magnesium, form polar highly covalent compounds.

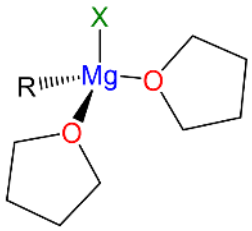
The chemistry of magnesium and beryllium demonstrates the danger of drawing an overly rigorous distinction between elements as metals, nonmetals, and metalloids. This is because both Be and Mg can form compounds with considerable covalent character and, as might be expected from their relative paucity of electrons, they share much in common with the electron deficient row 13 metalloids B and Al.

In terms of Mg, the influence of covalency is evident from the structures of the Grignard reagents that Mg forms on reaction between the metal and alkyl halides.

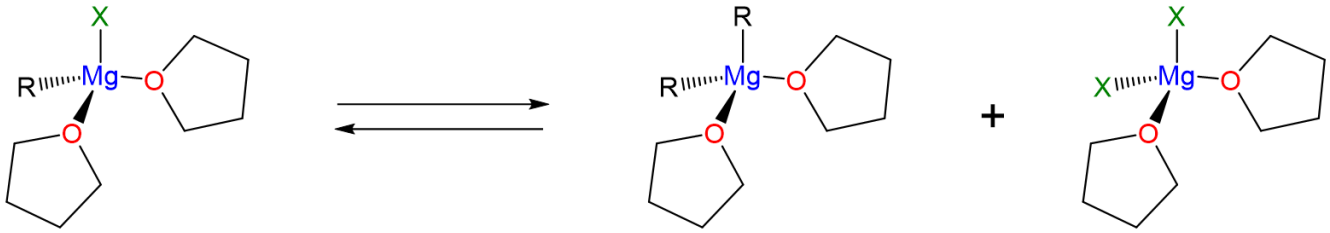
$$Mg(s) + R-X \xrightarrow{THF,\text{catalytic } I_2} R-Mg-X$$

The reaction is dependent on the presence of Lewis base donor ethers like Et_2O or THF, which coordinate the Mg^{2+}, completing its coordination sphere and giving tetrahedral complexes like that depicted in Scheme **7.5.2.II**.

Scheme 7.5.2.II. Structure of monomeric "RMgX" Grignard reagent in THF solution.



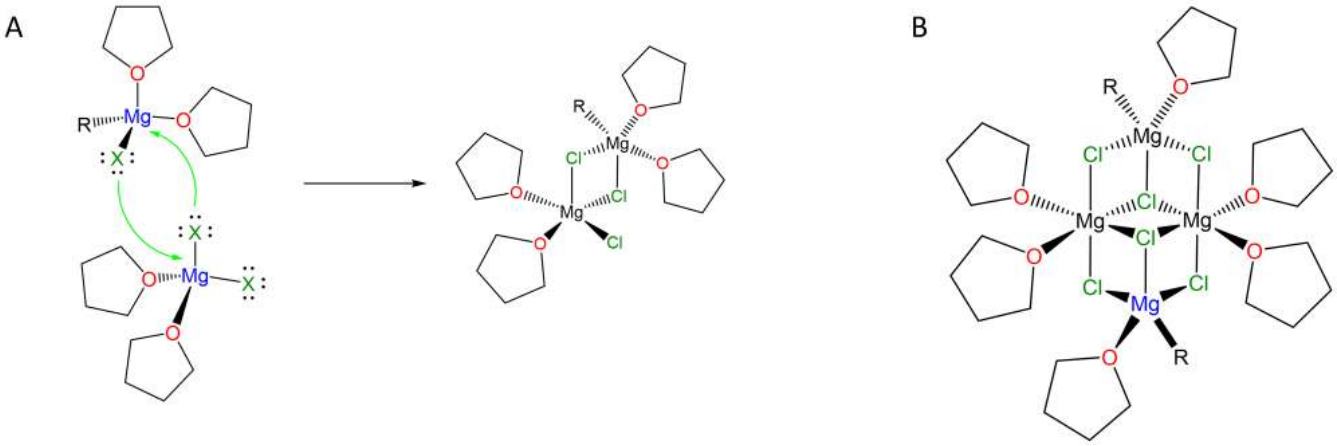
Like molecular compounds, Grignard reagents undergo ligand substitution reactions in solution according to the Schlenk equilibrium.



"RMgX" "R_2Mg" "MgX_2"

They also form clusters in which the halogen lone pairs are used to bridge multiple Mg centers, as illustrated by the complex in Scheme **7.5.2.III**.

Scheme 7.5.2.II. (A) Halogens like Cl can bridge multiple metal centers via their lone pairs, allowing for the formation of species like (B) "$(RMgCl)_2(MgCl_2)_2$". Redrawn from references 4 and 5.



The extent of covalency is even greater in the case of beryllium, which with a radius of only 113 Å and valence electrons that experience a Slater effective nuclear charge of +1.95 atomic charge units, has considerable ability to polarize nearby Lewis bases. As a result, beryllium tends to form polar covalent bonds rather than ionic ones.

Because beryllium only possesses two valence electrons, its compounds also tend to be electron deficient and bridging Be-X-Be bonds are common. Thus in liquid ammonia, Be forms species with bridging Be-N-Be bonds like the tetrameric cluster shown in Scheme **7.5.2.III**.

Scheme 7.5.2.III. Tetrameric Be cluster formed in liquid ammonia. Redrawn from reference 6.

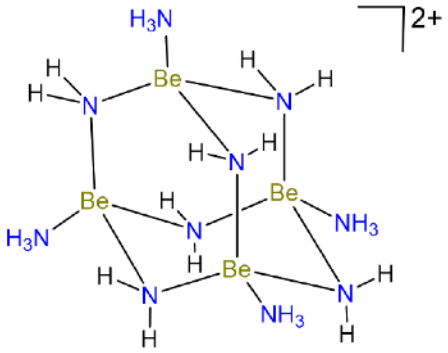


Figure **7.5.2.2**. At higher temperatures the polymeric chains dissociate into Be_2Cl_4 dimers and $BeCl_2$ monomers.

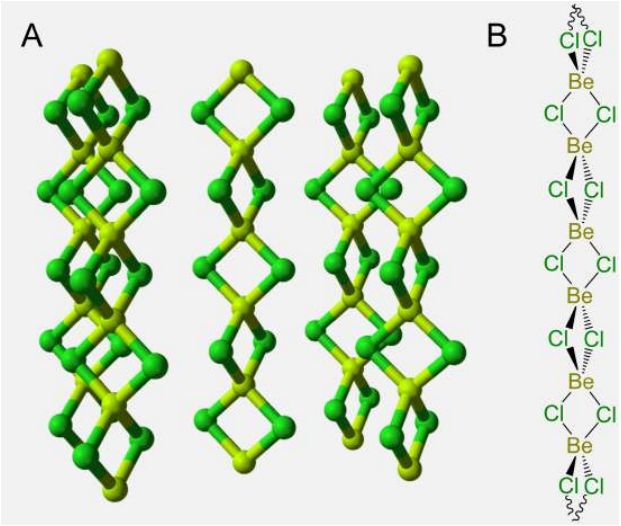


Figure **7.5.2.2**. (A) Structure of $BeCl_2$ consisting of (B) polymeric chains of edge-linked $BeCl_4$ tetrahedra. The structure of $BeCl_2$ is by Ben Mills - Own work, Public Domain, commons.wikimedia.org/w/inde...?curid=4759802, who rendered it from X-ray data reported in Rundle, R. E.;Lewis, P.H. *J. Chem. Phys.* **1952**, *20(1)*: 132-134.

One particularly remarkable structure is that of basic beryllium acetate in which a central oxygen bridges four Be atoms, as shown in Scheme **7.5.2.IV** along with that of $Be_4(NO_3)_6O$, which is thought to possess an anlogous structure.

Scheme 7.5.2.IV. (A) Structure of basic beryllium acetate, $Be_4(OAc)_6O$, (B) in which the central OBe_4 tetrahedron is circumscribed to make it easier to see that the structure consists of a OBe_4^{6+} tetrahedron in which the Be---Be edges are linked by bridging acetate ligands. Zinc forms an analogous structure. (C) The structure of $Be_4(NO_3)_6O$ is postulated to be analogous to that of basic beryllium acetate, with bridging nitrate ligands taking the place of the acetates.

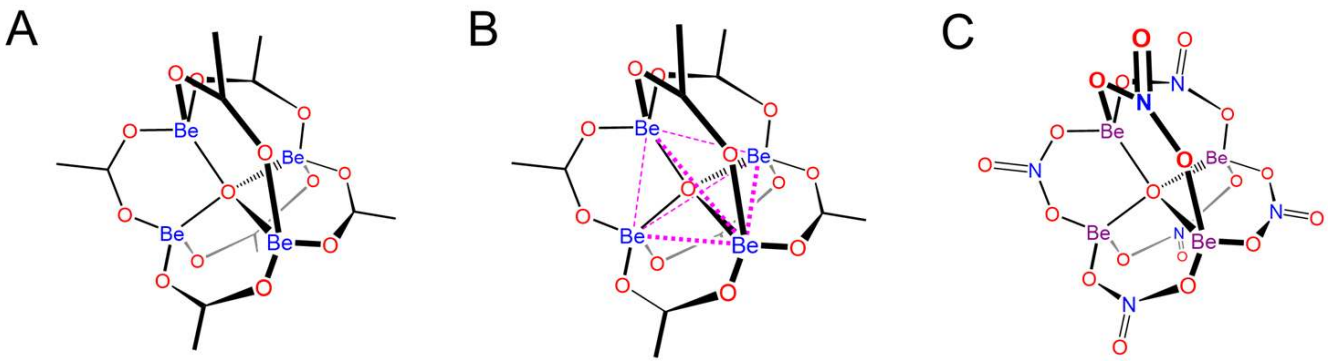


Figure **7.5.2.3**.

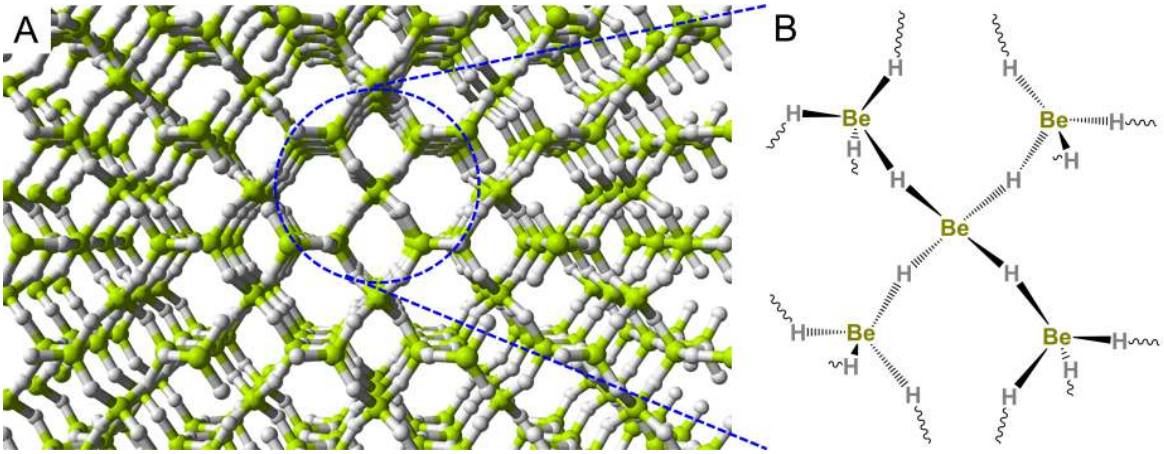
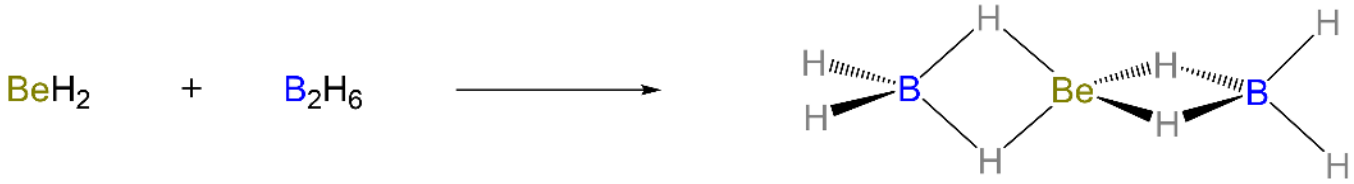


Figure **7.5.2.3**. (A) Structure of BeH_2 consisting of (B) a network of BeH_4 tetrahedra linked via 3-center-2-electron Be-H-Be bonds. The structure of BeH_2 is by Ben Mills - Own work, Public Domain, commons.wikimedia.org/w/inde...?curid=3930832, who rendered it from X-ray data reported in Smith, G.S.; Johnson, Q.C.; Smith, D. K.; Cox, D. E.; Snyder, R. L.; Zhou, R-S.; Zalkin, A. *Solid State Communications* **1988,** *67(5)*, 491-494.

Beryllium hydride even forms an adduct with two BH_3 to give a structure in which a central Be is linked to the terminal BH_2 groups by 3-center-2-electron Be-H-B bonds, as shown in Scheme **7.5.2.V**.[7]

Scheme 7.5.2.V. Formation of an adduct between BeH_2 and two BH_3 (in the form of B_2H_6).



References and Notes

1. Petrocelli, A.W. Superoxides. In Van Nostrand's Encyclopedia of Chemistry, G.D. Considine (Ed.). Wiley, 2005. doi:10.1002/0471740039.vec2421

2. The decomposition range midpoint for $MgCO_3$, $CaCO_3$, $SrCO_3$, and $BaCO_3$ are calculated from the data reported in Maitra, S., Chakrabarty, N., & Pramanik, J.. *Cerâmica* **2008**, *54*(331), 268-272.

3. The decomposition temperatures for $BeSO_4$, $MgSO_4$, $CaSO_4$, and $SrSO_4$ are from Massey, A. G., Main group chemistry. E. Horwood: New York, 1990, pg. 152.

4. Seyferth, D., The Grignard Reagents. Organometallics 2009, 28 (6), 1598-1605.

5. Toney, J.; Stucky, G. D. J. Organomet. Chem. **1971**, 28, 5.

6. Müller, M.; Karttunen, A. J.; Buchner, M. R., Speciation of Be^{2+} in acidic liquid ammonia and formation of tetra- and octanuclear beryllium amido clusters. Chemical Science 2020, 11 (21), 5415-5422.

7. The structure of BeB_2H_8 may also be thought of as an adduct between Be^{2+} and two BH_4^- ligands.

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7.6: Group 13 (and a note on the post-transition metals)

The group 13 elements comprise the elements Boron through Nihonium

The group 13 elements comprise the elements Boron through Nihonium in group 13 of the periodic table, as shown in Figure **7.6.1**.

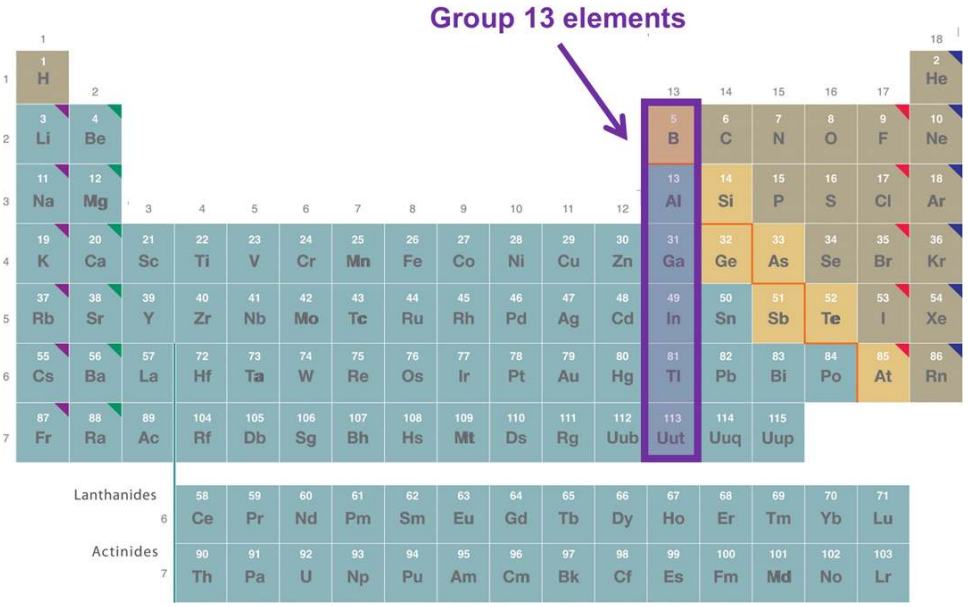


Figure **7.6.1**. Position of the group 13 elements in the periodic table. Note that since the periodic table used was developed, element 113 was named Nihonium and given the symbol Nh. Adapted from the periodic table at https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/02._Atoms%2C_Molecules%2C_and_Ions/2.5%3A_The_Periodic_Table

The group 13 elements are chemically diverse, comprising elements:

- Boron, B, an electron deficient 2nd row element sometimes classified as a nonmetal and occasionally as a metalloid;
- Aluminum, Al, an electron deficient 3rd row element sometimes classified as a metal and sometimes as a metalloid;
- Gallium (Ga), Indium (In), Thallium (Tl), and Nihonium (Nh, marked under its old symbol, Uut, in the Figures on this page), post transition metals that exhibit the inert pair effect to varying degrees.

The group 13 elements include post-transition metals.

The term **post-transition metals** refers to those elements that are metals following the transition metals. As with the metalloid concept there is no universal consensus as to what exactly is a post transition metal. Fortunately, in practice it is less important to precisely define what is and is not a post transition metal than to understand the reason why it might be helpful to classify an element as a post-transition metal.

The main features of the post transition metals are that they are relatively electron rich and electronegative compared to what is classically thought of as a metal. Roughly, this translates into relatively lower melting points (since more antibonding levels in the band structure tend to be occupied), increased preference for covalency, and greater brittleness than other metals (due to the resulting directional bonding). Their electron richness means that they tend to form soft cations.

Several systems are used to classify elements as belonging to the post transition metals. The main ones include:

1. *Metals which follow the d-block.* By this definition only the metals in groups 13 and higher and Rows 3 and higher which form relatively soft and electron rich cations and exhibit significant covalency in their bonding are included. However, if this scheme is adopted too rigidly Al is excluded since it technically doesn't follow the *d*-block (and has an unfilled (n-1)*d* subshell) and the metalloids are excluded, even though many of them also form relatively soft and electron rich cations with filled (n-1)*d* subshells. Another disadvantage of this system is that it entangles the issue of which elements should be classified as post-transition metals with the thorny issue of which elements should be classified as metals vs. metalloids.

2. *Metals and metalloids of the p-block.* This system has the advantage of emphasizing the interesting and unique properties of the metals and metalloids of *p*-block as well as continuities in those properties through the *p*-block. Consequently, it will be used here in the sections which follow. However, it has the disadvantage of excluding metals like Zn, Cd, and Hg, which form many compounds in which the metal has a (n-1)d^{10} configuration.
3. *Metals which follow the transition elements in the sense of forming ions with a completely full (n-1)d valence shell sometimes along with Al and the p-block metalloids*. This definition adds Zn, Cd, and Hg (and sometimes Cu, Ag, and Au) since they form ions with an (n-1)d^{10} valence electron configuration such as Zn^{2+}, Cd^{2+} and Hg^{2+}(and Cu^{+}, Ag^{+}, and Au^{+}). Since this chapter only considers the *p*-block elements, *for the purposes of this chapter* this system is functionally identical to system 2.

Whichever classification scheme one uses, it is often more helpful to think of the classification of elements as post-transition metals as a way to emphasize similarities in the chemical properties of a set of elements rather than as a way of emphasizing how post-transition metals differ from other metals. The post-transition metals are not the only ones which form soft cations or compounds better described as being held together by covalent bonds. As the previous sections made clear, even alkali metals form anions under the right circumstances, and many compounds of metals are better described in terms of covalency than ionic interactions. This was already evident in the chemistry of the alkaline earth metals Be and Mg discussed in the previous section. In subsequent chapters the bonding and reactivity in coordination complexes and organometallic compounds will largely be described in covalent terms.

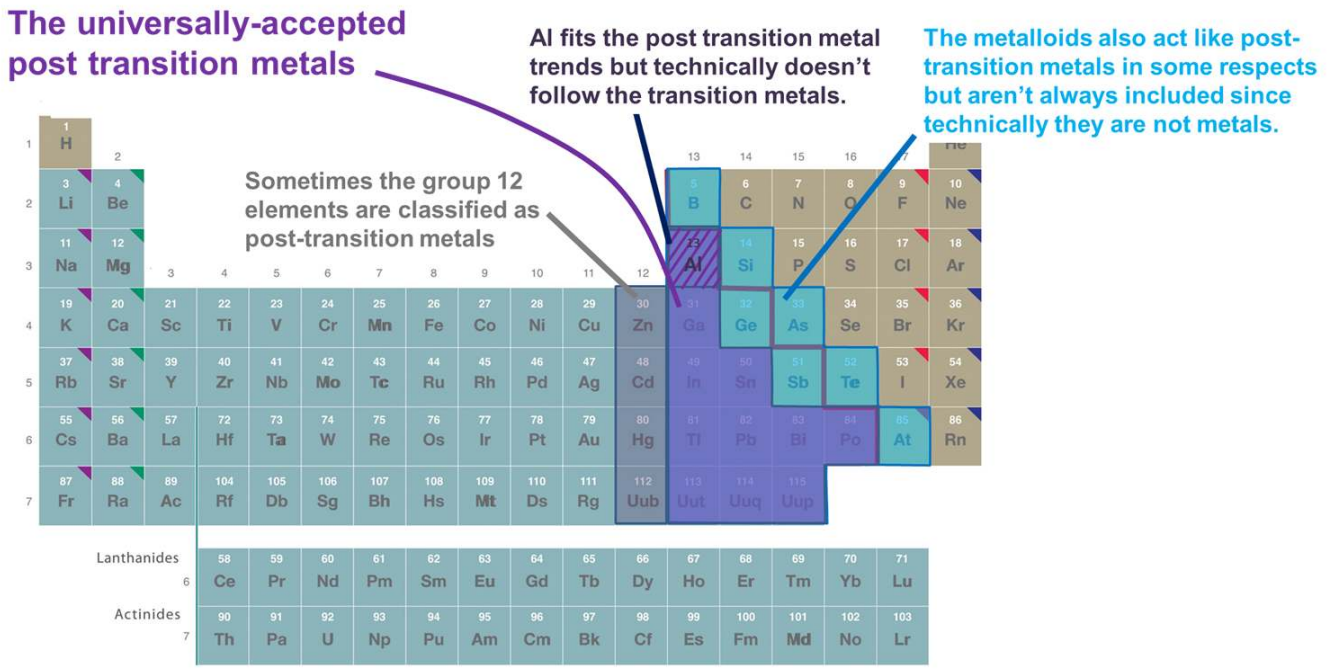


Figure **7.6.2**. Some of the elements classified as post transition metals. Those shown in purple are commonly accepted since they are metals and clearly follow the transition metals, while the metals in groups 12 (and sometimes 11), Al, and the metalloids are all sometimes included since they behave like the other post-transition metals in important respects. The periodic table is adapted from that at https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/02._Atoms%2C_Molecules%2C_and_Ions/2.5%3A_The_Periodic_Table.

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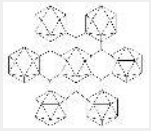
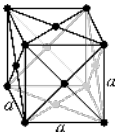
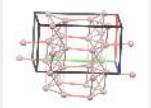
7.6.1: Properties of the Group 13 Elements and Boron Chemistry

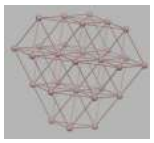
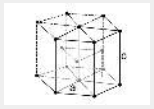
As elements, Boron acts like an electron deficient nonmetal and the other group 13 elements like metals that exhibit varying degrees of covalency.

Selected properties of the Group 13 elements are given in Table **7.6.1.1**.

Table 7.6.1.1. Selected Properties of Group 13 Elements other than Nihonium. For more information about how this data was

sourced see note 1.

Element	Elemental Form	Melting Point (°C)	Pauling Electronegativity	Ionization Energy (kJ/mol)	Electron Affinity (kJ/mol)	Atomic Radius (Å)	Covalent Radius (Å)
Boron, B	Network Covalent Solid characterized by the sharing of electrons in boron clusters, primarily linked icosahedra, like those depicted schematically below. 	2180	2.04	801	27	1.92	0.84
Aluminum or Aluminium,[2] Al	FCC Metal 	660	1.61	577	42	1.84	1.24
Gallium, Ga	Metal with a nonstandard crystal structure that may be described as packed Ga_2 units, which are shown linked by the thicker pink lines in the structure below. 	30	1.81	579	41	1.87	1.23
Indium, In	Distorted close packed metal	157	1.78	558	36	1.93	1.42

							
Thallium, Tl	HCP Metal 	304	1.8	589	28.9	1.96	1.44

From the data given in Table **7.6.1.1** several things are apparent:

1. There is a discontinuity between the properties of boron and the group 13 metals in rows 3 and higher.

2. Boron forms covalent compounds characterized by multicenter bonding and cluster formation; the other elements are metals that exhibit varying degrees of covalency.

3. Trends in the properties of the row 3+ group 13 metals are far from simple, likely in part because

- The atomic properties of Ga and In are influenced by the *d*-block contraction, giving both a relatively high electronegativity, which when combined with their small radii promote stronger covalent interactions.
- The atomic properties of Tl are also influenced by the lanthanide contraction, resulting in an increase in electronegativity and ionization energy relative to In.

4. The interplay between changing covalent and metallic bonding interactions on going from Al to Tl results in a decrease in melting point from Al to Ga followed by an increase in melting point on going from Ga to Tl.

The group 13 elements are prepared by reduction of halides or oxides or, in the case of boron, thermal decomposition of the hydride.

Boron can be prepared by reduction of its halides or high temperature thermal decomposition of its hydrides.

$$2\ BCl_3 + 3\ H_2 \longrightarrow 2\ B + 6\ HCl$$

$$B_2H_6 \xrightarrow{\Delta} 2\ B + 3\ H_2$$

The group 13 metals are made by electrolytic reduction of the cations in thermally accessible molten salts. The best known example is the production of aluminum in the **Hall-Héroult process**.

$$2\ Al_2O_3 + 3\ C(s,\ graphite) \xrightarrow{electrolysis,940-980^\circ C,KF,Na_2AlF_6} 4\ Al(s) + 3\ CO_2(g)$$

Boron forms covalent bonds and engages in cluster and/or bridge bonding when there are too few electrons to form enough pairwise bonds to satisfy an octet.

Boron possesses only three valence electrons and can be stablilized by sharing five more. It does this in three main ways.

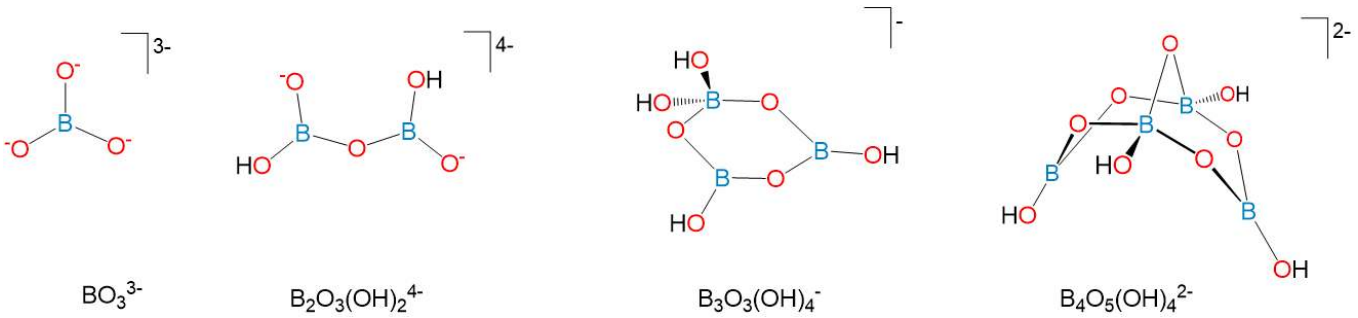
1. **Boron forms ordinary covalent bonds and/or gains electrons to give stable molecules or ions.** For example, while the boron of monomeric BH_3 may not have access to enough valence electrons to achieve a stable octet, it can satisfy its octet by forming an adduct with a Lewis base. A well known example is the borohydride anion, BH_4^-.

$$BH_3 + H^- \longrightarrow BH_4^-$$

A large number of boron compounds are of this sort. These include

a. *The borates and boric acid derivatives which comprise a few ppm of the Earth's crust.* These contain borate anions similar to the representative set shown in Scheme **7.6.1.II**. Of these, sodium borate or borox is commonly used in household detergents. More precisely, there is a mixture of boraxes, all of which are of formula $[Na(H_2O)_x]_2H_2B_4O_9$ (often written as $Na_2B_4O_7{\cdot}xH_2O$) and differ in the number of waters of hydration. All contain the tetraborate anion, $B_4O_5(OH)_4^{2-}$, which has the structure shown at right in Scheme **7.6.1.II**..

Scheme 7.6.1.II. The tetraborate anion.



As illustrated by the structures depicted in Scheme **7.6.1.II**, the boron in borates is found in BO_4 tetrahedra and trigonal planar BO_3 units linked together in various ways.

The borates illlustrate the acid-base properties of these conventional boron compounds. Borate anions may be considered as derived from hydrolysis of boric oxide to boric acid followed by acid dissociation.

$$\underset{\text{boric oxide}}{B_2O_3} + 3\,H_2O \longrightarrow \underset{\text{boric acid}}{2\,B(OH)_3}$$

$$B(OH)_3 \rightleftharpoons H^+ + B(OH)_2O^-$$

$$B(OH)_3 \rightleftharpoons 3\,H^+ + BO_3^{3-}$$

In this respect boron oxide, like all metal oxides, is capable of acting as a Brønsted acid, albeit a very weak one. Consequently the borate anions, as the conjugate bases of weak acids, are Brønsted bases.

The trigonal planar boron sites in species like boric acid illustrate the ability of trigonal planar boron to act as a Lewis acid, specifically by forming a Lewis base adduct.

$$B(OH)_3 + OH^- \rightleftharpoons B(OH)_4^-$$

Notice that the three coordinate boron centers in Scheme **7.6.1.II** are not drawn as possessing an octet, even though it would be possible to draw resonance forms which satisfy boron's octet by drawing resonance structures in which there are B=O bonds. This is because it is unclear that such resonance structures contribute significantly to the bonding in trigonal planar boron centers. To see why, it is helpful to consider the boron trihalides.

b. *The boron trihalides.* Structurally, boron trihalides like BCl_3 possess a trigonal planar structure like that in the BO_3 units of boric acid and metal borates. What is notable about the structure is that the B-X bonds are shorter than those in analogous tetrahedral structures, as illustrated in Scheme **7.6.1.III**.

Scheme 7.6.1.III. Increase in the B-Cl bond length as the boron center goes from trigonal pyramidal to tetrahedral coordination on formation of an adduct with ammonia. Reproduced from a drawing by Ben Mills based on reference 6.

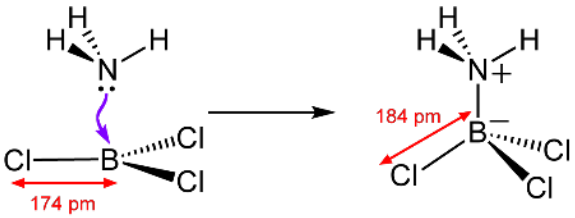


Figure **7.6.1.2C**.

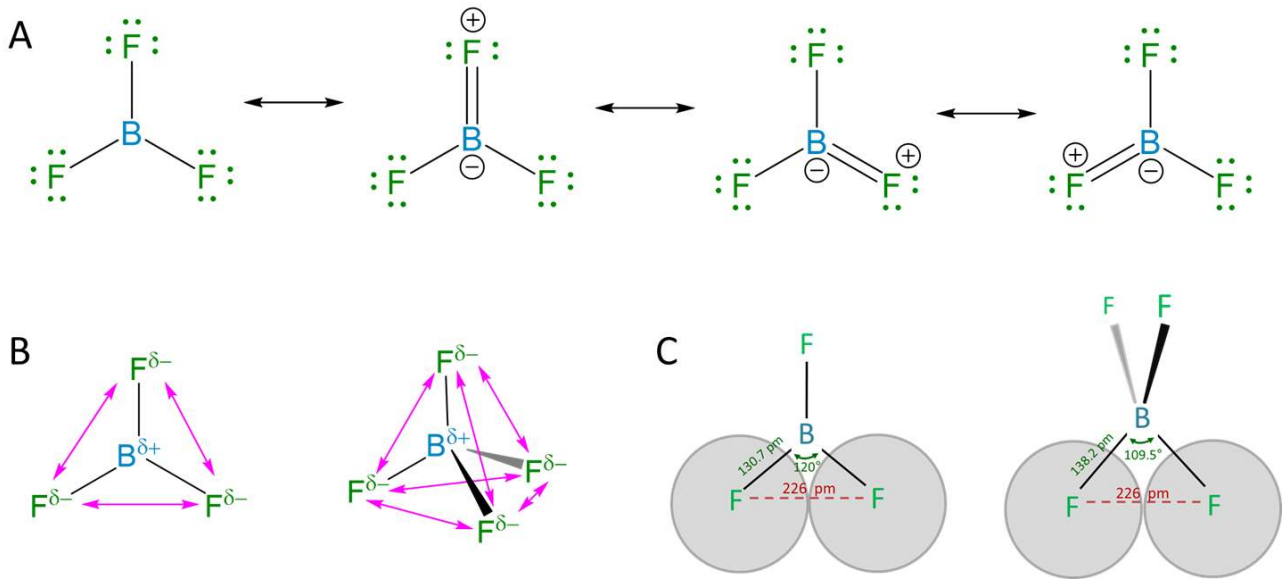


Figure **7.6.1.2**. (A) Resonance explanation for short B-F bonds involving contributions from structures in which the partial charges run counter to the expected $B^{\delta+}$-$X^{\delta-}$ polarity based on electronegativity and calculations, the latter of which support (B) an ionic explanation in terms of a need to reduce the strength of the greater number of repulsions (represented by magenta arrows) between F atoms in tetrahedral geometries compared to trigonal planar ones. (C) The shorter B-X bonds in trigonal planar vs. tetrahedral geometry may also be explained as following from the ligand close packing model. All distances are taken from reference 7.

c. *Borazine and the polymorphs of boron nitride.* One class of compounds in which multiple bonds involving boron are believed to play some role are borazine and the hexagonal polymorph of boron nitride, BN.

Borazine, $B_3N_3H_6$, is isoelectronic and isostructural to benzene, C_6H_6, and has very similar properties. Both have a planar hexagonal molecular structure, are nonpolar, and exist as relatively low boiling liquids at room temperature. The existence of delocalized π bonding in the borazine ring may be inferred in that the B-N bond distances of 1.44 Å in borazine is less than the ~1.6 Å B-N distances typical for B-N single bonds in tetrahedral systems[8] and close to the 1.42 Å C-C bond distance in benzene. While in benzene the electron delocalization is spread evenly around the carbon ring system, in borazine the greater electronegativity of N ensures that the electron density above and below the borazine is more heavily concentrated near the more electronegative N atoms. This is represented by the resonance and orbital descriptions of π bonding depicted in Scheme **7.6.1.IV**. As a result of the greater electron density on N and the resulting electron deficiency on B, the B and N atoms of borazine retain considerable Lewis acid and base character, respectively.

Scheme 7.6.1.IV. (A) Resonance representation of the bonding in borazine and (B) representation of the lowest energy π bonding MO in borazine showing the greater electron density on the more electronegative N atoms.

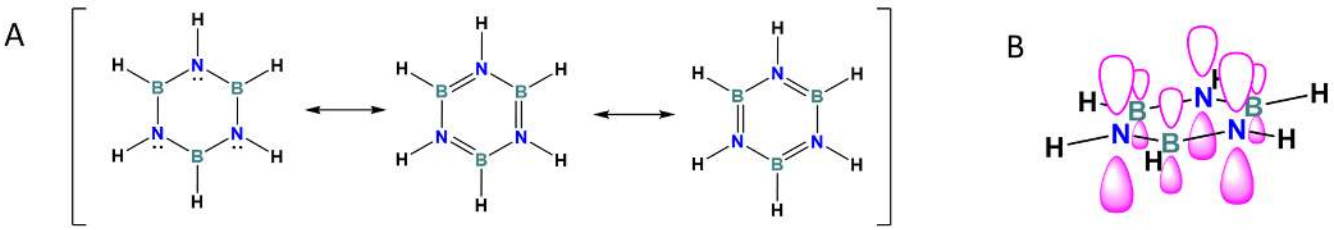


Figure **7.6.1.3A**. The B and N in each layer are trigonal planar and arranged in planar layers of interlocking hexagonal rings. As with borazine, the π system is delocalized, although again the electron density is somewhat localized on the N atoms and unlike graphite, hexagonal BN is not a good conductor. In keeping with the polarity of the B-N bonds and the respective electron densities on B and N, the layers are organized so that the B atoms in one layer are arranged directly above and below the N atoms in the next and vice versa, although the intersheet spacing of 3.3 Å suggests that there is no interlayer bonding. Further, as with graphite the ability of the sheets to move about relatively freely makes hexagonal BN a good lubricant.

Although the layered hexagonal structure of boron nitride is the most stable, BN also forms two polymorphs in which the B and N atoms are tetrahedrally coordinated; these are analogous to the cubic diamond and Lonsdaleite forms of carbon and are given in

Figures **7.6.1.3B** and **7.6.1.3C**. They may be thought of as consisting of layers of linked interlocking B_3N_3 chairs. The two forms differ in terms of whether the layers are arranged so as to be linked in the form of chair or boat conformation B_3N_3 rings.

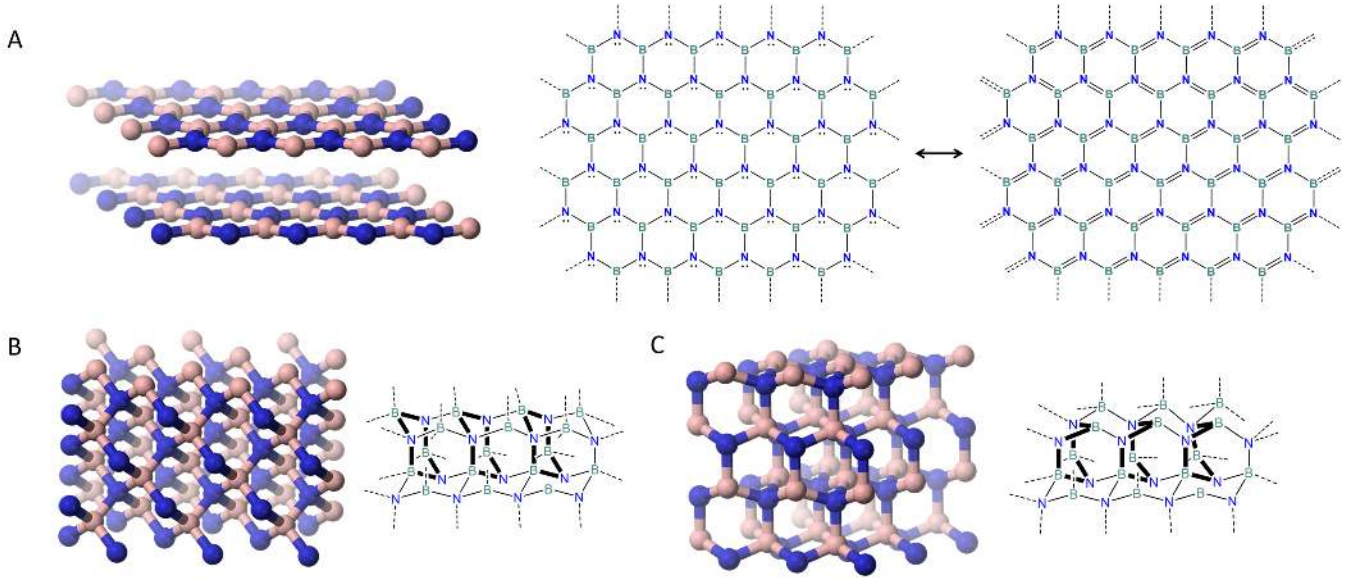


Figure **7.6.1.3**. (A) Layered structure of BN along with two resonance structures illustrating the bonding in a boron nitride layer, (B) cubic BN and a schematic depiction emphasizing the linking of layers of chair conformation B_3N_3 rings by chair conformation B_3N_3 rings and (C) Wurtzite-like hexagonal BN and a schematic depiction emphasizing the linking of layers by boat conformation B_3N_3 rings. The arrangement of B and N atoms in cubic and Wurtzitle-like hexagonal BN are analogous to those of C in cubic diamond and Lonsdaleite, respectively. The ball and stick images of layered, cubic, and Wurtzite-like hexagonal structures of BN are by Benjah-bmm27 - Own work, Public Domain, https://commons.wikimedia.org/w/inde...?curid=2129062, commons.wikimedia.org/w/inde...?curid=2129084, and commons.wikimedia.org/w/inde...?curid=2129086.

2. **Boron can achieve stable bonding configurations by sharing electrons via bridge bonds**. These are common in boron hydrides. For instance, another way the B of BH_3 can achieve an octet is to form two-center three-electron bridge bonds, as in diborane.

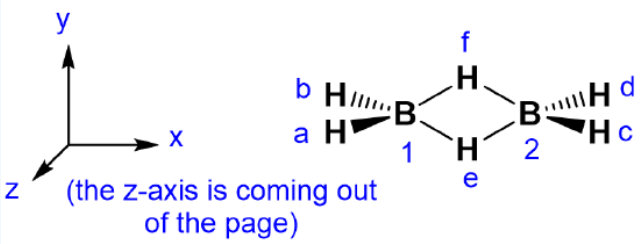


Valence bond and molecular orbital descriptions of the "two-electron three-center" bridge bonds in these molecules have already been given in 8.2.1. Hydrogen's Chemical Properties.

Those who wish to review the MO description of bonding are invited to consider the derivation of the MOs of diborane given in Example **7.6.1.1**.

? Exercise 7.6.1.1. The molecular orbitals of Diborane

Use the projection operator method to derive MOs for diborane. The structure of diborane is shown below, along with the atom labels and coordinate system which will be used in the answer key.



Answer

Diborane has D_{2h} symmetry, under which the following sets of orbitals will transform into one another and should be considered as a set:

$H_{1s,a}$, $H_{1s,b}$, $H_{1s,c}$, $H_{1s,d}$

$H_{1s,f}$, $H_{1s,e}$

$B_{1s,1}$, $B_{1s,2}$

$B_{px,1}$, $B_{px,2}$

$B_{py,1}$, $B_{py,2}$

$B_{pz,1}$, $B_{pz,2}$

Using the projection operator method with the following generator orbitals gives:

Generator orbital	**E**	**C_2 (z)**	**C_2 (y)**	**C_2 (x)**	**i**	**σ** (xy)	**σ** (xz)	**σ** (yz)
Set 1: $H_{1s,a}$	$H_{1s,a}$	$H_{1s,c}$	$H_{1s,d}$	$H_{1s,b}$	$H_{1s,d}$	$H_{1s,b}$	$H_{1s,a}$	$H_{1s,c}$
Set 2: $H_{1s,e}$	$H_{1s,e}$	$H_{1s,f}$	$H_{1s,e}$	$H_{1s,f}$	$H_{1s,f}$	$H_{1s,e}$	$H_{1s,f}$	$H_{1s,e}$
Set 3: $B_{1s,1}$	$B_{1s,1}$	$B_{1s,2}$	$B_{1s,2}$	$B_{1s,1}$	$B_{1s,2}$	$B_{1s,1}$	$B_{1s,1}$	$B_{1s,2}$
Set 4: $B_{px,1}$	$B_{px,1}$	$-B_{px,2}$	$-B_{px,2}$	$B_{px,1}$	$-B_{px,2}$	$B_{px,1}$	$B_{px,1}$	$-B_{px,2}$
Set 5: $B_{py,1}$	$B_{py,1}$	$-B_{py,2}$	$B_{py,2}$	$-B_{py,1}$	$-B_{py,2}$	$B_{py,1}$	$-B_{py,1}$	$B_{py,2}$
Set 6: $B_{pz,1}$	$B_{pz,1}$	$B_{pz,2}$	$-B_{pz,2}$	$-B_{pz,1}$	$-B_{pz,2}$	$-B_{pz,1}$	$B_{pz,1}$	$B_{pz,2}$

The use of these projections to generate orbitals is straightforward but a lot of work.

For Set 1, the terminal H 1s orbitals, taking the 1s orbital on H_a as the generator orbital:

$\Psi(A_g)? = [1(H_{1sa}) + (1)(H_{1sc}) + (1)(H_{1sd}) + (1)(H_{1sb}) + (1)(H_{1sd}) + (1)(H_{1sb}) + (1)(H_{1sa}) + (1)(H_{1sc})]$

$\Psi(A_g) = 2H_{1sa} + 2H_{1sb} + 2H_{1sc} + 2H_{1sd}$ So, there will be one a_g orbital (w/ all 1s in phase)

$\Psi(B_{1g})? = [1(H_{1sa}) + (1)(H_{1sc}) + (-1)(H_{1sd}) + (-1)(H_{1sb}) + (1)(H_{1sd}) + (1)(H_{1sb}) + (-1)(H_{1sa}) + (-1)(H_{1sc})]$

$\Psi(B_{1g}) = 0H_{1sa} + 0H_{1sb} + 0H_{1sc} + 0H_{1sd}$ No b_{1g} orbital

$\Psi(B_{2g})? = [1(H_{1sa}) + (-1)(H_{1sc}) + (1)(H_{1sd}) + (-1)(H_{1sb}) + (1)(H_{1sd}) + (-1)(H_{1sb}) + (1)(H_{1sa}) + (-1)(H_{1sc})]$

$\Psi(B_{2g}) = 2H_{1sa} - 2H_{1sb} - 2H_{1sc} + 2H_{1sd}$ So, there will be one b_{2g} orbital

$\Psi(B_{3g})? = [1(H_{1sa}) + (-1)(H_{1sc}) + (-1)(H_{1sd}) + (1)(H_{1sb}) + (1)(H_{1sd}) + (-1)(H_{1sb}) + (-1)(H_{1sa}) + (-1)(H_{1sc})]$

$\Psi(B_{3g}) = = 0H_{1sa} + 0H_{1sb} + 0H_{1sc} + 0H_{1sd}$ No b_{3g} orbital

$\Psi(A_u)? = [1(H_{1sa}) + (1)(H_{1sc}) + (1)(H_{1sd}) + (1)(H_{1sb}) + (-1)(H_{1sd}) + (-1)(H_{1sb}) + (-1)(H_{1sa}) + (-1)(H_{1sc})]$

$\Psi(A_u) = 0H_{1sa} + 0H_{1sb} + 0H_{1sc} + 0H_{1sd}$ So, there will be no a_u orbital

$\Psi(B_{1u})? = [1(H_{1sa}) + (1)(H_{1sc}) + (-1)(H_{1sd}) + (-1)(H_{1sb}) + (-1)(H_{1sd}) + (-1)(H_{1sb}) + (1)(H_{1sa}) + (1)(H_{1sc})]$

$\Psi(B_{1u}) = 2H_{1sa} - 2H_{1sb} + 2H_{1sc} - 2H_{1sd}$ So, there will be one b_{1u} orbital

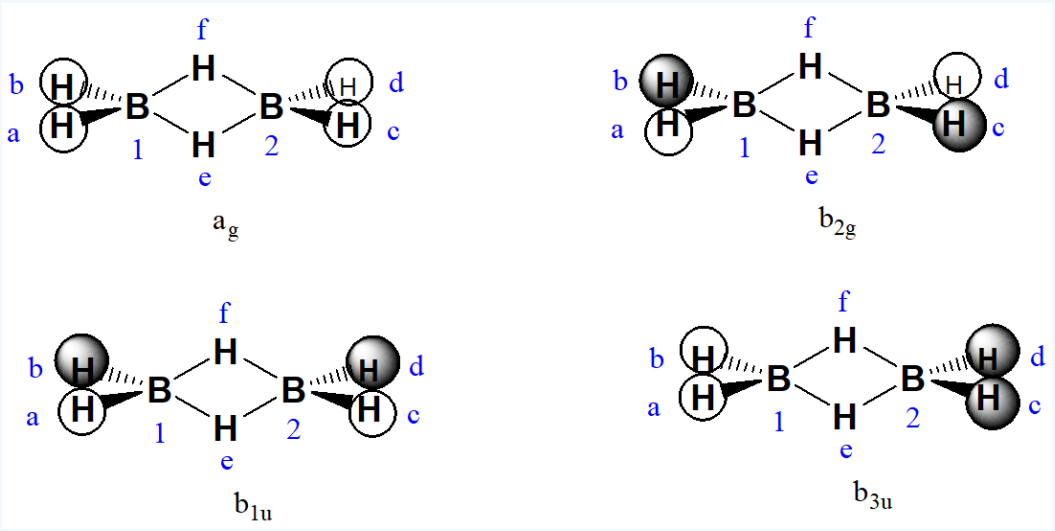
$\Psi(B_{2u})? = [1(H_{1sa}) + (-1)(H_{1sc}) + (1)(H_{1sd}) + (-1)(H_{1sb}) + (-1)(H_{1sd}) + (1)(H_{1sb}) + (-1)(H_{1sa}) + (1)(H_{1sc})]$

$\Psi(B_{2u}) = 0H_{1sa} + 0H_{1sb} + 0H_{1sc} + 0H_{1sd}$ So, there will be no b_{2u} orbital

$\Psi(B_{3u})? = [1(H_{1sa}) + (-1)(H_{1sc}) + (-1)(H_{1sd}) + (1)(H_{1sb}) + (-1)(H_{1sd}) + (1)(H_{1sb}) + (1)(H_{1sa}) + (-1)(H_{1sc})]$

$\Psi(B_{3u}) = 2H_{1sa} + 2H_{1sb} - 2H_{1sc} - 2H_{1sd}$ So, there will be one b_{3u} orbital

So the first set gives the following terminal hydrogen 1s group orbitals:



For Set 2, The H 1s orbitals on the bridging H, taking the 1s orbital on H_e as the generator orbital.

$\Psi(A_g)? = [1(H_{1se}) + (1)(H_{1sf}) + (1)(H_{1se}) + (1)(H_{1sf}) + (1)(H_{1sf}) + (1)(H_{1se}) + (1)(H_{1sf}) + (1)(H_{1se})]$

$\Psi(A_g) = 4H_{1se} + 4H_{1sf}$ So, there will be one a_g orbital (w/ both 1s in phase)

$\Psi(B_{1g})? = [1(H_{1se}) + (1)(H_{1sf}) + (-1)(H_{1se}) + (-1)(H_{1sf}) + (1)(H_{1sf}) + (1)(H_{1se}) + (-1)(H_{1sf}) + (-1)(H_{1se})$

$\Psi(B_{1g}) = 0H_{1se} + 0H_{1sf}$ No b_{1g} orbital

$\Psi(B_{2g})? = [1(H_{1se}) + (-1)(H_{1sf}) + (1)(H_{1se}) + (-1)(H_{1sf}) + (1)(H_{1sf}) + (-1)(H_{1se}) + (1)(H_{1sf}) + (-1)(H_{1se})]$

$\Psi(B_{2g}) = 0H_{1se} + 0H_{1sf}$ So, there will be no b_{2g} orbital

$\Psi(B_{2g})? = [1(H_{1se}) + (-1)(H_{1sf}) + (-1)(H_{1se}) + (1)(H_{1sf}) + (1)(H_{1sf}) + (-1)(H_{1se}) + (-1)(H_{1sf}) + (1)(H_{1se})]$

$\Psi(B_{3g}) = = 0H_{1sa} + 0H_{1sb} + 0H_{1sc} + 0H_{1sd}$ No b_{3g} orbital

$\Psi(A_u)? = [1(H_{1se}) + (1)(H_{1sf}) + (1)(H_{1se}) + (1)(H_{1sf}) + (-1)(H_{1sf}) + (-1)(H_{1se}) + (-1)(H_{1sf}) + (-1)(H_{1se})]$

$\Psi(A_u) = 0H_{1se} + 0H_{1sf}$ So, there will be no a_u orbital

$\Psi(B_{1u})? = [1(H_{1se}) + (1)(H_{1sf}) + (-1)(H_{1se}) + (-1)(H_{1sf}) + (-1)(H_{1sf}) + (-1)(H_{1se}) + (1)(H_{1sf}) + (1)(H_{1se})]$

$\Psi(B_{1u}) = 0H_{1se} + 0H_{1sf}$ So, there will be no b_{1u} orbital

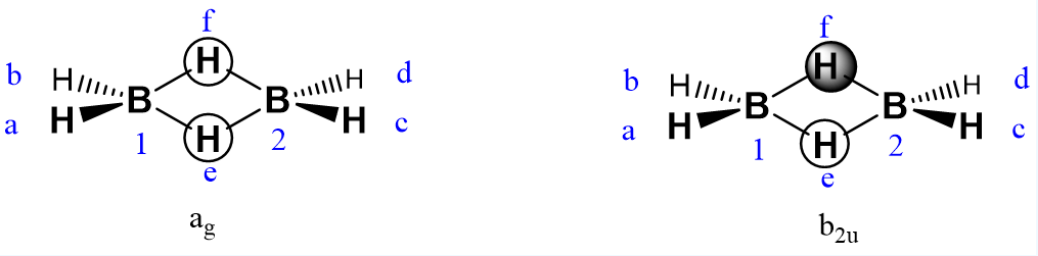
$\Psi(B_{2u})? = [1(H_{1se}) + (-1)(H_{1sf}) + (1)(H_{1se}) + (-1)(H_{1sf}) + (-1)(H_{1sf}) + (1)(H_{1se}) + (-1)(H_{1sf}) + (1)(H_{1se})]$

$\Psi(B_{2u}) = 4H_{1se} - 4H_{1sf}$ So, there will be a b_{2u} orbital

$\Psi(B_{3u})? = [1(H_{1se}) + (-1)(H_{1sf}) + (-1)(H_{1se}) + (1)(H_{1sf}) + (-1)(H_{1sf}) + (1)(H_{1se}) + (1)(H_{1sf}) + (-1)(H_{1se})]$

$\Psi(B_{3u}) = 0H_{1se} + 0H_{1sf}$ So, there will be no b_{3u} orbital

So the second set gives the following bridging hydrogen 1s group orbitals:



For Set 3, The B 2s orbitals, taking the 2*s* orbital on B1 as the generator orbital:

$\Psi(A_g)? = [1(B_{s1}) + (1)(B_{s2}) + (1)(B_{s2}) + (1)(B_{s1}) + (1)(B_{s2}) + (1)(B_{s1}) + (1)(B_{s1}) + (1)(B_{s2})]$

$\Psi(A_g) = 4B_{s,1} + 4B_{s,2}$ So, there will be one a_g orbital (w/ the B 1s in phase)

$\Psi(B_{1g})? = [1(B_{s1}) + (1)(B_{s2}) + (-1)(B_{s2}) + (-1)(B_{s1}) + (1)(B_{s2}) + (1)(B_{s1}) + (-1)(B_{s1}) + (-1)(B_{s2})]$

$\Psi(B_{1g}) = 0B_{s,1} + 0B_{s,2}$ No b_{1g} orbital

$\Psi(B_{2g})? = [1(B_{s1}) + (-1)(B_{s2}) + (1)(B_{s2}) + (-1)(B_{s1}) + (1)(B_{s2}) + (-1)(B_{s1}) + (1)(B_{s1}) + (-1)(B_{s2})]$

$\Psi(B_{2g}) = 0B_{s,1} + 0B_{s,2}$ No b_{2g} orbital

$\Psi(B_{2g})? = [1(B_{s1}) + (-1)(B_{s2}) + (-1)(B_{s2}) + (1)(B_{s1}) + (1)(B_{s2}) + (-1)(B_{s1}) + (-1)(B_{s1}) + (1)(B_{s2})]$

$\Psi(B_{3g}) = 0B_{s,1} + 0B_{s,2}$ No b_{3g} orbital

$\Psi(A_u)? = [1(B_{s1}) + (1)(B_{s2}) + (1)(B_{s2}) + (1)(B_{s1}) + (-1)(B_{s2}) + (-1)(B_{s1}) + (-1)(B_{s1}) + (-1)(B_{s2})]$

$\Psi(A_u) = 0B_{s,1} + 0B_{s,2}$ So, there will be no a_u orbital

$\Psi(B_{1u})? = [1(B_{s1}) + (1)(B_{s2}) + (-1)(B_{s2}) + (-1)(B_{s1}) + (-1)(B_{s2}) + (-1)(B_{s1}) + (1)(B_{s1}) + (1)(B_{s2})]$

$\Psi(B_{1u}) = 0B_{s1} + 0B_{s2}$ So, there will be no b_{1u} orbital

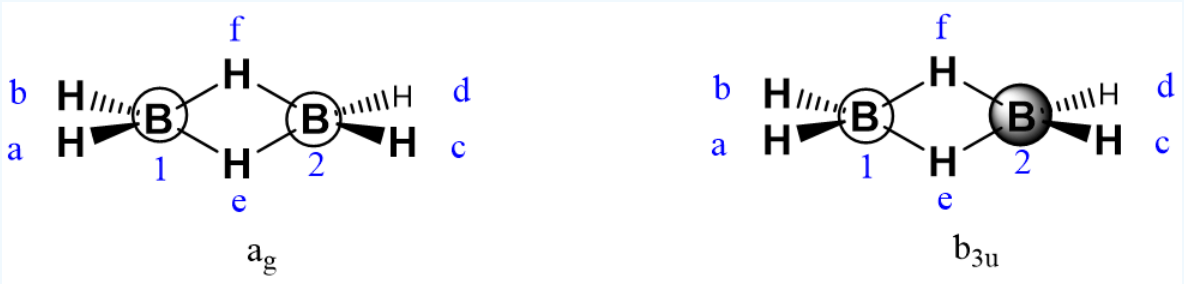
$\Psi(B_{2u})? = [1(B_{s1}) + (-1)(B_{s2}) + (1)(B_{s2}) + (-1)(B_{s1}) + (-1)(B_{s2}) + (1)(B_{s1}) + (-1)(B_{s1}) + (1)(B_{s2})]$

$\Psi(B_{2u}) = 0B_{s1} + 0B_{s2}$ So, there will be no b_{2u} orbital

$\Psi(B_{3u})? = [1(B_{s1}) + (-1)(B_{s2}) + (-1)(B_{s2}) + (1)(B_{s1}) + (-1)(B_{s2}) + (1)(B_{s1}) + (1)(B_{s1}) + (-1)(B_{s2})]$

$\Psi(B_{3u}) = 4B_{s1} - 4B_{s2}$ So, there will be one b_{3u} orbital

The boron 2*s* group orbitals are:



For Set 4: The B $2p_x$ orbitals, using the $2p_x$ orbital on B1 as the generator orbital:

$\Psi(A_g)? = [1(B_{px,1}) + (1)(-B_{px2}) + (1)(-B_{px2}) + (1)(B_{px1}) + (1)(-B_{px2}) + (1)(B_{px1}) + (1)(B_{px1}) + (1)(-B_{px2})]$

$\Psi(A_g) = 4B_{1px1} - 4B_{2px1}$ So, there will be one a_g orbital (w/ the B $2p_x$ antiphase)

$\Psi(B_{1g})? = [1(B_{px,1}) + (1)(-B_{px2}) + (-1)(-B_{px2}) + (-1)(B_{px1}) + (1)(-B_{px2}) + (1)(B_{px1}) + (-1)(B_{px1}) + (-1)(-B_{px2})]$

$\Psi(B_{1g}) = 0B_{1px1} + 0B_{1px2}$ No b_{1g} orbital

$\Psi(B_{2g})? = [1(B_{px,1}) + (-1)(-B_{px2}) + (1)(-B_{px2}) + (-1)(B_{px1}) + (1)(-B_{px2}) + (-1)(B_{px1}) + (1)(B_{px1}) + (-1)(-B_{px2})]$

$\Psi(B_{2g}) = 0B_{1px1} + 0B_{1px2}$ No b_{2g} orbital

$\Psi(B_{3g})? = [1(B_{px,1}) + (-1)(-B_{px2}) + (-1)(-B_{px2}) + (1)(B_{px1}) + (1)(-B_{px2}) + (-1)(B_{px1}) + (-1)(B_{px1}) + (1)(-B_{px2})]$

$\Psi(B_{3g}) = 0B_{1px1} + 0B_{1px2}$ No b_{3g} orbital

$\Psi(A_u)? = [1(B_{px,1}) + (1)(-B_{px2}) + (1)(-B_{px2}) + (1)(B_{px1}) + (-1)(-B_{px2}) + (-1)(B_{px1}) + (-1)(B_{px1}) + (-1)(-B_{px2})]$

$\Psi(A_u) = 0B_{1px1} + 0B_{1px2}$ So, there will be no a_u orbital

$\Psi(B_{1u})? = [1(B_{1s1}) + (1)(B_{1s2}) + (-1)(B_{1s2}) + (-1)(B_{1s1}) + (-1)(B_{1s2}) + (-1)(B_{1s1}) + (1)(B_{1s1}) + (1)(B_{1s2})]$

$\Psi(B_{1u}) = 0B_{1px1} + 0B_{1px2}$ So, there will be no b_{1u} orbital

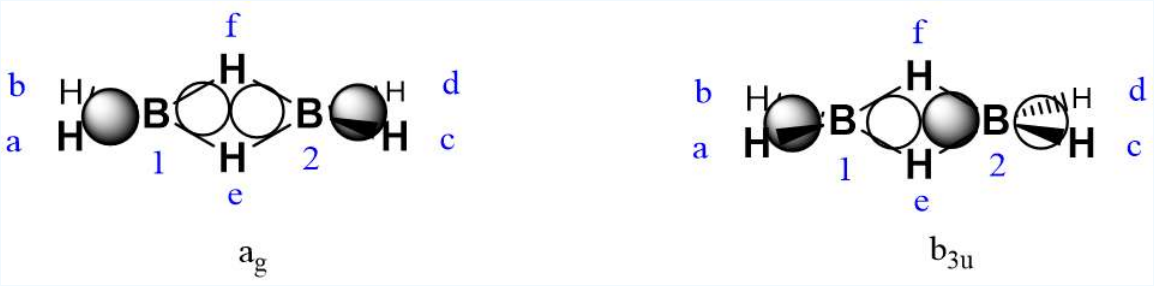
$\Psi(B_{2u})? = [1(B_{px,1}) + (-1)(-B_{px2}) + (1)(-B_{px2}) + (-1)(B_{px1}) + (-1)(-B_{px2}) + (1)(B_{px1}) + (-1)(B_{px1}) + (1)(-B_{px2})]$

$\Psi(B_{2u}) = 0B_{1px1} + 0B_{1px2}$ So, there will be no b_{2u} orbital

$\Psi(B_{3u})? = [1(B_{px,1}) + (-1)(-B_{px2}) + (-1)(-B_{px2}) + (1)(B_{px1}) + (-1)(-B_{px2}) + (1)(B_{px1}) + (1)(B_{px1}) + (-1)(-B_{px2})]$

$\Psi(B_{3u}) = 4B_{px1} + 4B_{px2}$ So, there will be one b_{3u} orbital

So the B 2p_x group orbitals are



For Set 5: The B 2p_y orbitals, taking 2p_y on B1 as the generator orbital:

$\Psi(A_g)? = [1(B_{py1}) + (1)(-B_{py2}) + (1)(B_{py2}) + (1)(-B_{py1}) + (1)(-B_{py2}) + (1)(B_{py1}) + (1)(-B_{py1}) + (1)(B_{py2})]$

$\Psi(A_g) = 0\ B_{py1} + 0B_{py2}$ So, there will be no a_g orbital

$\Psi(B_{1g})? = [1(B_{py1}) + (1)(-B_{py2}) + (-1)(B_{py2}) + (-1)(-B_{py1}) + (1)(-B_{py2}) + (1)(B_{py1}) + (-1)(-B_{py1}) + (-1)(B_{py2})]$

$\Psi(B_{1g}) = 2B_{py1} - 2B_{py2}$ One b_{1g} orbital

$\Psi(B_{2g})? = [1(B_{py1}) + (-1)(-B_{py2}) + (1)(B_{py2}) + (-1)(-B_{py1}) + (1)(-B_{py2}) + (-1)(B_{py1}) + (1)(-B_{py1}) + (-1)(B_{py2})]$

$\Psi(B_{2g}) = 0B_{py1} + 0B_{py2}$; No b_{2g} orbital

$\Psi(B_{2g})? = [1(B_{py1}) + (-1)(-B_{py2}) + (-1)(B_{py2}) + (1)(-B_{py1}) + (1)(-B_{py2}) + (-1)(B_{py1}) + (-1)(-B_{py1}) + (1)(B_{py2})]$

$\Psi(B_{2g}) = 0B_{py1} + 0B_{py2}$; No b_{3g} orbital

$\Psi(A_u)? = [1(B_{py1}) + (1)(-B_{py2}) + (1)(B_{py2}) + (1)(-B_{py1}) + (-1)(-B_{py2}) + (-1)(B_{py1}) + (-1)(-B_{py1}) + (-1)(B_{py2})]$

$\Psi(A_u) = 0B_{py1} + 0B_{py2}$; So, there will be no a_u orbital

$\Psi(B_{1u})? = [1(B_{py1}) + (1)(-B_{py2}) + (-1)(B_{py2}) + (-1)(-B_{py1}) + (-1)(-B_{py2}) + (-1)(B_{py1}) + (1)(-B_{py1}) + (1)(B_{py2})]$

$\Psi(B_{1u}) = 0B_{py1} + 0B_{py2}$; So, there will be no b_{1u} orbital

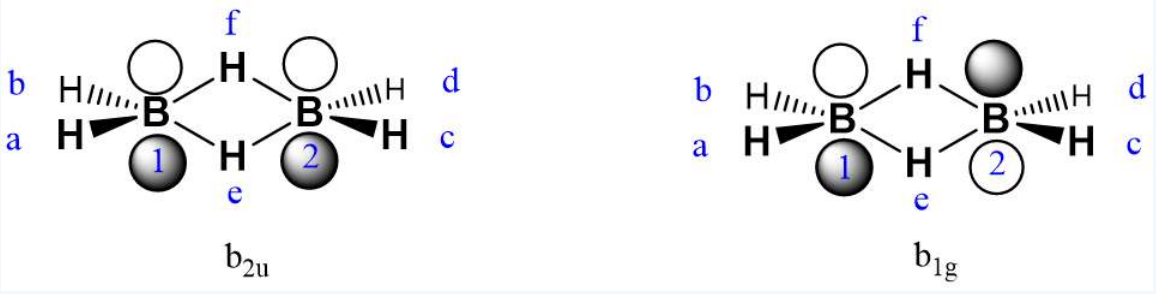
$\Psi(B_{2u})? = [1(B_{py1}) + (-1)(-B_{py2}) + (1)(B_{py2}) + (-1)(-B_{py1}) + (-1)(-B_{py2}) + (1)(B_{py1}) + (-1)(-B_{py1}) + (1)(B_{py2})]$

$\Psi(B_{2u}) = 4B_{py1} + 4B_{py2}$; So, there will be a b_{2u} orbital

$\Psi(B_{3u})? = [1(B_{py1}) + (-1)(-B_{py2}) + (-1)(B_{py2}) + (1)(-B_{py1}) + (-1)(-B_{py2}) + (1)(B_{py1}) + (1)(-B_{py1}) + (-1)(B_{py2})]$

$\Psi(B_{3u}) = 0B_{py1} + 0B_{py2}$; So, there will be no b_{3u} orbital

So the B 2p_y group orbitals are



For Set 6: The B 2p_z orbitals, taking the 2p_z orbital of B1 as the generator orbital.

$\Psi(A_g)? = [1(B_{pz1}) + (1)(B_{pz2}) + (1)(-B_{pz2}) + (1)(-B_{pz1}) + (1)(-B_{pz2}) + (1)(-B_{pz1}) +(1)(B_{pz1}) + (1)(B_{pz2})]$

$\Psi\ (A_g) = 0\ B_{pz1} + 0\ B_{pz2}$ So, there will be an a_g orbital

$\Psi(B_{1g})? = [1(B_{pz1}) + (1)(B_{pz2}) + (-1)(-B_{pz2}) + (-1)(-B_{pz1}) + (1)(-B_{pz2}) + (1)(-B_{pz1}) +(-1)(B_{pz1}) + (-1)(B_{pz2})]$

$\Psi\ (B_{1g}) = 0\ B_{pz1} + 0B_{pz2}$ So, there will be no b_{1g} orbital

$\Psi(B_{2g})? = [1(B_{pz1}) + (-1)(B_{pz2}) + (1)(-B_{pz2}) + (-1)(-B_{pz1}) + (1)(-B_{pz2}) + (-1)(-B_{pz1}) +(1)(B_{pz1}) + (-1)(B_{pz2})]$

$\Psi\ (B_{2g}) = 4\ B_{pz1} - 4B_{pz2}$ So, there will be a b_{2g} orbital

$\Psi(B_{3g})? = [1(B_{pz1}) + (-1)(B_{pz2}) + (-1)(-B_{pz2}) + (1)(-B_{pz1}) + (1)(-B_{pz2}) + (-1)(-B_{pz1}) +(-1)(B_{pz1}) + (1)(B_{pz2})]$

$\Psi\ (B_{3g}) = 0\ B_{pz1} + 0B_{pz2}$ So, there will be no b_{3g} orbital

$\Psi(A_u)? = [1(B_{pz1}) + (1)(B_{pz2}) + (1)(-B_{pz2}) + (1)(-B_{pz1}) + (-1)(-B_{pz2}) + (-1)(-B_{pz1}) +(-1)(B_{pz1}) + (-1)(B_{pz2})]$

$\Psi\ (A_u) = 0\ B_{pz1} + 0B_{pz2}$ So, there will be no a_u orbital

$\Psi(B_{1u})? = [1(B_{pz1}) + (1)(B_{pz2}) + (-1)(-B_{pz2}) + (-1)(-B_{pz1}) + (-1)(-B_{pz2}) + (-1)(-B_{pz1}) +(1)(B_{pz1}) + (1)(B_{pz2})]$

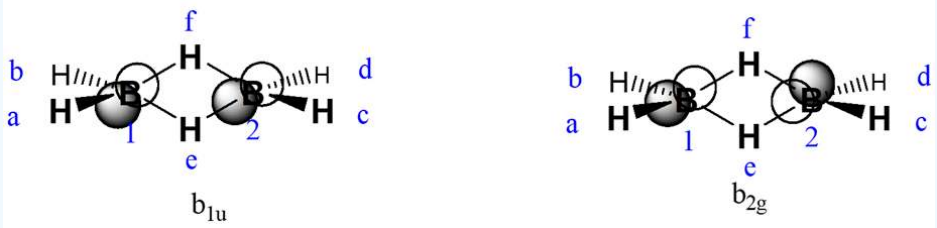
$\Psi\ (B_{1u}) = 4\ B_{pz1} + 4B_{pz2}$ So, there will be a b_{1u} orbital

$\Psi(B_{2u})? = [1(B_{pz1}) + (-1)(B_{pz2}) + (1)(-B_{pz2}) + (-1)(-B_{pz1}) + (-1)(-B_{pz2}) + (1)(-B_{pz1}) +(-1)(B_{pz1}) + (1)(B_{pz2})]\Psi\ (B_{2u}) = 0\ B_{pz1} + 0B_{pz2}$ So, there will be no b_{2u} orbital

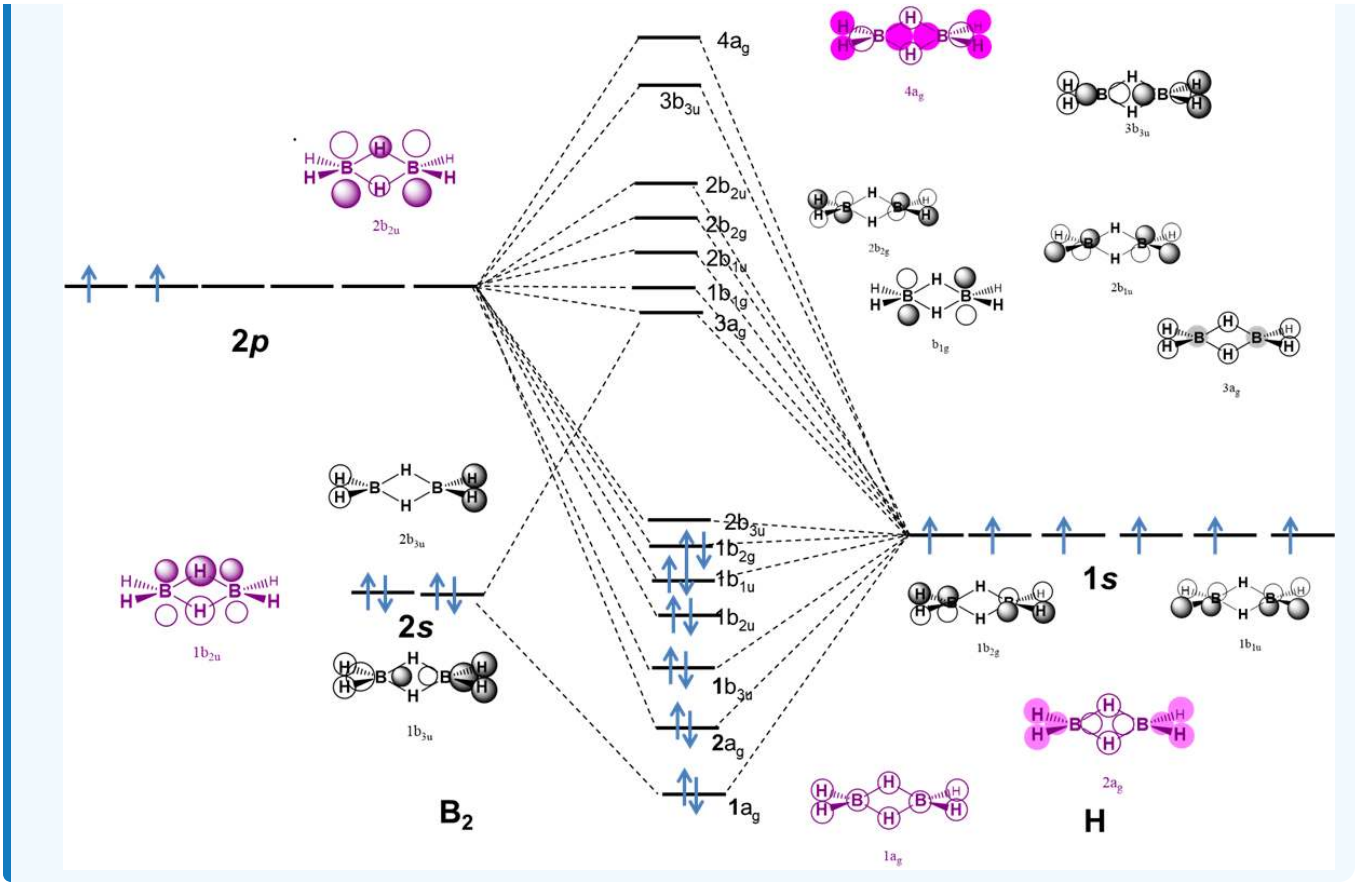
$\Psi(B_{3u})? = [1(B_{pz1}) + (-1)(B_{pz2}) + (-1)(-B_{pz2}) + (1)(-B_{pz1}) + (-1)(-B_{pz2}) + (1)(-B_{pz1}) +(1)(B_{pz1}) + (-1)(B_{pz2})]$

$\Psi\ (B_{3u}) = 0\ B_{pz1} + 0B_{pz2}$ So, there will be no b_{3u} orbital

So the B 2p_z group orbitals are

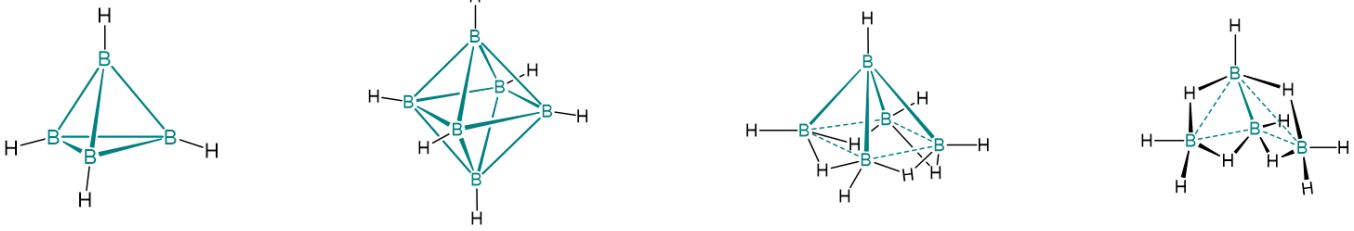


Finally, to construct MOs for the diborane group, orbitals of the same symmetry should be allowed to mix. The exact way in which this will occur should ideally be predicted by performing a quantum chemical calculation. However, an approximate diagram can be qualitatively estimated from the atomic orbital energies (which are conveniently available in a periodic table of atomic orbital energies). The result is given in 8.2.1. Hydrogen's Chemical Properties, reproduced for convenience below.



3. Share electrons among multiple boron and other atoms in a cluster. Such clusters are very common among the boron hydrides (boranes) and their derivatives. Examples are given in Scheme **7.6.1.V**.

Scheme 7.6.1.V. Examples of electron-deficient boron clusters. These consist of a cluster H-B: groups in which the B atoms are held together by sharing electrons among the atoms of the cluster. The B-B and B---B bonds in these images are drawn to help define the cluster shape, in which the B atoms tend to occupy the vertices of a deltahedron.



closo-$B_4H_4^{2-}$ *closo*-$B_6H_6^{2-}$ *nido*-B_5H_9 *arachno*-B_4H_{10}

Many aspects of the bonding in clusters will be explained in more detail in Section 15.4 Cluster Compounds, which also presents Wade's rules and the Polyhedral Skeletal Electron Pair Theory which may be used to rationalize their stability. This section instead focuses on outlining some features of borane chemistry.

Electron-deficient clusters are distinguished based on whether their shape is that of a complete deltahedron - a type of polyhedron in which all the faces are equilateral triangles. In *closo*-clusters the vertex atoms comprise a complete deltahedron while in *nido*-, *arachno*-, and *hypho*- clusters, one, two, and three of the deltahedron's vertices are unoccupied, respectively. For instance, in Scheme **7.6.1.V**, tetrahedral $B_4H_4^{2-}$ and octahedral $B_6H_6^{2-}$ are *closo*- while square pyramidal B_5H_9 is *nido*- since it corresponds to an octahedron with a missing vertex.

Notice also that there are bridging B-H-B bonds along the edges of the open vertices in the *nido*- and *arachno*- clusters of Scheme **7.6.1.IV**. This is a common feature of such clusters, although these bonds are not always present since the hydrogens can often be deprotonated to give stable anionic clusters.

$$B_5H_9 + MH \xrightarrow{\text{low T}} M^+ + B_5H_8^- + H_2 \qquad (M = \text{alkali metal})$$

Many boranes are anionic. The most iconic is icosahedral *closo*-dodecaborate, $B_{12}H_{12}^{2-}$, the structure of which is shown in Figure **7.6.1.3**.

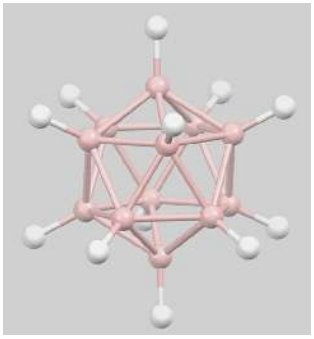
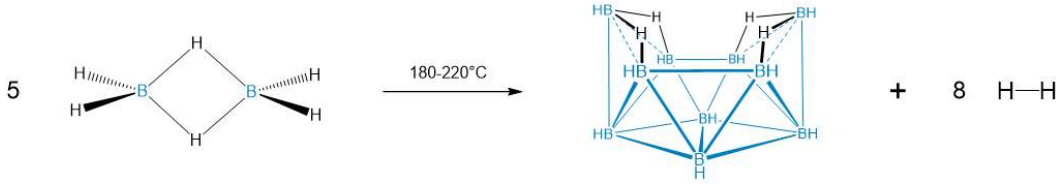
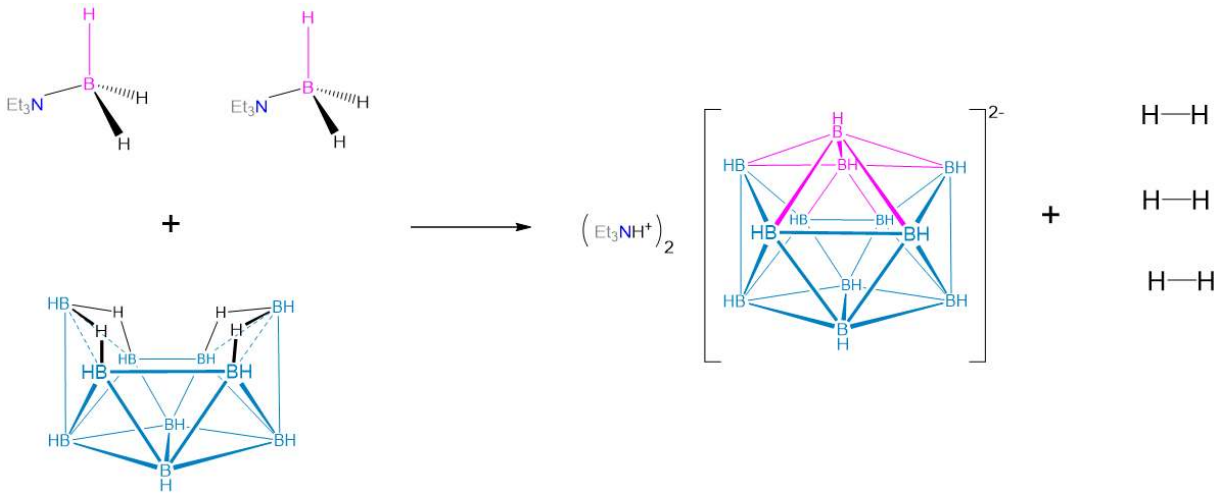


Figure **7.6.1.3**. Structure of *closo*-dodecaborate, $B_{12}H_{12}^{2-}$, showing boron atoms in cream and H atoms in white. The diameter of the cluster is similar to that of a benzene ring. Rendered from COD ID: 4306523 as reported in reference 9.

Typically, the higher boranes are formed by pyrolytic removal of H_2, H^- , and/or H^+ units from BH_3 or BH_4^-. This process may be conceptualized as giving rise to BH, BH^-, and BH_2 units which coalesce into clusters. The process may be seen in part by considering the preparation of *closo*-dodecaborate. First the diborane is pyrolyzed to give *arachno*-decaborane(14), $B_{10}H_{14}$, in a process in which the loss of B-H and B-H-B bonds is compensated for by the formation of cluster bonds in which multiple B atoms share the bonding electrons. The resulting *arachno*-decaborane(14), $B_{10}H_{14}$, has the icosahedral shape of dodecaborate.

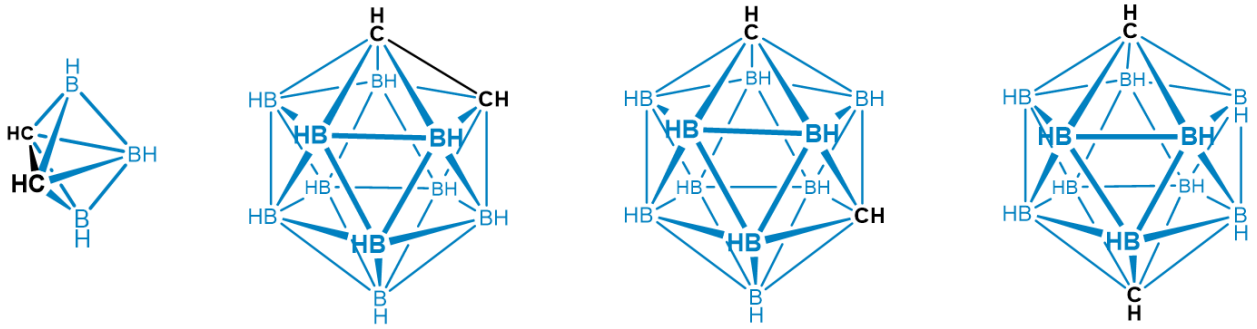


The two missing vertices in the *arachno*- cluster are added by allowing the cluster to react with additional BH_3 units, this time in the form of the Et_3N-BH_3 adduct.



Finally, it should be noted that elements other than boron can form clusters and that, consequently, boron forms mixed clusters with a variety of elements. Some examples include the carboranes depicted in Scheme **7.6.1.VI**.

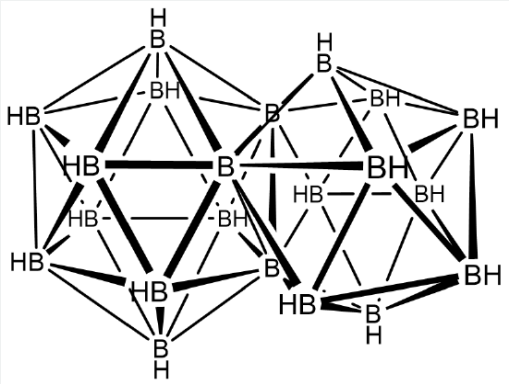
Scheme 7.6.1.VI. Some carborane clusters, including the *ortho*-, *meta*-, and *para*-"carborane", $C_2B_{10}H_{12}$.



Note 7.6.1.1: Conjuncto Boranes

In addition to ordinary *closo*-, *nido*-, *arachno*-, and *hypho*- boranes, there are *conjuncto*-boranes, which consist of two clusters joined via a B-B linkage, at a vertex, edge, or face. An example of such a cluster is shown in Scheme **7.6.1.VI**.

Scheme 7.6.1.VII. A face-sharing *conjuncto*- borane.



Note 7.6.1.2: Boron in Medicinal Chemistry: Neutron Capture Therapy

Boranes and their derivatives are the subject of ongoing research into effective neutron capture therapies for the treatment of tumors of the head and neck. The basis of these therapies is the nuclear chemistry of its ^{10}B isotope, which comprises 19.6% of naturally occurring boron (the remaining 80.4% is ^{11}B). Boron-10 can absorb neutrons to give excited ^{11}B, which undergoes radiative decay via alpha emission:

$$\text{Neutron capture :} \quad {}^{10}_{5}\mathrm{B} + {}^{1}_{1}\mathrm{n} \longrightarrow [{}^{11}_{5}\mathrm{B}]^{*}$$

$$\text{alpha emission :} \quad [{}^{11}_{5}\mathrm{B}]^{*} \longrightarrow {}^{7}_{3}\mathrm{Li} + {}^{4}_{2}\mathrm{He}$$

This sequence of reactions in medical applications to treat tumors is called neutron capture therapy. The basic principles of neutron capture therapy are summarized in Figure **7.6.1.4**.

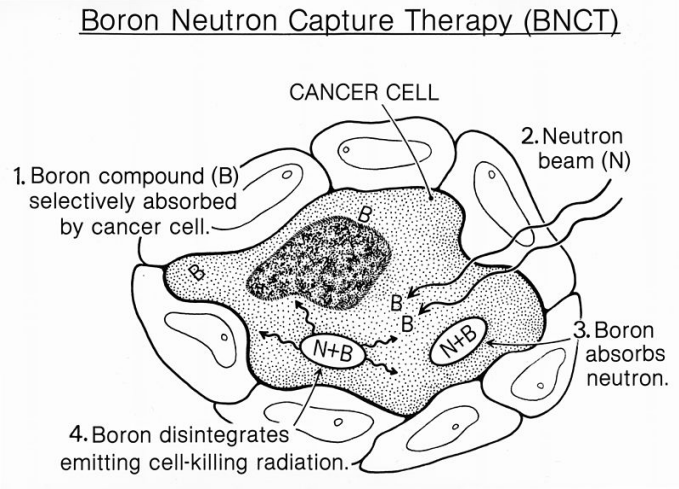


Figure **7.6.1.4**. Use of neutron capture therapy to destroy cancerous cells. The image is by Pat Kenny (Illustrator) / Public domain.

As can be seen from Figure **7.6.1.4**, the process involves irradiating the boron-infused tumor with neutrons. These neutrons are poorly absorbed by tissues comprised primarily of the big six elements of biochemistry (C, H, N, O, S, and P) and so minimally damage normal tissue. However, in boron-infused tumor cells, $[^{11}_{5}\mathrm{B}]^{*}$ produced by neutron capture degrades to give high energy $^{7}_{3}\mathrm{Li}$ and $^{4}_{2}\mathrm{He}$ that damage the surrounding cancerous tissue.

Effective neutron capture therapy requires the use of a boron reagent that is otherwise nontoxic and can be selectively delivered to cancer cells in therapeutically-effective concentrations. This has been a considerable research challenge and the development of such reagents is a subject of ongoing research. Many of the compounds tried so far are borane or carborane amino or nucleic acid analogues or conjugates of borane and various biomolecules, although borane-infused liposomes (liposomes are preferentially taken up and retained by tumors) have recently been shown effective against certain types of tumors in mice.

Notes and References

1. Nihonium is not included, since as a metastable synthetic element with isotope-dependent half-lives of less than 10 seconds it is poorly characterized. The boron structure is taken from https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Book%3A_Inorganic_Chemistry_(Saito)/04%3A_Chemistry_of_Nonmetallic_Elements/4.02%3A_Main_group_elements_of_2nd_and_3rd_periods_and_their_compounds. The FCC and HCP structures are original PNGs by Daniel Mayer and DrBob, traced in Inkscape by User:Stannered - Cubic, face-centered.png: Lattice face centered cubic.svg:, CC BY-SA 3.0, commons.wikimedia.org/w/inde...?curid=1735631; By !Original: DornelfVector: DePiep - Own work based on: Hexagonal close packed.png, CC BY-SA 3.0, commons.wikimedia.org/w/inde...curid=20183889; those of Ga and In are rendered using Mercury from data deposited in the Materials Project Database as reported in references 4 and 5, respectively. Electronegativity, ionization energy, electron affinity, and radii values are taken from the Royal Society of Chemistry periodic table database at https://www.rsc.org/periodic-table/.

2. Called Aluminium in the UK and other countries where British English is used.

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The Materials Project: A materials genome approach to accelerating materials innovation APL Materials, 2013, 1(1), 011002.

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6. Robinson, E. A.; Johnson, S. A.; Tang, T.-H.; Gillespie, R. J. *Inorganic Chemistry* 1997, 36 (14), 3022-3030.

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10. Kueffer, P. J.; Maitz, C. A.; Khan, A. A.; Schuster, S. A.; Shlyakhtina, N. I.; Jalisatgi, S. S.; Brockman, J. D.; Nigg, D. W.; Hawthorne, M. F., Boron neutron capture therapy demonstrated in mice bearing EMT6 tumors following selective delivery of boron by rationally designed liposomes. Proceedings of the National Academy of Sciences 2013, 110 (16), 6512-6517.

Contributors and Attributions

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7.6.2: Heavier Elements of Group 13 and the Inert Pair Effect

The group 13 metals also form conventional compounds as well as M-X-M type bridge bonds and metal-like clusters.

The group 13 metals form a wide variety of compounds that may be explained in terms of ionic or pairwise covalent bonding. These oxides can generally be explained as ionic. Thallium's main oxide, Tl_2O, crystallizes in the CdI_2 lattice, and consists of layers of edge-linked octahedra, as shown in Figure **7.6.2.1A**, while the most stable form of Al_2O_3 , corundum, consists of layers of edge-linked AlO_6 octahedra vertex-linked to adjacent layers as shown in Figure **7.6.2.1B**.

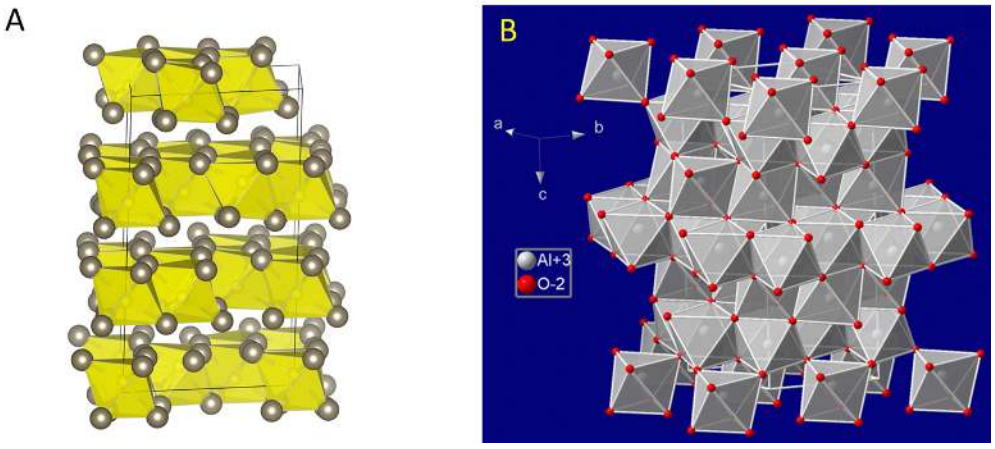


Figure **7.6.2.1**. (A) The CdI_2 structure adopted by Tl_2O showing layers of edge-linked Tl_6O octahedra and (B) Corundum Al_2O_3 structure consisting of layers of edge-linked AlO_6 octahedra (in the horizontal) vertex-linked adjacent layers (in the vertical direction). The CdI_2 structure image is by Speedpera / CC BY (https://creativecommons.org/licenses/by/4.0 and the Corundrum Al_2O_3 image is is by Materialscientist at English Wikipedia / CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0)

Nevertheless, although it is possible to explain the structural chemistry of Al_2O_3 as involving an ionic lattice, Al does form covalently-bonded oxyanions just as boron does. A particularly well known example is the $Al_6O_{18}^{18-}$ anion, which contains AlO_4 tetrahedra covalently vertex-linked into an Al_6O_6 ring as shown in Scheme **7.6.2.I**. The calcium salt of this anion is found in tricalcium aluminate cements, which as the name suggests are formed by mixing 3 equivalents of CaO with one of Al_2O_3.

Scheme 7.6.2.I. Two views of the $Al_6O_{18}^{18-}$ anion.

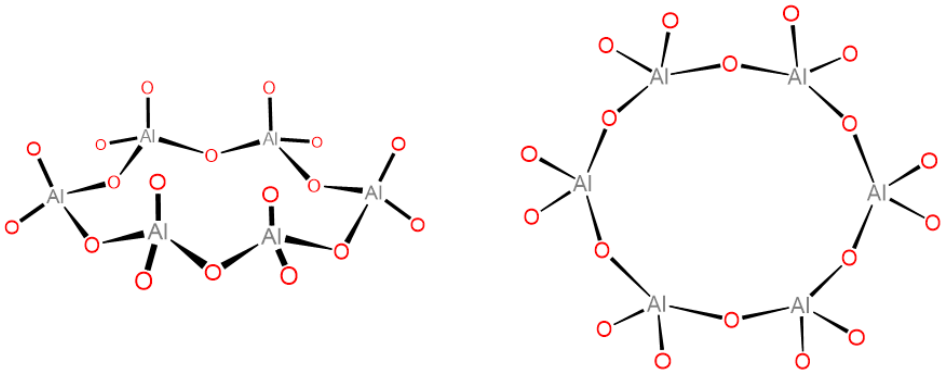


Figure **7.6.2.2** is illustrative. It forms a network structure as a solid, as liquid exists as a E_2X_6 dimer, and in the gas phase is a mixture of dimers and monomers, ultimately giving the monomer only at high temperatures.

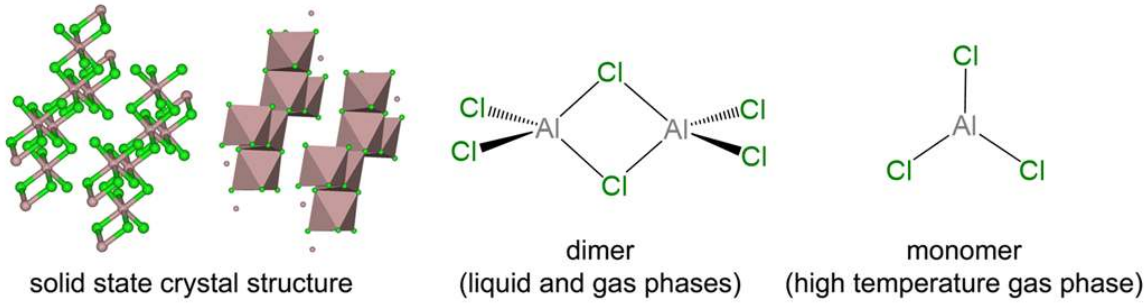
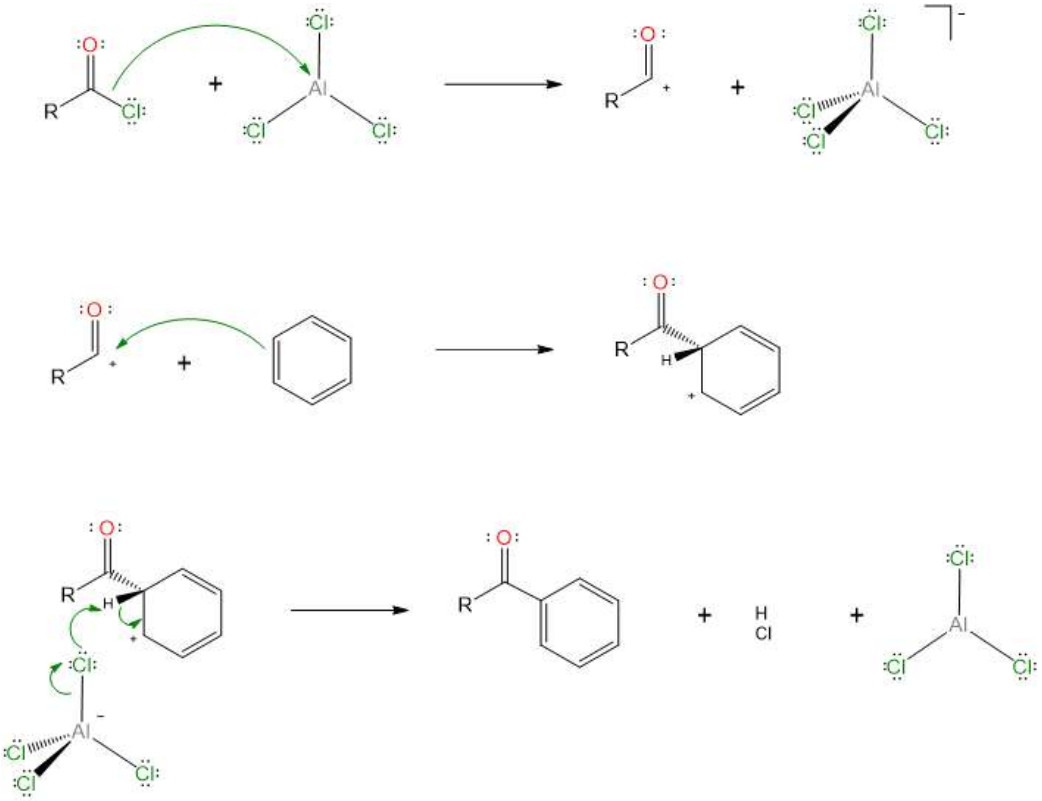


Figure **7.6.2.2**. Representative group 13 trihalides. The solid state structure and text are adapted from an image by Benjah-bmm27 taken from https://upload.wikimedia.org/wikipedia/commons/4/42/Aluminium-trichloride-3D-structures.png.

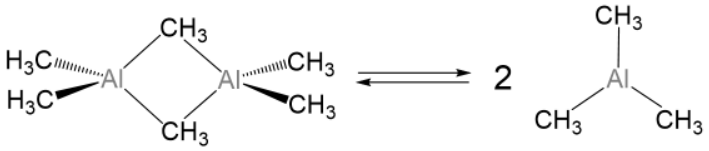
The aluminum trihalides are effective Lewis acids. This property serves as the basis for their use as a catalyst in Friedel-Crafts alkylations and acylations. In these reactions, $AlCl_3$ acts as a Lewis base to abstract a chloride ion from an alkyl or acyl halide, generating a carbon-based cation that can add to an aromatic ring in an electrophilic aromatic substitution reaction (Scheme **7.6.2.II**).

Scheme 7.6.2.II. $AlCl_3$ acts as a Lewis acid catalyst in facilitating Friedel Crafts acylation.



Trialkyl group 13 compounds also exist as monomers and dimers, although the monomer-dimer preference increasingly shifts towards monomer on going from Al to In. In general, GaR_3 and InR_3 species exist as monomers, while for Al the monomer and dimer are often in equilibrium (Scheme **7.6.2.II**) for smaller alkyl groups, shifting towards monomer with bulky ones.

Scheme 7.6.2.II. Dimer-monomer equilibrium of trimethyl aluminum.



As with their boron analogues, trialkyl aluminum and trialkylgallium compounds are effective Lewis acids, reacting with Lewis bases at the group 13 element to give tetrahedral species.

The low electronegativity of the group 13 metals also means that the alkyl groups of group 13 trialkyl complexes are nucleophilic and basic. This reactivity is employed in the commercial use of GaR_3 species for the chemical vapor deposition of semiconductor-grade GaAs via reaction of GaR_3 with AsH_3.

$$Ga(CH_3)_3 + AsH_3 \longrightarrow GaAs(s) + 3\ CH_4$$

Compounds containing Al-Al and Ga-Ga single and multiple bonds can be prepared, although Al≡Al bonds have so far only been demonstrated in the gas phase.[1] In the case of Ga, multiple bonds can be formed by reduction of compounds of type $RGaX_2$ by using extremely bulky R groups to prevent dimerization of any Ga=Ga or Ga≡Ga species formed. The nature of the multiply-bonded species formed this way have been the subject of much theoretical investigation. The 1997 report of the synthesis of a gallyne[2] in particular set off a storm of controversy about the nature of its Ga-Ga bond, leading to competing claims that the bond should be understood as involving single, triple, or even double bond interactions. Some of the options are depicted in Figure **7.6.2.3A**. Although no clear consensus has yet emerged, recent experimental and theoretical work[3] has pointed to the description of bonding as involving a σ bond, a conventional π bond, and a Klinkhammer-type slipped π bond, as shown in Figure **7.6.2.3**.

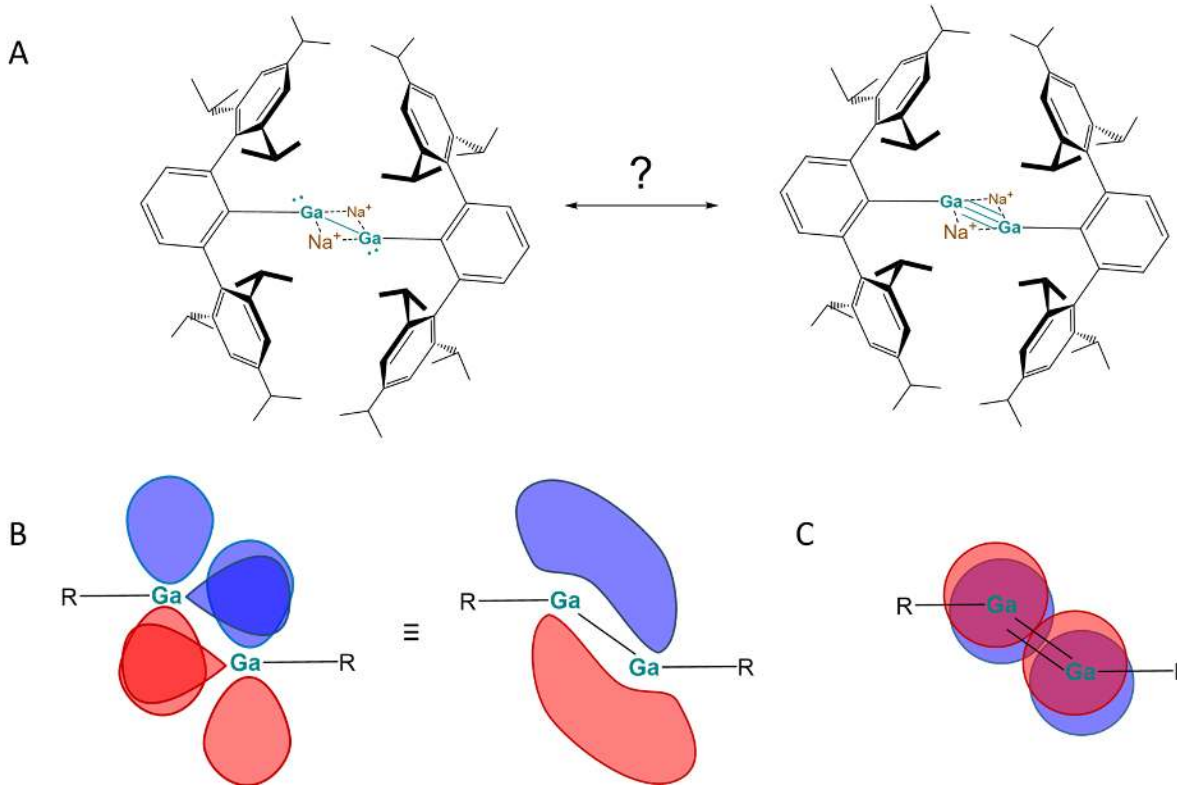


Figure **7.6.2.3**. (A) Two Lewis depictions of possible bonding arrangements in Robinson's Gallyne, in which the bond between the Ga atoms has been proposed to consist of (B) an overlap between σ type and *p* orbitals on the two Ga atoms, equivalent to the σ bond and a Klinkhammer-type slipped π bond. (C) The third bond of the triple bond is a conventional π bond perpendicular to the σ and slipped π bond and, in common with other π interactions involving row 3+ elements, features relatively weak overlap. The dotted lines to the Na^+ ions are intended to show the location of these ions in the structure without implying anything about how they participate in the bonding.

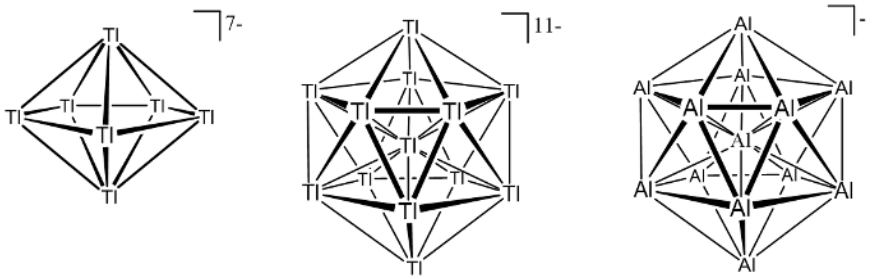
Aluminum and gallium are also known to form atomic clusters. There are two types:

1. **Naked metal clusters**

   Examples include anions like Tl_7^{7-} , Ga_{11}^{7-} , and Tl_{13}^{11-} formed by reaction of the metal or metal halide with a powerful reductant (usually an alkali or similar highly reducing metal) and "magic clusters" containing unusually stable species like Al_7^+ and Al_{13}^- formed by laser sputtering of aluminum (*i.e.*, irradiating an Al surface with a laser and watching what sort of clusters come off). Among these, Al_{13}^- is so stable that it can even be prepared by solution phase reduction of dendrimer-

encapsulated $AlCl_3$ by ketyl radicals. The chemical behavior of the Al_{13}^- anion may be rationalized by thinking about it as analogous to a "halide," specifically of the superatom Al_{13}. Superatoms like Al_{13} are clusters that possess well-defined energy levels and directional valence orbitals just as atoms do; consequently, they exhibit atom-like reactivity in tending to gain, lose, or share electrons to fill a shell of low energy orbitals. In the case of Al_{11}, its reactivity mimics that of the halogens and so it is described as a superhalogen.

Examples of naked metal cluster structures are given in Figure **7.6.2.4**.



Tl_7^{7-} Tl_{13}^{11-} Al_{13}^-

Figure **7.6.2.4**. Structures of some naked metal clusters. The shapes of these are often analogous to those of stable boranes, although in many of them, one of the atoms occupies the cluster interior.

As may be seen from the structures in Figure **7.6.2.4**, these clusters adopt shapes similar to those of the boranes, although as is the case with Tl_{13}^{11-} and Al_{13}^- sometimes one of the metal atoms resides in the cluster interior. As might be expected, the stability of many of these clusters is analogous to that of the boranes in being explicable in terms of Wade's rules, although given that Tl_{13}^{11-} and Al_{13}^- are isostructural and both stable while differing in their valence electron counts by ten electrons it is clear that this is not always the case.

The existence of multiple stable electron counts in group 13 superatom clusters like Al_{13}^- has been explained by the **jellium model** of cluster stability, which treats clusters like Al_{13}^- as consisting of an "ionic core" consisting of the nuclei and their core electrons $(Al^{3+})_{13}$ surrounded by the "jelly" of valence electrons. In the case of Al_{13} clusters, this model gives stable sets of energy levels allowing for configurations containing the "magic numbers" of 2, 8, 18, 20, 34, or 40 electrons. In this model, the 40 valence electrons in Al_{13}^- correspond to the last of these stable states. Thus Tl_{13}^{11-} and Al_{13}^- represent different regimes of stability, one consistent with a Wade-type cluster similar to the boranes explicable in terms of molecular orbitals formed by combinations of atomic orbitals and the other one explicable in terms of the orbitals given by treating Al_{13} as a superatom in the jellium model.

2. **Metalloid clusters**

Metalloid clusters consist of a small particle of metal surrounded by ligands. Some such Al and Ga clusters even contain upwards of 69 atoms. Examples include clusters with formulas $[Al_{69}\{N(SiMe_3)_2\}_{18}]^{3-}$ and $[Al_{77}N(SiMe_3)_2\}_{20}]^{2-}$. The structure of a relatively small example is given in Figure **7.6.2.5**.

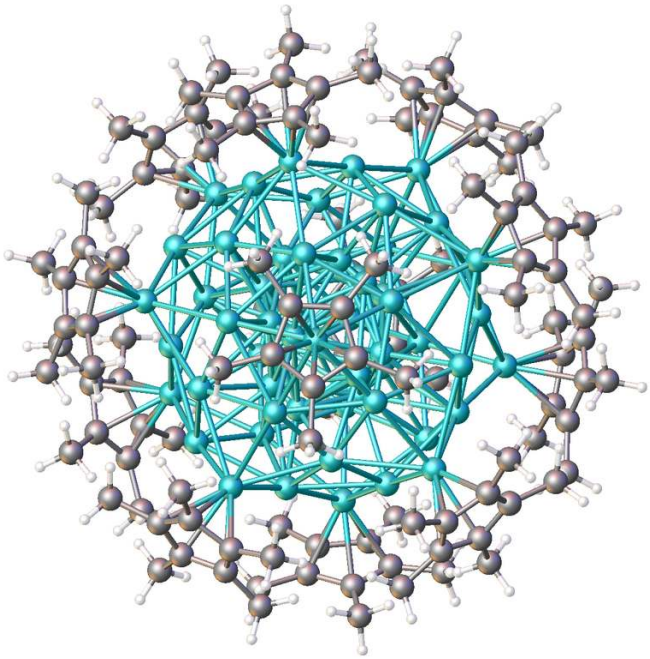
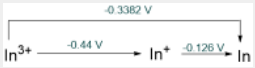
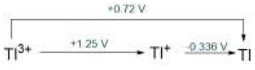


Figure **7.6.2.5**. Structure of $Cp^*_{10}Al_{50}$ (Cp^* = $C_5(CH_3)_5^-$). By Smokefoot - Own work, CC BY-SA 4.0, commons.wikimedia.org/w/inde...curid=87686580

Although the group 13 metals have varying tendencies to form covalent bonds, they tend to act chemically as metals.

Some representative features of these elements illustrative of their chemistry are summarized in Table **7.6.2.1**.

Table 7.6.2.1. Illustrative properties of the group 13 metals.[9,10]

Group 13 Metal	Natural Source	**Oxides** (major product of reaction of the element with O_2 is given in bold)	Illustrative Stable Mononuclear Halides	Redox Behavior in Acidic Solution
Aluminum, Al	**Aluminosilicates** like • feldspars of formula $MAlSi_3O_8$ or $M'Al_2Si_2O_8$ where M = alkali metal and M' = alkaline earth metal • clays like kaolinite, $Al_2Si_2O_5(OH)_4$ • Bauxites containing $Al_2O_3{\cdot}xH_2O$	**Al_2O_3**	AlX_3 (X = F, Cl, Br, I)	
Gallium, Ga	As impurities in Aluminum and Fe/Zn ores • Bauxites, $Al_2O_3{\cdot}xH_2O$ • Sphalerites, ZnS Small amounts in Gallite, $CuGaS_2$	**Ga_2O_3** Ga_2O	Network covalent GaF_3 Dimeric Ga_2X_6 (X = Cl, Br, I) $Ga^{I}Ga^{III}{}_2Cl_7$ $Ga^{I}Ga^{III}X_4$ (X = Cl, Br, I)	
Indium, In	As impurities in Zn and Cu/Fe ores • Sphalerites, ZnS • Chalcopyrite, $CuFeS_2$	**In_2O_3**	InX_3 (X = F, Cl, Br, I) $In^{I}_3(In^{III}X_6)$ (X = Cl, Br) $In^{I}In^{III}X_4$ (X = Br, I) InX (X = Cl, Br, I)	
Thallium, Tl	As impurities in sulfide-rich ores • $CuFeS_2$, CuS, Cu_2S • PbS • ZnS small amounts in minerals like $TlCu_7Se_4$, $TlPbAs_5S_9$, others	Tl_2O_3 **Tl_2O**	TlF_3 TlX (X = F, Cl, Br, I) thallium(I) triiodide, $Tl^{I}(I_3)$	

As may be seen from the data in Table **7.6.2.1**, on moving down group 13 from Al to Tl

1. Geologic occurrence of the elements in oxide ores (Al, Ga) becomes increasingly replaced by a preference for occurrence in sulfides and selenides (Ga, In, Tl). This is consistent with *increasing softness on moving down group 13*.
2. There is an increasing preference for the +1 oxidation state. This may be seen from
    - the standard potentials for reduction of M^{3+} and M^{+} to the metal. These show a decrease in the stability of the +3 ion on going down the group. In the case of Tl, Tl^{3+}(aq) is even less stable than Tl^{+}(aq).
    - an increase in prevalence of the +1 oxidation state in the monomeric halides. The aluminum monohalides, AlX, are highly unstable; the bromide and chloride of Ga^{I} stabilizable (but perhaps not monomeric); the In^{I} halides stable only for the less oxidizing halogens Cl, Br, and I; and for thallium, TlF_3 is the only stable Tl^{3+} halide.

This increasing preference for an oxidation state two lower than maximum valence is not restricted to the group 13 elements. It is a common feature of post transition element chemistry that these elements can act as if their ns^2 valence electrons are inert, on account of which this tendency has been referred to somewhat misleadingly as the **inert pair effect**.

Post-transition metals exhibit the inert pair effect, in which they act as if their ns^2 valence electrons do not contribute to bonding.

Metals and metalloids of the *p* block commonly possess two stable oxidation states, with one corresponding to the loss of all their n*s* and n*p* valence electrons and one the loss of two fewer electrons. This is evident from the well-known ions and oxidation states observed for the group 13, 14, and 15 metals and metalloids shown in Scheme **7.6.2.III**.

Scheme 7.6.2.III. Common oxidation states of group 13, 14, and 15 metals and metalloids.

13	14	15
Al^{+}, Al^{3+}		
Ga^{+}, Ga^{3+}	Ge^{II}, Ge^{IV}	As^{III}, As^{V}
In^{+},In^{3+}	Sn^{2+},Sn^{4+}	Sb^{III},Sb^{V}
Tl^{+}, Tl^{3+}	Pb^{2+}, Pb^{4+}	Bi^{3+}, Bi^{5+}

Moreover, there is an increasing preference for the lower oxidation state on going down a group in the periodic table so that

- The higher (n+) oxidation state is favored for lighter elements so that the order of preference is

$$Al^{3+} > Ga^{3+} > In^{3+} > Tl^{3+}$$

- The lower (n - 2)+ oxidation state is favored for heavier elements

$$Al^{+} < Ga^{+} < In^{+} < Tl^{+}$$

This is why the most stable oxide and chloride of Al are Al_2O_3 and $AlCl_3$ while the most stable oxides and Cl of Tl are Tl_2O and TlCl.

The classical explanation for the existence of this behavior is to postulate that the heavier elements' ns^2 valence electrons are chemically inert - *i.e.*, an inert pair. For this reason the observation that many post transition elements have stable n+ and (n-2)+ oxidation states and that there is an increasing preference for the lower oxidation state on moving down a group has been termed the **inert pair effect**.

The inert pair effect is due to the decrease in bond energies down a group.

However, the term inert pair effect is a misnomer. There are two reasons for this

1. *The ns electrons do not become significantly more inert (a.k.a. lower in energy) as one descends the groups of the periodic table.* A cursory look at the valence *s* and *p* orbital energies of the main group elements reveals that it is simply not the case that the n*s* orbitals become lower in energy on going down a group of the periodic table. As may be seen from the energies given in Figure **7.6.2.6**, the energy of the n*s* orbitals is generally lowest for period 1 and 2 elements, after which the only overall trend that may be noted is that the ns orbital energies of the rows 3-6 elements generally do not differ by more than 20% across the entire range.

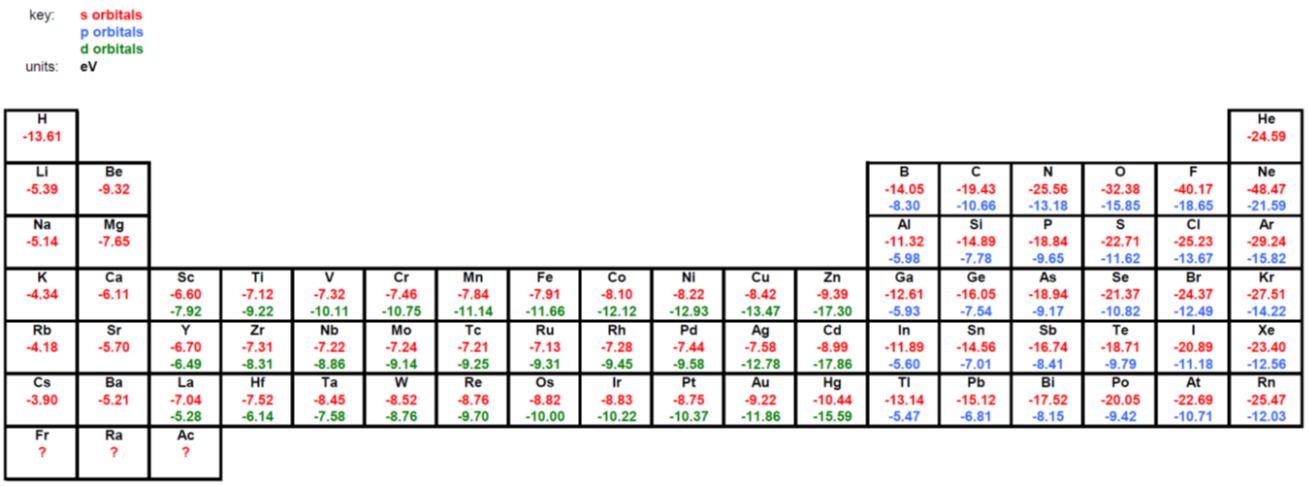


Figure **7.6.2.6**. Valence orbital energies of the main group elements and transition metals in eV. By Emily V Eames and taken from http://www.graylark.com/eve/orbital-energies-table.html

2. *The inert pair effect is due to the decrease in bond energies as bond lengths increase down a group of the periodic table*. To see how this leads to the appearance of ns electron inertness as one descends the periodic table, consider that the process of forming an E-X bond generally involves

- endergonic oxidation of the metal
- exergonic formation of a M-X bond

Consider the interplay between these two energies in the case of forming the monohalides and trihalides of the group 13 elements. The cost of oxidation of the metal reflects a balance between the ionization energies given in Table **7.6.2.2** and bond energies given in Table **7.6.2.3**.[15]

Table 7.6.2.2. Ionization energy costs for formation of M^+ and M^{3+}. Recalculated from the similar table of ionization energies at en.Wikipedia.org/wiki/Inert_pair_effect.

Process	B	Al	Ga	In	Tl
$M \rightarrow M^+$ IE_1 (kJ/mol)	800	577	578	558	589
$M \rightarrow M^{3+}$ $IE_1 + IE_2 + IE_3$ (kJ/mol)	6886	5137	5520	5082	5438
Inert pair oxidation: $M^+ \rightarrow M^{3+}$ $IE_2 + IE_3$ (kJ/mol)	6,086	4,560	4,942	4,524	4,849

Table 7.6.2.3. M-Cl homolytic bond energies in kJ/mol.[15]

Bond	B-Cl	Al-Cl	Ga-Cl	In-Cl	Tl-Cl
Typical E-Cl Bond Dissociation energy (kJ/mol)	536	494	481	439	372.8

As may be seen from Table **7.6.2.3**, the energy cost for ionization of the "inert pair" is greatest for boron, drops by ~25% on going to Al, and then remains approximately constant for the remaining members of the group. In contrast, the compensating bond dissociation energies drop more slowly on going from B to Tl, with successive ~10% and ~20% decreases on going from Ga to In and In to Tl. Because bond energies drop on going from Al to Tl while ionization energies do not, it is thought that the inert pair

effect isn't due to the inertness of the ns electrons but rather due to the weakening of bond energies. When the stabilization energy due to M-E bond formation is no longer enough to pay the cost needed to oxidize away the ns electrons, the lower oxidation state will be more stable than the higher one, just as it would if the ns electrons really were inert.

The inert pair of electrons exerts structural effects.

Regardless of the origin of the inert pair effect, the inert pair of electrons influences the structure of compounds in the (n-2)+ oxidation state. Electron pairs that do this by altering the observed geometry of compounds are said to be **stereochemically active inert pairs**. The lone pairs of $Sn^{II}Cl_2$ are the classic example. As shown in Figure **7.6.2.7A**, gas phase $Sn^{II}Cl_2$ exhibits an AX_2E VSEPR geometry, while $Sn^{II}Cl_2$ in its solid state, hydrates, and salts all exhibit AX_3E geometries, consistent with the influence of a lone pair of electrons.

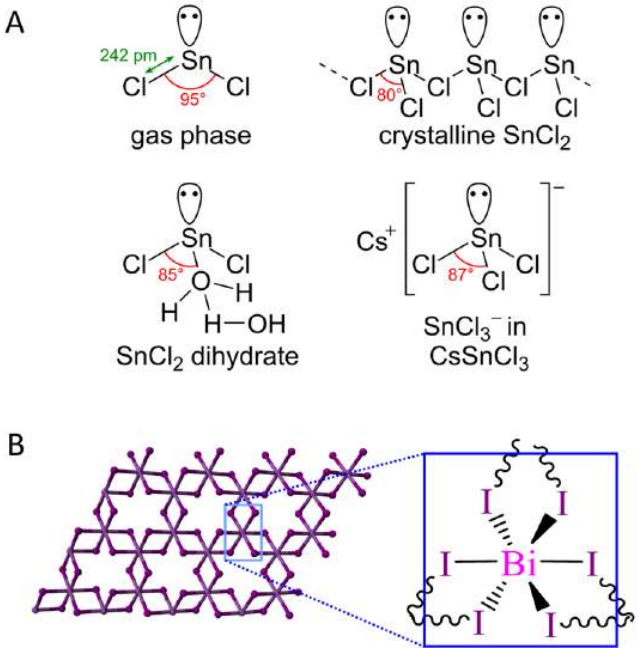


Figure **7.6.2.7**. (A) Steroechemically active inert pairs in $SnCl_2$ and several of its Lewis base adducts. (B) Stereochemically inert lone pairs in BiI_3. The $SnCl_2$ image is by Hbf878 - Own work, CC0, commons.wikimedia.org/w/inde...curid=64768302. The BiI_3 image is adapted from the structure drawn by Ben Mills, Benjah-bmm27 / Public domain, and taken from commons.wikimedia.org/wiki/F...r-3D-balls.png.

Sometimes the coordination geometry of an element is exactly that which would be expected if the inert pair were not present. In such cases the inert pair is said to be **stereochemically inert**. In general, when the element's coordination number is less than six, the inert pairs will be stereochemically active, while for coordination numbers of six or more the pair may be stereochemically active or stereochemically inert.

Even when an inert pair appears stereochemically inert, it does not mean that it exerts no effect on the structure of the compound. It may be that the pair is simply fluxional and only appears to be inert because it is rapidly adjusting its position among possible locations. For instance, in the structure of BiI_3 shown in Figure **7.6.2.7B**, the lone pair is likely interchanging between the six faces of the octahedron defining the coordination sphere, as is the case for XeF_6 (Figure **7.6.2.8**).

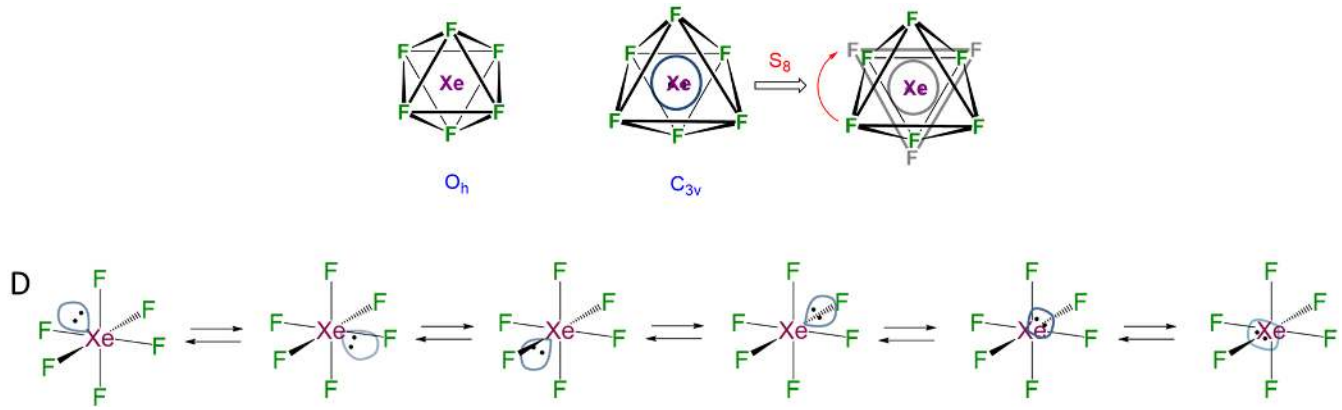


Figure **7.6.2.8**. The appearance of stereochmeical inactivity on the part of the inert pair in BiI_3 can likely be explained in terms of fluxional behavior similar to that believed to take place in XeF_6. (A) If the lone pair of XeF_6 were stereochemically inactive, the compound would possess true O_h symmetry. (B) The opening of a face of XeF_6's coordination octahedron by a stereochemically active lone-pair reduces the symmetry of the octahedron to C_{3v} symmetry, (C) as may be seen in that F atoms on opposite faces no longer interchange under an S_8 operation. (D) However, fluxionality in XeF_6 involving interchange of the stereochemically active lone pair among the six faces of the XeF_6 octahedron is so fast that on most timescales the opening of all six faces is averaged and the structure appears octahedral.

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9. The list of halides are selected from those listed in references 4-6 and element halide Wikipedia pages, checked against the original literature. The specific pages used include en.Wikipedia.org/wiki/Aluminium_halide, en.Wikipedia.org/wiki/Gallium_halides, en.Wikipedia.org/wiki/Indium_halides, and en.Wikipedia.org/wiki/Thallium_halides.

10. All potentials are taken from Bard, A. J.; Parsons, R.; Jordan, J. Standard potentials in aqueous solution. M. Dekker: New York, 1985. Note that this reference reports a $Ga^{2+/0}$ potential in addition to the $Ga^{3+/0}$ potential given. This couple was not included since the nature of the Ga^{2+} species referenced ($GaCl_2$ produced by reacting Ga and $GaCl_3$) was unclear (*i.e.*, it may be a $Ga^{I}Ga^{III}$ species or possess a Ga-Ga bond).

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7.7: Group 14

The group 14 elements comprise the elements carbon (C) through flerovium (Fl) in group 14 of the periodic table, as shown in Figure **7.7.1**.

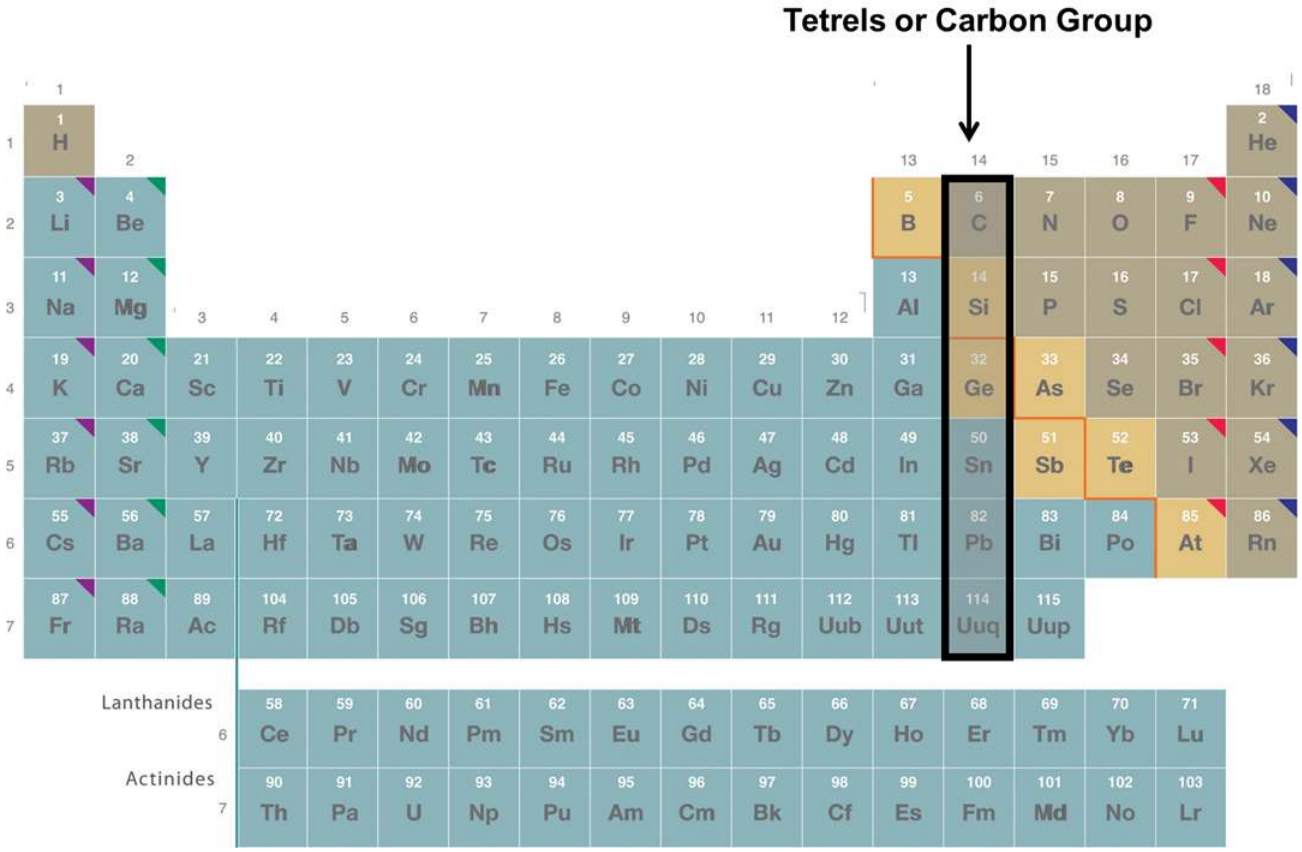


Figure **7.7.1**. The Group 14 elements. Note that since the periodic table used was developed element 115 was named Flerovium and given the symbol Fl. Adapted from the periodic table at https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/02._Atoms%2C_Molecules%2C_and_Ions/2.5%3A_The_Periodic_Table

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7.7.1: The Group 14 Elements and the Many Allotropes of Carbon

As an element, carbon's ability to form strong multiple bonds enables it to form many allotropes, while the remaining elements in this group are network covalent or metallic solids.

Selected properties of the Group 14 elements are given in Table **7.7.1.1**.

Table **7.7.1.1**: Selected Properties of Group 14 Elements other than Flerovium. For more information about how this data was sourced see note 1.

Property	Carbon	Silicon	Germanium	Tin	Lead
atomic symbol	C	Si	Ge	Sn	Pb
atomic number	6	14	32	50	82
atomic mass (amu)	12.01	28.09	72.64	118.71	207.2
valence electron configuration*	$2s^2 2p^2$	$3s^2 3p^2$	$4s^2 4p^2$	$5s^2 5p^2$	$6s^2 6p^2$
melting point/boiling point (°C)	4489 (at 10.3 MPa)/3825	1414/3265	938/2833	232/2586	327/1749
density (g/cm^3) at 25°C	2.2 (graphite), 3.51 (diamond)	2.33	5.32	7.27(white)	11.30
atomic radius (Å)	1.70	2.10	2.11	2.17	2.02
covalent radius (Å)	0.75	1.14	1.20	1.40	1.45
first ionization energy (kJ/mol)	1086	787	762	709	716
electron affinity (kJ/mol)	−122	−134	−119	−107	−35
Pauling electronegativity	2.55	1.90	2.01	1.96	1.8
product of reaction with O_2	CO_2, CO	SiO_2	GeO_2	SnO_2	PbO
type of oxide	acidic (CO_2)	acidic neutral (CO)	amphoteric	amphoteric	amphoteric
product of reaction with N_2	none	Si_3N_4	none	Sn_3N_4	none
product of reaction with X_2‡	CX_4	SiX_4	GeX_4	SnX_4	PbX_2
product of reaction with H_2	CH_4	none	none	none	none

*The configuration shown does not include filled d and f subshells.

†The values cited are for six-coordinate +4 ions in the most common oxidation state, except for C^{4+} and Si^{4+}, for which values for the four-coordinate ion are estimated.

‡X is Cl, Br, or I. Reaction with F_2 gives the tetrafluorides (EF_4) for all group 14 elements, where E represents any group 14 element.

As may be seen from the data in Table **7.7.1.1**, consistent with general atomic property trends, atomic radii increase down the group while electron affinities, ionization energies, and electronegativities generally decrease. The trends are not always monotonic, however, likely due to the impact of the *d*-block contraction on the atomic properties of Ge and also the lanthanide and actinide contractions on those of Sn and Pb.

From the common elemental forms of the group 14 elements in Table **7.7.1.1** two trends are apparent:

1. In keeping with the second row uniqueness principle, carbon forms a wider variety of allotropes than the other group 14 elements. Specifically, carbon's ability to form strong π bonds enables it to form delocalized sheet-like structures in the form of graphite and graphene (planar sheets) and nanotubes and fullerenes, which may be considered as sheets wrapped over to form tubes and ball-like structures, respectively.
2. There is a decreasing tendency towards covalency down the group. While C, Si, and Ge form network covalent structures and Pb a metallic one, tin forms both network covalent and metallic structures, which differ so slightly in their stability that the metallic form interconverts to the network covalent one above 13°C.

Carbon's ability to form strong multiple bonds enables it to form a host of molecular and network covalent allotropes

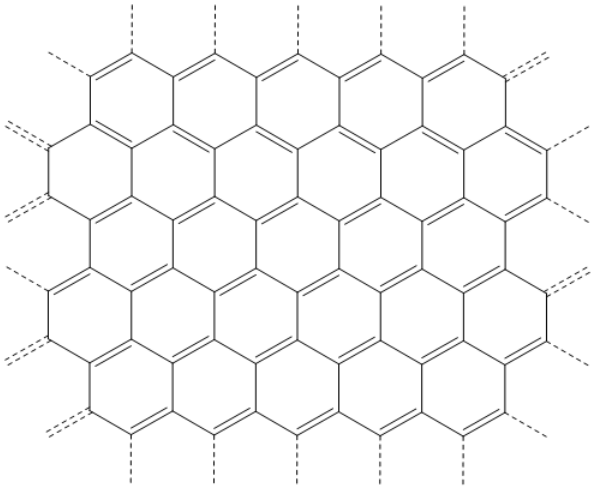
Carbon's ability to form strong multiple bonds enables it to form a host of molecular and network covalent allotropes. Some of these allotropes have been known since ancient times; some are a focus of much active research. The major classes of allotropes include:

1. α- and β-**Graphite.** The α form of graphite is the most stable carbon allotrope. It is formed naturally through the decomposition of carbonaceous material in sediments but may also be made synthetically by vaporizing the Si out of SiC.

$$\mathrm{SiC} \xrightarrow{\Delta} \mathrm{C(s)} + \mathrm{Si(g)}$$

The structure of α-graphite consists of hexagonal layers of interconnected rings of graphene sheets, the structure of which is shown in Scheme **7.7.1.I**.

Scheme 7.7.1.I. One resonance structure depiction of part of a graphene sheet.



All the carbons in the graphene sheet are trigonal planar and connected by a network of covalent bonds that may be adequately described as involving sigma overlaps between sp^2 -orbitals and a delocalized π bond network. This delocalized π bonding system involves a half-filled valence band of π type orbitals and is responsible for graphite's good electrical conductivity.

In terms of the impact of the delocalized π bonds on graphite's structure, it ensures that the graphene sheets are planar with delocalized π clouds above and below the carbon plane. Because of this, the sheets may be stacked together in various arrangements in which the carbons in adjacent layers may be eclipsed or staggered with respect to one another, as shown in Figure

7.7.1.1. The stable α-graphite form possesses staggered layers alternating an AB pattern, while in the slightly less stable β-graphite, the layers are staggered in an ABC arrangement (Figure **7.7.1.1b**).

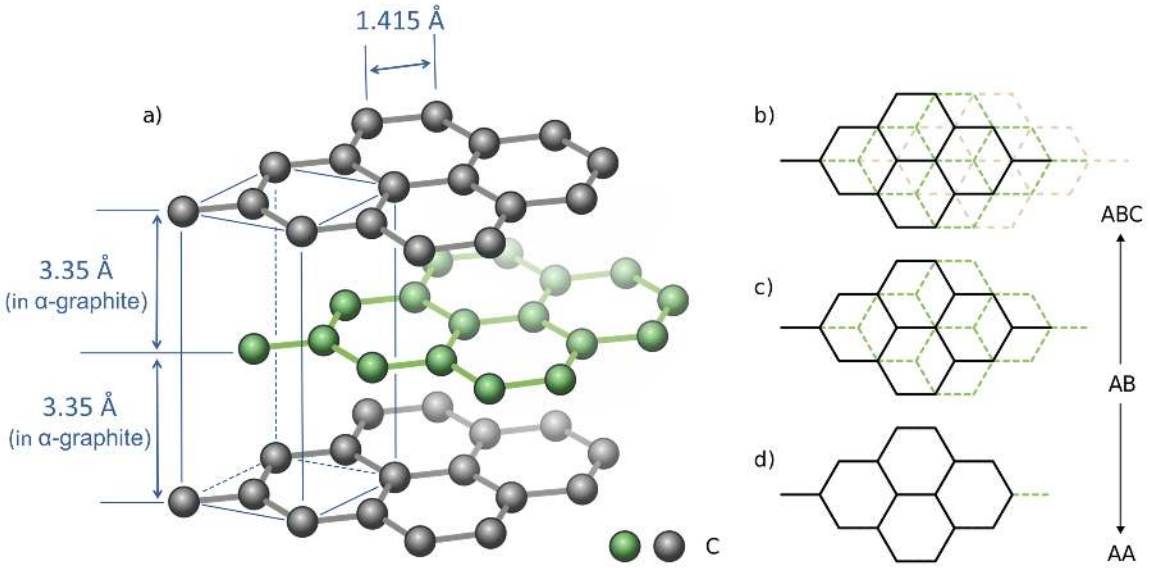


Figure **7.7.1.1**. Graphite structures. (a) Structure of α-graphite showing the offset of adjacent graphene layers that alternate in an AB pattern along with (b-d) additional stacking arrangements of the graphene layers. The AB stacking arrangement corresponds to α-graphite and the ABC arrangement to β-graphite. The image is a slightly modified form of an image by Jozef Sivek - Own work, CC BY-SA 4.0, commons.wikimedia.org/w/inde...curid=39574577

Since the forces between the graphene layers do not vary much as the sheets move past one another, it is relatively easy for layer slip to occur; graphite thus functions effectively as a lubricant. In addition, it is possible to exfoliate individual graphene sheets using scotch tape and chemical exfoliation methods.

2. Graphene. Individual graphene sheets like that depicted in Scheme **7.7.1.I** have been the subject of intense experimental and theoretical investigation as a 2D nanomaterial. Owing to the strong carbon-carbon bonds that hold the sheet together, defect-free graphene is the strongest material known, albeit a brittle one; it also has a band structure that makes it a good conductor of electricity and leads to unusual optical properties. Among the latter, even a single graphene layer is visible to the naked eye, as shown in Figure **7.7.1.2**.



Figure **7.7.1.2**. Though only a single layer of C atoms thick, graphene can be observed with the naked eye due to its high absorptivities in the visible range. The image is public Domain, en.Wikipedia.org/w/index.php?curid=19900701

3. Diamond and Lonsdaleite. When subjected to extremes of heat and pressure, graphite converts to its more dense diamond allotrope, in which all the carbons are tetrahedral and held together by sigma bonds, as shown in Figure **7.7.1.3**. In this structure, all the carbons are tetrahedral and connected in chair conformation rings. As might be expected from such a tightly interconnected structure, diamond is extremely hard, although analogous structures which also possess chair form rings, specifically Wurtzite-like hexagonal BN and its all-carbon analogue Lonsdaleite, are even harder. As might be expected from diamond's all-σ structure, it is a poor electrical conductor, and the 1.544 Å C-C bond length in diamond is longer than the 1.415 Å C-C bond length in graphite (1.415 Å).

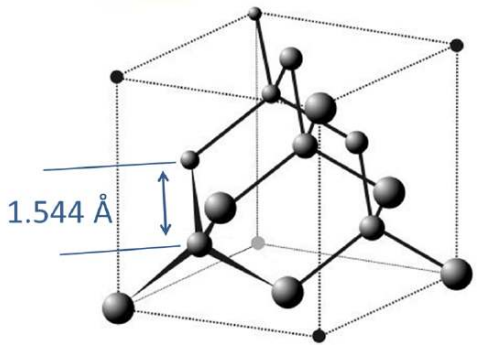


Figure **7.7.1.3**. Diamond structure. The image is extracted and slightly modified from Diamond_and_graphite.jpg: by User:Itubderivative work: Materialscientist (talk) - Diamond_and_graphite.jpgFile:Graphite-tn19a.jpg, CC BY-SA 3.0, commons.wikimedia.org/w/inde...?curid=7223557.

4. Fullerenes. Since the late 1980s discovery of the sixty-carbon European football (soccer ball) shaped buckminsterfullerene shown in Figure **7.7.1.4A**, it has been recognized that such molecules have long been present in soot, carbon black, and related materials. Produced today by electrolytic or laser ablation or pyrolysis, a large number of such structures have been produced, some of which are shown in Figure **7.7.1.4B**.

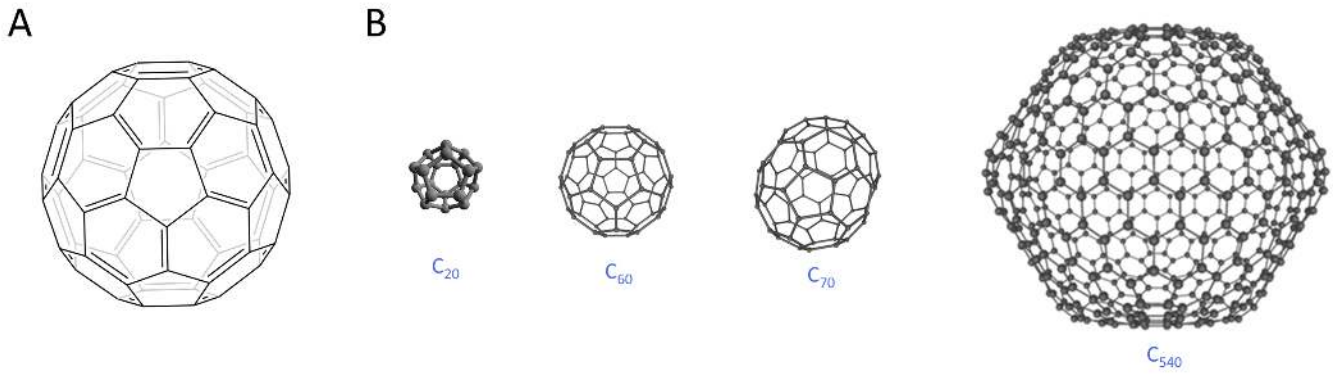


Figure 7.7.1.4.
Structures of several fullerenes: (A) buckminsterfullerene, C_{60}, named after the American architect Buckminster Fuller, who popularized the use of geodesic domes; (B) C_{20}, C_{60}, C_{70}, and (C) C_{540}
The image of C_{60} is taken from By Perditax - Own work, CC0, commons.wikimedia.org/w/inde...curid=15480223; the 3D images of C_{20}, C_{60}, C_{70}, and C_{540} are remixed from the image Created by Michael Ströck (mstroeck) - Created by Michael Ströck (mstroeck), CC BY-SA 3.0, commons.wikimedia.org/w/inde...p?curid=584786

Figure **7.7.1.5**. These exist in different arrangements classified according to how the graphite sheet is oriented relative to the nanotube axis.

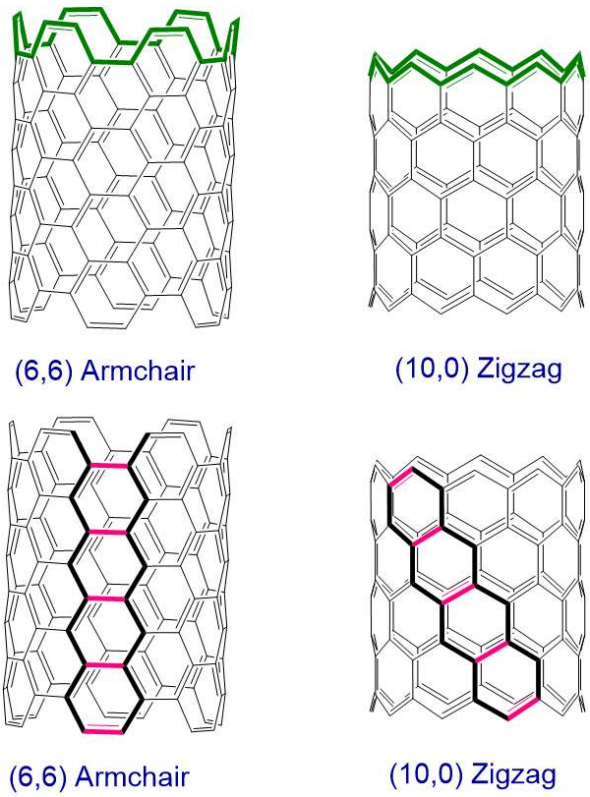


Figure **7.7.1.5**. An example of an armchair and a zigzag nanotube. Note that contrary to what some textbooks claim, armchair and zigzag nanotubes do not represent different nanotube conformations but rather different configurations of carbons in a nanotube.

As shown in Figure **7.7.1.6**, the overall linear chains of connected carbon atoms within a graphene sheet can be classified as taking on either a **zigzag** or **armchair** arrangement. Nanotubes then are classified as armchair or zigzag based on the arrangement of the bonds perpendicular to the tube axis (Figure **7.7.1.7**, top). Alternatively, armchair nanotubes may be envisioned as formed by connecting the zigzag path ends of a graphene sheet in which the direction of the zigzag path is oriented along the nanotube axis, while in zigzag nanotubes the connected zigzag paths are angled relative to the helix axis (Figure **7.7.1.7**, bottom).

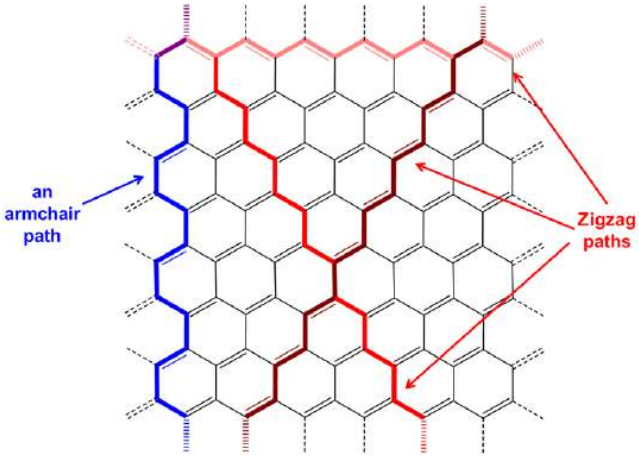


Figure **7.7.1.6**. Connected paths of bonds in a graphene sheet are classified as involving armchair paths or zigzag paths.

In ordinary carbon nanotubes the armchair or zigzag path around the tube forms a closed loop. Such carbon nanotubes are relatively linear. In **helical nanotubes** like that shown in Figure **7.7.1.7**, the armchair or zigzag paths form a helical spiral around the nanotube surface instead. In order for this to take place, the carbon rings cannot be perfectly hexagonal but are instead twisted, and to relieve the resulting strain helical nanotubes take on a coiled shape.

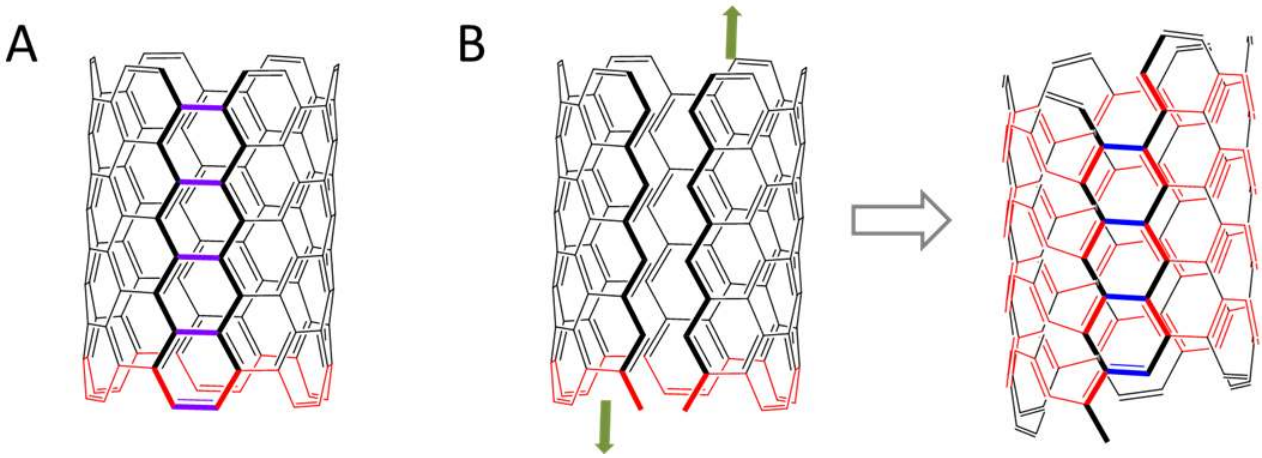


Figure **7.7.1.7**. (A) The armchair and zigzag paths that define a nanotube as armchair or zigzag wrap form circular paths in an ordinary nanotube. In a helical nanotube the paths are coiled in a helix arrangement. (B) Such helical nanotubes may be thought of as formed by connecting the zigzag ends of a graphene sheet in such a way that one loop of helices is shifted relative to the other. Again, despite what some texts claim, helical nanotubes are not conformers of other types of nanotubes but rather isomers. For example, the helical nanotube shown in C is a configurational isomer of the 6,6-armchair nanotube shown in A.

Depending on the size of the nanotube, it is sometimes even possible to nest multiple nanotubes inside one another, to "bud" fullerenes off the side of a nanotube, or even to fit fullerenes inside to give a "carbon peapod". Some of the possibilities are depicted in **Figure 7.7.1.8.**

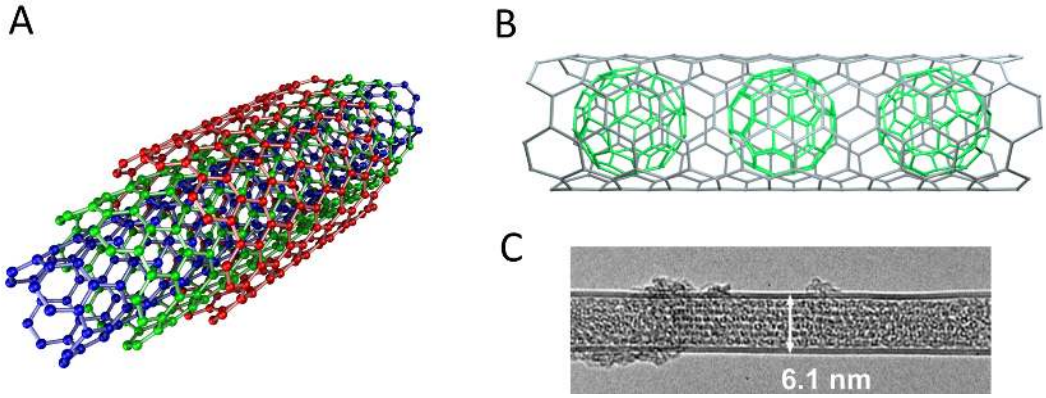


Figure **7.7.1.8**. (A) Model of a triple wall carbon nanotube; (B) Carbon peapod structure consisting of C_{60} chains in a single walled carbon nanotube; (C) TEM image of a 6.1 nm wide double walled carbon nanotube filled with C_{60} molecules (for reference a 6-membered aromatic ring is ~0.00025 nm wide). The triple walled carbon nanotube image is by Eric Wieser - Own work, CC BY-SA 3.0, commons.wikimedia.org/w/inde...curid=12453670; the carbon peapod image is from Chem171 W15 - Own work, CC BY-SA 4.0, commons.wikimedia.org/w/inde...curid=39071978; that of the double walled carbon naotube filled with buckyballs by Hamid Reza Barzegar et al. (listed as reference 3 - http://pubs.acs.org/doi/full/10.1021/nl503388f), CC BY 4.0, commons.wikimedia.org/w/inde...curid=45374138

The chemical properties of fullerenes and nanotubes reflect their structure in the following ways:

1. They possess a delocalized π structure and so can undergo facile oxidation and reduction reactions. For instance, buckminsterfullerene can be electrochemically reduced in six successive one-electron steps to give C_{60}^{6-}. Similar reductions can occur by reacting a fullerene with an active metal. In many cases this simply results in a salt of a fulleride anion, but in some cases the metal goes inside the fullerene cage to give an **endohedral fullerene**, designated M@C_{60}. A model of such a fullerene is given in Figure **7.7.1.9**.
2. The carbons in these systems are all quaternary and so generally only undergo addition reactions, not substitutions.
3. While the planar sheets of graphite contain trigonal planar carbons, the carbons in fullerenes and nanotubes must be slightly bent into a pyramidal shape in order to accommodate the concavity of those structures. This results in considerable steric strain that can be relieved when addition occurs at a carbon to render it tetrahedral. Because of this, fullerenes undergo a variety of nucleophilic and cycloaddition reactions, primarily at the C=C bonds joining two six-membered rings.

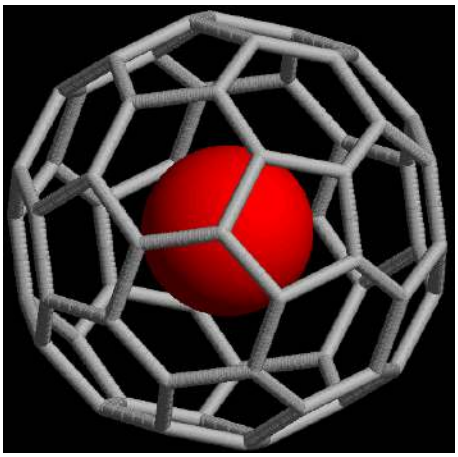


Figure 7.7.1.9. Model of an endohedral complex of buckminsterfullerene, $M@C_{60}$. Such complexes can form in conjunction with oxidation of the metal and reduction of the fullerene and so might be described as $M^{z+}@C_{60}^{z-}$. However, many examples of neutral endohedral complexes are also known, including $Ne@C_{60}$ and $H_2O@C_{60}$. (Hajv01, Endohedral fullerene, CC BY-SA 4.0)

Readers desiring a more thorough presentation of the chemistry of fullerenes are invited to read this summary of carbon nanomaterials by Andrew Barron of Rice University.

6. Vitreous carbon. Glass-like carbon, commonly referred to as glassy or vitreous carbon, is believed to consist of a mixture of concave graphene-like sheets, similar to those in nanotubes and fullerenes but not completely wrapped to form closed balls or tubes. Such forms of carbon are commonly used in electrode materials in electrochemistry (*e.g.*, glassy carbon electrodes).

7. High-carbon content amorphous materials. These are technically not a single form or a pure allotrope but rather a family of high-carbon content materials that include amorphous carbon, carbon black, soot, pyrolyzed coal, coal, and charcoal. These contain varying amounts of hydrocarbons (particularly polycyclic aromatic hydrocarbons) and other organic material. Many of these materials contain small crystallites of diamond and graphite-like regions interconnected by an amorphous matrix of carbon-rich material. Some representative structures are given in Figure 7.7.1.10.

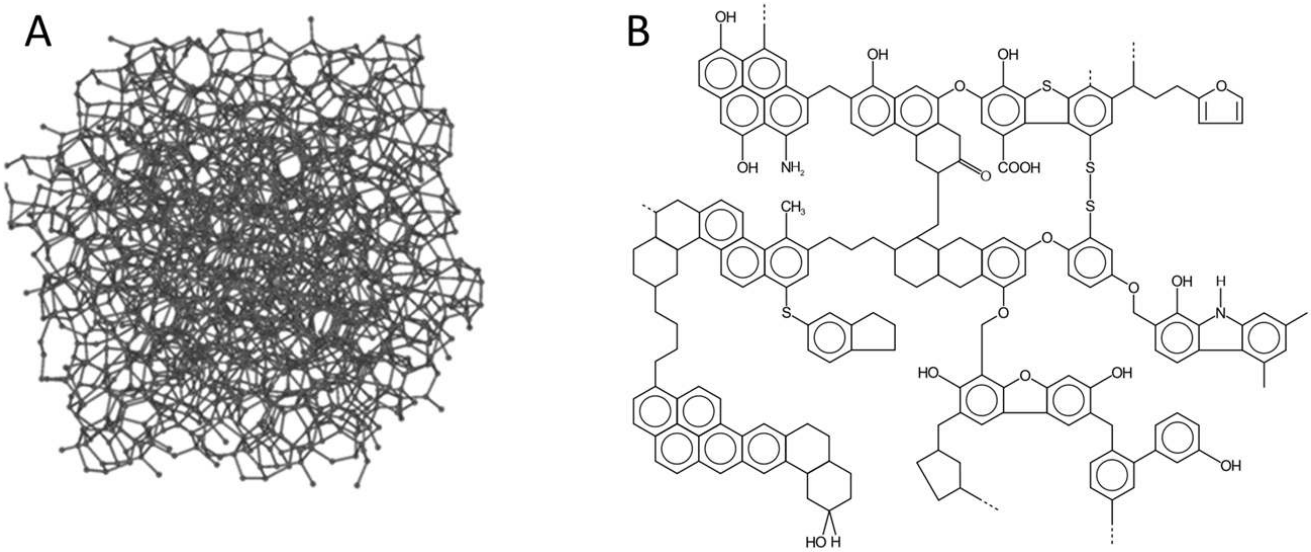


Figure 7.7.1.10. Models illustrative of the molecular structure of (A) amorphous carbon and (B) coal. Although the presence of non-carbon material is most apparent in the structure of coal, neither are not true allotropes since they contain C-H bonds and other organic material. The image of amorphous carbon is extracted from an image created by Michael Ströck (mstroeck) - Created by Michael Ströck (mstroeck), CC BY-SA 3.0, commons.wikimedia.org/w/inde...p?curid=584786; the model for the structure of coal is by real name: Karol Głąbpl.wiki: Karol007commons: Karol007e-mail: kamikaze007 (at) tlen.pl - own work from: Loretta Jones, Peter Atkins, "Chemia ogólna. Cząsteczki, materia, reakcje" tł. Jerzy Kuryłowicz, Wydawnictwo Naukowe PWN, Warszawa 2004. ISBN: 83-01-13810-6This W3C-unspecified vector image was created with Inkscape., CC BY-SA 3.0, https://commons.wikimedia.org/w/inde...?curid=1521998

8. Graphyne - a possible future carbon allotrope? The discovery of fullerene and carbon nanotube structures held together exclusively by interconnected C-C and C=C bonds raises the issue of whether it might be possible to construct forms of carbon that include or are even primarily comprised of C≡C bonds. These materials, called **graphynes**, by analogy with the double bonded structure of graphene, are predicted to be theoretically stable but as yet have been neither observed in nature nor made experimentally. A selection of proposed graphyne structures is given in **Figure 7.7.1.11.**

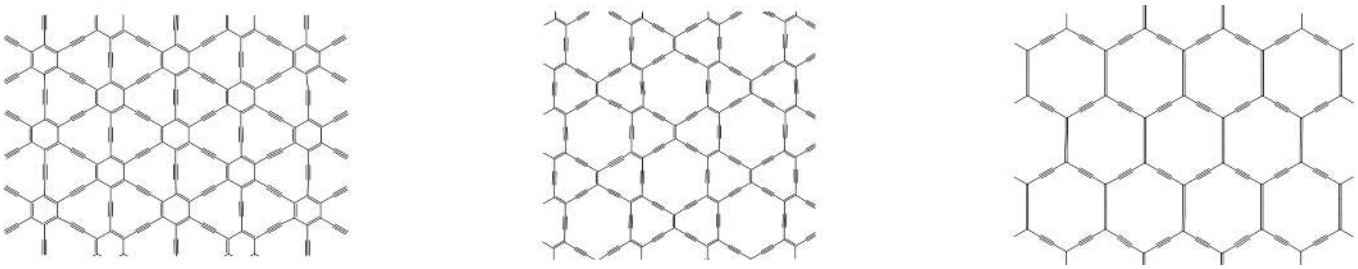


Figure **7.7.1.11**. A variety of graphyne structures that have been proposed as theoretically stable. As of July 2020 no sample of stable graphyne has been made experimentally.

Note: A few analytically notable group 14 isotopes

A number of group 14 isotopes find use in analytical applications. These include:

^{13}C, a spin 1/2 NMR active isotope comprising 1% of natural carbon. It is widely used in carbon-13 NMR to structurally characterize organic and organometallic compounds. For more information on carbon 13 NMR and its use in organic chemistry see this page.

^{14}C, an unstable isotope that occurs at ~ 1 parts per trillion in the atmosphere and undergoes radioactive decay with a half-life of 5730 years. Since the level of ^{14}C in organisms is approximately equal to atmospheric levels at their time of death and decays thereafter, the ratio of ^{14}C to ^{12}C in a biologically-derived sample may be used to estimate the age of objects ~60,000 years old or less. For more information on radiocarbon dating see this chem libre texts page.

^{29}Si, a spin 1/2 NMR active isotope comprising ~5% of naturally occurring silicon. Silicon-29 NMR is useful as a structural tool for characterizing silicon compounds ranging from glasses to organosilanes. Although there is not yet a Chem Libre texts page describing the technique, a brief introduction may be found here.

^{73}Ge, a spin 9/2 nucleus, and spin 1/2 **^{115}Sn**, **^{117}Sn**, **^{119}Sn**, and **^{207}Pb** are also NMR active isotopes that can be used to structurally characterize compounds of these elements. Their use is beyond the scope of this introductory text but for those interested, more information about the use of these nuclei in NMR is available for Ge, Sn, and Pb. In addition ^{73}Ge is Mössbauer active, although relatively few examples of its use in the characterization of Ge in Ge-containing materials exist.

References

1. Atomic and physical property data are taken from those listed by the Royal Society of Chemistry at https://www.rsc.org/periodic-table. Many are rounded to a smaller number of significant figures. The structure images are taken from

2. Lee, C.; Wei, X.; Kysar, J. W.; Hone, J., Measurement of the Elastic Properties and Intrinsic Strength of Monolayer Graphene. Science 2008, 321 (5887), 385-388.

3. Barzegar, H. R.; Gracia-Espino, E.; Yan, A.; Ojeda-Aristizabal, C.; Dunn, G.; Wågberg, T.; Zettl, A., C60/Collapsed Carbon Nanotube Hybrids: A Variant of Peapods. Nano Letters 2015, 15 (2), 829-834.

Contributors and Attributions

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7.7.2: Inorganic Compounds of the Group 14 Elements

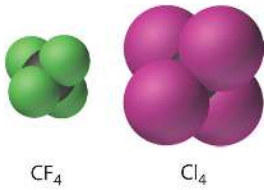
Reactions and Compounds of Carbon

Carbon is the building block of all organic compounds, including biomolecules, fuels, pharmaceuticals, and plastics, whereas inorganic compounds of carbon include metal carbonates, which are found in substances as diverse as fertilizers and antacid tablets, halides, oxides, carbides, and carboranes. Like boron in group 13, the chemistry of carbon differs sufficiently from that of its heavier congeners to merit a separate discussion.

The structures of the allotropes of carbon—diamond, graphite, fullerenes, and nanotubes—are distinct, but they all contain simple electron-pair bonds (Figure 7.18). Although it was originally believed that fullerenes were a new form of carbon that could be prepared only in the laboratory, fullerenes have been found in certain types of meteorites. Another possible allotrope of carbon has also been detected in impact fragments of a carbon-rich meteorite; it appears to consist of long chains of carbon atoms linked by alternating single and triple bonds, $(–C{\equiv}C–C{\equiv}C–)_n$. Carbon nanotubes ("buckytubes") are being studied as potential building blocks for ultramicroscale detectors and molecular computers and as tethers for space stations. They are currently used in electronic devices, such as the electrically conducting tips of miniature electron guns for flat-panel displays in portable computers.

Although all the carbon tetrahalides (CX_4) are known, they are generally not obtained by the direct reaction of carbon with the elemental halogens (X_2) but by indirect methods such as the following reaction, where X is Cl or Br:

$$CH_{4(g)} + 4X_{2(g)} \rightarrow CX_{4(l,s)} + 4HX_{(g)} \tag{7.7.2.1}$$



The carbon tetrahalides all have the tetrahedral geometry predicted by the valence-shell electron-pair repulsion (VSEPR) model, as shown for CF_4 and CI_4. Their stability decreases rapidly as the halogen increases in size because of poor orbital overlap and increased crowding. Because the C–F bond is about 25% stronger than a C–H bond, fluorocarbons are thermally and chemically more stable than the corresponding hydrocarbons, while having a similar hydrophobic character. A polymer of tetrafluoroethylene ($F_2C{=}CF_2$), analogous to polyethylene, is the nonstick Teflon lining found on many cooking pans, and similar compounds are used to make fabrics stain resistant (such as Scotch-Gard) or waterproof but breathable (such as Gore-Tex).

> *The stability of the carbon tetrahalides decreases with increasing size of the halogen due to increasingly poor orbital overlap and crowding.*

Carbon reacts with oxygen to form either CO or CO_2, depending on the stoichiometry. Carbon monoxide is a colorless, odorless, and poisonous gas that reacts with the iron in hemoglobin to form an Fe–CO unit, which prevents hemoglobin from binding, transporting, and releasing oxygen in the blood (see Figure 23.26). In the laboratory, carbon monoxide can be prepared on a small scale by dehydrating formic acid with concentrated sulfuric acid:

$$HCO_2H(l) \xrightarrow{H_2SO_4(l)} CO(g) + H_3O^+(aq) + HSO_4^- \tag{7.7.2.2}$$

Carbon monoxide also reacts with the halogens to form the oxohalides (COX_2). Probably the best known of these is phosgene ($Cl_2C{=}O$), which is highly poisonous and was used as a chemical weapon during World War I:

$$CO(g) + Cl_2(g) \xrightarrow{\Delta} Cl_2C{=}O(g) \tag{7.7.2.3}$$

Despite its toxicity, phosgene is an important industrial chemical that is prepared on a large scale, primarily in the manufacture of polyurethanes.

Carbon dioxide can be prepared on a small scale by reacting almost any metal carbonate or bicarbonate salt with a strong acid. As is typical of a nonmetal oxide, CO_2 reacts with water to form acidic solutions containing carbonic acid (H_2CO_3). In contrast to its reactions with oxygen, reacting carbon with sulfur at high temperatures produces only carbon disulfide (CS_2):

$$C(s) + 2S(g) \xrightarrow{\Delta} CS_2(g) \quad (7.7.2.4)$$

The selenium analog CSe_2 is also known. Both have the linear structure predicted by the VSEPR model, and both are vile smelling (and in the case of CSe_2, highly toxic), volatile liquids. The sulfur and selenium analogues of carbon monoxide, CS and CSe, are unstable because the C≡Y bonds (Y is S or Se) are much weaker than the C≡O bond due to poorer π orbital overlap.

> *π bonds between carbon and the heavier chalcogenides are weak due to poor orbital overlap.*

Binary compounds of carbon with less electronegative elements are called carbides. The chemical and physical properties of carbides depend strongly on the identity of the second element, resulting in three general classes: ionic carbides, interstitial carbides, and covalent carbides. The reaction of carbon at high temperatures with electropositive metals such as those of groups 1 and 2 and aluminum produces ionic carbides, which contain discrete metal cations and carbon anions. The identity of the anions depends on the size of the second element. For example, smaller elements such as beryllium and aluminum give methides such as Be_2C and Al_4C_3, which formally contain the C^{4-} ion derived from methane (CH_4) by losing all four H atoms as protons. In contrast, larger metals such as sodium and calcium give carbides with stoichiometries of Na_2C_2 and CaC_2. Because these carbides contain the C^{4-} ion, which is derived from acetylene (HC≡CH) by losing both H atoms as protons, they are more properly called acetylides. Reacting ionic carbides with dilute aqueous acid results in protonation of the anions to give the parent hydrocarbons: CH_4 or C_2H_2. For many years, miners' lamps used the reaction of calcium carbide with water to produce a steady supply of acetylene, which was ignited to provide a portable lantern.



19th-century miner's lamp. The lamp uses burning acetylene, produced by the slow reaction of calcium carbide with water, to provide light.

The reaction of carbon with most transition metals at high temperatures produces interstitial carbides. Due to the less electropositive nature of the transition metals, these carbides contain covalent metal–carbon interactions, which result in different properties: most interstitial carbides are good conductors of electricity, have high melting points, and are among the hardest substances known. Interstitial carbides exhibit a variety of nominal compositions, and they are often nonstoichiometric compounds whose carbon content can vary over a wide range. Among the most important are tungsten carbide (WC), which is used industrially in high-speed cutting tools, and cementite (Fe_3C), which is a major component of steel.

Elements with an electronegativity similar to that of carbon form covalent carbides, such as silicon carbide (SiC; Equation ???) and boron carbide (B_4C). These substances are extremely hard, have high melting points, and are chemically inert. For example, silicon carbide is highly resistant to chemical attack at temperatures as high as 1600°C. Because it also maintains its strength at high temperatures, silicon carbide is used in heating elements for electric furnaces and in variable-temperature resistors.

> *Carbides formed from group 1 and 2 elements are ionic. Transition metals form interstitial carbides with covalent metal–carbon interactions, and covalent carbides are chemically inert.*

Example 7.7.2.1

For each reaction, explain why the given product forms.

a. $CO(g) + Cl_2(g) \rightarrow Cl_2C{=}O(g)$
b. $CO(g) + BF_3(g) \rightarrow F_3B{:}C{\equiv}O(g)$
c. $Sr(s) + 2C(s) \xrightarrow{\Delta} SrC_2(s)$

Given: balanced chemical equations

Asked for: why the given products form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

Solution

a. Because the carbon in CO is in an intermediate oxidation state (+2), CO can be either a reductant or an oxidant; it is also a Lewis base. The other reactant (Cl_2) is an oxidant, so we expect a redox reaction to occur in which the carbon of CO is further oxidized. Because Cl_2 is a two-electron oxidant and the carbon atom of CO can be oxidized by two electrons to the +4 oxidation state, the product is phosgene ($Cl_2C{=}O$).
b. Unlike Cl_2, BF_3 is not a good oxidant, even though it contains boron in its highest oxidation state (+3). Nor can BF_3 behave like a reductant. Like any other species with only six valence electrons, however, it is certainly a Lewis acid. Hence an acid–base reaction is the most likely alternative, especially because we know that CO can use the lone pair of electrons on carbon to act as a Lewis base. The most probable reaction is therefore the formation of a Lewis acid–base adduct.
c. Typically, both reactants behave like reductants. Unless one of them can also behave like an oxidant, no reaction will occur. We know that Sr is an active metal because it lies far to the left in the periodic table and that it is more electropositive than carbon. Carbon is a nonmetal with a significantly higher electronegativity; it is therefore more likely to accept electrons in a redox reaction. We conclude, therefore, that Sr will be oxidized, and C will be reduced. Carbon forms ionic carbides with active metals, so the reaction will produce a species formally containing either C^{4-} or C_2^{2-}. Those that contain C^{4-} usually involve small, highly charged metal ions, so Sr^{2+} will produce the acetylide (SrC_2) instead.

Exercise 7.7.2.1

Predict the products of the reactions and write a balanced chemical equation for each reaction.

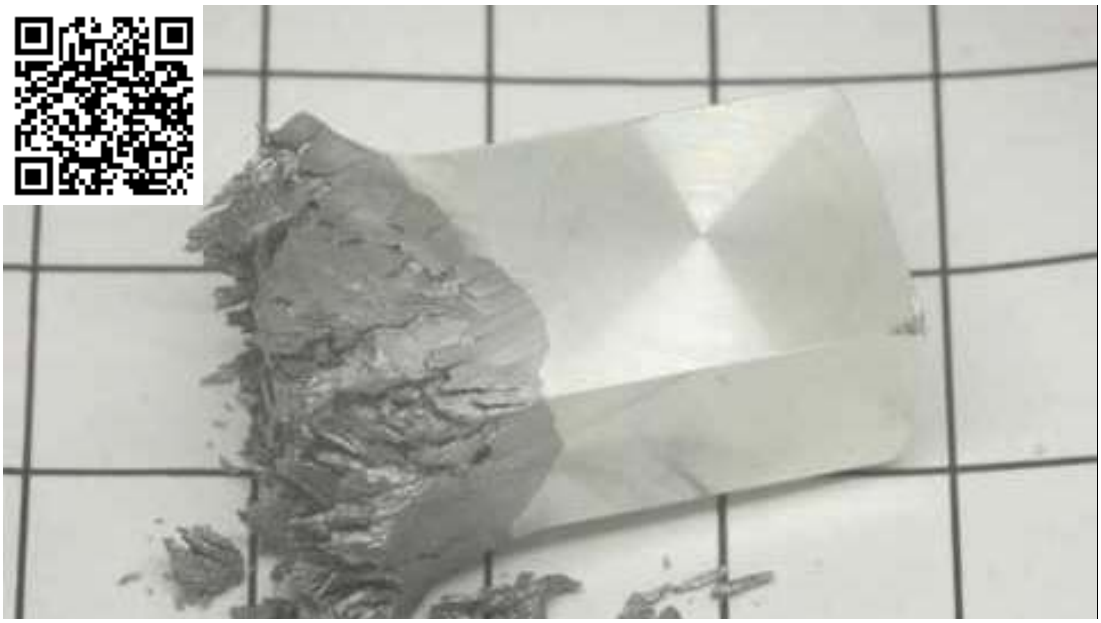
a. $C(s) + \text{excess } O_2(g) \xrightarrow{\Delta}$
b. $C(s) + H_2O(l) \rightarrow$
c. $NaHCO_3(s) + H_2SO_4(aq) \rightarrow$

Answer

a. $C(s) + \text{excess } O_2(g) \xrightarrow{\Delta} CO_2(g)$
b. $C(s) + H_2O(l) \rightarrow$ no reaction
c. $NaHCO_3(s) + H_2SO_4(aq) \rightarrow CO_2(g) + NaHSO_4(aq) + H_2O(l)$

Reactions and Compounds of the Heavier Group 14 Elements

Although silicon, germanium, tin, and lead in their +4 oxidation states often form binary compounds with the same stoichiometry as carbon, the structures and properties of these compounds are usually significantly different from those of the carbon analogues. Silicon and germanium are both semiconductors with structures analogous to diamond. Tin has two common allotropes: white (β) tin has a metallic lattice and metallic properties, whereas gray (α) tin has a diamond-like structure and is a semiconductor. The metallic β form is stable above 13.2°C, and the nonmetallic α form is stable below 13.2°C. Lead is the only group 14 element that is metallic in both structure and properties under all conditions.



***Video* 7.7.2.1**: *Time lapse tin pest reaction.*

Based on its position in the periodic table, we expect silicon to be amphoteric. In fact, it dissolves in strong aqueous base to produce hydrogen gas and solutions of silicates, but the only aqueous acid that it reacts with is hydrofluoric acid, presumably due to the formation of the stable SiF_6^{2-} ion. Germanium is more metallic in its behavior than silicon. For example, it dissolves in hot oxidizing acids, such as HNO_3 and H_2SO_4, but in the absence of an oxidant, it does not dissolve in aqueous base. Although tin has an even more metallic character than germanium, lead is the only element in the group that behaves purely as a metal. Acids do not readily attack it because the solid acquires a thin protective outer layer of a Pb^{2+} salt, such as $PbSO_4$.

All group 14 dichlorides are known, and their stability increases dramatically as the atomic number of the central atom increases. Thus CCl_2 is dichlorocarbene, a highly reactive, short-lived intermediate that can be made in solution but cannot be isolated in pure form using standard techniques; $SiCl_2$ can be isolated at very low temperatures, but it decomposes rapidly above −150°C, and $GeCl_2$ is relatively stable at temperatures below 20°C. In contrast, $SnCl_2$ is a polymeric solid that is indefinitely stable at room temperature, whereas $PbCl_2$ is an insoluble crystalline solid with a structure similar to that of $SnCl_2$.

> *The stability of the group 14 dichlorides increases dramatically from carbon to lead.*

Although the first four elements of group 14 form tetrahalides (MX_4) with all the halogens, only fluorine is able to oxidize lead to the +4 oxidation state, giving PbF_4. The tetrahalides of silicon and germanium react rapidly with water to give amphoteric oxides (where M is Si or Ge):

$$MX_{4(s,l)} + 2H_2O_{(l)} \rightarrow MO_{2(s)} + 4HX_{(aq)} \tag{7.7.2.5}$$

In contrast, the tetrahalides of tin and lead react with water to give hydrated metal ions. Because of the stability of its +2 oxidation state, lead reacts with oxygen or sulfur to form PbO or PbS, respectively, whereas heating the other group 14 elements with excess O_2 or S_8 gives the corresponding dioxides or disulfides, respectively. The dioxides of the group 14 elements become increasingly basic as we go down the group.

> *The dioxides of the group 14 elements become increasingly basic down the group.*

Because the Si–O bond is even stronger than the C–O bond (~452 kJ/mol versus ~358 kJ/mol), silicon has a strong affinity for oxygen. The relative strengths of the C–O and Si–O bonds contradict the generalization that bond strengths decrease as the bonded atoms become larger. This is because we have thus far assumed that a formal single bond between two atoms can always be described in terms of a single pair of shared electrons. In the case of Si–O bonds, however, the presence of relatively low-energy, empty d orbitals on Si and nonbonding electron pairs in the p or sp^n hybrid orbitals of O results in a partial π bond (Figure **7.7.2.3**). Due to its partial π double bond character, the Si–O bond is significantly stronger and shorter than would otherwise be expected. A

similar interaction with oxygen is also an important feature of the chemistry of the elements that follow silicon in the third period (P, S, and Cl). Because the Si–O bond is unusually strong, silicon–oxygen compounds dominate the chemistry of silicon.

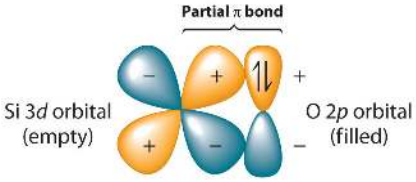
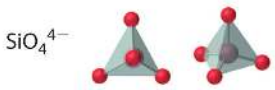


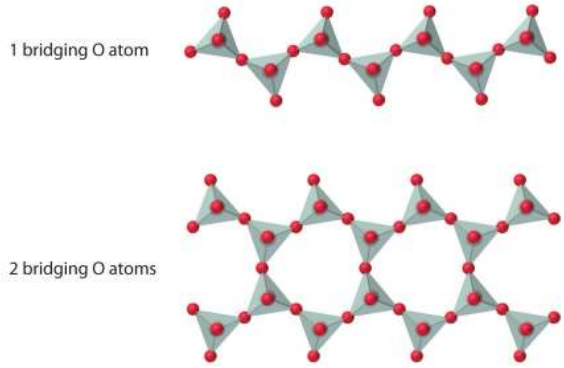
Figure **7.7.2.3**: π Bonding between silicon and oxygen. Silicon has relatively low-energy, empty 3d orbitals that can interact with filled 2p hybrid orbitals on oxygen. This interaction results in a partial π bond in which both electrons are supplied by oxygen, giving the Si–O bond partial double bond character and making it significantly stronger (and shorter) than expected for a single bond.

> *Because silicon–oxygen bonds are unusually strong, silicon–oxygen compounds dominate the chemistry of silicon.*

Compounds with anions that contain only silicon and oxygen are called silicates, whose basic building block is the SiO_4^{4-} unit:



The number of oxygen atoms shared between silicon atoms and the way in which the units are linked vary considerably in different silicates. Converting one of the oxygen atoms from terminal to bridging generates chains of silicates, while converting two oxygen atoms from terminal to bridging generates double chains. In contrast, converting three or four oxygens to bridging generates a variety of complex layered and three-dimensional structures, respectively.



In a large and important class of materials called aluminosilicates, some of the Si atoms are replaced by Al atoms to give aluminosilicates such as zeolites, whose three-dimensional framework structures have large cavities connected by smaller tunnels (Figure **7.7.2.4**). Because the cations in zeolites are readily exchanged, zeolites are used in laundry detergents as water-softening agents: the more loosely bound Na^+ ions inside the zeolite cavities are displaced by the more highly charged Mg^{2+} and Ca^{2+} ions present in hard water, which bind more tightly. Zeolites are also used as catalysts and for water purification.

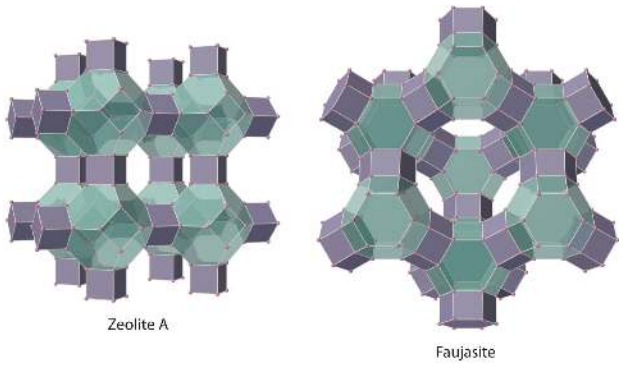


Figure 7.7.2.4: Zeolites are aluminosilicates with large cavities connected by channels. The cavities normally contain hydrated cations that are loosely bound to the oxygen atoms of the negatively charged framework by electrostatic interactions. The sizes and arrangements of the channels and cavities differ in different types of zeolites. For example, in zeolite A the aluminosilicate cages are arranged in a cubic fashion, and the channels connecting the cavities intersect at right angles. In contrast, the cavities in faujasite are much larger, and the channels intersect at 120° angles. In these idealized models, the oxygen atoms that connect each pair of silicon atoms have been omitted.

Silicon and germanium react with nitrogen at high temperature to form nitrides (M_3N_4):

$$3Si_{(l)} + 2N_{2(g)} \rightarrow Si_3N_{4(s)} \tag{7.7.2.6}$$

Silicon nitride has properties that make it suitable for high-temperature engineering applications: it is strong, very hard, and chemically inert, and it retains these properties to temperatures of about 1000°C.

Because of the diagonal relationship between boron and silicon, metal silicides and metal borides exhibit many similarities. Although metal silicides have structures that are as complex as those of the metal borides and carbides, few silicides are structurally similar to the corresponding borides due to the significantly larger size of Si (atomic radius 111 pm versus 87 pm for B). Silicides of active metals, such as Mg_2Si, are ionic compounds that contain the Si^{4-} ion. They react with aqueous acid to form silicon hydrides such as SiH_4:

$$Mg_2Si_{(s)} + 4H^+_{(aq)} \rightarrow 2Mg^{2+}_{(aq)} + SiH_{4(g)} \tag{7.7.2.7}$$

Unlike carbon, catenated silicon hydrides become thermodynamically less stable as the chain lengthens. Thus straight-chain and branched silanes (analogous to alkanes) are known up to only n = 10; the germanium analogues (germanes) are known up to n = 9. In contrast, the only known hydride of tin is SnH_4, and it slowly decomposes to elemental Sn and H_2 at room temperature. The simplest lead hydride (PbH_4) is so unstable that chemists are not even certain it exists. Because E=E and E≡E bonds become weaker with increasing atomic number (where E is any group 14 element), simple silicon, germanium, and tin analogues of alkenes, alkynes, and aromatic hydrocarbons are either unstable (Si=Si and Ge=Ge) or unknown. Silicon-based life-forms are therefore likely to be found only in science fiction.

> *The stability of group 14 hydrides decreases down the group, and E=E and E≡E bonds become weaker.*

The only important organic derivatives of lead are compounds such as tetraethyllead [$(CH_3CH_2)_4Pb$]. Because the Pb–C bond is weak, these compounds decompose at relatively low temperatures to produce alkyl radicals (R·), which can be used to control the rate of combustion reactions. For 60 yr, hundreds of thousands of tons of lead were burned annually in automobile engines, producing a mist of lead oxide particles along the highways that constituted a potentially serious public health problem. (Example 6 in Section 22.3 examines this problem.) The use of catalytic converters reduced the amount of carbon monoxide, nitrogen oxides, and hydrocarbons released into the atmosphere through automobile exhausts, but it did nothing to decrease lead emissions. Because lead poisons catalytic converters, however, its use as a gasoline additive has been banned in most of the world.

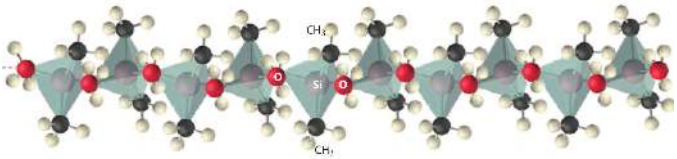


Figure 7.7.2.5 Silicones are polymers with long chains of alternating silicon and oxygen atoms. The structure of a linear silicone polymer is similar to that of quartz, but two of the oxygen atoms attached to each silicon atom are replaced by the carbon atoms of organic groups, such as the methyl groups ($–CH_3$) shown here. The terminal silicon atoms are bonded to three methyl groups. Silicones can be oily, waxy, flexible, or elastic, depending on the chain length, the extent of cross-linking between the chains, and the type of organic group.

Compounds that contain Si–C and Si–O bonds are stable and important. High-molecular-mass polymers called silicones contain an $(Si–O–)_n$ backbone with organic groups attached to Si (Figure 7.7.2.5). The properties of silicones are determined by the chain length, the type of organic group, and the extent of cross-linking between the chains. Without cross-linking, silicones are waxes or oils, but cross-linking can produce flexible materials used in sealants, gaskets, car polishes, lubricants, and even elastic materials, such as the plastic substance known as Silly Putty.



A child playing with Silly Putty, a silicone polymer with unusual mechanical properties. Gentle pressure causes Silly Putty to flow or stretch, but it cannot be flattened when hit with a hammer. This is called a "Non-Newtonian Fluid".

Example 7.7.2.2

For each reaction, explain why the given products form.

a. $Pb(s) + Cl_2(g) \rightarrow PbCl_2(s)$
b. $Mg_2Si(s) + 4H_2O(l) \rightarrow SiH_4(g) + 2Mg(OH)_2(s)$
c. $GeO_2(s) + 4OH^-(aq) \rightarrow GeO_4^{4-}(aq) + 2H_2O(l)$

Given: balanced chemical equations

Asked for: why the given products form

Strategy:

Classify the type of reaction. Using periodic trends in atomic properties, thermodynamics, and kinetics, explain why the observed reaction products form.

Solution

a. Lead is a metal, and chlorine is a nonmetal that is a strong oxidant. Thus we can expect a redox reaction to occur in which the metal acts as a reductant. Although lead can form compounds in the +2 and +4 oxidation states, Pb^{4+} is a potent oxidant (the inert-pair effect). Because lead prefers the +2 oxidation state and chlorine is a weaker oxidant than fluorine, we expect $PbCl_2$ to be the product.
b. This is the reaction of water with a metal silicide, which formally contains the Si^{4-} ion. Water can act as either an acid or a base. Because the other compound is a base, we expect an acid–base reaction to occur in which water acts as an acid. Because Mg_2Si contains Si in its lowest possible oxidation state, however, an oxidation–reduction reaction is also a possibility. But water is a relatively weak oxidant, so an acid–base reaction is more likely. The acid (H_2O) transfers a proton to the base (Si^{4-}), which can accept four protons to form SiH_4. Proton transfer from water produces the OH^- ion, which will combine with Mg^{2+} to give magnesium hydroxide.

c. We expect germanium dioxide (GeO_2) to be amphoteric because of the position of germanium in the periodic table. It should dissolve in strong aqueous base to give an anionic species analogous to silicate.

? Exercise 7.7.2.2

Predict the products of the reactions and write a balanced chemical equation for each reaction.

a. $PbO_2(s) \xrightarrow{\Delta}$
b. $GeCl_4(s) + H_2O(l) \rightarrow$
c. $Sn(s) + HCl(aq) \rightarrow$

Answer

a. $\mathbf{PbO_2(s) \xrightarrow{\Delta} PbO(s) + \frac{1}{2}O_2(g)}$
b. $GeCl_4(s) + 2H_2O(l) \rightarrow GeO_2(s) + 4HCl(aq)$
c. $Sn(s) + 2HCl(aq) \rightarrow Sn^{2+}(aq) + H_2(g) + 2Cl^-(aq)$

Summary

The group 14 elements show the greatest diversity in chemical behavior of any group; covalent bond strengths decease with increasing atomic size, and ionization energies are greater than expected, increasing from C to Pb. The group 14 elements show the greatest range of chemical behavior of any group in the periodic table. Because the covalent bond strength decreases with increasing atomic size and greater-than-expected ionization energies due to an increase in Z_{eff}, the stability of the +2 oxidation state increases from carbon to lead. The tendency to form multiple bonds and to catenate decreases as the atomic number increases. The stability of the carbon tetrahalides decreases as the halogen increases in size because of poor orbital overlap and steric crowding. Carbon forms three kinds of carbides with less electronegative elements: ionic carbides, which contain metal cations and C^{4-} (methide) or C_2^{2-} (acetylide) anions; interstitial carbides, which are characterized by covalent metal–carbon interactions and are among the hardest substances known; and covalent carbides, which have three-dimensional covalent network structures that make them extremely hard, high melting, and chemically inert. Consistent with periodic trends, metallic behavior increases down the group. Silicon has a tremendous affinity for oxygen because of partial Si–O π bonding. Dioxides of the group 14 elements become increasingly basic down the group and their metallic character increases. Silicates contain anions that consist of only silicon and oxygen. Aluminosilicates are formed by replacing some of the Si atoms in silicates by Al atoms; aluminosilicates with three-dimensional framework structures are called zeolites. Nitrides formed by reacting silicon or germanium with nitrogen are strong, hard, and chemically inert. The hydrides become thermodynamically less stable down the group. Moreover, as atomic size increases, multiple bonds between or to the group 14 elements become weaker. Silicones, which contain an Si–O backbone and Si–C bonds, are high-molecular-mass polymers whose properties depend on their compositions.

Contributors and Attributions

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7.7.3: Chemistry of Carbon (Z=6)

Carbon is the fourth most abundant element in the known universe but not nearly as common on the earth, despite the fact that living organisms contain significant amounts of the element. Common carbon compounds in the environment include the gases carbon dioxide (CO_2) and methane (CH_4).

Inorganic Chemistry of Carbon

Inorganic carbon is carbon extracted from ores and minerals, as opposed to organic carbon found in nature through plants and living things. Some examples of inorganic carbon are carbon oxides such as carbon monoxide and carbon dioxide; polyatomic ions, cyanide, cyanate, thiocyanate, carbonate and carbide. Carbon is an element that is unique to itself. Carbon forms strong single, double and triple bonds; therefore, it would take more energy to break these bonds than if carbon were to bond to another element.

For carbon monoxide the reaction is as follows:

$$2C_{(s)} + O_2 \rightarrow 2CO_{(g)} \quad \Delta H = -110.52\ kJ/mol\ CO$$

$$C_{(s)} + O_2 \rightarrow CO_{2(g)} \quad \Delta H = -393.51\ kJ/mol\ CO_2$$

CO and CO_2 are both gases. CO has no odor or taste and can be fatal to living organisms if exposed at even very small amounts (about a thousandth of a gram). This is because CO will bind to the hemoglobin that carries oxygen in the blood. CO_2 will not become fatal unless living organisms are exposed to larger amounts of it, about 15%. CO_2 influences the atmosphere and affects the temperature through the greenhouse gas effect. As heat is trapped in the atmosphere by CO_2 gases, the Earth's temperature increases. The main source for CO_2 in our atmosphere, amongst many, is volcanoes.

Allotropes

Carbon exists in several forms called allotropes. Diamond is one form with a very strong crystal lattice, known as a precious gem from the most ancient records. Another allotrope is graphite, in which the carbon atoms are arranged in planes which are loosely attracted to one another (hence its use as a lubricant). The recently discovered fullerenes are yet another form of carbon.

- Inorganic carbon may come in the form of diamond as a transparent, isotropic crystal. It is the hardest naturally occurring material on this earth. Diamond has four valence electrons, and when each electron bonds with another carbon it creates an sp^3-hybridized atom. The boiling point of diamond is 4827°C.
- Unlike diamond, graphite is opaque, soft, dull and hexagonal. Graphite can be used as a conductor (electrodes) or even in pencils. Graphite consists of planes of sp^2 hybridized carbon atoms in which each carbon is attached to three other carbons.
- Fullerenes are carbon cages with the formula C_2n where $n > 13$. The most abundant fullerene is the spherical C_{60}. Fullerene may contain atoms or molecules inside the cage (endohedral fullerenes) or covalently attached outside (exhedral or adduct fullerenes). The discovery of fullerenes is accredited to Richard Smalley and his team in 1985 at Rice University, who found it after photoablating the surface of graphite with a laser.

Applications

Carbon has a very high melting and boiling point and rapidly combines with oxygen at elevated temperatures. In small amounts it is an excellent hardener for iron, yielding the various steel alloys upon which so much of modern construction depends. An important (but rare) radioactive isotope of carbon, C-14, is used to date ancient objects of organic origin. It has a half-life of 5730 years, but there is only 1 atom of C-14 for every 1012 atoms of C-12 (the usual isotope of carbon).

References

1. General Chemistry Principles & Modern Applications Ninth Edition by Petrucci pg. 84-90
2. Microsoft Encarta Encyclopedia 2002 CD-ROM
3. Inorganic Chemistry Third Edition by Housecroft, Catherine

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7.7.4: Chemistry of Silicon (Z=14)

Silicon, the second most abundant element on earth, is an essential part of the mineral world. Its stable tetrahedral configuration makes it incredibly versatile, and it is used in various ways in our everyday lives. Found in everything from spaceships to synthetic body parts, silicon can be found all around us, and sometimes even in us.

Introduction

The name for silicon is taken from the Latin silex which means "flint". The element is second only to oxygen in abundance in the earth's crust and was discovered by Berzelius in 1824. The most common compound of silicon, SiO_2, is **the most abundant chemical compound in the earth's crust;** we know it better as common beach sand.

Properties

Silicon is a crystalline semi-metal or metalloid. One of its forms is shiny, grey, and very brittle (it will shatter when struck with a hammer). It is a group 14 element in the same periodic group as carbon, but chemically behaves distinctly from all of its group counterparts. Silicon shares the bonding versatility of carbon, with its four valence electrons, but is otherwise a relatively inert element. However, under special conditions, silicon can be made to be a good deal more reactive. Silicon exhibits metalloid properties, is able to expand its valence shell, and is able to be transformed into a semiconductor, distinguishing it from its periodic group members.

Table 1: Properties of Silicon

Symbol	Si
Atomic Number	14
Group	14 (Carbon Family)
Electron Configuration	$[Ne]3s^2 3p^2$
Atomic Weight	28.0855 g
Density	2.57 g/mL
Melting Point	1414^oC
Boiling Point	3265^oC
Oxidation States	4, 3, 2, 1, -1, -2, -3, -4
Electronegativity	1.90
Stable Isotopes	^{28}Si, ^{29}Si, ^{30}Si

Where Silicon is Found

27.6% of the Earth's crust is made up of silicon. Although it is so abundant, it is not usually found in its pure state, but rather its dioxide and hydrates. SiO_2 is silicon's only stable oxide and is found in many crystalline varieties. Its purest form is quartz, but it is also found as jasper and opal. Silicon can also be found in feldspar, micas, olivines, pyroxenes and even in water (Figure 1). In another allotropic form, silicon is a brown amorphous powder most familiar in "dirty" beach sand. The crystalline form of silicon is the foundation of the semiconductor age.



Figure 1: Sand is an easy to find silicon deposit

Silicates

Silicon is most commonly found in silicate compounds. Silica is the one stable oxide of silicon, and has the empirical formula SiO_2. Silica is not a silicon atom with two double bonds to two oxygen atoms. Silica is composed of one silicon atom with four single bonds to four oxygen molecules (Figure 2).

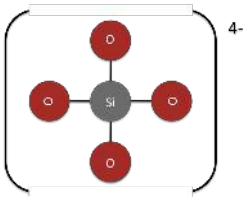


Figure 2: The net charge of silica is minus 4

Silica, i.e. silicon dioxide, takes on this molecular form, instead of carbon dioxide's characteristic shape, because silicon's 3p orbitals make it more energetically favorable to create four single bonds with each oxygen rather than make two double bonds with each oxygen atom. This leads to silicates linking together in -Si-O-Si-O- networks called silicates. The empirical form of silica is SiO_2 because, with respect to the net average of the silicate, each silicon atom has two oxygen atoms.

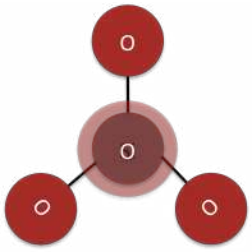


Figure 3: This is a representation of the tetrahedral silica complex

The tetrahedral SiO_4^{4-} complex (see Figure 3), the core unit of silicates, can bind together in a variety of ways, creating a wide array of minerals. Silicon is an integral component in minerals, just as Carbon is an essential component of organic compounds.

Nesosilicates

In nesosilicates, the silicate tetrahedral does not share any oxygen molecules with other silicate tetrahedrals, and instead balances out its charge with other metals. The core structure of nesosilicate is simply a lone tetrahedral silica unit (Figure 4). The empirical formula for the core structure of a nesosilicate is SiO_4^{4-}.

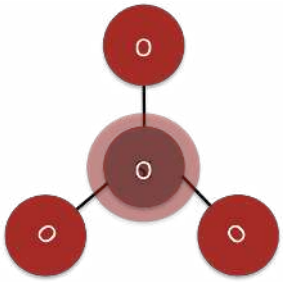


Figure 4: The core of a nesosilicate

Nesosilicates make up the outer fringes of a group of minerals known as olivines.

Sorosilicates

In sorosilicates, two silicate tetrahedrals join together by sharing an oxygen atom at one of their corners. The core structure of a sorosilicate is a pair of silica tetrahedra. (see Figure 5)

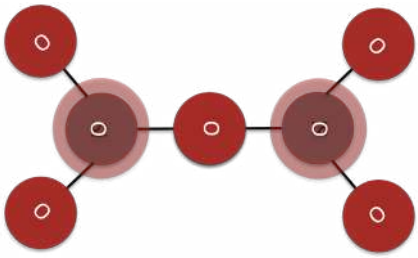


Figure 5: The core of a sorosilicate

The mineral thortveitie is an example of a sorosilicate complex.

Cyclosilicates

In cyclosilicates, three or more silica tetrahedrals share two corners of an oxygen atom. The core structure of a cyclosilicate is a closed ring of silica tetrahedra. (see Figure 6)

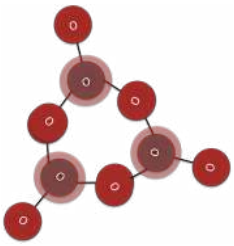


Figure 6: The core of a cyclosilicate

The mineral beryl is an example of a cyclosilicate complex.

Inosilicates

Inosilicates are complexes where each tetrahedral shares two corners with another silica tetrahedral to create a single chain (see Figure 7) or three corners to create a double chain (Figure 8). The core structure of an inosilicate is either an infinite single or double chain of silica tetrahedrals.

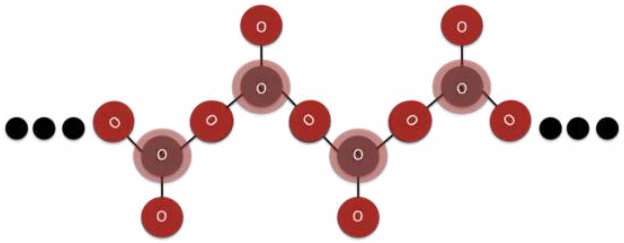


Figure 7: The core of a single chain inosilicate

The mineral group pyroxenes are examples of single chain inosilicates.

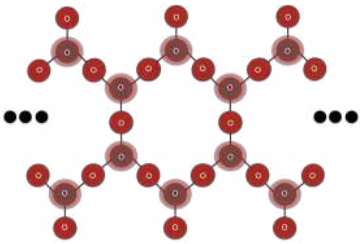


Figure 8: The core of a double chain inosilicate

The mineral amphibole is an example of a double chain inosilicate.

Phyllosilicates

Phyllosilicates are silica complexes where each tetradedral shares three corners and creates a sheet of silicon and oxygen. (see Figure 9) The core complex of a phyllosilicate is an infinite sheet of connected silica tetrahedrals.

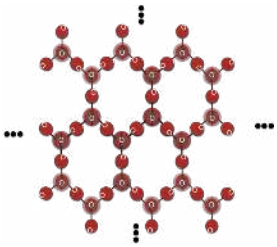


Figure 9: The core of phyllosilicate

The mineral talc is an example of a phyllosilicate complex.

Tectosilicates

Tectosilicates are three-dimensional silicate structures. The core structure of a tectosilicate is an infinite network of connected silica tetrahedrals. (see Figure 10)

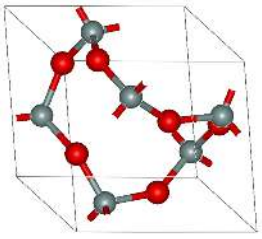


Figure 10: The 3d core of tectosilicate

The mineral quartz is an example of a tectosilicate complex.

Although many silica complexes form network covalent solids, quartz is a particularly good example of a network solid. Silicates in general share the properties of covalent solids, and this affiliated array of properties makes them very useful in modern day

industry.

Silanes

Silanes are silicon-hydrogen compounds. Carbon-hydrogen compounds form the backbone of the living world with seemingly endless chains of hydrocarbons. With the same valence configuration, and thus the same chemical versatility, silicon could conceivably play a role of similar organic importance. But silicon does not play an integral role in our day to day biology. One principal reason underlies this.

Like hydrocarbons, silanes progressively grow in size as additional silicon atoms are added. But there is a very quick end to this trend. The largest silane has a maximum of six silicon atoms (see Figure 11).

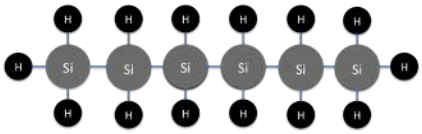


Figure 11: The largest silane, hexasilane

Hexasilane is the largest possible silane because Si-Si bonds are not particularly strong. In fact, silanes are rather prone to decomposition. Silanes are particularly prone to decomposition via reaction with oxygen. Silanes also have a tendency to swap out their hydrogens for other elements and become *organosilanes*. (see Figure 12)

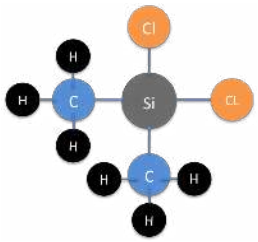


Figure 12: The organosilane, dichlorodimethylsilane

Silanes have a variety of industrial and medical uses. Among other things, silanes are used as water repellents and sealants.

Silicones

Silicones are a synthetic silicon compound; they are not found in nature. When specific silanes are made to undergo a specific reaction, they are turned into silicone, a very special silicon complex. Silicone is a polymer and is prized for its versatility, temperature durability, low volatility, general chemical resistance and thermal stability. Silicone has a unique chemical structure, but it shares some core structural elements with both silicates and silanes. (See Figure 13)

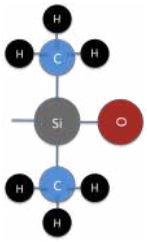


Figure 13: The core unit of a silicone

Silicone polymers are used for a huge array of things. Among numerous other things, breast implants are made out of silicone.

Silicon Halides

Silicon has a tendency to react readily with halogens. The general formula depicting this is SiX_4, where X represents any halogen. Silicon can also expand its valence shell, and the laboratory preparation of $[SiF_6]^{2-}$ is a definitive example of this. However, it is unlikely that silicon could create such a complex with any halogen other than fluorine, because six of the larger halogen ions cannot physically fit around the central silicon atom.

Silicon halides are synthesized to purify silicon complexes. Silicon halides can easily be made to give up their silicon via specific chemical reactions that result in the formation of pure silicon.

Applications

Silicon is a vital component of modern day industry. Its abundance makes it all the more useful. Silicon can be found in products ranging from concrete to computer chips.

Electronics

The high tech sector's adoption of the title Silicon Valley underscores the importance of silicon in modern day technology. *Pure* silicon, that is, essentially pure silicon, has the unique ability of being able to discretely control the number and charge of the current that passes through it. This makes silicon play a role of utmost importance in devices such as transistors, solar cells, integrated circuits, microprocessors, and semiconductor devices, where such current control is a necessity for proper performance. Semiconductors exemplify silicon's use in contemporary technology.

Semiconductors

Semiconductors are unique materials that have neither the electrical conductivity of a conductor nor that of an insulator. Semiconductors lie somewhere in between these two classes, giving them a very useful property. Semiconductors are able to manipulate electric current. They are used to rectify, amplify, and switch electrical signals and are thus integral components of modern day electronics.

Semiconductors can be made out of a variety of materials, but the majority of semiconductors are made out of silicon. But semiconductors are not made out of silicates, or silanes, or silicones; they are made out of *pure* silicon, that is, essentially pure silicon crystal. Like carbon, silicon can make a diamond-like crystal. This structure is called a silicon lattice. (see Figure 15) Silicon is perfect for making this lattice structure because its four valence electrons allow it to perfectly bond to four of its silicon neighbors.

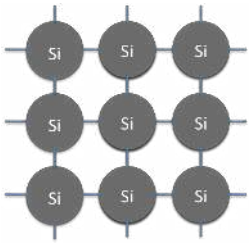


Figure 15: An example of a silicon lattice

However, this silicon lattice is essentially an insulator, as there are no free electrons for any charge movement, and is therefore not a semiconductor. This crystalline structure is turned into a semiconductor when it is doped. Doping refers to a process by which impurities are introduced into ultra-pure silicon, thereby changing its electrical properties and turning it into a semiconductor. Doping turns pure silicon into a semiconductor by adding or removing a very, very small number of electrons, thereby making it neither an insulator nor a conductor, but a semiconductor with limited charge conduction. Subtle manipulation of pure silicon lattices via doping generates the wide variety of semiconductors that modern day electrical technology requires.

Semiconductors are made out of silicon for two fundamental reasons. Silicon has the properties needed to make semiconductors, and silicon is the second most abundant element on earth.

Glasses

Glass is another silicon derivate that is widely utilized by modern day society. If sand, a silica deposit, is mixed with sodium and calcium carbonate at temperatures near 1500 degrees Celsius, when the resulting product cools, glass forms. Glass is a particularly interesting state of silicon. Glass is unique because it represents a solid non-crystalline form of silicon. The tetrahedral silica elements bind together, but in no fundamental pattern behind the bonding. (see Figure 16)

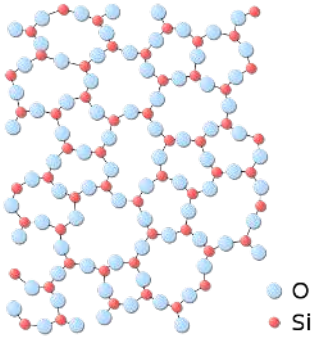


Figure 16: Non-crystalline silica

The end result of this unique chemical structure is the often brittle, typically optically transparent material known as glass. This silica complex can be found virtually anywhere human civilization is found.

Glass can be tainted by adding chemical impurities to the basal silica structure. (see Figure 17) The addition of even a little Fe_2O_3 to pure silica glass gives the resultant mixed glass a distinctive green color.



Figure 17: Non-crystalline silica with unknown impurities

Fiber Optics

Modern fiber optic cables must relay data via undistorted light signals over vast distances. To undertake this task, fiber optic cables must be made of special ultra-high purity glass. The secret behind this ultra-high purity glass is ultra pure silica. To make fiber optic cables meet operational standards, the impurity levels in the silica of these fiber optic cables has been reduced to parts per billion. This level of purity allows for the vast communications network that our society has come to take for granted.

Ceramics

Silicon plays an integral role in the construction industry. Silicon, specifically silica, is a primary ingredient in building components such as bricks, cement, ceramics, and tiles.

Additionally, silicates, especially quartz, are very thermodynamically stable. This translates to silicon ceramics having high heat tolerance. This property makes silicon ceramics particularly useful for things ranging from space ship hulls to engine components. (see Figure 18)



Silica ceramics on the underside of the orbital are used for rentry

Figure 18

Polymers

Silicone polymers represent another facet of silicon's usefulness. They are generally characterized by their flexibility, resistance to chemical attack, impermeability to water, and their ability to retain their properties at both high and low temperatures. This array of properties makes silicone polymers very useful. They are used in insulation, cookware, high temperature lubricants, medical equipment, sealants, adhesives, and even as an alternative to plastic in toys.

Production

As silicon is not normally found in its pure state, it must be chemically extracted from its naturally occurring compounds. The most prevalent form of naturally occurring silicon is silica. Silica is a strongly bonded compound, and it requires a good deal of energy to extract the silicon out of the silica complex. The principal means of extraction is via a chemical reaction at a very high temperature.

The synthesis of silicon is fundamentally a two-step process. First, use a powerful furnace to heat up the silica to temperatures over 1900 degrees celsius, and second, add carbon. At temperatures over 1900 degrees celsius, carbon will reduce the silica compound to pure silicon.

Purification

For some silicon applications, the purity of freshly produced silicon is not satisfactory. To meet the demand for high purity silicon, techniques have been devised to further refine the purity of extracted silicon.

Purification of silicon essentially involves taking synthesized silicon, turning it into a silicon compound that can be easily distilled, and then breaking up this newly formed silicon compound to yield an ultra pure silicon product. There are several distinct purification methods available, but most chemical forms of purification involve both silane and silicon halide complexes.

Trivia

- Silicon is the eighth most abundant element in the universe.
- Silicon was first identified in 1787 but first discovered as an element in 1824.
- Silicon is an important element in the metabolism of plants, but not very important in the metabolism of animals.
- Silicon is harmless to ingest and inject into the body but it is harmful to inhale.
- *Silicosis* is the name of the disease associated with inhaling too much of the silicon compound silica. It primarily afflicts construction workers.
- Silica is a major chemical component of asbestos.

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Problems

Highlight area next to "Ans" to see answer

How many oxides does silicon have, and what are they?

Ans:

How does a silicate tetrahedral balance its charge if not bonded with another silicate?

Ans:

Carbon is to organic compounds as silica is to:

Ans:

How big is the largest silicon-hydrogen compound?

Ans:

Why is silicon important to computers?

Ans:

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7.7.4.1: Silicates

Silicates are some of the most abundant minerals on Earth. They are some of the most common of the raw material that takes over 75% of the Earth's crust. A majority of igneous rocks and sedimentary rocks are made of silicate minerals. The most common type of silicate is $(SiO_4)^{4-}$.

There are many different types of silicates. Most of them have a general chemical formula of $X_xY_y(Z_zO_o)W_w$.

- X = +1 or +2 cations
- Y = +2, +3, or +4 cations
- Z = + 3 or +4 cations
- O = oxygen
- W = usually OH-, F-, or Cl-
- x, y, z, o, w = subscript numbers

Some of the subcategories of silicates are the following:

- Nesosilicates
- Sorosilicates
- Cyclosilicates
- Inosilicates
- Phyllosilicates
- Tectosilicates

Nesosilicates

Nesosilicates are made up of units of independent tetrahedrals. Some of the minerals that contain nesosilicates are olivine, garnet, zircon, kyanite, topaz, and staurolite. Olivine is important in the processes of igneous rock forming. It has a general formula of $(Mg, Fe)_2SiO_4$. Garnet belongs to the isomorphic group, where it often occurs as dodecahedron crystals such as pyrope, almandine, and grossularite. It is usually found in metamorphic rocks, and is known for being the January birthstone. Zircon, on the other hand, is marketed as gemstone and is oxidized to produce gemstones that are similar to diamonds known as cubic zirconia. Kyanite is a part of a polymorphic group (Al_2OSiO_4).

Ex. $\mathbf{(SiO_4)^{-4}}$ **or** $\mathbf{(Si_3O_{12})^{-12}}$

Sorosilicates

Sorosilicate is made up of two tetrahedrals shared by an oxygen. Some of the minerals that are classified as sorosilicates are hemimorphite, epidote, and allanite. Hemimorphite is usually found as bladed crystals. Epidote belongs to the isomorphic group, which is important in forming minerals. Lastly, allanite has a metamict structure that is usually black with no cleavage.

ex. $\mathbf{(Si_2O_7)^{-6}}$

Cyclosilicates

Cyclosilicates are made up of closed ring units of tetrahedrals sharing two oxygen atoms. They are known for their hardness and consist of a variety of gemstones. They also have poor cleavage. Some minerals that are classified as cyclosilicates are beryl, cordierite, and tourmaline. The gemstones that are classified as beryl include emerald (deep green), aquamarine (greenish-blue), and morganite (red). Tourmalines also have a variety of gemstones, which include rubellite (red-pink) and indicolite (dark blue). As for cordierite, it often show dichroism, meaning that it shows different colors at different concentrations.

Ex. $\mathbf{(Si_6O_{18})^{-12}}$

Inosilicates

Inosilicates are made up of continuous double chain units of tetrahedrals, each sharing 2 and 3 oxygens. They include the pyroxene group, which are single chain minerals without hydroxides, and the amphibole group, which are double chains with hydroxides. The pyroxene group has two directional 90 degree cleavages. Some examples are enstatite-ferrosilite, diopside-hedenbergite,

augite, and spodumene. As for the amphibole group, it has two directional cleavages at 124-56 degrees. Some examples are tremolite-actinolite and hornblende. Both of these groups are rock-forming minerals.

Ex. **$(SiO_3)^{-2}$ or $(Si_2O_6)^{-4}$**

Phyllosilicates

Phyllosilicates comprise continuous sheet units of tetrahedrals, each sharing 3 oxygen atoms. They include the clay and mica minerals, which are rock-forming minerals. The clay group is made of hydrous aluminum layered silicates. Some examples are kaolinite and talc. On the other hand, the mica group consists of thin sheets and a multitude of ionic substitutions of Al^{3+} and Si^{4+}. Some examples are muscovite (light color), biotite (black or dark colored), and lepidolite (pink colored and a source of lithium). The serpentine group also belongs to the phyllosilicates. Some examples are serpentine and crysotile.

Ex. **$(Si_2O_5)^{-2}$ or $(Al\ Si_3O_{10})^{-5}$**

Tectosilicates

Tectosilicates consist of a continuous framework of tetrahedrals, each sharing all 4 oxygen atoms. Their structure has a great amount of Al-Si substitution. Some of the groups that are classified as tectosilicates are the SiO_2 polymorphic group, the K-feldspar polymorphic group, the feldspathoid group, and the zeolite group. The SiO_2 polymorphic group has a variety of quartz, such as smoky quartz, amethyst, and jasper. Some minerals in the K-felspar polymorphic group include orthoclase and microcline. Microcline has 1 Pb^{2+} ion replacing every 2 K^{1+} ions, showing an omission solid solution and causing a blue-green color in the mineral. The felspathoid group minerals are similar to feldspars but only have two-thirds of the amount of silica; they form a silica-deficient magma. Some examples are leucite and sodalite. Lastly, the zeolite group has hydrous silicates with ionic exchange and absorption properties that can act as water softeners by exchanging Na^{1+} ions for Ca^{2+} ions in solution. For example:

$$Na_2Al_2Si_3O_{10} - 2H_2O \rightarrow CaAl_2Si_3O_{10} - 2H_2O.$$

Ex. **(SiO_2), $(AlSiO_4)^{-1}$, $(Al_2Si_2O_8)^{-2}$, or $(Al_2Si_4O_{12})^{-2}$**

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7.7.4.2: Silicon and Group 14 Elements

Learning Objectives

- Predict some chemical reactions for a set of conditions.
- Describe some chemical and physical properties of C and Si.

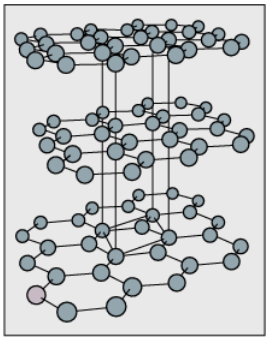
Group 14 Elements C, Si, Ge, Sn, Pb

Group 14 elements play more important roles in our lives and our civilization than elements of any other group. Thus, every educated person should know something about them.

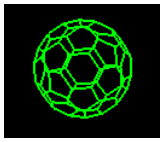
- Carbon - The element of organic chemistry and life.
- Silicon - The element of information technology.
- Germanium - The element of transistor bases.
- Tin and lead - Elements known to alchemists.

Chemistry of Carbon

Carbon exists as diamond, graphite, fullerenes, and charcoal. Their structures are interesting; so are their properties. You probably know a lot about diamond and graphite, but the fullerenes were discovered after 1970, and this discovery has opened a door for a lot of interesting research. Read about them in books, magazines and journals. You might find yourself working with them some day.



Among the fullerenes, one of the most common "molecules" has 60 C atoms, and is represented by C_{60}; a diagram is shown here. If you connect the 60 carbon atoms with bonds, the structure looks like a cage with 5- and 6- member rings. Synthesis, bonding, symmetry and stability of the cagelike fullerenes have already attracted a lot of attention, and their properties are even more fascinating.



Regarding carbon compounds, you already know something about CO_2 and CO, including their roles in the environment. The hard carbides such as Fe_3C, WC, and TiC are more interesting to material scientists and engineers for their application in cutting tools. The calcium carbide CaC_2 produced by reducing CaO by carbon was a valuable commodity at one time due to its reaction with water to give acetylene gas:

$$CaC_2 + 2\,H_2O \rightarrow Ca(OH)_2 + C_2H_{2(g)}$$

Acetylene is an important industrial gas for the manufacture of polymers.

Silicon

Do you know that:

- Si comprises 27.7 % of the Earth's crust?
- silicates, SiO_2 based minerals, are everywhere?
- Si is an essential element for bone growth?
- Si crystals are the bases of computer chips?
- the structure of Si is the same as that of diamond, and this feature is important for computer chips?
- How we convert SiO_2 into Si element?

Silicates

By weight, silicon is the most abundant element in the Earth's crust. It usually exists in the form of an oxide, SiO_2. This formula does not do justice to so many different materials we call silicates, but these substances are indeed SiO_2. Some of the minerals contain impurities.

In pure form, SiO_2 is quartz. Small particles of quartz are sand. They are hard. In the structure at the atomic level, every silicon atom is bonded to 4 oxygen atoms, and every oxygen is bonded to two Si atoms. The four Si—O bonds point towards the corners of a tetrahedron, as do the C—C bonds in the diamond structure. When an impurity is present, the quartz may be colored. Due to various arrangements of the Si—O—Si bonds, the same substance appears in many forms.

A basic unit of silicate structures is SiO_4^{4-}. The gemstone zircon has a formula $ZrSiO_4$, and olivine has a chemical formula of $(MgFe)_2SiO_4$. Two SiO_4^{4-} units combine to give the pyrosilicate unit $Si_2O_7^{6-}$, and it appears in akermanite, $Ca_2MgSi_2O_7$. When the number of units increases, the tetrahedral units combine to form rings, chains, layers and 3-dimensional networks. Thus, the structure and classification of silicate is a major part of minerals. (This site has some interesting pictures.)

Silicon and Silane

Elemental silicon can be obtained from reduction of silicates. The reduction of sand, SiO_2 by carbon at 3300 K in the reaction,

$$SiO_2 + 2\,C \rightarrow Si_{(l)} + 2\,CO \quad \text{at 3300 K}$$

gives liquid silicon. The silicon so obtained is usually not pure, and for the computer industry, the element must be purified. Crystal growth and silicon fabrication dominated the industry in the 1980s and 1990s, and perhaps into the next century, and the production of the element is only the beginning of the process.

If a more reactive element, Mg, is used in the reduction, Mg_2Si is formed,

$$SiO_2 + 4\,Mg \rightarrow Mg_2Si + 2\,MgO$$

Mg_2Si is a compound, and it reacts with water to form silane.

Silane, SiH_4, can be produced by reacting Mg_2Si with acids

$$Mg_2Si + 4\,H_2O \rightarrow 2\,Mg(OH)_2 + SiH_4$$

and SiH_4 is ignited when it contacts air, being much more reactive than methane,

$$SiH_4 + O_2 \rightarrow SiO_2 + H_2O$$

In a basic solution, SiH_4 reacts with water to give $SiO(OH)_3^-$,

$$SiH_4 + OH^- + 3\,H_2O \rightarrow SiO(OH)_3^- + 4\,H_2$$

Silicon Halides

Silicon tetrafluoride is formed when glass (SiO_2) is exposed to HF, and when Si reacts with F_2,

$$SiO_2 + 4\,HF_{(aq)} \rightarrow 2\,H_2O + SiF_{4(g)}$$
$$Si + 2\,F_2 \rightarrow SiF_{4(g)}$$

When chlorine passes through hot sand (SiO_2) and carbon, $SiCl_4$ is produced,

$$SiO_2 + C + 2\,Cl_2 \rightarrow 2\,CO + SiCl_{4(g)}$$

$SiCl_4$ and SiF_4 react with water to give silicic acid,

$$SiCl_4 + 4\,H_2O \rightarrow 4\,HCl + Si(OH)_{4(aq)},$$
$$SiF_4 + 4\,H_2O \rightarrow 4\,HF + Si(OH)_{4(aq)}.$$

Silicone Polymers

Silicones are polymers with the general formula $(R_2SiO_2)_n$ or $(RSiO_3)_n$, (R = CH_3, C_2H_5, C_6H_5, etc). The chain is held together by Si–O–Si bonds. A simple one is $((CH_3)_2SiO_2)_n$,

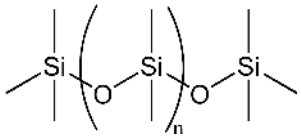


Figure 2: *Chemical structure of the silicone polydimethylsiloxane (PDMS).*

Of course, the 4 bonds around the Si atoms point to the corners of a tetrahedron. These siloxane polymers are widely used as sealants, adhesives, additives, flame retardants, and lubricants. They have a wide application in industries. Depending on the organic group attached to silicon, the inorganic polymer silicones have been an important class of materials.

Questions

1. **Which one lists the group 14 elements in order of increasing atomic weight?**
   a. B Al Ga In Tl
   b. C Si Ge Sn Pb
   c. N P As Sb Bi
   d. O S Se Te Po
   e. F Cl Br I At
2. **Which allotrope of carbon is the hardest: diamond, graphite, or fullerenes?**
3. **What compound of carbon reacts with water to give acetylene gas?**
4. **When you want to extract silicon element, what do you use to reduce the sand: SiO_2, C or Mg?**
5. **Which is stable towards air: methane or silane?**
6. **Give the name of polymers whose chains are held together by Si–O–Si bonds.**
7. **In the crystal structure of Si, how many other Si atoms are connected to a particular Si atom?**

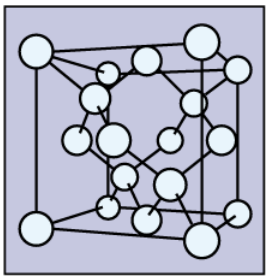
Solutions

1. *Answer* b
   Hint...
   Knowing the groups of elements enables us to correlate their chemical properties. Each list of choices is a group of elements on the period table.
   a = 3A, b = 14, c = 5A, d = 6A, e = 7A.
2. *Answer* diamond
   Hint...
   Diamond is the hardest thing in the world. Fullerenes are large molecules consisting of 40 to hundreds of carbon atoms, with C_{60} being the most common.
3. *Answer* . . .CaC_2
   Hint...
   The reaction to produce acetylene gas is

   $$CaC_2 + H_2O \rightarrow C_2H_2 + Ca(OH)_2$$

   Acetylene is still an important industrial gas, as raw material for polymers.

4. *Answer* ...**C**
   Hint...
   Carbon or coke is used for silicon metal, because Mg_2Si is formed if **Mg** is used.
5. *Answer* ... methane is stable
   Hint...
   Methane is the major component of natural gas, and it will not react with air until ignited, whereas silane ignites explosively as soon as it contacts air.
6. *Answer* ...silicones
   Hint...
   Silicon polymers are an important class of materials invented not too long ago.
7. *Answer* ... 4
   Hint...
   Silicon and diamond have the same crystal structure. The edge of unit cells of **Si** is larger than that of diamond.



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7.7.5: Chemistry of Germanium (Z=32)

Germanium, categorized as a metalloid in group 14, the carbon family, has five naturally occurring isotopes. Germanium, abundant in the Earth's crust, has been said to improve the immune system of cancer patients. It is also used in transistors, but its most important use is in fiber-optic systems and infrared optics.

Introduction

The metalloid was one of the elements predicted by Mendeleev in 1871 (ekasilicon) to fill out his periodic table and was discovered in 1886 by Winkler. In a mine near Freiberg, Saxony, a new mineral was found in 1885. First the mineral was called argyrodite, but later, when Clemens Winkler examined this mineral he discovered that it was similar to antimony. At first he wanted to name it neptunium, but because this name was already taken he named it germanium in honor of his fatherland Germany.

The position of where germanium should be placed on the periodic table was under discussion during the time due to its similarities to arsenic and antimony. Due to Mendeleev's prediction of ekasilicon, germanium's place on the periodic table was confirmed because of the similar properties predicted and similar properties deduced from examining the mineral.



Figure **7.7.5.1**: polycrystalline germanium. (CC BY 3.0; Jurii via Wikipedia)

Characteristics

Like silicon, germanium is used in the manufacture of semi-conductor devices. Unlike silicon, it is rather rare (only about 1 part in 10 million parts in the earth's crust). The physical and chemical properties of germanium closely parallel those of silicon. Germanium (Ge) has an atomic number of 32. It is grayish-white, lustrous, hard, and has similar chemical properties to tin and silicon. Germanium is brittle and silvery-white under standard conditions. Under these conditions, germanium is known as α-

germanium, which has a diamond cubic crystal structure. When germanium is under pressure above 120 kilobars, it has a different allotrope known as *β-germanium*. Germanium is one of the few substances like water that expands when it solidifies.

Atomic Number:	32
Atomic Symbol:	Ge
Atomic Weight:	72.59
Atomic Radius:	122.5 pm
Series:	Metalloid
Group:	14
Density:	5.353 g/cm^3
Specific Heat:	0.32J/gK
Electronic Configuration:	[Ar] 4s^{2}3d^{10}4p^2
Melting Point:	938.25 C
Boiling Point:	2833 C
Common Oxidation States:	4,2

Germanium, a semiconductor, is the first metallic metal to become a superconductor in the presence of a strong electromagnetic field.

Isotopes

The five naturally occurring isotopes of germanium have atomic masses of 70, 72, 73, 74, and 76. Germanium 76 is slightly radioactive and is the least common. Germanium 74 is the most common isotope, having the greatest natural abundance of the five. When it is bombarded with alpha particles, Germanium 72 generates stable Se 77.

Chemical Properties

At a temperature of 250 °C, germanium slowly oxidizes to GeO_2. Germanium dissolves slowly in concentrated sulfuric acid, and is insoluble in diluted acids and alkalis. It will react violently with molten alkalis to produce $[GeO_3]^{2-}$. The common oxidation states of germanium are +4 and +2. Under rare conditions, germanium also occurs in oxidation states of +3, +1, and -4.

There are two forms of germanium oxides: germanium dioxide (GeO_2) and germanium monoxide (GeO). By roasting germanium sulfide, germanium dioxide can be obtained. As for germanium monoxide, it can be obtained by the high temperature reaction of germanium dioxide and germanium metal. Germanium dioxide has the unusual property of a refractive index for light but transparency to infrared light.

Applications and Uses

Like silicon, germanium is used in the manufacture of semi-conductor devices. Unlike silicon, it is rather rare (only about 1 part in 10 million parts in the earth's crust). Although it forms a compound, germanium dioxide, just like silicon, it is generally extracted from the by-products of zinc refining.

Germanium is used mainly for fiber-optic systems and infrared optics. It is also used for polymerization catalysts, electronics, and as phosphors, for metallurgy, and for chemotherapy. Because germanium dioxide has a high index of refraction and low optical dispersion, it is useful for wide-angle camera lenses. As stated before, it is an important semi-conductor, so it is used in transistors.

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7.7.6: Chemistry of Tin (Z=50)

Mentioned in the Hebrew scriptures, tin is of ancient origins. Tin is an element in Group 14 (the carbon family) and has mainly metallic properties. Tin has atomic number 50 and an atomic mass of 118.710 atomic mass units.

Introduction

Mentioned in the Hebrew scriptures, tin is of ancient origins. Early metal smiths were quick to learn that mixing copper with tin created a more durable metal (bronze), and it is principally for its alloys that tin is valued today. Named after the Etruscan god Tinia, the chemical symbol for tin is taken from the Latin *stannum*. The metal is silvery white and very soft when pure. It has the look of freshly cut aluminum, but the feel of lead.

Polished tin is slightly bluish. It has been used for many years in the coating of steel cans for food because it is more resistant to corrosion than iron. It forms a number of useful low-melting alloys (solders) which are used to connect electrical circuits. Bending a bar of tin produces a characteristic squealing sound called "tin cry". Tin shares chemical similarities with germanium and lead. Tin mining began in Australia in 1872, and today tin is used extensively in industry and commerce.

Table 1: Basic Properties of tin

Color	white with blueish tinge
Hardness	softer than gold, harder than lead
Atomic Radius	140 pm
Density	$5.77 g/cm^3$
Melting Point	232 degrees Celsius
Boiling Point	2623 degrees Celsius
Electrical Conductivity	about 1/7th that of silver
Electrode Potential	>0.192V
First Ionization Energy	709 kJ/mol
Ionic Radius	93 pm

Reactions of Tin

Hydrogen	Tin not affected
Nitrogen	Tin absorbs it instead of hydrogen in electric discharge
Argon	No sign of a combination of tin with argon
Fluorine	Does not react with tin at low temperatures, but at 100 degrees Celsius they form stannic fluoride. Perhaps one of the most familiar of tin compounds, SnF_2, tin(II) fluoride, goes by the trade name of *fluoristan* and is found in some fluoride toothpastes.
Chlorine	Acts on tin at room temperature
Bromine	Acts on tin at room temperature
Sulfur	Unites directly with tin when heated
Selenium	Reacts vigorously with tin
Tellurium	Reacts vigorously with tin
Nitrogen	Forms a compound by direct union with tin
Arsenic	Reacts with tin under heat and light
Antimony	Is dissolved by molten tin

Reaction of tin with oxygen

When heated in oxygen, tin produces stannic oxide:

$$Sn_{(s)} + O_{2(g)} \rightarrow SnO_{2(s)}$$

Reaction of tin with water (steam)

$$Sn_{(s)} + 2H_2O_{(g)} \rightarrow SnO_{2(s)} + 2H_{2(g)}$$

Isotopes

There are 10 known stable isotopes of tin, the most of any elements on the periodic table. This high number of stable isotopes could be attributed to the fact that the atomic number of $^{50}\mathrm{Sn}$ is a 'magic number' in nuclear physics.

Table 4: Isotopes of tin

Isotope	% Natural Abundance
112 amu	0.95%
116 amu	14.24%
117 amu	7.57%
118 amu	24.01%
119 amu	8.58%
120 amu	32.97%
122 amu	4.71%
124 amu	5.98%

Allotropes of Tin

Tin has 3 allotropes: alpha, beta and gamma tin. Alpha tin is the most unstable form. Beta tin is the most commonly found allotrope of tin, and gamma tin only exists at very high temperatures.

Oxidation States of Tin

Tin, although it is found in Group 14 of the periodic table, is consistent with the trend found in Group 13, where the lower oxidation state is favored farther down a group. Tin can exist in two oxidation states, +2 and +4, but it displays a tendency to exist in the +4 oxidation state.

Common Compounds of Tin

Tin forms two main oxides, SnO and SnO_2 (amphoteric).

Electron Configuration of Tin

Tin has a ground state electron configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^2$ and can form covalent tin (II) compounds with its two unpaired p-electrons. In the three dimensional figure below, the first and most inner electron shell is represented by blue electrons, the second electron shell made up of eight electrons is represented by red electrons, the third shell containing eighteen electrons is represented with green electrons, and the next outer shell again contains eighteen electrons and is represented in purple.

Uses of Tin

Early metal smiths were quick to learn that mixing copper with tin created a more durable metal (bronze) and it is principally for its alloys that tin is valued today. Nearly half of the tin metal produced is used in solders, which are low melting point alloys used to join wires. Solders are important in electrician work and plumbing. Tin is also used as a coating for lead, zinc, and steel to prevent corrosion. Tin cans are widely used for storing foods; the first tin can was used in London in 1812.

Questions

Find the oxidation state of tin in the following compounds:

a. $SnCl^2$ Answer:2

b. SnO^2 Answer:4

Write an equation for the reaction of tin with water. Under what conditions does this reaction take place?

Answer: $Sn(s) + 2H_2O(g) \rightarrow SnO_2(s) + 2H_2(g)$ Reaction takes place if water is heated to a high temperature to form steam.

Which of these reactions take place?

a. tin with oxygen Answer: YES

b. tin with hydrogen Answer: NO

c. tin with argon Answer: NO

d. tin with chlorine Answer: YES

Arrange the following in order of increasing atomic radius: Sn, K, Ag, C, Pb.

Answer: C<Sn<Pb<Ag<K

Arrange the following in order of decreasing ionization energy: Sn, Si, Pb, I, In.

Answer: Si> I > Sn > In > Pb

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7.7.7: Chemistry of Lead (Z=82)

Known to the ancients, lead takes its name from the Anglo-Saxon word for the metal, and its symbol comes from the Latin plumbum (from which we get the modern word "plumber" since old plumbing was done with lead pipes).

Although lead is not very common in the earth's crust, what is there is readily available and easy to refine. Its chief use today is in lead-acid storage batteries such as those used in automobiles. In pure form it is too soft to be used for much else. Lead has a blue-white color when first cut but quickly dulls on exposure to air, forming Pb_2O, one of the few lead(I) compounds. Most stable lead compounds contain lead in oxidation states of +2 or +4.

Various isotopes of lead come at the end of the natural decay series of elements like uranium, thorium and actinium. These are Pb-206, Pb-207 and Pb-208.

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7.7.7.1: Lead Plumbate

Lead plumbate, also called red lead, minium or Mennige (in German), is a mineral showing colors from light red to brown/yellow tints. As a pure chemical it shows a vivid red. Minium is rare and occurs in lead mineral deposits that have been subjected to severe oxidizing conditions. It also occurs as a result of mine fires. It is most often associated with galena, cerussite, massicot, litharge, native lead, wulfenite and mimetite.

Lead plumbate is obtained by heating lead monoxide (PbO) to 450-480°C in air:

$$3PbO + 1/2O_2 \rightarrow Pb_3O_4$$

or by oxidative annealing of lead white:

$$3Pb_2CO_3(OH)_2 + O_2 \rightarrow 2Pb_3O_4 + 3CO_2 + 3H_2O$$

Lead plumbate decomposes into lead monoxide and oxygen above 550°C.

Pb_3O_4 can be seen formally as a lead(II)plumbate(IV), $Pb_2[PbO_4]$, or $2PbO \cdot PbO_2$. In nitric acid, the lead(II) oxide reacts forming lead nitrate, while the insoluble lead(IV) oxide is left unchanged:

$$Pb_3O_4 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O$$

Lead plumbate is virtually insoluble in water. However, it dissolves in hydrochloric acid (which is present in the stomach), and is therefore toxic when ingested. Lead plumbate (in a mixture with linseed oil or other organic adhesives) has been used as an anti-corrosion paint for iron. It forms insoluble iron(II) and iron(III) plumbates when brought into contact with iron oxides and with elementary iron. However, its use as a protective undercoat paint is limited due to its toxicity.

Lead plumbate was used as a red pigment in ancient and medieval periods for paintings and the production of illuminated manuscripts (the term miniature is connected to the name of the substance).

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SECTION OVERVIEW

7.8: The Nitrogen Family

The nitrogen family includes the following compounds: nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb), and bismuth (Bi). All Group 15 elements have the electron configuration ns^2np^3 in their outer shell, where n is the principal quantum number.

7.8.1: General Properties and Reactions

7.8.1.1: Nitrogen Group (Group 5) Trends

7.8.2: Chemistry of Nitrogen (Z=7)

7.8.3: Chemistry of Phosphorus (Z=15)

7.8.4: Chemistry of Antimony (Z=51)

7.8.5: Chemistry of Bismuth (Z=83)

7.8.6: Chemistry of Moscovium (Z=115)

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7.8.1: General Properties and Reactions

The nitrogen family includes the following compounds: nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb), and bismuth (Bi). All Group 15 elements have the electron configuration ns^2np^3 in their outer shell, where n is equal to the principal quantum number. The nitrogen family is located in the p-block in Group 15.

Periodic Trends

All Group 15 elements tend to follow the general periodic trends:

- Electronegativity (the atom's ability to attract electrons) decreases down the group.
- Ionization energy (the amount of energy required to remove an electron from the atom in its gas phase) decreases down the group.
- Atomic radii increase in size down the group.
- Electron affinity (the ability of the atom to accept an electron) decreases down the group.
- Melting point (amount of energy required to break bonds to change a solid phase substance to a liquid phase substance) increases down the group.
- Boiling point (amount of energy required to break bonds to change a liquid phase substance to a gas) increases down the group.
- Metallic character increases down the group.

Properties of Group 15 Elements

Element/Symbol	Atomic Number	Mass	Electron Configuration	Covalent Radius (pm)	Electronegativity	First Ionizaton Energy (kJ/mol)	Common Physical Form(s)
Nitrogen (N)	7	14.01	$1s^2\ 2s^2\ 2p^3$	75	3.0	1402	Colorless Gas
Phosphorus (P)	15	30.97	$[Ne]3s^2\ 3p^3$	110	2.1	1012	White Solid / Red Solid
Arsenic (As)	33	74.92	$[Ar]\ 3d^{10}\ 4s^2\ 4p^3$	121	2.0	947	Yellow Solid / Gray Solid
Antimony (Sb)	51	121.76	$[Kr]\ 4d^{10}\ 5s^2\ 5p^3$	140	1.9	834	Yellow Solid / Silver-White Metallic Solid
Bismuth (Bi)	83	208.98	$[Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^3$	155	1.9	703	Pink-White Metallic Solid

Nitrogen

Nitrogen was discovered in 1770 by Scheele and Priestley. This nonmetallic element has no color, taste, or odor, and is present in nature as a noncombustible gas. When compared with the rest of Group 15, nitrogen has the highest electronegativity, which makes it the most nonmetallic of the group. The common oxidation states of nitrogen are +5, +3, and -3. Nitrogen makes up about 0.002% of the earth's crust; however, it constitutes 78% of the earth's atmosphere by volume. Nitrogen has also been discovered in the atmospheres of Venus and Mars. Venus has a 3.5% nitrogen volume in its atmosphere and Mars has a 2.7% nitrogen volume in its atmosphere. Nitrogen is found naturally in animal and plant proteins and in fossilized remains of ancient plant life. Important nitrogen-containing minerals are niter, KNO_3, and soda niter, $NaNO_3$, which are found in desert regions and are important components of fertilizers. Before the process of converting nitrogen into ammonia was discovered, sources of nitrogen were limited. One of the processes of converting nitrogen to ammonia, the Haber-Bosch process, is very important for the production of nitrogen. Nitrogen has very little solubility in liquids. N_2 does not have any allotropes.

The unusually stable $N_2(g)$ nitrogen gas is the source from which all nitrogen compounds are ultimately derived. $N_2(g)$ is stable due to its electronic structure: the bond between the two nitrogen atoms of N_2 is a triple covalent bond, which is strong and hard to

break. The enthalpy change associated with breaking the bonds in N_2 is highly endothermic: ΔH = +945.4 kJ. Nitrogen gas is used as a refrigerant, metal treatment, and pressurized gas for oil recovery. Additionally, the Gibbs energies of formation of nitrogen compounds show that their formations are nonspontaneous, and the following process does not occur at normal temperatures:

$$1/2N_{2(g)} + 1/2O_2 \rightarrow NO_{(g)}$$

with

$$\Delta G_f = +86.55\ kJ\,mol^{-1}$$

The oxides and oxyacids of nitrogen include nitrous oxide (N_2O), nitrogen oxide (NO), and nitrogen dioxide (NO_2). Nitrous oxide, also called “laughing gas,” is used in dental work, child birth, and to increase the speed of cars. Nitrogen oxide is found in smog and neurotransmitters. Hydrazine, N_2H_4, is a poisonous, colorless liquid that explodes in air. Hydrazine is a good reducing agent, and methyl hydrazine is commonly used as a rocket fuel.

Phosphorus

Phosphorus is a nonmetallic element. The most common oxidation state of phosphorus is -3. Phosphorus is the eleventh most abundant element, making up 0.11% of the earth's crust. The main source of phosphorus compounds is phosphorus rocks. Phosphorous is not found pure in nature, but in the form of apatite ores. These include compounds such as fluorapatite ($Ca_5(PO_4)_3F$), which in fluoridated water is used to strengthen teeth, and hydroxylapatite ($Ca_{10}(OH)_2(PO_4)_6$), a major component of tooth enamel and bone material. Phosphorus exhibits allotropic forms: the most common forms at room temperature are white phosphorus and red phosphorus. White phosphorus is a white, waxy solid that can be cut with a knife. It forms a tetrahedral molecule, P_4. White phosphorus is toxic, while red phosphorus is nontoxic. Red phosphorous forms when white phosphorous is heated to 573 Kelvin and not exposed to air. Red phosphorus is less reactive than white phosphorus. Red phosphorus has a chain-like polymeric structure, and is more stable. Both white and red phosphorus are incendiary and have been used to make match tips, although the use of white phosphorus has been largely discontinued due to toxicity. Phosphorus has many applications: phosphorus trichloride (PCl_3) is used in soaps, detergents, plastics, synthetic rubber nylon, motor oils, insecticides and herbicides; phosphoric acid, H_3PO_4, is used in fertilizers; phosphorus is also prevalent in the food industry, used in baking powders, instant cereals, cheese, the curing of ham, and in the tartness of soft drinks.

Arsenic

Arsenic is a highly poisonous metalloid. Because it is a metalloid, arsenic has a high density, moderate thermal conductivity, and a limited ability to conduct electricity. The oxidation states of arsenic are +5, +3, +2, +1, and -3. The three allotropic forms of arsenic are yellow, black, and gray; the gray allotrope is the most common. Compounds of arsenic are used in insecticides, weed killers, and alloys. The oxide of arsenic is *amphoteric*, meaning it can act as both an acid and a base. Arsenic is mainly obtained by heating arsenic-containing sulfides. The chemical formula for this process is given below:

$$FeAsS_{(s)} \rightarrow FeS_{(s)} + As_{(g)}$$

The $As_{(g)}$ deposits as $As_{(s)}$, which can then be used to make other compounds. Arsenic can also be obtained by the reduction of arsenic(III) oxide with $CO_{(g)}$.

Antimony

Antimony is also a metalloid. The oxidation states of antimony are +3, -3, and +5. Antimony exhibits allotropy; the most stable allotrope is the metallic form, which is similar in properties to arsenic: high density, moderate thermal conductivity, and a limited ability to conduct electricity. The oxide of antimony is antimony (III) oxide, which is amphoteric, meaning it can act as both an acid and a base. Antimony is obtained mainly from its sulfide ores, and it vaporizes at low temperatures. Along with arsenic, antimony is commonly used in alloys. Arsenic, antimony, and lead form an alloy with desirable properties for electrodes in lead-acid batteries. Arsenic and antimony are also used to produce semiconductor materials such as GaAs, GaSb, and InSb in electronic devices.

Bismuth

Bismuth is a metallic element. The oxidation states of bismuth are +3 and +5. Bismuth is a poor metal (one with significant covalent character) that is similar to both arsenic and antimony. Bismuth is commonly used in cosmetic products and medicine. Out of the group, bismuth has the lowest electronegativity and ionization energy, which means that it is more likely to lose an electron than the rest of the Group 15 elements. This is why bismuth is the most metallic of Group 15. Bismuth is also a poor electrical conductor. The oxide of bismuth is bismuth(III) oxide; it acts as a base, as expected for a metal oxide. Bismuth is obtained as a by-product of the refining of other metals, allowing other metals to recycle their by-products into bismuth.

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Problems

1. How much of the earth's crust is made up of nitrogen?
2. How much of earth's crust is not made up of phosphorus?
3. What kind of bond does N_2 have?
4. How are red phosphorus and white phosphorus related to each other?
5. What is the electron configuration of arsenic?
6. Does bismuth have metallic properties or nonmetallic properties?
7. True or False: nitrogen and phosphorus are metals.
8. Which Group 15 element has the greatest atomic radius?
9. Which Group 15 element is the strongest reducing agent?
10. True or False: bismuth exhibits the most metallic character.
11. What is the most common physical form of nitrogen?
12. What is the process in which nitrogen can convert into ammonia?
13. Which element has the highest first ionization energy?
14. Complete and balance the following reaction: $\_N_2(g) + \_H_2(g) \rightarrow$ ____
15. What is the common oxidation state of all Group 15 elements?

Answers

1. 0.002% of the earth's crust is made up of nitrogen.
2. The earth's crust is made up of 0.11% phosphorus, so 99.89% of the earth's crust is not made up of phosphorus.
3. N_2 has a triple covalent bond that is strong and hard to break.
4. Red phosphorus and white phosphorus are both allotropes of phosphorus. Red phosphorus comes from white phosphorus when it is heated to about 573 Kelvin.
5. [Ar] $3d^{10}\ 4s^2\ 4p^3$
6. Bismuth has metallic properties.
7. False; both nitrogen and phosphorus are nonmetals.
8. According to periodic trends, bismuth has the greatest atomic radius.
9. According to periodic trends, bismuth is the strongest reducing agent since it has an electronegativity value of 1.9, which is the same as antimony, but it has a lower ionization energy of 703 kJ/mol, which means it is more likely to get oxidized.
10. True; bismuth is the only metallic element of Group 15.
11. The most common physical form of nitrogen is a colorless gas.
12. The process of converting nitrogen into ammonia is known as the Haber-Bosch process.
13. According to periodic trends, nitrogen would have the highest first ionization energy, which means that it does not want to lose an electron the most.
14. $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

15. The common oxidation state for all Group 15 elements is -3.

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7.8.1.1: Nitrogen Group (Group 5) Trends

Summary of Nitrogen Group (Group VA) Trends:

1. The hydrides become less thermally stable and more reactive down the column. The M-H and M-CH3 mean bond enthalpies decrease in strength down the group and consequently the hydrides and alkyls become less stable.

2. The majority of nitrogen compounds are covalent. The main exceptions being those based on the nitride ion.

3. Multiple bond formation:

- Nitrogen forms very strong multiple p_{π}-p_{π} bonds to itself and neighboring elements belonging to the same row, *e.g.*, CN^-, N_2, NO^+. Compounds of P, As, and Bi with multiple bonds may be obtained if large groups are introduced into the molecules, *e.g.*, P_2R_2 and As_2R_2. Similar multiply bonded compounds of Sb are not known.

4. Coordination numbers:

- The coordination numbers increase down the group. For nitrogen, 3 and 4 coordination predominate. Phosphorous and arsenic in addition form octahedral complexes, and higher coordination numbers are observed for Sb and Bi.

5. Increased metallic character

- The elements become increasingly metallic down the column in their chemical and physical properties. Down the group the oxo cations, *e.g.*, SbO^+ and BiO^+, become more prevalent.

6. The oxides become more basic down the column.

- Phosphorous and arsenic oxides are acidic, antimony oxide is amphoteric, and that of bismuth is basic.

7. The halides become more ionic and increasingly adopt infinite structures in preference to molecular ones.

8. Catenation occurs in the order: N < P > As > Sb > Bi. Phosphorous forms a wide range of ring and cage compounds because of the favorable P-P bond enthalpy.

9. Negative oxidation states:

- For nitrogen the N^{3-} ion is well established in the ionic nitrides of the electropositive elements. The anionic derivatives of the heavier elements frequently retain element-element bonds, *e.g.*, Sb_4^{2-}, Bi_4^{2-}, Sb_7^{3-}, and As_{11}^{3-}.

10. The donor/acceptor behavior of R3M:

- Donor/Lewis base ability: N < P > As > Sb > Bi
- Steric effects: N > P ~ As > Sb > Bi and increase with bulk of substituents: $PR_3 > PR_2H > PRH_2 > PH_3$
- π-acidity: $R_3P > R_3As > R_3Sb > R_3Bi$
- Lewis acidity of the +5 fluorides: $PF_5 > AsF_5 > SbF_5$

11. Hydrolysis of halides:

- In the +5 oxidation state, PF_5 is not readily hydrolyzed, AsF_5 hydrolyses, SbF_5 reacts vigorously with water. BiF_5 reacts explosively with water. In the +3 oxidation state, NF_3 is unreactive, PF_3 reacts only with OH^- not OH_2, AsF_3 and SbF_3 are soluble in water, and BiF_3 is insoluble in water but soluble in inorganic acids.

12. Stabilization of the +3 oxidation state relative to +5 oxidation state. The trend is less well defined than that of group IVa and in fact an alternation in stabilities is observed. This may be illustrated by the following halide stabilities:

	N	P	As	Sb	Bi
EF_5	unknown	stable	stable	stable	stable
ECl_5	unknown	stable	known but unstable	stable	unknown
EBr_5	unknown	stable	unknown	stable	unknown
EI_5	unknown	stable	unknown	stable	unknown
EF_3	stable	stable	stable	stable	stable
ECl_3	known but unstable	stable	stable	stable	stable
EBr_3	known but unstable	stable	stable	stable	stable
EI_3	known but unstable	stable	stable	stable	stable

- The + 5 oxidation state halides are unknown for N, well defined for P, only stable for As as fluoride, well defined for the fluoride and chloride of antimony, and only known for the fluoride for Bi.
- For both oxidation states the stability order is F > Cl . Br >I as anticipated by the ordering of the mean enthalpies, *i.e.,* fluoride forms the strongest bonds and iodine the weakest.
- The oxides show a similar trend. Bi^V and N^V oxides and oxoacids are strongly oxidizing, whereas P^V oxides and oxoacids are very stable and As^V and Sb^V oxides and oxoacids are mildly oxidizing.

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7.8.2: Chemistry of Nitrogen (Z=7)

Nitrogen is present in almost all proteins and plays important roles in both biochemical applications and industrial applications. Nitrogen forms strong bonds because of its ability to form a triple bond with itself and other elements. Thus, there is a lot of energy in the compounds of nitrogen. Before 100 years ago, little was known about nitrogen. Now, nitrogen is commonly used to preserve food and as a fertilizer.

Introduction

Nitrogen is found to have either 3 or 5 valence electrons and lies at the top of Group 15 on the periodic table. It can have either 3 or 5 valence electrons because it can bond in the outer 2p and 2s orbitals. Molecular nitrogen (N_2) is not reactive at standard temperature and pressure and is a colorless and odorless gas.

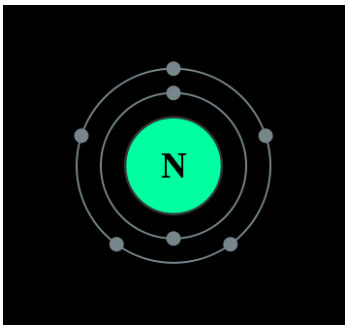


Figure **7.8.2.1 :** *A Bohr diagram of the nitrogen atom.*

Nitrogen is a non-metal element that occurs most abundantly in the atmosphere; nitrogen gas (N_2) comprises 78.1% of the volume of the Earth's air. It only appears in 0.002% of the earth's crust by mass. Compounds of nitrogen are found in foods, explosives, poisons, and fertilizers. Nitrogen is found in DNA in the form of nitrogenous bases as well as in neurotransmitters. It is one of the most produced industrial gases, and is produced commercially as a gas and a liquid.

Table 1: General Properties of Nitrogen

Name and Symbol	Nitrogen, N
Category	non-metal
Atomic Weight	14.0067
Group	15
Electron Configuration	$1s^2\ 2s^2\ 2p^3$
Valence Electrons	2, 5
Phase	Gas

History

Nitrogen, which makes up about 78% of our atmosphere, is a colorless, odorless, tasteless and chemically unreactive gas at room temperature. Its name is derived from the Greek nitron + genes for soda forming. For many years during the 1500's and 1600's, scientists hinted that there was another gas in the atmosphere besides carbon dioxide and oxygen. It was not until the 1700's that scientists could prove there was in fact another gas that took up mass in the atmosphere of the Earth.

Nitrogen was discovered in 1772 by Daniel Rutherford (and independently by others such as Priestly and Cavendish); Rutherford was able to remove oxygen and carbon dioxide from a contained tube full of air. He showed that there was residual gas that did not support combustion as did oxygen or carbon dioxide. While his experiment was the one that proved that nitrogen existed, other experiments were also going on in London, where they called the substance "burnt" or "dephlogisticated air".

Nitrogen is the fourth most abundant element in humans, and it is more abundant in the known universe than carbon or silicon. Most commercially produced nitrogen gas is recovered from liquefied air. Of that amount, the majority is used to manufacture ammonia (NH_3) via the Haber process. Much is also converted to nitric acid (HNO_3).

Isotopes

Nitrogen has two naturally occurring isotopes, **nitrogen-14** and **nitrogen-15,** which can be separated with chemical exchanges or thermal diffusion. Nitrogen also has isotopes with masses of 12, 13, 16, and 17, but they are radioactive.

- **Nitrogen 14** is the most abundant form of nitrogen and makes up more than 99% of all nitrogen found on Earth. It is a stable compound and is non-radioactive. Nitrogen-14 has the most practical uses, and is found in agricultural practices, food preservation, biochemicals, and biomedical research. It is found in abundance in the atmosphere and among many living organisms. It has 5 valence electrons and is not a good electrical conductor.
- **Nitrogen-15** is the other stable form of nitrogen. It is often used in medical research and preservation. The element is non-radioactive and therefore can also be sometimes used in agricultural practices. Nitrogen-15 is also used in brain research, specifically nuclear magnetic resonance spectroscopy (NMR), because unlike nitrogen-14 (nuclear spin of 1), it has a nuclear spin of 1/2, which has benefits when it comes to MRI research and NMR observations. Lastly, nitrogen-15 can be used as a label or in some proteins in biology. Scientists mainly use this compound for research purposes and have not yet seen its full potential for uses in brain research.

Compounds

The two most common compounds of nitrogen are potassium nitrate (KNO_3) and sodium nitrate ($NaNO_3$). These two compounds are formed by decomposing organic matter that has potassium or sodium present and are often found in fertilizers and byproducts of industrial waste. Most nitrogen compounds have a positive Gibbs free energy (i.e., reactions are not spontaneous).

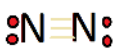


Figure **7.8.2.2** *: Lewis Dot structure of molecular nitrogen*

The dinitrogen molecule (N_2) is an "unusually stable" compound, particularly because nitrogen forms a triple bond with itself. This triple bond is difficult to break. For dinitrogen to follow the octet rule, it must have a triple bond. Nitrogen has a total of 5 valence electrons, so doubling that, we would have a total of 10 valence electrons with two nitrogen atoms. The octet requires an atom to have 8 total electrons in order to have a full valence shell, therefore it needs to have a triple bond. The compound is also very inert, since it has a triple bond. Triple bonds are very hard to break, so they keep their full valence shell instead of reacting with other compounds or atoms. Think of it this way: each triple bond is like a rubber band; with three rubber bands, the nitrogen atoms are very attracted to each other.

Nitrides

Nitrides are compounds of nitrogen with a less electronegative atom; in other words they are compounds with atoms that have a less full valence shell. These compounds form with lithium and Group 2 metals. Nitrides usually have an oxidation state of -3.

$$3Mg + N_2 \rightarrow Mg_3N_2 \tag{7.8.2.1}$$

When mixed with water, nitride will form ammonia; the nitride ion acts as a very strong base.

$$N^{3-} + 3H_2O_{(l)} \rightarrow NH_3 + 3OH^-_{(aq)} \tag{7.8.2.2}$$

When nitrogen forms compounds with other atoms, it primarily forms covalent bonds. These are normally formed with other metals and look like: MN, M_3N, and M_4N. These compounds are typically hard, inert, and have high melting points because of nitrogen's ability to form triple covalent bonds.

Ammonium Ions

Nitrogen goes through fixation by reaction with hydrogen gas over a catalyst. This process is used to produce ammonia. As mentioned earlier, this process allows us to use nitrogen as a fertilizer because it breaks down the strong triple bond held by N_2.

The famous Haber-Bosch process for synthesis of ammonia looks like this:

$$N_2 + 3H_2 \rightarrow 2NH_3 \tag{7.8.2.3}$$

Ammonia is a base and is also used in typical acid-base reactions.

$$2NH_{3(aq)} + H_2SO_4 \rightarrow (NH_4)_2SO_{4(aq)} \tag{7.8.2.4}$$

Nitride ions are very strong bases, especially in aqueous solutions.

Oxides of Nitrogen

Nitrogen uses a variety of different oxidation numbers from +1 to +5 for oxide compounds. Almost all the oxides that form are gasses, and exist at 25 degrees Celsius. Oxides of nitrogen are acidic and easily attach protons.

$$N_2O_5 + H_2O \rightarrow 2HNO_{3(aq)} \tag{7.8.2.5}$$

The oxides play a large role in living organisms. They can be useful, yet dangerous.

- Dinitrogen monoxide (N_2O) is an anesthetic used by dentists, also known as laughing gas.
- Nitrogen dioxide (NO_2) is harmful. It binds to hemoglobin molecules, not allowing the molecule to release oxygen throughout the body. It is released from cars and is very toxic.
- Nitrate (NO_3^-) is a polyatomic ion.
- The more unstable nitrogen oxides allow for space travel.

Hydrides

Hydrides of nitrogen include ammonia (NH_3) and hydrazine (N_2H_4).

- In aqueous solution, ammonia forms the ammonium ion, which we described above, and it has special amphiprotic properties.
- Hydrazine is commonly used as rocket fuel.

Applications of Nitrogen

- Nitrogen provides a blanketing for our atmosphere and is used for the production of chemicals and electronic compartments.
- Nitrogen is used as fertilizer in agriculture to promote growth.
- Pressurized gas for oil production.
- Refrigerant (such as freezing food fast).
- Explosives.
- Metal treatment/protectant via exposure to nitrogen instead of oxygen.

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Problems

- Complete and balance the following equations

  N_2 + ___H_2 → ___NH_

  $H_2N_2O_2$ → ?

  $2NH_3 + CO_2$ → ?

  __Mg + N_2 → Mg_N_

  $N_2H_5 + H_2O$ → ?

- What are the different isotopes of nitrogen?
- List the oxidation states of various nitrogen oxides: N_2O, NO, N_2O_3, N_2O_4, N_2O_5

- List the different elements that nitrogen will react with to make it basic or acidic....
- List some uses of nitrogen

Answers

- Complete and balance the following equations

  $N_2 + 3H_2 \rightarrow 2NH_3$(Haber process)

  $H_2N_2O_2 \rightarrow 2HNO$

  $2NH_3 + CO_2 \rightarrow (NH_2)_2CO + H_2O$

  $2Mg + 3N_2 \rightarrow Mg_3N_2$

  $N_2H_5 + H_2O \rightarrow N_2 + H^+ + H_2O$

- What are the different isotopes of nitrogen?

  Stable forms include nitrogen-14 and nitrogen-15.

- List the oxidation states of various nitrogen oxides: +1, +2, +3, +4, +5 respectively.
- List the different elements that nitrogen will react with to make it basic or acidic :Nitride ion is a strong base when reacted with water; ammonia is generally a weak acid.
- Uses of nitrogen include anesthetic, refrigerant, and metal protector.

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7.8.3: Chemistry of Phosphorus (Z=15)

Learning Objectives

- Compare properties of Group 15 elements.
- Explain the major application of phosphate.
- Describe the equilibria of the ionization of phosphoric acid.

Phosphorus (P) is an essential part of life as we know it. Without the phosphates in biological molecules such as ATP, ADP and DNA, we would not be alive. Phosphorus compounds can also be found in the minerals in our bones and teeth. It is a necessary part of our diet. In fact, we consume it in nearly all of the foods we eat. Phosphorus is quite reactive. This quality of the element makes it an ideal ingredient for matches because it is so flammable. Phosphorus is a vital element for plants and that is why we put phosphates in our fertilizer to help them maximize their growth.

Introduction

Phosphorus plays a big role in our existence but it can also be dangerous. When fertilizers containing phosphorus enter the water, it produces rapid algae growth. This can lead to eutrophication of lakes and rivers; i.e., the ecosystem has an increase of chemical nutrients and this can led to negative environmental effects. With all the excess phosphorus, plants grow rapidly then die, causing a lack of oxygen in the water and an overall reduction of water quality. It is thus necessary to remove excess phosphorus from our wastewater. The process of removing the phosphorus is done chemically by reacting the phosphorus with compounds such as ferric chloride, ferric sulfate, and aluminum sulfate or aluminum chlorohydrate. Phosphorus, when combined with aluminum or iron, becomes an insoluble salt. The solubility equilibrium constants of $FePO_4$ and $AlPO_4$ are 1.3×10^{-22} and 5.8×10^{-19}, respectively. With solubilitys this low, the resulting precipitates can then be filtered out.



Figure 1. Phosphates can lead to excessive algae growth, which can be undesirable

Another example of the dangers of phosphorus is in the production of matches. The flammable nature and cheap manufacturing of white phosphorus made it possible to easily make matches around the turn of the 20th century. However, white phosphorus is highly toxic. Many workers in match factories developed brain damage and a disease called "phosphorus necrosis of the jaw" from exposure to toxic phosphorus vapors. Excess phosphorus accumulation caused their bone tissue to die and rot away. For this reason, we now use red phosphorus or phosphorus sesquisulfide in "safety" matches.

Discovery of Phosphorus

Named from the Greek word phosphoros ("bringer of light"), elemental phosphorus is not found in its elemental form because this form is quite reactive. Because of this factor it took a long period of time for it to be "discovered". The first recorded isolation of phosphorus was by alchemist Hennig Brand in 1669, involving about 60 pails of urine. After letting a large amount of urine putrefy for a long time, Brand distilled the liquid to a paste, heated the paste, discarded the salt formed, and put the remaining substance under cold water to form solid white phosphorus. Brand's process was not very efficient; the salt he discarded actually contained most of the phosphorus. Nevertheless, he obtained some pure, elemental phosphorus for his efforts. Others of the time improved the efficiency of the process by adding sand, but still continued to discard the salt. Later, phosphorus was manufactured from bone ash. Currently, the process for manufacturing phosphorus does not involve large amounts of putrefied urine or bone ash. Instead, manufacturers use calcium phosphate and coke (Emsley).

Allotropes of Phosphorus

Phosphorus is a nonmetal, solid at room temperature, and a poor conductor of heat and electricity. Phosphorus occurs in at least 10 allotropic forms, the most common (and reactive) of which is so-called white (or yellow) phosphorus, which looks like a waxy

solid or plastic. It is very reactive and will spontaneously inflame in air, so it is stored under water. The other common form of phosphorus is red phosphorus, which is much less reactive and is one of the components on the striking surface of a match book. Red phosphorus can be converted to white phosphorus by careful heating.

White phosphorus consists of $\mathbf{P_4}$ molecules, whereas the crystal structure of red phosphorus has a complicated network of bonding. White phosphorus has to be stored in water to prevent natural combustion, but red phosphorus is stable in air.



Figure 2: The four common allotropes of phosphorus. from Wikipedia.

When burned, red phosphorus also forms the same oxides as those obtained in the burning of white phosphosrus, $\mathbf{P_4O_6}$ when air supply is limited, and $\mathbf{P_4O_{10}}$ when sufficient air is present.

Diphosphorus (P_2)

Diphosphorus ($\boldsymbol{P_2}$) is the gaseous form of phosphorus that is thermodynamically stable above 1200 °C and until 2000 °C. It can be generated by heating white phosphorus (see below) to 1100 K and is very reactive with a bond-dissociation energy (117 kcal/mol or 490 kJ/mol) half that of dinitrogen ($\boldsymbol{N_2}$).

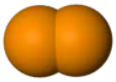


Figure 2: Diphosphorus molecule. (CC-SA-BY 3.0; Wikipedia)

White Phosphorus (P_4)

White phosphorus (P_4) has a tetrahedral structure. It is soft and waxy, but insoluble in water. Its glow occurs as a result of its vapors slowly being oxidized by the air. It is so thermodynamically unstable that it combusts in air. It was once used in fireworks and the U.S. military still uses it in incendiary bombs.

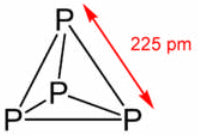


Figure 3: Structure of white phosphorus. (CC-SA-BY 3.0; Wikipedia)

This Youtube video link shows various experiments with white phosphorus, which help show the physical and chemical properties of it. It also shows white phosphorus combusting with air.

Red Phosphorus and Violet Phosphorus (Polymeric)

Red Phosphorus has more atoms linked together in a network than white phosphorus does, which makes it much more stable. It is not quite as flammable, but given enough energy it still reacts with air. For this reason, we now use red phosphorus in matches.



Figure 4: red phosphorus is in safety matches. (CC-SA-BY 3.0; Wikipedia)

Violet phosphorus is obtained from heating and crystallizing red phosphorus in a certain way. The phosphorus forms pentagonal "tubes".

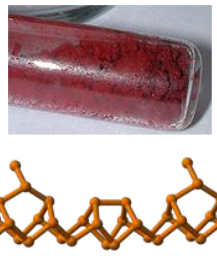


Figure 5. Structure of Violet Phosphorus. (CC-SA-BY 3.0; Wikipedia)

Black Phosphorus (Polymeric)

Black phosphorus is the most stable form; the atoms are linked together in puckered sheets, like graphite. Because of these structural similarities black phosphorus is also flaky like graphite and possesses other similar properties.

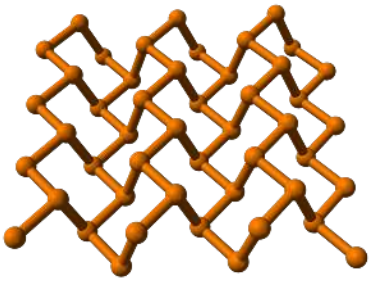


Figure 6. Ball-and-stick model of a sheet of phosphorus atoms in black phosphorus. (CC-SA-BY 3.0; Wikipedia)

Isotopes of Phosphorus

There are many isotopes of phosphorus, only one of which is stable (^{31}P). The rest of the isotopes are radioactive with generally very short half-lives, which vary from a few nanoseconds to a few seconds. Two of the radioactive phosphorus isotopes have longer half-lives: ^{32}P has a half-life of 14 days and ^{33}P has a half-life of 25 days. These half-lives are long enough to be useful for analysis, and for this reason the isotopes can be used to mark DNA.

^{32}P played an important role in the 1952 Hershey-Chase Experiment. In this experiment, Alfred Hershey and Martha Chase used radioactive isotopes of phosphorus and sulfur to determine that DNA was genetic material and not proteins. Sulfur can be found in proteins but not DNA, and phosphorus can be found in DNA but not proteins. This made phosphorus and sulfur effective markers of DNA and protein, respectively. The experiment was set up as follows: Hershey and Chase grew one sample of a virus in the presence of radioactive ^{35}S and another sample of a virus in the presence of ^{32}P. Then, they allowed both samples to infect bacteria. They blended the ^{35}S and the ^{32}P samples separately and centrifuged the two samples. Centrifuging separated the genetic material from the non-genetic material. The genetic material penetrated the solid that contained the bacterial cells at the bottom of the tube while the non-genetic material remained in the liquid. By analyzing their radioactive markers, Hershey and Chase found that the ^{32}P remained with the bacteria, and the ^{35}S remained in the supernatant liquid. These results were confirmed by further tests involving the radioactive phosphorus..

Phosphorus and Life

We get most elements from nature in the form of minerals. In nature, phosphorus exists in the form of phosphates. Rocks containing phosphate are fluoroapatite ($3\,Ca_3(PO_4)_2 \cdot CaF_2$), chloroapaptite, ($3\,Ca_3(PO_4)_2 \cdot CaCl_2$), and hydroxyapatite ($3\,Ca_3(PO_4)_2 \cdot Ca(OH)_2$). These minerals are very similar to the bones and teeth. The arrangements of atoms and ions of bones and teeth are similar to those of the phosphate-containing rocks. In fact, when the OH^- ions of the teeth are replaced by F^-, the teeth resist decay. This discovery led to a series of social and economical issues.

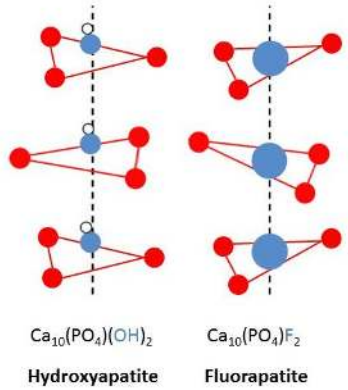


Figure 6: (left) Fluoride ions (F^-) replace hydroxyl groups (OH^-) in hydroxyapatite to form fluorapatite in the tooth enamel. (right) A portion of the apatite crystal lattice is depicted showing the replacement of hydroxide by fluoride (big blue circles). (Public Domain; Delmar Larsen).

Nitrogen, phosphorus and potassium are key ingredients for plants, and their contents are key in all forms of fertilizers. From an industrial and economical viewpoint, phosphorus-containing compounds are important commodities. Thus, the chemistry of phosphorus has academic, commercial and industrial interests.

Chemistry of Phosphorus

As a member of the Nitrogen Family, Group 15 on the Periodic Table, phosphorus has 5 valence shell electrons available for bonding. Its valence shell configuration is $3s^2 3p^3$. Phosphorus forms mostly covalent bonds. Any phosphorus rock can be used for the production of elemental phosphorus. Crushed phosphate rocks and sand (SiO_2) react at 1700 K to give phosphorus oxide, P_4O_{10}:

$$2\,Ca_3(PO_4)_2 + 6\,SiO_2 \rightarrow P_4O_{10} + 6\,CaSiO_3 \tag{7.8.3.1}$$

P_4O_{10} can be reduced by carbon:

$$P_4O_{10} + 10\,C \rightarrow P_4 + 10\,CO. \tag{7.8.3.2}$$

Waxy solids of white phosphorus are molecular crystals consisting of P_4 molecules. They have an interesting property in that they undergo spontaneous combustion in air:

$$P_4 + 5\,O_2 \rightarrow P_4O_{10} \tag{7.8.3.3}$$

The structure of P_4 can be understood by thinking of the electronic configuration ($s^2\ p^3$) of P in bond formation. Sharing three electrons with other P atoms gives rise to the 6 P–P bonds, leaving a lone pair occupying the 4th position in a distorted tetrahedron.

When burned with insufficient oxygen, P_4O_6 is formed:

$$P_4 + 3\,O_2 \rightarrow P_4O_6 \tag{7.8.3.4}$$

Into each of the P–P bonds, an O atom is inserted.

Burning phosphorus with excess oxygen results in the formation of P_4O_{10}. An additional O atom is attached to the P directly:

$$P_4 + 5\,O_2 \rightarrow P_4O_{10} \tag{7.8.3.5}$$

Thus, the oxides P_4O_6 and P_4O_{10} share interesting features. Oxides of phosphorus, P_4O_{10}, dissolve in water to give phosphoric acid,

$$P_4O_{10} + 6\,H_2O \rightarrow 4\,H_3PO_4 \tag{7.8.3.6}$$

Phosphoric acid is a polyprotic acid, and it ionizes in three stages:

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \tag{7.8.3.7}$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \tag{7.8.3.8}$$

$$HPO_4^{2-} \rightarrow H^+ + PO_4^{3-} \quad (7.8.3.9)$$

Phosphoric Acid

Phosphoric acid is a polyprotic acid, which makes it an ideal buffer. It gets harder and harder to separate the hydrogen from the phosphate, making the pK_a values increase in basicity: 2.12, 7.21, and 12.67. The conjugate bases $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} can be mixed to form buffer solutions.

Table 1: Ionization constants for the successive deprotonation of phosphoric acid states

Reaction	Dissociation Constant
$H_3PO_4 + H_2O \rightarrow H_3O^+ + H_2PO^{4-}$	$K_{a1}=7.5x10^{-3}$
$H_2PO_4^- + H_2O \rightarrow H_3O^+ + HPO_4^{2-}$	$K_{a2}=6.2x10^{-8}$
$H_2PO_4^- + H_2O \rightarrow H_3O^+ + PO_4^{3-}$	$K_{a3}=2.14x10^{-13}$
Overall: $H_3PO_4 + 3H_2O \rightarrow 3H_3O^+ + PO_4^{3-}$	

Past and Present Uses of Phosphorus

Commercially, phosphorus compounds are used in the manufacture of phosphoric acid (H_3PO_4) (found in soft drinks and used in fertilizer compounding). Other compounds find applications in fireworks and, of course, phosphorescent compounds which glow in the dark. Phosphorus compounds are currently used in foods, toothpaste, baking soda, matches, pesticides, nerve gases, and fertilizers. Phosphoric acid is not only used in buffer solutions; it is also a key ingredient of Coca Cola and other sodas! Phosphorus compounds were once used in detergents as a water softener until they raised concerns about pollution and eutrophication. Pure phosphorus was once prescribed as a medicine and an aphrodisiac until doctors realized it was poisonous (Emsley).

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2. Emsley, John. The 13th Element: The Sordid Tale of Murder, Fire, and Phosphorus. John Wiley and Sons, Inc. 2000.
3. Corbridge, D.E.C. The Structural Chemistry of Phosphorus. Elsevier Scientific Publishing Company. 1974.

Questions

1. About 85% of the total industrial output of phosphoric acid is used
   a. in the detergent industry
   b. to produce buffer solutions
   c. in the paint industry
   d. to produce superphosphate fertilizers
   e. in the manufacture of plastics
2. What is the product when phosphorus pentoxide P_4O_{10} reacts with water? Give the formula of the product.
3. What is the phosphorus-containing product when PCl_3 reacts with water? Give the formula.

Solutions

1. *Answer...* d

   The middle number, (for example, 6-5-8) specifies the percentage of phosphorus compound in a fertilizer. Phosphorus is an important element for plant life.

2. *Answer* H_3PO_4

$$P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$$

3. *Answer* H_3PO_3

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

   This is a weaker acid than H_3PO_4.

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7.8.4: Chemistry of Antimony (Z=51)

Antimony and its compounds have been known for centuries. Scientific study of the element began during the early 17th century, much of the important work being done by Nicolas Lemery. The name of the element comes from the Greek anti + monos for "not alone", while the modern symbol is rooted in the Latin-derived name of the common ore, stibnite. Antimony is a hard, brittle metalloid which is alloyed with other metals to increase hardness. It is also used in some semi-conductor devices. The recovery of elemental antimony parallels that of arsenic: the sulfide ore (stibnite) is roasted in air and then heated with carbon.

Antimony trisulfide

Antimony trisulfide, Sb_2S_3, is a sulfide mineral commonly called *stibnite* or *antimonite*. Antimony trisulfide exists as a gray/black crystalline solid (orthorhombic crystals) and an amorphous red-orange powder. It turns black due to oxidation by air. Antimony trisulfide is the most important source for antimony. It is insoluble in water and melts at 550°C. The chemical symbol of antimony (Sb) is derived from stibnite.

Amorphous (red to yellow-orange) antimony trisulfide can be prepared by treating an antimony trichloride solution with hydrogen sulfide:

$$2SbCl_3 + 3H_2S \rightarrow Sb_2S_3 + 6HCl$$

When antimony trisulfide is melted with iron at approximately 600°C, the following reaction yields elementary antimony:

$$Sb_2S_3 + 3Fe \rightarrow 2Sb + 3FeS$$

Sb_2S_3 is used as a pigment, in pyrotechnics (glitter and fountain mixtures) and on safety matches. In combination with antimony oxides it is also used as a yellow pigment in glass and porcelain. Antimony trisulfide photoconductors are used in vidicons for CCTV.

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7.8.5: Chemistry of Bismuth (Z=83)

Bismuth, the heaviest non-radioactive naturally occurring element, was isolated by Basil Valentine in 1450. It is a hard, brittle metal with an unusually low melting point (271°C). Alloys of bismuth with other low-melting metals such as tin and lead have even lower melting points and are used in electrical solders, fuse elements and automatic fire sprinkler heads.

The metal can be found in nature, often combined with copper or lead ores, but can also be extracted from bismuth(III) oxide by roasting with carbon. Compounds of bismuth are used in pigments for oil paintings and one is in a popular pink preparation for the treatment of common stomach upset.

Contributors and Attributions

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7.8.6: Chemistry of Moscovium (Z=115)

In studies announced jointly by the Joint Institute for Nuclear Research in Dubna, Russia, and the Lawrence Livermore National Laboratory in the U.S., four atoms of element 113 were produced in 2004 via decay of element 115 after the fusion of Ca-48 and Am-243.

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SECTION OVERVIEW

7.9: The Oxygen Family (The Chalcogens)

The oxygen family, also called the chalcogens, consists of the elements found in Group 16 of the periodic table and is considered among the main group elements. It consists of the elements oxygen, sulfur, selenium, tellurium and polonium. These can be found in nature in both free and combined states.

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7.9.1: General Properties and Reactions

The oxygen family, also called the chalcogens, consists of the elements found in Group 16 of the periodic table and is considered among the main group elements. It consists of the elements oxygen, sulfur, selenium, tellurium and polonium. These can be found in nature in both free and combined states. The group 16 elements are intimately related to life. We need oxygen all the time throughout our lives. Did you know that sulfur is also one of the essential elements of life? It is responsible for some of the protein structures in all living organisms. Many industries utilize sulfur, but emission of sulfur compounds is often seen more as a problem than the natural phenomenon. The metallic properties of Group 16 elements increase as the atomic number increases. The element polonium has no stable isotopes, and the isotope with mass number 209 has the longest half life of 103 years.

Properties and Periodic Trends

Properties of oxygen are very different from those of other elements of the group, but they all have 2 elections in the outer s orbital, and 4 electrons in the p orbitals, usually written as s^2p^4.

The electron configurations for each element are given below:

- **Oxygen**: $1s^2\ 2s^2\ 2p^4$
- **Sulfur**: $1s^2\ 2s^2p^6\ 3s^2p^4$
- **Selenium**: $1s^2\ 2s^2p^6\ 3s^2p^6d^{10}\ 4s^2p^4$
- **Tellurium**: $1s^2\ 2s^2p^6\ 3s^2p^6d^{10}\ 4s^2p^6d^{10}\ 5s^2p^4$
- **Polonium**: $1s^2\ 2s^2p^6\ 3s^2p^6d^{10}\ 4s^2p^6d^{10}f^{14}\ 5s^2p^6d^{10}\ 6s^2p^4$

Example 7.9.1.1: Polonium

Polonium can be written as [Xe] $6s^2\ 4f^{14}\ 5d^{10}\ 6p^4$

The trends of the properties in this group are interesting. Knowing the trend allows us to predict their reactions with other elements. Most trends are true for all groups of elements, and the group trends are due mostly to the size of the atoms and number of electrons per atom. The trends are described below:

1. The metallic properties increase in the order oxygen, sulfur, selenium, tellurium, or polonium. Polonium is essentially a metal. It was discovered by M. Curie, who named it after her native country Poland.
2. Electronegativity, ionization energy (or ionization potential IP), and electron affinity decrease for the group as atomic weight increases.
3. The atomic radii and melting points increase.
4. Oxygen differs from sulfur in chemical properties due to its small size. The differences between O and S are more than the differences between other members.

Metallic character increases down the group, with tellurium classified as a metalloid and polonium as a metal. Melting point, boiling point, density, atomic radius, and ionic radius all increase down the group. Ionization energy decreases down the group. The most common oxidation state is -2; however, sulfur can also exist at a +4 and +6 state, and +2, +4, and +6 oxidation states are possible for Se, Te, and Po.

Table **7.9.1.1**: Select properties of Group 16 elements

	Oxygen	Sulfur	Selenium	Tellurium	Polonium
Boiling Pt (°C)	-182.962	444.674	685	989.9	962
Ionization Energy (kJ/mol)	1314	1000	941	869	812
Ionic Radius (pm)	140	184	198	221	

Oxygen

Oxygen is a gas at room temperature and 1 atm, and is colorless, odorless, and tasteless. It is the most abundant element by mass in both the Earth's crust and the human body. It is second to nitrogen as the most abundant element in the atmosphere. There are many commercial uses for oxygen gas, which is typically obtained through fractional distillation. It is used in the manufacture of iron, steel, and other chemicals. It is also used in water treatment, as an oxidizer in rocket fuel, for medicinal purposes, and in petroleum refining.

Oxygen has two **allotropes**, O_2 and O_3. In general, O_2 (or dioxygen) is the form referred to when talking about the elemental or molecular form because it is the most common form of the element. The O_2 bond is very strong, and oxygen can also form strong bonds with other elements. However, compounds that contain oxygen are considered to be more thermodynamically stable than O_2.

The latter allotrope, ozone, is a pale-blue poisonous gas with a strong odor. It is a very good oxidizing agent, stronger than dioxygen, and can be used as a substitute for chlorine in purifying drinking water without giving the water an odd taste. However, because of its unstable nature it disappears and leaves the water unprotected from bacteria. Ozone at very high altitudes in the atmosphere is responsible for protecting the Earth's surface from ultraviolet radiation; however, at lower altitudes it becomes a major component of smog.

Oxygen's primary oxidation states are -2, -1, 0, and -1/2 (in O_2^-), but **-2** is the most common. Typically, compounds with oxygen in this oxidation state are called **oxides**. When oxygen reacts with metals, it forms oxides that are mostly ionic in nature. These can dissolve in water and react to form hydroxides; they are therefore called **basic anhydrides** or **basic oxides**. Nonmetal oxides, which form covalent bonds, are simple molecules with low melting and boiling points.

Compounds with oxygen in an oxidation state of -1 are referred to as *peroxides*. Examples of this type of compound include Na_2O_2 and BaO_2. When oxygen has an oxidation state of -1/2, as in O_2^-, the compound is called a *superoxide*.

Oxygen is rarely the central atom in a structure and can never bond with more than 4 elements due to its small size and its inability to create an expanded valence shell. Oxygen reacts with hydrogen to form water, which is extensively hydrogen-bonded, has a large dipole moment, and is considered a universal solvent.

There are a wide variety of oxygen-containing compounds, both organic and inorganic: oxides, peroxides and superoxides, alcohols, phenols, ethers, and carbonyl-containing compounds such as aldehydes, ketones, esters, amides, carbonates, carbamates, carboxylic acids and anhydrides.

Sulfur

Sulfur is a solid at room temperature and 1 atm pressure. It is usually yellow, tasteless, and nearly odorless. It is the sixteenth most abundant element in Earth's crust. It exists naturally in a variety of forms, including elemental sulfur, sulfides, sulfates, and organosulfur compounds. Since the 1890s, sulfur has been mined using the Frasch process, which is useful for recovering sulfur from deposits that are under water or quicksand. Sulfur produced from this process is used in a variety of ways including in vulcanizing rubber and as fungicide to protect grapes and strawberries.

Sulfur is unique in its ability to form a wide range of allotropes, more than any other element in the periodic table. The most common state is the solid S_8 ring, as this is the most thermodynamically stable form at room temperature. Sulfur exists in the gaseous form in five different forms (S, S_2, S_4, S_6, and S_8). In order for sulfur to convert between these compounds, sufficient heat must be supplied.

Two common oxides of sulfur are sulfur dioxide (SO_2) and sulfur trioxide (SO_3). Sulfur dioxide is formed when sulfur is combusted in air, producing a toxic gas with a strong odor. These two compounds are used in the production of sulfuric acid, which is used in a variety of reactions. Sulfuric acid is one of the top manufactured chemicals in the United States, and is primarily used in the manufacture of fertilizers.

Sulfur also exhibits a wide range of oxidation states, with values ranging from -2 to +6. It is often the central ion in a compound and can easily bond with up to 6 atoms. In the presence of hydrogen it forms the compound hydrogen sulfide, H_2S, a poisonous gas incapable of forming hydrogen bonds and with a very small dipole moment. Hydrogen sulfide can easily be recognized by its strong odor that is similar to that of rotten eggs, but this smell can only be detected at low, nontoxic concentrations. This reaction

with hydrogen epitomizes how differently oxygen and sulfur act despite their common valence electron configuration and common nonmetallic properties.

A variety of sulfur-containing compounds exist, many of them organic. The prefix *thio-* in front of the name of an oxygen-containing compound means that the oxygen atom has been substituted with a sulfur atom. General categories of sulfur-containing compounds include thiols (mercaptans), thiophenols, organic sulfides (thioethers), disulfides, thiocarbonyls, thioesters, sulfoxides, sulfonyls, sulfamides, sulfonic acids, sulfonates, and sulfates.

Selenium

Selenium appears as a red or black amorphous solid, or a red or grey crystalline structure; the latter is the most stable. Selenium has properties very similar to those of sulfur; however, it is more metallic, though it is still classified as a nonmetal. It acts as a semiconductor and therefore is often used in the manufacture of rectifiers, which are devices that convert alternating currents to direct currents. Selenium is also photoconductive, which means that in the presence of light the electrical conductivity of selenium increases. It is also used in the drums of laser printers and copiers. In addition, it has found increased use now that lead has been removed from plumbing brasses.

It is rare to find selenium in its elemental form in nature; it must typically be removed through a refining process, usually involving copper. It is often found in soils and in plant tissues that have bioaccumulated the element. In large doses, the element is toxic; however, many animals require it as an essential micronutrient. Selenium atoms are found in the enzyme glutathione peroxidase, which destroys lipid-damaging peroxides. In the human body it is an essential cofactor in maintaining the function of the thyroid gland. In addition, some research has shown a correlation between selenium-deficient soils and an increased risk of contracting the HIV/AIDS virus.

Tellurium

Tellurium is the metalloid of the oxygen family, with a silvery white color and a metallic luster similar to that of tin at room temperature. Like selenium, it is also displays photoconductivity. Tellurium is an extremely rare element, and is most commonly found as a telluride of gold. It is often used in metallurgy in combination with copper, lead, and iron. In addition, it is used in solar panels and memory chips for computers. It is not toxic or carcinogenic; however, when humans are exposed to too much of it they develop a garlic-like smell on their breaths.

Polonium

Polonium is a very rare, radioactive metal. There are 33 different isotopes of the element and all of the isotopes are radioactive. It exists in a variety of states, and has two metallic allotropes. It dissolves easily into dilute acids. Polonium does not exist in nature in compounds, but it can form synthetic compounds in the laboratory. It is used as an alloy with beryllium to act as a neutron source for nuclear weapons.

Polonium is a highly toxic element. The radiation it emits makes it very dangerous to handle. It can be immediately lethal when applied at the correct dosage, or cause cancer if chronic exposure to the radiation occurs. Methods to treat humans who have been contaminated with polonium are still being researched, and it has been shown that chelation agents could possibly be used to decontaminate humans.

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Problems

1. What properties increase down the oxygen family?
2. What element can form the most allotropes in the periodic table?
3. What is photoconductivity and which elements display this property?
4. Ozone (O_3) is a contributor to smog: True or False
5. How many electrons do elements of the oxygen family have in their outermost shell?
6. What does the term "peroxide" refer to?
7. How many elements in the oxygen family are metals, and which one(s)?
8. What is the most common oxidation state for elements in the oxygen family?
9. What is the most abundant element by mass in the Earth's crust and in the human body?

Solutions

1. Melting point, boiling point, density, atomic radius, and ionic radius.
2. Sulfur.
3. Photoconductivity is when the electrical conductivity of an element increases in the presence of light. Both selenium and tellurium display this property.
4. True.
5. Six.
6. A compound that contains oxygen in the oxidation state of -1.
7. 1; Polonium.
8. -2.
9. Oxygen.

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7.9.1.1: Oxygen Group (Group VIA) Trends

Summary of Oxygen Group (Group VIA) Trends:

1. The elements become progressively more metallic down the column. Polonium has chemical and physical properties of a metal and tellurium is borderline.

2. Chemically the metallic character of the heavier elements is reflected in their increased tendency to form cationic species, the ionic character and basicities of their oxides, and their increased tendency to form complexes.

3. The non-metal character of the earlier members of the Group is the molecular nature of the stable elemental allotrophs, the ability to form anions, e.g. O2- and S2-, which result from completing the octet. Compounds resulting from these anions, e.g. Na2E, CaE (E = O, S, Se ..) become progressively more covalent down the Group as a result of the decreasing electronegativiety of the chalcogens (group VIA).

4. The thermal stabilities of the hydrides EH2 decrease down the column primarily because of the decreasing EH mean bond enthalpies.

5. The abilities of these hydrides to form hydrogen bonds decreases rapidly down the Group after oxygen and this has a dramatic effect on the boiling and melting points of the hydrides.

6. The formation of molecular compounds with strong multiple bonds is particularly important for oxygen which forms strong pπ-pπ bonds, e.g. CO, dπ-pπ bonds with transition metals, e.g. OsO4, “allow” main group compounds to achieve hypervalency, e.g. R3PO, and even fπ-pπ bonding, e.g. UO22+. Multiple bonding is less significant for the heavier elements, although sulfur and selenium provide some examples, e.g. selenoketones, R3PS, and R3PSe.

7. The increasing size of the atoms leads to compounds with progressively larger maximum coordination numbers (coordinative unsaturation). Oxygen usually has a coordination number of 2 or 3 with a few examples of 4 coordination, sulfur exhibits a maximum coordination number of 6, and higher coordination numbers of 8 have been observed for Te.

   These maximum coordination numbers have an impact on the case of hydrolysis of the halides, *e.g.* the rate of hydrolysis is: $TeF_6 > SeF_6 > SF_6$

   Also, the octahedral anionic complexes $[MX_6]^{2-}$ (X = halide) are more commonly observed for Se, Te, and Po.

8. Oxygen has a strong preference for the -2 formal oxidation state, whereas the heavier elements exhibit oxidation states of 2, 4, and 6. The alternation in oxidation state stability effect is observed far more in Group VIa than Group Va.

9. The tendency towards catenation reaches a maximum at sulfur, which forms a wide range of ring and chain compounds, e.g. Sn, XSnX, [O3S(Sn)SO3]2-,and S82+.

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7.9.2: Chemistry of Oxygen (Z=8)

Oxygen is an element that is widely known by the general public because of the large role it plays in sustaining life. Without oxygen, animals would be unable to breathe and would consequently die. Oxygen not only is important to supporting life, but also plays an important role in many other chemical reactions. Oxygen is the most common element in the earth's crust and makes up about 20% of the air we breathe. Historically the discovery of oxygen as an element essential for combustion stands at the heart of the phlogiston controversy (see below).

The Origin and History

Oxygen is found in the group 16 elements and is considered a chalcogen. Named from the Greek oxys + genes, "acid-former", oxygen was discovered in 1772 by Scheele and independently by Priestly in 1774. Oxygen was given its name by the French scientist, Antoine Lavoisier.

Scheele discovered oxygen through an experiment which involved burning manganese oxide. Scheele came to find that the hot manganese oxide produced a gas which he called "fire air". He also came to find that when this gas was able to come into contact with charcoal, it produced beautiful bright sparks. All of the other elements produced the same gas. Although Scheele discovered oxygen, he did not publish his work until three years after another chemist, Joseph Priestly, discovered oxygen. Joseph Priestly, an English chemist, repeated Scheele's experiment in 1774 using a slightly different setup. Priestly used a 12 in burning glass and aimed the sunlight directly towards the compound that he was testing, mercuric oxide. As a result, he was able to "discover better air" that was shown to expand a mouse's lifetime to four times as long and caused a flame to burn with higher intensity. Despite these experiments, both chemists were not able to pinpoint exactly what this element was. It was not until 1775 that Antoine Lavoisier, a French chemist, was able to recognize this unknown gas as an element.

Our atmosphere currently contains about 21% of free oxygen. Oxygen is produced in various ways. The process of photochemical dissociation in which water molecules are broken up by ultraviolet rays produces about 1-2% of our oxygen. Another process that produces oxygen is photosynthesis which is performed by plants and photosynthetic bacteria. Photosynthesis occurs through the following general reaction:

$$CO_2 + H_2O + h\nu \rightarrow \text{organic compounds} + O_2$$

The Dangers of Phlogiston

Phlogiston theory is the outdated belief that a fire-like element called phlogiston is contained within combustible bodies and released during combustion. The name comes from the Ancient Greek φλογιστόν phlogistón (burning up), from φλόξ phlóx (flame). It was first stated in 1667 by Johann Joachim Becher, and then put together more formally by Georg Ernst Stahl. The theory attempted to explain burning processes such as combustion and rusting, which are now collectively known as oxidation.

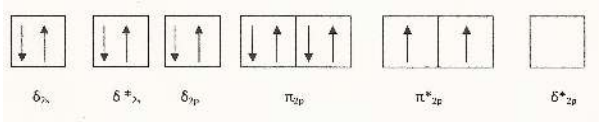
Properties

- Element number: 8
- Atomic weight 15.9994
- Color: gas form- colorless, liquid- pale blue
- Melting point: 54.36K
- Boiling point: 90.2 K
- Density: .001429
- 21% of earth's atmosphere
- Third most abundant element in the universe
- Most abundant element in Earth's crust at 45.4%
- 3 Stable isotopes
- Ionization energy: 13.618 eV
- Oxygen is easily reduced and is a great oxidizing agent making it readily reactive with other elements



Magnetic Properties of Oxygen

Oxygen (O_2) is paramagnetic. An oxygen molecule has six valence electrons, so the O_2 molecule has 12 valence electrons with the electron configuration shown below:



As shown, there are two unpaired electrons, which causes O_2 to be paramagnetic. There are also eight valence electrons in the bonding orbitals and four in antibonding orbitals, which makes the bond order 2. This accounts for the double covalent bond that is present in O_2.



Video* 7.9.2.1*: *A chemical demonstration of the paramagnetism of molecular oxygen, as shown by the attraction of liquid oxygen to magnets.*

As shown in Video **7.9.2.1**, since molecular oxygen (***O_2***) has unpaired electrons, it is paramagnetic and is attracted to the magnet. In contrast, molecular nitrogen (***N_2***) has no unpaired electrons and is not attracted to the magnet.

General Chemistry of Oxygen

Oxygen normally has an oxidation state of -2, but is capable of having oxidation states of -2, -1, -1/2, 0, +1, and +2. The oxidation states of oxides, peroxides and superoxides are as follows:

- Oxides: O^{-2} ,

- peroxides: O_2^{-2} ,
- superoxide: O_2^{-1}.

Oxygen does not react with itself, nitrogen, or water under normal conditions. Oxygen does, however, dissolve in water at 20 degrees Celsius and 1 atmosphere. Oxygen also does not normally react with bases or acids. Group 1 metals (alkaline metals) are very reactive with oxygen and must be stored away from oxygen in order to prevent them from becoming oxidized. The metals at the bottom of the group are more reactive than those at the top. The reactions of a few of these metals are explored in more detail below.

Lithium: Reacts with oxygen to form white lithium oxide in the reaction below.

$$4\,Li + O_2 \rightarrow 2\,Li_2O \tag{7.9.2.1}$$

Sodium: Reacts with oxygen to form a white mixture of sodium oxide and sodium peroxide. The reactions are shown below.

- Sodium oxide:

$$4\,Na + O_2 \rightarrow 2\,Na_2O \tag{7.9.2.2}$$

- Sodium peroxide:

$$2\,Na + O_2 \rightarrow Na_2O_2 \tag{7.9.2.3}$$

Potassium: Reacts with oxygen to form a mixture of potassium peroxide and potassium superoxide. The reactions are shown below.

- Potassium peroxide:

$$2\,K + O_2 \rightarrow 2\,K_2O_2 \tag{7.9.2.4}$$

- Potassium superoxide:

$$K + O_2 \rightarrow KO_2 \tag{7.9.2.5}$$

Rubidium and Cesium: Both metals react to produce superoxides through the same process as that of the potassium superoxide reaction.

> *The oxides of these metals form metal hydroxides when they react with water. These metal hydroxides make the solution basic or alkaline, hence the name alkaline metals.*

Group 2 metals (alkaline earth metals) react with oxygen through the process of burning to form metal oxides but there are a few exceptions.

Beryllium is very difficult to burn because it has a layer of beryllium oxide on its surface which prevents further interaction with oxygen. Strontium and barium react with oxygen to form peroxides. The reaction of barium and oxygen is shown below, and the reaction with strontium would be the same.

$$Ba\,(s) + O_2\,(g) \rightarrow BaO_2\,(s) \tag{7.9.2.6}$$

Group 13 reacts with oxygen in order to form oxides and hydroxides that are of the form X_2O_3 and $X(OH)_3$. The variable X represents the various group 13 elements. As you go down the group, the oxides and hydroxides get increasingly basic.

Group 14 elements react with oxygen to form oxides. The oxides formed at the top of the group are more acidic than those at the bottom of the group. Oxygen reacts with silicon and carbon to form silicon dioxide and carbon dioxide. Carbon is also able to react with oxygen to form carbon monoxide, which is slightly acidic. Germanium, tin, and lead react with oxygen to form monoxides and dioxides that are amphoteric, which means that they react with both acids and bases.

Group 15 elements react with oxygen to form oxides. The most important are listed below.

- Nitrogen: N_2O, NO, N_2O_3, N_2O_4, N_2O_5
- Phosphorus: P_4O_6, P_4O_8, P_2O_5
- Arsenic: As_2O_3, As_2O_5

- Antimony: Sb_2O_3, Sb_2O_5
- Bismuth: Bi_2O_3, Bi_2O_5

Group 16 elements react with oxygen to form various oxides. Some of the oxides are listed below.

- Sulfur: SO, SO_2, SO_3, S_2O_7
- Selenium: SeO_2, SeO_3
- Tellurium: TeO, TeO_2, TeO_3
- Polonium: PoO, PoO_2, PoO_3

Group 17 elements (halogens) fluorine, chlorine, bromine, and iodine react with oxygen to form oxides. Fluorine forms two oxides with oxygen: F_2O and F_2O_2. Both fluorine oxides are called oxygen fluorides because fluorine is the more electronegative element. One of the fluorine reactions is shown below.

$$\mathbf{O_2\,(g) + F_2\,(g) \rightarrow F_2O_2\,(g)} \tag{7.9.2.7}$$

Group 18: Some would assume that the Noble Gases would not react with oxygen. However, xenon does react with oxygen to form $\mathbf{XeO_3}$ and $\mathbf{XeO_4}$. The ionization energy of xenon is low enough for the electronegative oxygen atom to "steal away" electrons. Unfortunately, $\mathbf{XeO_3}$ is HIGHLY unstable, and it has been known to spontaneously detonate in a clean, dry environment.

Transition metals react with oxygen to form metal oxides. However, gold, silver, and platinum do not react with oxygen. A few reactions involving transition metals are shown below:

$$2Sn_{(s)} + O_{2(g)} \rightarrow 2SnO_{(s)} \tag{7.9.2.8}$$

$$4Fe_{(s)} + 3O_{2(g)} \rightarrow 2Fe_2O_{3(s)} \tag{7.9.2.9}$$

$$4Al_{(s)} + 3O_{2(g)} \rightarrow 2Al_2O_{3(s)} \tag{7.9.2.10}$$

Reaction of Oxides

We will be discussing metal oxides of the form X_2O. The variable X represents any metal that is able to bond to oxygen to form an oxide.

- **Reaction with water:** The oxides react with water to form a metal hydroxide.

$$X_2O + H_2O \rightarrow 2XOH$$

- **Reaction with dilute acids:** The oxides react with dilute acids to form a salt and water.

$$X_2O + 2HCl \rightarrow 2XCl + H_2O$$

Reactions of Peroxides

The peroxides we will be discussing are of the form X_2O_2. The variable X represents any metal that can form a peroxide with oxygen.

Reaction with water: If the temperature of the reaction is kept constant despite the fact that the reaction is exothermic, then the reaction proceeds as follows:

$$X_2O_2 + 2H_2O \rightarrow 2XOH + H_2O_2$$

If the reaction is not carried out at a constant temperature, then the reaction of the peroxide and water will result in decomposition of the hydrogen peroxide that is produced into water and oxygen.

Reaction with dilute acid: This reaction is more exothermic than that with water. The heat produced causes the hydrogen peroxide to decompose to water and oxygen. The reaction is shown below.

$$X_2O_2 + 2HCl \rightarrow 2XCl + H_2O_2$$

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

Reaction of Superoxides

The superoxides we will be talking about are of the form XO_2, with X representing any metal that forms a superoxide when reacting with oxygen.

Reaction with water: The superoxide and water react in a very exothermic reaction that is shown below. The heat that is produced in forming the hydrogen peroxide will cause the hydrogen peroxide to decompose to water and oxygen.

$$2XO_2 + 2H_2O \rightarrow 2XOH + H_2O_2 + O_2$$

Reaction with dilute acids: The superoxide and dilute acid react in a very exothermic reaction that is shown below. The heat produced will cause the hydrogen peroxide to decompose to water and oxygen.

$$2XO_2 + 2HCl \rightarrow 2XCl + H_2O_2 + O_2$$

Allotropes of Oxygen

There are two allotropes of oxygen; dioxygen (O_2) and trioxygen (O_3) which is called ozone. The reaction of converting dioxygen into ozone is very endothermic, causing it to occur rarely and only in the lower atmosphere. The reaction is shown below:

$$3O_{2(g)} \rightarrow 2O_{3(g)} \quad \Delta H^o = +285\ kJ$$

Ozone is unstable and quickly decomposes back to oxygen but is a great oxidizing agent.

Miscellaneous Reactions

Reaction with Alkanes: The most common reactions that involve alkanes occur with oxygen. Alkanes are able to burn and it is the process of oxidizing the hydrocarbons that makes them important as fuels. An example of an alkane reaction is the reaction of octane with oxygen as shown below.

$$C_8H_{18}(l) + 25/2\ O_2(g) \rightarrow 8CO_2(g) + 9H_2O(l)\ \Delta H_o = -5.48\ X\ 10^3\ kJ$$

Reaction with ammonia: Oxygen is able to react with ammonia to produce dinitrogen (N_2) and water (H_2O) through the reaction shown below.

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

Reaction with Nitrogen Oxide: Oxygen is able to react with nitrogen oxide in order to produce nitrogen dioxide through the reaction shown below.

$$NO + O_2 \rightarrow NO_2$$

Problems

1. Is oxygen reactive with noble gases?
2. Which transition metals does oxygen not react with?
3. What is produced when an oxide reacts with water?
4. Is oxygen reactive with alkali metals? Why are the alkali metals named that way?
5. If oxygen is reactive with alkali metals, are oxides, peroxides or superoxides produced?

Solutions

1. No, noble gases are unreactive with oxygen.
2. Oxygen is mostly unreactive with gold and platinum.
3. When an oxide reacts with water, a metal hydroxide is produced.
4. Oxygen is very reactive with alkali metals. Alkali metals are given the name alkali because the oxides of these metals react with water to form a metal hydroxide that is basic or alkaline.
5. Lithium produces an oxide, sodium produces a peroxide, and potassium, cesium, and rubidium produce superoxides.

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Contributors and Attributions

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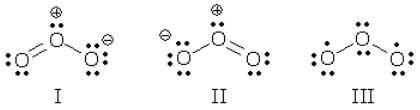
7.9.2.1: Ozone

Ozone is an allotropic form of oxygen. Its molecular formula is O_3 and molar mass is 48 g mol^{-1}.

Occurrence of ozone

Schonbein (1840) concluded that Van Marum's observations in 1785 of a peculiar smell, when an electric discharge was passed through oxygen (or air), was in fact a new gas. He named it ozone, which is derived from a Greek word ozoaterr meaning smell. In 1860, Soret assigned the molecular formula O_3. Ozone occurs in small amounts, in the upper layer of the atmosphere, where it is formed due to the action of ultraviolet rays on the oxygen of the air. It is also present in seawater where it is formed due to the reaction of fluorine with water.

In the structure of ozone, the bond length of 127.8 pm is intermediate between a single bond (bond length 148 pm) and a double bond (bond length 110 pm). Ozone is, therefore, considered to be a resonance hybrid of the following canonical forms:



Uses of ozone

- For air purification in crowded places like cinema halls and tunnel railways. Due to its strong oxidizing power it also destroys the foul smell in slaughter houses.
- In sterilizing drinking water by oxidizing all germs and bacteria.
- For preservation of meat in cold storage.
- For bleaching delicate fabrics such as silk, ivory, oils, starch and wax.
- It helps to locate a double bond in any unsaturated organic compound by ozonolysis.

Preparation of ozone

When a silent electric discharge is passed through dry oxygen, ozone is formed. Oxygen is never converted into ozone completely and we always obtain a mixture of oxygen and ozone. This mixture is called ozonized oxygen.

$$3\,O_2 \xrightarrow[\text{discharge}]{\text{electric}} 2\,O_3 \quad \Delta H = +284.5\ kJ/mol$$

The reaction is initiated by a sparkless or silent electric discharge, to produce less heat, as ozone is prone to decomposing back into oxygen with an increase in temperature (Le Chatelier's Principle). Hence, ozone is prepared in a specially designed apparatus called an ozonizer to facilitate the above conditions. An 'Ozonizer' is the apparatus used to prepare ozone by the passage of silent electrical discharge. Two types of ozonizers are commonly used: the Siemen's and the Brodie Ozonizers.

Siemen's Ozonizer

Seimen's ozonizer consists of two co-axial glass tubes fused together. Tin foil is used to coat the inner side of the inner tube and the outer side of the outer tube. The inner and outer tin coatings are connected to the terminals of an induction coil, which produces a current at high voltage. A slow current of pure and dry oxygen is passed through the annular space. On subjecting oxygen to silent electrical discharge, ozonized oxygen containing 10-15% ozone is formed. By taking the following precautions, the yield of ozone can be increased in the ozonized oxygen:

- Only pure and dry oxygen should be used.
- The ozonizer should be perfectly dry.
- A fairly low temperature (around 0°C) should be maintained.
- There should be no sparking.

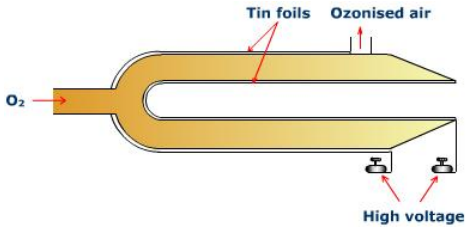


Figure 1: Siemen's ozonizer

Brodie's ozonizer

In principle, this ozonizer is like the Siemen's ozonizer, but dilute sulfuric acid replaces the tin foil. Two carbon electrodes are dipped in the acid and connected to an induction coil. A current of dry oxygen is passed through the space between the tubes. Ozonized oxygen containing about 5% O_3 comes out at the other end. If the apparatus is kept cool, the proportion of ozone may go up 20-25%.

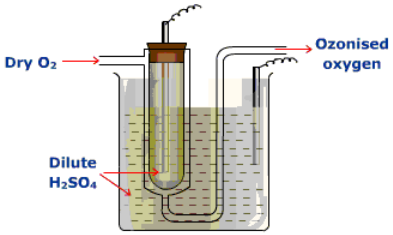


Figure 2: Brodie's ozonizer

Problems

1. How is ozone formed in the upper atmosphere?

Solution

1. Ozone is formed in the upper atmosphere in two steps:

    i) Photodissociation of oxygen by ultraviolet radiation of wavelength less than 240 nm.

$$O_2 \xrightarrow{h\nu} O^{\cdot} + O^{\cdot}$$

Oxygen atoms are really diradicals with two unpaired p-orbital electrons, but are represented with a single electron here.

    ii) Combination of highly reactive oxygen atoms with oxygen molecules.

$$O_2 + O^{\cdot} \rightarrow O_3$$

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7.9.2.1.1: Ozone Layer and Ozone Hole

Contrary to a common misconception, ozone is not in the form of a thick layer surrounding the atmosphere. Equally untrue is another misconception that there is a hole in this ozone layer. To understand how ozone spreads in the atmosphere, one needs to know the structure and composition of the atmosphere.

Depletion of Ozone

Ozone in the ionosphere, mesosphere, and stratosphere is being depleted. The concentration of ozone is gradually being reduced. As the content of ozone is highest in the ionosphere with the air itself being very thin, the depletion is negligible in the ionosphere. But in the mesosphere and stratosphere, the air is thicker and the ozone content is less. The depletion of ozone is of a higher order in these layers. The so-called hole in the ozone layer simply means that above some continents (specifically Antarctica, Asia, and parts of South America), the mesosphere and stratosphere have lost their original level of ozone content.

The depletion of the ozone layer is a global phenomenon in terms of both cause and effect. The geographical limits of countries are not barriers to either dispersal of gases in the layers of the atmosphere or depletion of gases. The causes for depletion may arise in any country. The effects (in terms of depletion) may arise in any other country. The effects (in terms of ozone depletion) need not be exactly above the country causing the depletion.

Causes of Depletion

It is now established that chlorofluorocarbon (CFC) chemicals evolved from various refrigerants, coolants, and propellants are the primary reason for the depletion of the ozone. CFCs are a group of chlorine-bearing gases of low specific gravity. They rise to the stratosphere and mesosphere. Due to ionizing solar radiation in these layers (which is the primary reason for production of ozone), fresh chlorine gas is produced from CFCs. This nascent chlorine gas has the capacity to react with ozone and bring down the level of ozone substantially.

Destruction of ozone in the ozone layer

The ozone in the ozone layer protects the earth from harmful ultraviolet radiation by trapping this radiation. The ozone layer has been thinning gradually and poses potential health hazards for the future. The thinning of the ozone layer has been attributed to the presence of chlorofluorohydrocarbons (e.g., $CFCl_3$ and CF_2Cl_2) in the atmosphere. These chemicals have been used as aerosol propellants and cooling mixtures in refrigerators. How these chemicals affect ozone concentration is illustrated with the equations given below.

$$CF_2Cl_2 + h\nu \rightarrow CF_2Cl^{\cdot} + Cl^{\cdot} \tag{7.9.2.1.1.1}$$

Chlorine atoms, being highly reactive, react with ozone (O_3):

$$Cl^{\cdot} + O_3 \rightarrow ClO^{\cdot} + O_2 \tag{7.9.2.1.1.2}$$

The monoxide of chlorine further reacts with another molecule of O_3:

$$ClO^{\cdot} + O_3 \rightarrow Cl^{\cdot} + 2\,O_2 \tag{7.9.2.1.1.3}$$

The chlorine atom so obtained reacts with another ozone molecule. Hence, steps 7.9.2.1.1.2 and 7.9.2.1.1.3 are repeated again and again, and lead to the depletion of the concentration of ozone.

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7.9.3: Chemistry of Sulfur (Z=16)

Learning Objectives

- Describe the chemistry of the oxygen group.
- Give the trend of various properties.
- Remember the names of Group 16 elements.
- Explain the Frasch process.
- Describe properties and applications of $\mathbf{H_2SO_4}$.
- Explain properties and applications of $\mathbf{H_2S}$.

Sulfur is a chemical element that is represented with the chemical symbol "S" and the atomic number 16 on the periodic table. Because it is 0.0384% of the Earth's crust, sulfur is the seventeenth most abundant element following strontium. Sulfur also takes on many forms, which include elemental sulfur, organo-sulfur compounds in oil and coal, $H_2S(g)$ in natural gas, and mineral sulfides and sulfates. This element is extracted by using the Frasch process (discussed below), a method where superheated water and compressed air are used to draw liquid sulfur to the surface. Offshore sites, Texas, and Louisiana are the primary sites that yield extensive amounts of elemental sulfur. However, elemental sulfur can also be produced by reducing H_2S, commonly found in oil and natural gas. For the most part, though, sulfur is used to produce $SO_2(g)$ and H_2SO_4.

Known from ancient times (mentioned in the Hebrew scriptures as brimstone) sulfur was classified as an element in 1777 by Lavoisier. Pure sulfur is tasteless and odorless with a light yellow color. Samples of sulfur often encountered in the lab have a noticeable odor. Sulfur is the tenth most abundant element in the known universe.

Sulfur at a Glance

Atomic Number	16
Atomic Symbol	S
Atomic Weight	32.07 grams per mole
Structure	orthorhombic
Phase at room temperature	solid
Classification	nonmetal

Physical Properties of Sulfur

Sulfur has an atomic weight of 32.066 grams per mole and is part of group 16, the oxygen family. It is a nonmetal and has a specific heat of 0.706 J g^{-1} $^oC^{-1}$. The electron affinity is 200 kJ mol^{-1} and the electronegativity is 2.58 (unitless). Sulfur is typically found as a light-yellow, opaque, and brittle solid in large amounts of small orthorhombic crystals. Not only does sulfur have twice the density of water, but it is also insoluble in water. On the other hand, sulfur is highly soluble in carbon disulfide and slightly soluble in many common solvents. Sulfur can also vary in color and blackens upon boiling due to carbonaceous impurities. Even as little as 0.05% of carbonaceous matter darkens sulfur significantly.



Figure **7.9.3.1**: A piece of sulfur burning with a blue flame that can hardly be seen in daylight, but it can be seen in this photograph if you look closely. Image by Johannes Hemmerlein and used with permission.

Most sulfur is recovered directly as the element from underground deposits by injecting super-heated water and piping out molten sulfur (sulfur melts at 112° C). Compared to other elements, sulfur has the most allotropes. While the S_8 ring is the most common allotrope, there are 6 other structures with up to 20 sulfur atoms per ring.

- Under appropriate conditions, sulfur vapor can contain S, S_2, S_4, S_6, and S_8.
- At room temperature, **rhombic sulfur (S_α)** is a stable solid comprising cyclic S_8 molecules.
- At 95.5 °C, rhombic sulfur becomes **monoclinic sulfur (S_β)**. The crystal structure found in monoclinic sulfur differs from that of rhombic sulfur. Monoclinic sulfur is also made up of S_8molecules.
- Monoclinic sulfur becomes **liquid sulfur (S_λ)** at 119 °C. Liquid sulfur is a straw-colored liquid made up of S_8 molecules and other cyclic molecules containing a range of six to twenty atoms.
- At 160 °C, this becomes a dark, viscous liquid called **liquid sulfur (S_μ)**. The molecules are still made up of eight sulfur atoms, but the molecule opens up and transforms from a circle into a long spiral-chain molecule.
- At 180 °C, the chain length and viscosity reach their maximum. Chains break and viscosity decreases at temperatures that exceed 180 °C.
- **Sulfur vapor** is produced when liquid boils at 445 °C. In the vapor that is produced, S_8 molecules dominate, but as the vapor continues to heat up, the molecules break up into smaller groups of sulfur atoms.
- To produce **plastic sulfur**, S is poured into cold water. Plastic sulfur is rubberlike and is made up of long, spiral-chain molecules. If plastic sulfur sits for long, it will reconvert to rhombic sulfur.

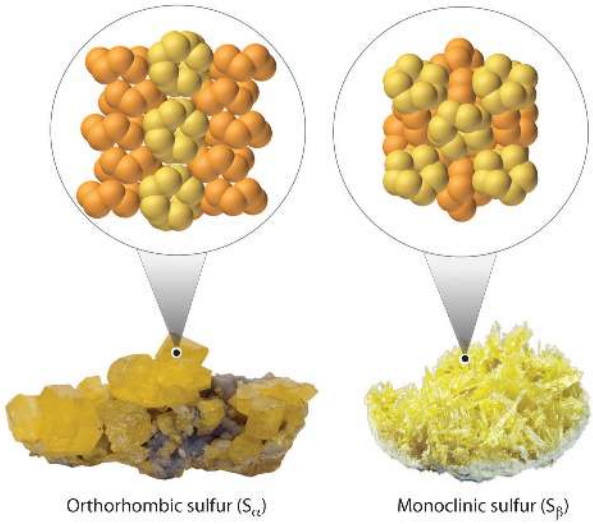


Figure **7.9.3.2**: Two allotropes of sulfur.

While oxygen has fewer allotropes than sulfur, including O, O_2, O_3, O_4, O_8, metallic O (and four other solid phases), many of these actually have a corresponding sulfur variant. However, sulfur has more tendency to catenate (the linkage of atoms of the same element into longer chains). Here are the values of the single and double bond enthalpies:

O–O	142 kJ/mol
S–S	268 kJ/mol
O=O	499 kJ/mol
S=S	352 kJ/mol

This means that O=O is stronger than S=S, while O–O is weaker than S–S. So, in sulfur, single bonds are favored and catenation is easier than in oxygen compounds. It seems that the reason for the weaker S=S double bonds has its roots in the size of the atom: it's harder for the two atoms to come to a small enough distance, so that the p orbital overlap is small and the π bond is weak. This is attested by looking down the periodic table: Se=Se has an even weaker bond enthalpy of 272 kJ/mol.

> What happens when the solid sulfur melts? The S_8 molecules break up. When suddenly cooled, long chain molecules are formed in the plastic sulfur which behave like rubber. Plastic sulfur transforms into rhombic sulfur over time.

Compounds

Reading the following reactions, figure out and notice the change of the oxidation state of S in the reactants and products. Common oxidation states of sulfur are -2, 0, +4, and +6. Sulfur (brimstone, stone that burns) reacts with O_2 giving a blue flame (Figure 7.9.3.1):

$$S + O_2 \rightarrow SO_2$$

SO_2 is produced whenever a metal sulfide is oxidized. It is recovered and oxidized further to give SO_3, for production of H_2SO_4. SO_2 reacts with H_2S to form H_2O and S.

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

$$SO_3 + H_2O \rightleftharpoons H_2SO_4 \quad \text{(a valuable commodity)}$$

$$SO_3 + H_2SO_4 \rightleftharpoons H_2S_2O_7 \quad \text{(pyrosulfuric acid)}$$

Sulfur reacts with sulfite ions in solution to form thiosulfate,

$$S + {SO_3}^{2-} \longrightarrow {S_2O_3}^{2-}$$

but the reaction is reversed in an acidic solution.

Oxides

There are many different stable sulfur oxides, but the two that are commonly found are sulfur dioxide and sulfur trioxide. Sulfur dioxide is a commonly found oxide of sulfur. It is a colorless, pungent, and nonflammable gas. It has a density of 2.8 kg/m^3 and a melting point of -72.5 ^{o}C. Because organic materials are more soluble in SO_2 than in water, the liquid form is a good solvent. SO_2 is primarily used to produce SO_3. The direct combustion of sulfur and the roasting of metal sulfides yield SO_2 via the contact process:

$$\underbrace{S(s) + O_2(g) \rightarrow SO_2(g)}_{\text{Direct combustion}}$$

$$\underbrace{2ZnS(s) + 3O_2(g) \rightarrow 2ZnO(s) + 2SO_2(g)}_{\text{Roasting of metal sulfides}}$$

Sulfur trioxide is another one of the commonly found oxides of sulfur. It is a colorless liquid with a melting point of 16.9 ^{o}C and a density of kg/m^3. SO_3 is used to produce sulfuric acid. SO_2 is used in the synthesis of SO_3:

$$\underbrace{2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)}_{\text{Exothermic, reversible reaction}}$$

This reaction needs a catalyst to be completed in a reasonable amount of time with V_2O_5 being the catalyst most commonly used.

Hydrogen Sulfide H_2S

- Hydrogen sulfide, $\mathbf{H_2S}$, is a diprotic acid. The equilibria below,

$$\mathbf{H_2S \rightleftharpoons HS^- + H^+}$$

$$\mathbf{HS^- \rightleftharpoons S^{2-} + H^+}$$

have been discussed in connection with Polyprotic Acids.

Other Sulfur-containing Compounds

Perhaps the most significant compound of sulfur used in modern industrialized societies is sulfuric acid ($\boldsymbol{H_2SO_4}$). Sulfur dioxide ($\boldsymbol{SO_2}$) finds practical applications in bleaching and refrigeration but it is also a nuisance gas resulting from the burning of sulfurous coals. Sulfur dioxide gas then reacts with the water vapor in the air to produce a weak acid, sulfurous acid ($\boldsymbol{H_2SO_3}$), which contributes to the acid rain problem.

- **Sulfuric acid**, H_2SO_4, is produced by reacting $\boldsymbol{SO_3}$ with water. However, this often leads to pollution problems. SO_3(g) is reacted with 98% H_2SO_4 in towers full of ceramic material to produce $H_2S_2O_7$ or **oleum**. Water is circulated in the tower to maintain the correct concentration and the acid is diluted with water at the end in order to produce the correct concentration. Pure sulfuric acid has no color and odor, and it is an oily, hygroscopic liquid. However, sulfuric acid vapor produces heavy, white smoke and a suffocating odor.
- **Dilute sulfuric acid**, H_2SO_4(aq), reacts with metals and acts as a strong acid in common chemical reactions. It is used to produce H_2(g) and liberate CO_2(g) and can neutralize strong bases.
- **Concentrated sulfuric acid**, H_2SO_4 (conc.), has a strong affinity for water. In some cases, it removes H and O atoms. Concentrated sulfuric acid is also a good oxidizing agent and reacts with some metals.

$$\boldsymbol{C_{12}H_{22}O_{11}(s) \rightarrow 12C(s) + 11H_2O(l)}$$

(Concentrated sulfuric acid used in forward reaction to remove H and O atoms.)

Applications of Sulfuric Acid

- as a strong acid for making $\mathbf{HCl}$ and $\mathbf{HNO_3}$.
- as an oxidizing agent for metals.
- as a dehydrating agent.
- for manufacture of fertilizer and other commodities.

- **Sulfurous acid** (H_2SO_3) is produced when $\boldsymbol{SO_2}$(g) reacts with water. It cannot be isolated in its pure form; however, it forms salts as sulfites. Sulfites can act as both reducing agents and oxidizing agents.

$$O_2(g) + 2\ SO_3^{2-}(aq) \rightarrow 2\ SO_4^{2-}\ (aq)\ \text{(Reducing agent)}$$

$$2\ H_2S(g) + 2\ H^+(aq) + SO_3^{2-}(aq) \rightarrow 3\ H_2O(l) + 3\ S(s)\ \text{(Oxidizing agent)}$$

H_2SO_3 is a diprotic acid that acts as a weak acid in both steps, and H_2SO_4 is also a diprotic acid but acts as a strong acid in the first step and a weak acid in the second step. Acids like $NaHSO_3$ and $NaHSO_4$ are called acid salts because they are the product of the first step of these diprotic acids.

Boiling elemental sulfur in a solution of sodium sulfite yields **thiosulfate**. Not only are thiosulfates important in photographic processing, but they are also common analytical reagents used with iodine (like in the following two reactions).

$$\boldsymbol{2Cu^{2+}_{(aq)} + 5I^-_{(aq)} \rightarrow 2CuI_{(s)} + I^-_{3(aq)}}$$

$$\boldsymbol{I^-_{3(aq)} + 2S_2O^{2-}_{3(aq)} \rightarrow 3I^-_{(aq)} + S_4O^{2-}_{6(aq)}}$$

with excess triiodide ion titrated with $Na_2S_2O_3$(aq).

Other than sulfuric acid, perhaps the most familiar compound of sulfur in the chemistry lab is the foul-smelling hydrogen sulfide gas, $\boldsymbol{H_2S}$, which smells like rotten eggs.

- **Sulfur halides** are compounds formed between sulfur and the halogens. Common compounds include SF_2, S_2F_2, SF_4, and SF_6. While SF_4 is a powerful fluorinating agent, SF_6 is a colorless, odorless, unreactive gas. Compounds formed by sulfur and chloride include S_2Cl_2, SCl_4, and SCl_2. SCl_2 is a red, bad-smelling liquid that is utilized to produce mustard gas ($S(CH_2CH_2Cl)_2$).

$$SCl_2 + 2CH_2CH_2 \rightarrow S(CH_2CH_2Cl)_2$$

Production -The Frasch Process

Sulfur can be mined by the Frasch process. This process has made sulfur a high purity (up to 99.9 percent pure) chemical commodity in large quantities. Most sulfur-containing minerals are metal sulfides, and the best known is perhaps pyrite (FeS_2, known as fool's gold because of its golden color). The most common sulfate-containing mineral is gypsum, $CaSO_4 \cdot 2H_2O$, also known as plaster of Paris.

The Frasch process is based on the fact that sulfur has a comparatively low melting point. The process forces (99.5% pure) sulfur out by using hot water and air. In this process, superheated water is forced down the outermost of three concentric pipes. Compressed air is pumped down the center tube, and a mixture of elemental sulfur, hot water, and air comes up the middle pipe. Sulfur is melted with superheated water (at 170 °C under high pressure) and forced to the surface of the earth as a slurry.

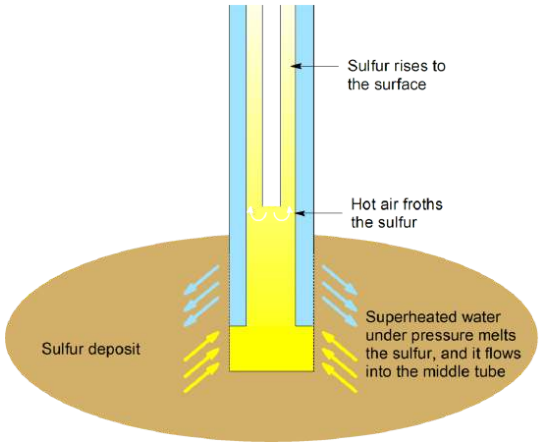


Figure **7.9.3.1**: Pictorial representation of the Frasch process. Adapted from Wolfgang Nehb, Karel Vydra (2005), "Sulfur", Ullmann's Encyclopedia of Industrial Chemistry, Weinheim: Wiley-VCH. (Public Domain; Rifleman 82)

Sulfur is mostly used for the production of sulfuric acid, H_2SO_4. Most sulfur mined by the Frasch process is used in industry for the manufacture of sulfuric acid. Sulfuric acid, the most abundantly produced chemical in the United States, is manufactured by the contact process. Most (about 70%) of the sulfuric acid produced in the world is used in the fertilizer industry. Sulfuric acid can act as a strong acid, a dehydrating agent, and an oxidizing agent. Its applications use these properties. Sulfur is an essential element of life in sulfur-containing proteins.

Applications

Sulfur has many practical applications. As a fungicide, sulfur is used to counteract apple scab in organically farmed apple production. Other crops that utilize sulfur fungicides include grapes, strawberries, and many vegetables. In general, sulfur is effective against mildew diseases and black spot. Sulfur can also be used as an organic insecticide. Sulfites are frequently used to bleach paper and preserve dried fruit.

The vulcanization of rubber includes the use of sulfur as well. Cellophane and rayon are produced with carbon disulfide, a product of sulfur and methane. Sulfur compounds can also be found in detergents, acne treatments, and agrichemicals. Magnesium sulfate (epsom salt) has many uses, ranging from bath additives to exfoliants. Sulfur is being increasingly used as a fertilizer as well. Because standard sulfur is hydrophobic, it is covered with a surfactant by bacteria before oxidation can occur. Sulfur is therefore a slow-release fertilizer. Lastly, sulfur functions as a light-generating medium in sulfur lamps.

Concentrated sulfuric acid was once one of the most produced chemicals in the United States; the majority of the H_2SO_4 that is now produced is used in fertilizer. It is also used in oil refining, production of titanium dioxide, and in emergency power supplies

and car batteries. The mineral gypsum, or calcium sulfate dihydrate, is used in making plaster of Paris. Over one million tons of aluminum sulfate is produced each year in the United States by reacting H_2SO_4 and Al_2O_3. This compound is important in water purification. Copper sulfate is used in electroplating. Sulfites are used in the paper making industry because they produce a substance that coats the cellulose in the wood and frees the fibers of the wood for treatment.

Emissions and the Environment

Particles, SO_2(g), and H_2SO_4 mist are the components of industrial smog. Because power plants burn coal or high-sulfur fuel oils, SO_2(g) is released into the air. When catalyzed on the surfaces of airborne particles, SO_2 can be oxidized to SO_3. A reaction with NO_2 works as well as shown in the following reaction:

$$SO_{2(g)} + NO_{2(g)} \rightarrow SO_{3(g)} + NO_{(g)}$$

H_2SO_4 mist is then produced after SO_3 reacts with water vapor in the air. If H_2SO_4 reacts with airborne NH_3, $(NH_4)_2SO_4$ is produced. When SO_2(g) and H_2SO_4 reach levels that exceed 0.10 ppm, they are potentially harmful. By removing sulfur from fuels and controlling emissions, acid rain and industrial smog can be kept under control. Processes like fluidized bed combustion have been presented to remove SO_2 from smokestack gases.

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Problems

1. Draw a diagram that summarizes the allotropy of sulfur. Use symbols, arrows, and numbers.
2. Direct combustion of sulfur is the only method for producing SO_2(g). True or False.
3. Sulfites are not oxidizing agents. They are good reducing agents. True or False.
4. Give the reaction for the production of sulfur trioxide.
5. Choose the incorrect statement.
    a. Sulfur produces cellophane and rayon.
    b. Standard sulfur is hydrophobic.
    c. SO_2 can oxidize to SO_3
    d. Sulfur influences the development of acid rain and industrial smog.
    e. All of the above are correct.
6. Which reaction is responsible for the destruction of limestone and marble statues and buildings?
    a. $CaCO_3 \rightarrow CaO + CO_2$
    b. $SO_2 + H_2O \rightarrow H_2SO_3$
    c. $BaO + CO_2 \rightarrow BaCO_3 \rightarrow BaSO_3$ upon reaction with SO_2
    d. $CaCO_3 + H_2O \rightarrow Ca(OH)_2 + CO_2$

e. $CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2 \rightarrow CaSO_4$ upon oxidation

7. Give the formula of thiosulfate ion.
8. What is the oxidation state of S in SF_6, H_2SO_4, $NaHSO_4$, SO_4^{2-}, and SO_3?
9. What is the phase of sulfur at 298 K? Enter the type of crystals.
10. Give the name of the process by which sulfur is forced out of the ground using hot water and air.

Solutions

1. The diagram may be drawn in any way. However, the symbols (S_2), (S_4), (S_6), ($S_?$), and (S_8(g)) must be included. The temperatures should be written next to the arrows.
2. False
3. False
4. $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$
5. A
6. e.

   Consider...

   SO_2 in H_2SO_3 is the acid in acid rain, which attacks $CaCO_3$, marble. SO_2 reduces pigments in organic matter.
7. $S_2O_3^{2-}$

   Consider...

   Sulfate is SO_4^{2-}; replacement of an O by an S gives thiosulfate $S_2O_3^{2-}$. The two S in $S_2O_3^{2-}$ have different oxidation states: one is +6, the other is (-2), average +2.
8. 6

   Consider...

   Oxidation state for S in H_2SO_3, SO_3^{2-}, SO_2, etc. is 4. The oxidation state of S is the same for all in the list.
9. rhombic sulfur

   Consider...

   The term rhombic describes a type of crystal. Monoclinic sulfur is meta stable at 298 K.
10. Frasch process

    Consider...

    The Frasch process is used to mine elemental sulfur.

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7.9.4: Chemistry of Selenium (Z=34)

Element number 34, selenium, was discovered by Swedish chemist Jons Jacob Berzelius in 1817. Selenium is a non-metal and can be compared chemically to its other non-metal counterparts found in Group 16: The Oxygen Family, such as sulfur and tellurium.

Properties

Chemical Symbol:	Se
Atomic Number:	34
Atomic Weight:	78.96
Electron Configuration:	[Ar] $4s^2 3d^{10} 4p^4$
Melting Point:	493.65 K
Boiling Point:	958 K
Electronegativity:	2.55 (Pauling)
Oxidation States:	Se^{-2}, Se^{+6}, Se^{+4}
Ionization Energies:	First: 941 kJ/mol
	Second: 2045 kJ/mol
	Third: 2973.7 kJ/mol

History

Selenium was discovered by Berzelius in 1818. It is named for the Greek word for "moon", selene. The discovery of selenium was an important finding, but at the same time seemingly accidental. Fellow scientist Martin Klaproth discovered a contamination of sulfuric acid creating a red colored product which he believed to be due to the element tellurium. However, Berzelius went on to further analyze the impurity and came to the conclusion that it was an unknown element that shared properties similar to those of tellurium. Based on the Greek word “selene,” meaning moon, Jons Berzelius decided to call the newly found element selenium.

Allotropes and Physical Properties

Selenium can exist in multiple allotropes that are essentially different molecular forms of an element with varying physical properties. For example, one allotrope of selenium can be seen as an amphorous (“without crystalline shape”) red powder. Selenium also takes a crystalline hexagonal structure, forming a metallic gray allotrope which is known to be stable. The most thermodynamically stable allotrope of selenium is trigonal selenium, which also appears as a gray solid. Most selenium is recovered from the electrolytic copper refining process. This is usually in the form of the red allotrope.

Selenium is mostly noted for its important chemical properties, especially those dealing with electricity. Unlike sulfur, selenium is a semiconductor, meaning that it conducts some electricity, but not as well as conductors. Selenium is a photoconductor, which means it has the ability to change light energy into electrical energy. Not only is selenium able to convert light energy into electrical energy, but it also displays the property of photoconductivity. Photoconductivity is the idea that the electrical conductivity of selenium increases due to the presence of light -- or, in other words, it becomes a better photoconductor as light intensity increases.

Isotopes

Isotopes of an element are atoms that have the same atomic numbers but a different number of neutrons (different mass numbers) in their nuclei. Selenium is known to have over 20 different isotopes; however, only 5 of them are stable. The five stable isotopes of selenium are ^{74}Se, ^{76}Se, ^{77}Se, ^{78}Se, ^{80}Se.

Uses

Due to selenium's property of photoconductivity, it is known to be used in photocells, exposure meters in photography, and also in solar cells. Selenium can also be seen in the products of plain-paper photocopiers, laser printers and photographic toners. Besides its uses in the electronic industry, selenium is also popular in the glass-making industry. When selenium is added to glass, it is able to negate the color of other elements found in the glass and essentially decolorizes it. Selenium is also able to create a ruby-red colored glass when added. The element can also be used in the production of alloys and is an additive to stainless steel.

Health Hazards

Selenium, a trace element, is important in the diet and health of both plants and animals, but can be only taken in very small amounts. Exposure to an excess amount of selenium is known to be toxic and causes health problems. With an upper intake level of 400 micrograms per day that can be tolerated, too much selenium can lead to selenosis and may result in health problems and even death. Compounds of selenium are also known to be carcinogenic.

Chemical Reactivity

Reaction with hydrogen

Selenium forms hydrogen selenide, H_2Se, a colorless flammable gas, when reacted with hydrogen.

Reaction with oxygen

Selenium burns in air, displaying a blue flame, and forms solid selenium dioxide.

$$Se_{8(s)} + 8O_{2(g)} \rightarrow 8SeO_{2(s)}$$

Selenium is also known to form selenium trioxide, SeO_3.

Reaction with halides

Selenium reacts with fluorine, F_2, and burns to form selenium hexafluoride.

$$Se_{8(s)} + 24F_{2(g)} \rightarrow 8SeF_{6(l)}$$

Selenium also reacts with chlorine and bromine to form diselenium dichloride, Se_2Cl_2 and diselenium dibromide, Se_2Br_2.

$$Se_8 + 4Cl_2 \rightarrow 4Se_2Cl_{2(l)}$$

$$Se_8 + 4Br_2 \rightarrow 4Se_2Br_{2(l)}$$

Selenium also forms SeF_4, $SeCl_2$ and $SeCl_4$.

Selenides

Selenium reacts with metals to form selenides. Example: Aluminum selenide

$$3Se_8 + 16Al \rightarrow 8Al_2Se_3$$

Selenites

Selenium reacts to form salts called selenites, e.g., silver selenite (Ag_2SeO_3) and sodium selenite (Na_2SeO_3).

Problems

1. Describe selenium's property of photoconductivity.
2. Does selenium react with hydrogen? If so, what compound is produced?
3. Describe selenium's purpose as a trace element.
4. What are some common uses for selenium?
5. Does selenium react with oxygen?

Solutions

1. Selenium's ability to change light energy into electrical energy increases as light intensity increases.
2. Yes, selenium reacts with hydrogen and forms hydrogen selenide, H_2Se.
3. Selenium is important to the health of plants and animals, but is only safe in small amounts. Too much selenium can be toxic and cause serious health problems.
4. Selenium is used in the glass-making industry and also in electronics. It is used in photo cells, solar cells, photocopiers, laser printers and also photographic toners.
5. Selenium burns in air and forms selenium dioxide. It is also able to form selenium trioxide.

Reference

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7.9.5: Chemistry of Tellurium (Z=52)

Discovered by von Reichenstein in 1782, tellurium is a brittle metalloid that is relatively rare. It is named from the Latin tellus for "earth". Tellurium can be alloyed with some metals to increase their machinability and is a basic ingredient in the manufacture of blasting caps. Elemental tellurium is occasionally found in nature but is more often recovered from various gold ores, all containing $AuTe_2$.

History

Tellurium was discovered in a gold ore from the mines in Zlatna, near present day Sibiu, Transylvania. The ore was known as "Faczebajer weißes blättriges Golderz" (white leafy gold ore from Faczebaja) or antimonalischer Goldkies (antimonic gold pyrite). In 1782, while serving as the Austrian chief inspector of mines in Transylvania, Franz-Joseph Müller von Reichenstein concluded that a certain ore did not contain antimony, but that it contained bismuth sulfide. However, the following year, he reported that this was erroneous and that the ore contained mostly gold and an unknown metal very similar to antimony. After 3 years of testing, Müller determined the specific gravity of the mineral and noted the radish-like odor of the white smoke, which passed off when the new metal was heated. In 1789, another Hungarian scientist, Pál Kitaibel, also discovered the element independently in an ore from Deutsch-Pilsen which had been regarded as argentiferous molybdenite, but later he gave the credit to Müller. In 1798, it was named by Martin Heinrich Klaproth, who earlier isolated it from the mineral calaverite.

Properties

Tellurium is a semimetallic, lustrous, crystalline, brittle, silver-white element. It is usually available as a dark grey powder and has metal and non-metal properties. Te forms many compounds corresponding to those of sulfur and selenium. When burned in the air, tellurium has a greenish-blue flame and forms tellurium dioxide as a result. Tellurium is unaffected by water or hydrochloric acid, but dissolves in nitric acid. It has an atomic mass of 127.6 g/mol^{-1} and a density of 6.24 g-cm^{-3}. Its boiling point is 450 degrees Celsius and its melting point is 1390 °C.

Source and Abundance

There are eight naturally occurring isotopes of tellurium, of which three are radioactive. Tellurium is among the rarest stable solid elements in the Earth's crust. At 0.005 ppm, it is comparable to platinum in abundance. However, tellurium is far more abundant in the wider universe. Tellurium was originally and is most commonly found in gold tellurides. However, the largest source for modern production of tellurium is as a byproduct of blister copper refinement. The treatment of 500 tons of copper ore results in 0.45 kg of tellurium. Tellurium can also be found in lead deposits. Other tellurium sources, known as subeconomic deposits because the cost of abstraction outweighs the yield in tellurium, are lower-grade copper and some coal.

Originally, the copper tellurium ore is treated with sodium bicarbonate and elemental oxygen to produce a tellurium oxide salt, copper oxide, and carbon dioxide:

$$Cu_2Te + Na_2CO_3 + 2O_2 \rightarrow 2CuO + Na_2TeO_3 + CO_2$$

Then, the sodium tellurium oxide is treated with sulfuric acid to precipitate out tellurium dioxide, which can be treated with aqueous sodium hydroxide to reduce to pure tellurium and oxygen gas:

$$TeO_2 + 2NaOH \rightarrow Na_2TeO_3 + H_2O \rightarrow Te + 2NaOH + O_2$$

Industrial and Commercial Use

Tellurium has many unique industrial and commercial uses that improve product quality and quality-of-life. Many of the technologies that utilize tellurium have important uses for the energy industry, the military, and health industries. Tellurium is used to color glass and ceramics and can improve the machining quality of metal products. When added to copper alloys, tellurium makes the alloy more ductile, whereas it can prevent corrosion in lead products. Tellurium is an important component of infrared detectors used by the military as well as x-ray detectors used by a variety of fields including medicine, science, and security. In addition, tellurium-based catalysts are used to produce higher-quality rubber. CdTe films are one of the highest efficiency photovoltaics, metals that convert sunlight directly into electrical power, at 11-13% efficiency and are, therefore, widely used in solar panels. CdTe is a thin-film semiconductor that absorbs sunlight.

Tellurium can be replaced by other elements in some of its uses. For many metallurgical uses, selenium, bismuth, or lead are effective substitutes. Both selenium and sulfur can replace tellurium in rubber production. Technologies based on tellurium have global impacts. As a photovoltaic, CdTe is the second most utilized solar cell in the world, soon said to surpass crystalline silicon and become the first. According to the US military, tellurium-based infrared detectors are the reason that the military has such an advantage at night, an advantage which, in turn, has an effect on global and domestic politics.

Environmental Impacts

Tellurium extraction, as a byproduct of copper refinement, shares environmental impacts associated with copper mining and extraction. While a generally safe process, the removal of copper from other impurities in the ore can lead to leaching of various hazardous sediments. In addition, the mining of copper tends to lead to reduced water flow and quality, disruption of soils and erosion of riverbanks, and reduction of air quality.

Resource Limitations v. Demand

About 215-220 tons of tellurium are mined across the globe every year. In 2006, the US produced 40% of the global production, Peru produced 30%, Japan produced 20%, and Canada produced 10% of the world's tellurium supply (since the chart can't be any bigger). The leading countries in production are the United States with 50 tons per year, Japan with 40 tons per year, Canada with 16 tons per year, and Peru with 7 tons per year (year 2009). When pure, tellurium costs $24 per 100 grams. Because tellurium is about as rare as platinum on earth, the United States Department of Energy expects a supply shortfall by the year 2025, despite the always improving extraction methods. As demand increases to provide the tellurium needed for solar panels and other such things, supply will continue to decrease and thus the price will skyrocket. This will cause waves in the sustainable energy movement as well as military practices and modern medicine.

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7.9.6: Chemistry of Polonium (Z=84)

Polonium was discovered in 1898 by Marie Curie and named for her native country of Poland. The discovery was made by extraction of the remaining radioactive components of pitchblende following the removal of uranium. There is only about 10^{-6} g per ton of ore! Current production for research purposes involves the synthesis of the element in the lab rather than its recovery from minerals. This is accomplished by producing Bi-210 from the abundant Bi-209. The new isotope of bismuth is then allowed to decay naturally into Po-210. The sample pictured above is actually a thin film of polonium on stainless steel.

Although radioactive, polonium has a few commercial uses. You can buy your own sample of polonium at a photography store. It is part of the special anti-static brushes for dusting off negatives and prints.

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7.9.7: Chemistry of Livermorium (Z=116)

In May of 2012 the IUPAC approved the name "Livermorium" (symbol Lv) for element 116. The new name honors the Lawrence Livermore National Laboratory (1952). A group of researchers of this laboratory with the heavy element research group of the Flerov Laboratory of Nuclear Reactions took part in the work carried out in Dubna on the synthesis of superheavy elements including element 116. Atoms of Lv were formed by the reaction of Cm-248 with Ca-48. The resulting Lv-292 decays by alpha emission to Fl-288.

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SECTION OVERVIEW

7.10: The Halogens

The halogens are located on the left of the noble gases on the periodic table. These five toxic, non-metallic elements make up Group 17 of the periodic table and consist of: fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At). Although astatine is radioactive and only has short-lived isotopes, it behaves similar to iodine and is often included in the halogen group. Because the halogen elements have seven valence electrons, they only require one additional electron to form a full octet. This characteristic makes them more reactive than other non-metal groups.

7.10.1: Physical Properties of the Halogens

- 7.10.1.1: Atomic and Physical Properties of Halogens
- 7.10.1.2: General Properties of Halogens
- 7.10.1.3: Halogen Group (Group 17) Trends
- 7.10.1.4: Physical Properties of the Group 17 Elements

7.10.2: Chemical Properties of the Halogens

- 7.10.2.1: Halide Ions as Reducing Agents
- 7.10.2.2: Halogens as Oxidizing Agents
- 7.10.2.3: Interhalogens
- 7.10.2.4: More Reactions of Halogens
- 7.10.2.5: Oxidizing Ability of the Group 17 Elements
- 7.10.2.6: Testing for Halide Ions
- 7.10.2.7: The Acidity of the Hydrogen Halides

7.10.3: Chemistry of Fluorine (Z=9)

7.10.4: Chemistry of Chlorine (Z=17)

- 7.10.4.1: The Manufacture of Chlorine

7.10.5: Chemistry of Bromine (Z=35)

7.10.6: Chemistry of Iodine (Z=53)

7.10.7: Chemistry of Astatine (Z=85)

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7.10.1: Physical Properties of the Halogens

Some chemical and physical properties of the halogens are summarized in Table **7.10.1.1**. It can be seen that there is a regular increase in many of the properties of the halogens proceeding down group 17 from fluorine to iodine. This includes their melting points, boiling points, the intensity of their color, the radius of the corresponding halide ion, and the density of the element. On the other hand, there is a regular decrease in the first ionization energy as we go down this group. As a result, there is a regular increase in the ability to form high oxidation states and a decrease in the oxidizing strength of the halogens from fluorine to iodine.

Table **7.10.1.1**: Properties of Group 17 (The Halogens)

Property	F	Cl	Br	I
Atomic number, Z	9	17	35	53
Ground state electronic configuration	[He]$2s^2$ $2p^5$	[Ne]$3s^2$ $3p^5$	[Ar]$3d^{10}$ $4s^2$ $4p^5$	[Kr]$4d^{10}$ $5s^2$ $5p^5$
color	pale yellow gas	yellow-green gas		
Density of liquids at various temperatures, /kg m^{-3}	1.51 (85 °K)	1.66 (203 °K)	3.19 (273 °K)	3.96 (393 °K)
Melting point, /K	53.53	171.6	265.8	386.85
Boiling point, /K	85.01	239.18	331.93	457.5
Enthalpy of atomization, $\Delta_a H°$ (298K) / kJ mol^{-1}	79.08	121.8	111.7	106.7
Standard enthalpy of fusion of X_2, $\Delta_{fus}H°$(mp) / kJ mol^{-1}	0.51	6.4	10.57	15.52
Standard enthalpy of vaporization of X_2, $\Delta_{vap}H°$(bp) / kJ mol^{-1}	6.62	20.41	29.96	41.57
First ionization energy, IE_1 / kJ mol^{-1}	1681	1251.1	1139.9	1008.4
$\Delta_{EA}H_1°$(298K) / kJ mol^{-1}	-333	-348	-324	-295
$\Delta_{hyd}H°(X^-,g)$ / kJ mol^{-1}	-504	-361	-330	-285
$\Delta_{hyd}S°(X^-,g)$ / JK^{-1} mol^{-1}	-150	-90	-70	-50
$\Delta_{hyd}G°(X^-,g)$ / kJ mol^{-1}	-459	-334	-309	-270
Standard redox potential, $E°(X_2/2X^-)$ /V	2.87	1.36	1.09	0.54
Covalent radius, r_{cov} = ½ X-X bond length /pm	72	100	114.2	133.3
Ionic radius, r_{ion} for X^- /pm	133	181	196	220
van der Waals radius, r_v /pm	135	180	195	215
X-X(g)bond energy /kJ mol^{-1}	159	243	193	151
H-X(g)bond energy /kJ mol^{-1}	562	431	366	299
C-X(g)bond energy /kJ mol^{-1}	484	338	276	238
Pauling	3.98	3.16	2.96	2.66

Property	F	Cl	Br	I
electronegativity, χ^P				

Color

The origin of the color of the halogens stems from the excitation between the highest occupied π* molecular orbital and the lowest unoccupied σ* molecular orbital. The energy gap between the HOMO and LUMO decreases according to $F_2 > Cl_2 > Br_2 > I_2$. The amount of energy required for excitation depends upon the size of the atom. Fluorine is the smallest element in the group and the force of attraction between the nucleus and the outer electrons is very large. As a result, it requires a large excitation energy and absorbs violet light (high energy) and so appears pale yellow. On the other hand, iodine needs significantly less excitation energy and absorbs yellow light of low energy. Thus it appears dark violet. Using similar arguments, it is possible to explain the greenish yellow color of chlorine and the reddish brown color of bromine.

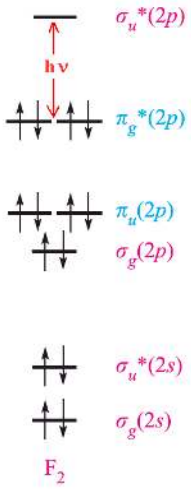


Figure* 7.10.1.1*: *Molecular orbital diagram for fluorine.*

The halogens show a variety of colors when dissolved in different solvents. Solutions of iodine can be bright violet in CCl_4, pink or reddish brown in aromatic hydrocarbons, and deep brown in alcohols, for example. This variety can be explained by weak donor-acceptor interaction and complex formation. The presence of charge-transfer bands further supports this since they are thought to be derived from interaction with the HOMO σ_u^* orbital.

The X-ray structure of some of these complexes have been obtained, and often the intense color can be used for characterization and determination such as the bright blue color of iodine in the presence of starch. In the case of the solid formed between dibromine and benzene, the structure is shown below and a new charge transfer band occurs at 292 nm. The Br-Br bond length is essentially unchanged from that of dibromine (228 pm).

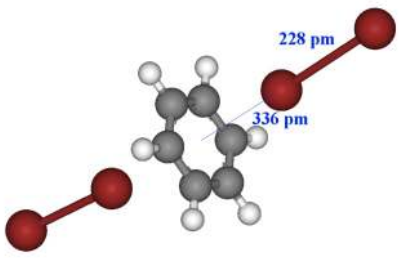


Figure* 7.10.1.2*: *Structure of dibromine and benzene complex*

In a study of the reaction of dibromine with substituted phosphines in diethyl ether, all but one showed a tetrahedral arrangement where one bromine was linked to the phosphorus.[3]

$$R_3P + Br_2(Et_2O, N_2/r.t.) \rightarrow R_3PBr_2 \qquad (7.10.1.1)$$

The X-ray study of the triethylphosphine was interpreted as $[Et_3PBr]Br$, where the Br-Br separation was 330 pm. This is considerably longer than the 228 pm found above and was taken to mean that the compound was ionic. In the case of the tri(perfluorophenyl)phosphine, however, the structure showed both bromines linked to give a trigonal bipyramid arrangement with D_3 symmetry. Why $(C_6F_5)_3PBr_2$ was the only R_3PBr_2 compound that adopted trigonal bipyramidal geometry was reasoned to be due to the very low basicity of the parent tertiary phosphine.

Melting and Boiling Points

Intermolecular forces are the attractive forces between molecules without which all substances would be gases. The various types of these interactions span large differences in energy and for the halogens and interhalogens are generally quite small. The dispersion forces involved in these cases are called London forces (after Fritz Wolfgang London, 1900-1954). They are derived from momentary oscillations of electron charge in atoms and hence are present between all particles (atoms, ions and molecules).

The ease with which the electron cloud of an atom can be distorted to become asymmetric is termed the molecule's **polarizability**. The greater the number of electrons an atom has, the farther the outer electrons will be from the nucleus, and the greater the chance for them to shift positions within the molecule. This means that larger nonpolar molecules tend to have stronger London dispersion forces. This is evident when considering the diatomic elements in group 17, the Halogens. All of these diatomic elements are nonpolar, covalently bonded molecules. Descending the group, fluorine and chlorine are gases, bromine is a liquid, and iodine is a solid. For nonpolar molecules, the farther you go down the group, the stronger the London dispersion forces.

To picture how this occurs, compare the situation 1) where the electrons are evenly distributed and then consider 2) an instantaneous dipole that would arise from an uneven distribution of electrons on one side of the nucleus. When two molecules are close together, the instantaneous dipole of one molecule can induce a dipole in the second molecule. This results in synchronized motion of the electrons and an attraction between them. 3) Multiply this effect over numerous molecules and the overall result is that the attraction keeps these molecules together, and for diiodine is sufficient to make this a solid.

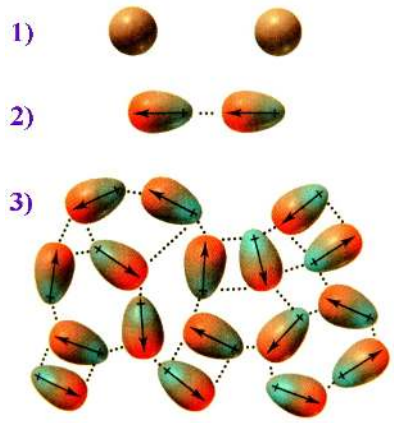


Figure* 7.10.1.3*: *On average the electron cloud for molecules can be considered to be spherical in shape. When two non-polar molecules approach, attractions or repulsions between the electrons and nuclei can lead to distortions in their electron clouds (i.e., dipoles are induced). When more molecules interact, these induced dipoles lead to intermolecular attraction.*

The changes seen in the variation of MP and BP for the dihalogens and binary interhalogens can be attributed to the increase in the London dispersion forces of attraction between the molecules. In general they increase with increasing atomic number.

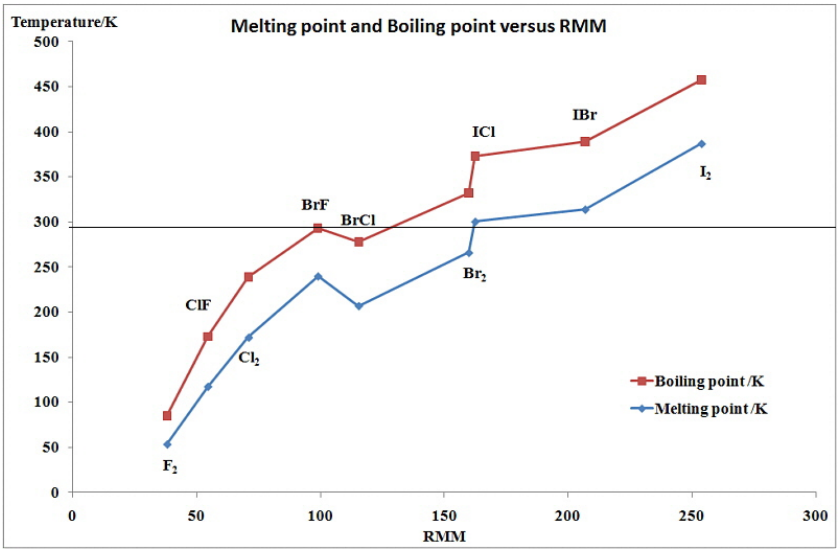


Figure 4:

Redox Properties

The most characteristic chemical feature of the halogens is their oxidizing strength. Fluorine has the strongest oxidizing ability, so that a simple chemical preparation is almost impossible and it must be prepared by electrolysis. Note that since fluorine reacts explosively with water, oxidizing it to dioxygen, finding reaction conditions for any reaction can be difficult. When fluorine is combined with other elements they generally exhibit high oxidation states. Chlorine is the next strongest oxidizing agent, but it can be prepared by chemical oxidation. Most elements react directly with chlorine, bromine and iodine, with decreasing reactivity going down the group, but often the reaction must be activated by heat or UV light. [2] The energy changes in redox process are:

1. Enthalpy of atomization,
2. $\Delta_{EA}H_1$,
3. $\Delta_{hyd}H°(X^-,g)$

The redox potential, E°, $X_2/2X^-$, measures a free-energy change, usually dominated by the ΔH term. The values in the Table below show that there is a decrease in oxidizing strength proceeding down the group (2.87, 1.36, 1.09, 0.54 V). This can be explained by comparing the steps shown above.

- 1) atomization of the dihalide is the energy required to break the molecule into atoms:

$$\tfrac{1}{2}X_{2(g)} \rightarrow X_{(g)} \tag{7.10.1.2}$$

Note that only F_2 and Cl_2 are gases in their natural states, so the energies associated with atomization of Br_2 and I_2 require converting the liquid or solid to gas first.

- 2) $\Delta_{EA}H_1$ is the energy liberated when the atom is converted into a negative ion and is related to the Electron Affinity

$$X_{(g)} + e^- \rightarrow X^-_{(g)} \tag{7.10.1.3}$$

Addition of an electron to the small F atom is accompanied by larger e^-/e^- repulsion than is found for the larger Cl, Br or I atoms. This would suggest that the process for F should be less exothermic than for Cl and not fit the trend that shows a general decrease going down the group.

- 3) $\Delta_{hyd}H°(X^-,g)$ is the energy liberated upon the hydration of the ion, the Hydration energy.

$$X^-_{(g)} + H_2O \rightarrow X^-_{(aq)} \tag{7.10.1.4}$$

The overall reaction is then:

$$\tfrac{1}{2}X_{2(g)} \rightarrow X^-_{(aq)} \tag{7.10.1.5}$$

Table 7.10.1.2

Halogen	atomization energy (kJ mol^{-1})	$\Delta_{EA}H_1$ (kJ mol^{-1})	hydration enthalpy (kJ mol^{-1})	overall (kJ mol^{-1})
F	+79.08	-333	-504	-758
Cl	+121.8	-348	-361	-587
Br	+111.7	-324	-330	-542
I	+106.7	-295	-285	-473

This shows a very negative energy change for the fluoride compared to the others in the group. This comes about because of two main factors: the high hydration energy and the low atomization energy. For F_2 2) is less than for Cl_2, but since the energy needed to break the F-F bond is also less and the hydration more, the total energy drop is much greater. In spite of their lower atomization energies, Br_2 and I_2 are weaker oxidizing agents than Cl_2 and this is due to their smaller $\Delta_{EA}H_1$ and smaller $\Delta_{hyd}H°$.

It can be seen that the $\Delta_{EA}H_1$ value for fluorine is in between those for chlorine and bromine and so this value alone does not provide a good explanation for the observed variation.

Each of the halogens is able to oxidize any of the heavier halogens situated below it in the group. They can oxidize hydrogen and nonmetals such as:

$$X_2 + H_{2(g)} \rightarrow 2HX_{(g)} \tag{7.10.1.6}$$

In water, the halogens disproportionate according to:

$$X_2 + H_2O_{(l)} \rightarrow HX_{(aq)} + HXO_{(aq)} \tag{7.10.1.7}$$

where $X = Cl, Br, I$. When base is added then the reaction goes to completion forming hypohalites, or at higher temperatures, halates; for example, heating dichlorine:

$$3Cl_{2(g)} + 6OH^-_{(aq)} \rightarrow ClO^-_{3(aq)} + 5Cl^-_{(aq)} + 3H_2O(l) \tag{7.10.1.8}$$

First Ionization Energies

The trend seen for the complete removal of an electron from the gaseous halogen atoms is that fluorine has the highest IE_1 and iodine the lowest. To overcome the attractive force of the nucleus means that energy is required, so the Ionization Energies are all positive. The variation with size can be explained, since as the size increases it take less energy to remove an electron. This inverse relationship is seen for all the groups, not just group 17. As the distance from the nucleus to the outermost electrons increases, the attraction decreases so that those electrons are easier to remove. The high value of IE_1 for fluorine is such that it does not exhibit any positive oxidation states, whereas Cl, Br and I can exist in oxidation states as high as 7.

Oxidation states

Fluorine is the most electronegative element in the periodic table and exists in all its compounds in either the -1 or 0 oxidation state. Chlorine, bromine, and iodine, however, can be found in a range of oxidation states including: +1, +3, +5, and +7, as shown below.

Table 7.10.1.3: Common Oxidation States for the Halogens

Oxidation States	Examples
-1	CaF_2, HCl, NaBr, AgI
0	F_2, Cl_2, Br_2, I_2
1	H**Cl**O, **Cl**F
3	H**Cl**O_2, **Cl**F_3
5	H**Cl**O_3, **Br**F_5, [**Br**F_6]$^-$, **I**F_5
7	H**Cl**O_4, **Br**F_6^+, **I**F_7, [**I**F_8]$^-$

In general, odd-numbered groups (like group 17) form odd-numbered oxidation states, and this can be explained since all stable molecules contain paired electrons (free radicals are obviously much more reactive). When covalent bonds are formed or broken, two electrons are involved, so the oxidation state changes by 2.

When difluorine reacts with diiodine, initially iodine monofluoride is formed.

$$I_2 + F_2 \rightarrow 2IF$$

Adding a second difluorine uses two more iodine valence electrons to form two more bonds:

$$2IF + F_2 \rightarrow IF_3$$

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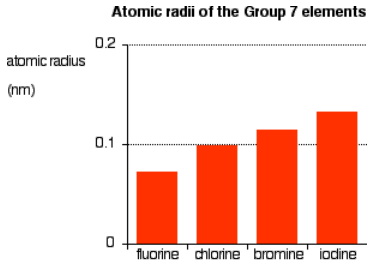
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7.10.1.1: Atomic and Physical Properties of Halogens

This page discusses the trends in the atomic and physical properties of the Group 7 elements (the halogens): fluorine, chlorine, bromine and iodine. Sections below cover the trends in atomic radius, electronegativity, electron affinity, melting and boiling points, and solubility, including a discussion of the bond enthalpies of halogen-halogen and hydrogen-halogen bonds.

Trends in Atomic Radius



The figure above shows the increase in atomic radius down the group.

Explaining the increase in atomic radius

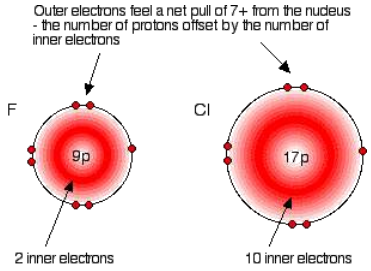
The radius of an atom is determined by:

- the number of layers of electrons around the nucleus
- the pull the outer electrons feel from the nucleus.

Compare the numbers of electrons in each layer of fluorine and chlorine:

F		2,7
Cl		2,8,7

In each case, the outer electrons feel a net +7 charge from the nucleus. The positive charge on the nucleus is partially neutralized by the negative inner electrons.

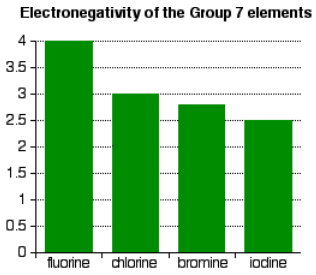


This is true for all the atoms in Group 7: the outer electrons experience a net charge of +7..

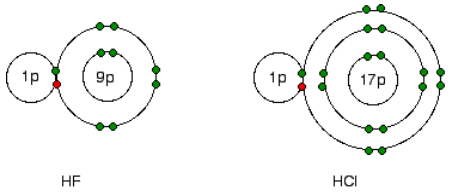
The only factor affecting the size of the atom is therefore the number of layers of inner electrons surrounding the atom. More layers take up more space due to electron repulsion, so atoms increase in size down the group.

Trends in Electronegativity

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons. It is usually measured on the Pauling scale, on which the most electronegative element (fluorine) is assigned an electronegativity of 4.0. The figure below shows electronegativities for each halogen:



Notice that electronegativity decreases down the group. The atoms become less effective at attracting bonding pairs of electrons. This effect is illustrated below using simple dots-and-crosses diagrams for hydrogen fluoride and hydrogen chloride:



The bonding pair of electrons between the hydrogen and the halogen experiences the same net pull of +7 from both the fluorine and the chlorine. However, in the chlorine case, the nucleus is farther away from the bonding electrons, which are therefore not as strongly attracted as in the fluorine case.

The stronger attraction from the closer fluorine nucleus makes fluorine more electronegative than chlorine.

Summarizing the trend down the Group

As the halogen atoms increase in size, any bonding pair gets farther away from the halogen nucleus, and so is less strongly attracted toward it. Hence, down the group, the elements become less electronegative.

Trends in First Electron Affinity

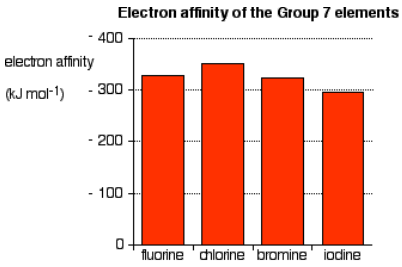
The first electron affinity is the energy released when 1 mole of gaseous atoms each acquire an electron to form 1 mole of gaseous 1- ions. In other words, it is the energy released in the following process:

$$X(g) + e^- \rightarrow X^-(g)$$

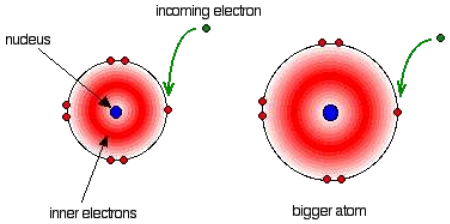
First electron affinities have negative values by convention. For example, the first electron affinity of chlorine is -349 kJ mol^{-1}. The negative sign indicates a release of energy.

The first electron affinities of the Group 7 elements

The electron affinity is a measure of the attraction between the incoming electron and the nucleus. There is a positive correlation between attraction and electron affinity. The trend down the group is illustrated below:



Notice that the trend down the group is inconsistent. The electron affinities generally decrease (meaning less heat is emitted), but the fluorine value deviates from this trend.



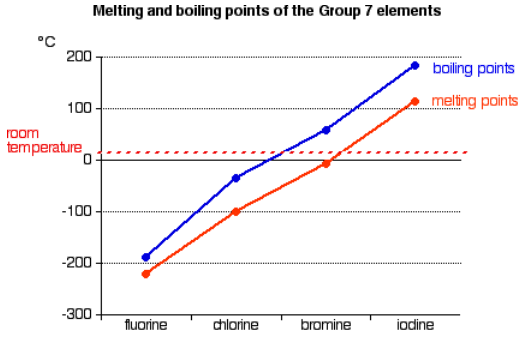
In the larger atom, the attraction from the more positive nucleus is offset by the additional screening electrons, so each incoming electron feels the effect of a net +7 charge from the center.

As the atom increases in size, the incoming electron is farther from the nucleus and so feels less attraction. The electron affinity therefore decreases down the group. However fluorine is a very small atom, with the incoming electron relatively close to the nucleus, and yet the electron affinity is smaller than expected.

Another effect must be considered in the case of fluorine. As the new electron comes approaches the atom, it enters a region of space already very negatively charged because of the existing electrons. The resulting repulsion from these electrons offsets some of the attraction from the nucleus.

Because the fluorine atom is very small, its existing electron density is very high. Therefore, the extra repulsion is particularly great and diminishes the attraction from the nucleus enough to lower the electron affinity below that of chlorine.

Trends in Melting Point and Boiling Point



Melting and boiling points increase down the group. As indicated by the graph above, fluorine and chlorine are gases at room temperature, bromine is a liquid and iodine a solid.

Explaining the trends in melting point and boiling point

All the halogens exist as diatomic molecules—F_2, Cl_2, and so on. van der Waals dispersion forces are the primary intermolecular attractions between one molecule and its neighbors. Larger molecules farther down the group have more electrons which can move around and form the temporary dipoles that create these forces.

The stronger intermolecular attractions down the group require more heat energy for melting or vaporizing, increasing their melting or boiling points.

Solubilities

Solubility in water

Fluorine reacts violently with water to produce aqueous or gaseous hydrogen fluoride and a mixture of oxygen and ozone; its solubility is meaningless. Chlorine, bromine, and iodine all dissolve in water to some extent, but there is again no discernible pattern. The following table shows the solubility of the three elements in water at 25°C:

	solubility (mol dm^{-3})
chlorine	0.091
bromine	0.21
iodine	0.0013

Chlorine dissolved in water produces a pale green solution. Bromine solution adopts a range of colors from yellow to dark orange-red depending on the concentration. Iodine solution in water is very pale brown. Chlorine reacts with water to some extent, producing a mixture of hydrochloric acid and chloric(I) acid (also known as hypochlorous acid). The reaction is reversible, and at any time only about a third of the chlorine molecules have reacted.

$$Cl_2 + H_2O \rightleftharpoons HCl + HClO$$

Chloric(I) acid is sometimes symbolized as HOCl, indicating the actual bonding pattern. Bromine and iodine form similar compounds, but to a lesser extent. In both cases, about 99.5% of the halogen remains unreacted.

The solubility of iodine in potassium iodide solution

Although iodine is only slightly soluble in water, it dissolves freely in potassium iodide solution, forming a dark red-brown solution. A reversible reaction between iodine molecules and iodide ions gives I_3^- ions. These are responsible for the color. In the laboratory, iodine is often produced through oxidation of iodide ions. As long as there are any excess iodide ions present, the iodine reacts to form I_3^-. Once the iodide ions have all reacted, the iodine is precipitated as a dark gray solid.

Solubility in hexane

The halogens are much more soluble in organic solvents such as hexane than they are in water. Both hexane and the halogens are non-polar molecules, so the only intermolecular forces between them are van der Waals dispersion forces. Because of this, the attractions broken (between hexane molecules and between halogen molecules) are similar to the new attractions made when the two substances mix. Organic solutions of iodine are pink-purple in color.

Bond enthalpies (bond energies or bond strengths)

Bond enthalpy is the heat required to break one mole of covalent bonds to produce individual atoms, starting from the original substance in the gas state, and ending with gaseous atoms. For chlorine, $Cl_{2(g)}$, it is the heat energy required for the following reaction, per mole:

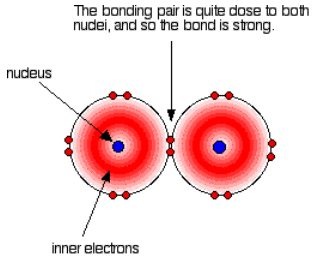
$$Cl-Cl(g) \rightarrow 2Cl(g)$$

Although bromine is a liquid, the bond enthalpy is defined in terms of gaseous bromine molecules and atoms, as shown below:

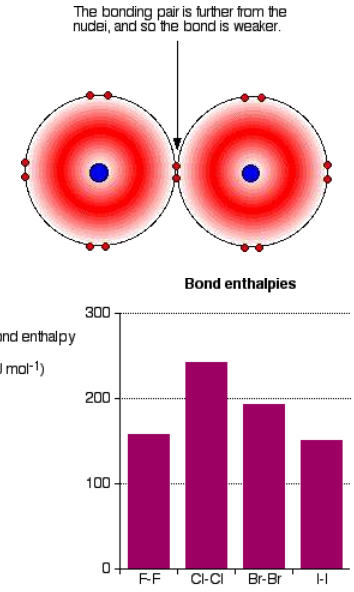


Bond enthalpy in the halogens, $X_2(g)$

Covalent bonding is effective because the bonding pair is attracted to both the nuclei at either side of it. It is that attraction which holds the molecule together. The extent of the attraction depends in part on the distances between the bonding pair and the two nuclei. The figure below illustrates such a covalent bond:



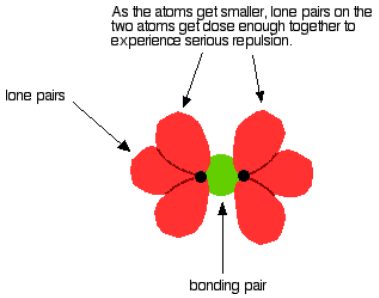
In all halogens, the bonding pair experiences a net +7 charge from either end of the bond, because the charge on the nucleus is offset by the inner electrons. As the atoms get larger down the group, the bonding pair is further from the nuclei and the strength of the bond should, in theory, decrease, as indicated in the figure below. The question is whether experimental data matches this prediction.



As is clear from the figure above, the bond enthalpies of the Cl-Cl, Br-Br and I-I bonds decreases as predicted, but the F-F bond enthalpy deviates.

Because fluorine atoms are so small, a strong bond is expected—in fact, it is remarkably weak. There must be another factor for consideration.

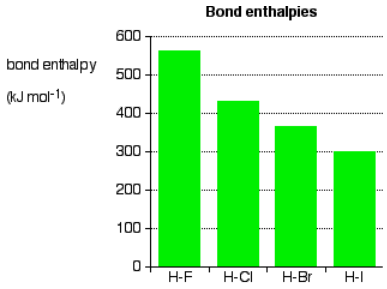
In addition to the bonding pair of electrons between the two atoms, each atom has 3 lone pairs of electrons in the outer shell. If the bond is very short,as in F-F, the lone pairs on the two atoms are close enough to cause significant repulsion, illustrated below:



In the case of fluorine, this repulsion is great enough to counteract much of the attraction between the bonding pair and the two nuclei. This weakens the bond.

Bond enthalpies in the hydrogen halides, $H_X(g)$

If the halogen atom is attached to a hydrogen atom, this does not occur; there are no lone pairs on a hydrogen atom. Bond enthalpies for halogen-hydrogen bonds are given below:



As larger halogens are involved, the bonding pair is more distant from the nucleus. The attraction is lessened, and the bond should be weaker; this is supported by the data, without exception. This fact has significant implications for the thermal stability of the hydrogen halides— they are easily broken into hydrogen and the halogen on heating.

Hydrogen fluoride and hydrogen chloride are thermally very stable under typical laboratory conditions. Hydrogen bromide breaks down to some extent into hydrogen and bromine on heating, and hydrogen iodide is even less stable when heated. Weaker bonds are more easily broken.

Contributors and Attributions

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7.10.1.2: General Properties of Halogens

The halogens are located on the left of the noble gases on the periodic table. These five toxic, non-metallic elements make up Group 17 of the periodic table and consist of: fluorine (F), chlorine (Cl), bromine (Br), iodine (I), and astatine (At). Although astatine is radioactive and only has short-lived isotopes, it behaves similarly to iodine and is often included in the halogen group. Because the halogen elements have seven valence electrons, they only require one additional electron to form a full octet. This characteristic makes them more reactive than other non-metal groups.

Introduction

Halogens form diatomic molecules (of the form X_2, where X denotes a halogen atom) in their elemental states. The bonds in these diatomic molecules are non-polar covalent single bonds. However, halogens readily combine with most elements and are never seen uncombined in nature. As a general rule, fluorine is the most reactive halogen and astatine is the least reactive. All halogens form Group 1 salts with similar properties. In these compounds, halogens are present as halide anions with charge of -1 (e.g., Cl^-, Br^-, etc.). Replacing the -ine ending with an -ide ending indicates the presence of halide anions; for example, Cl^- is named "chloride." In addition, halogens act as oxidizing agents—they exhibit the property to oxidize metals. Therefore, most of the chemical reactions that involve halogens are oxidation-reduction reactions in aqueous solution. When in the -1 oxidation state, with carbon or nitrogen in organic compounds, the halogens often form single bonds. When a halogen atom is substituted for a covalently-bonded hydrogen atom in an organic compound, the prefix *halo-* can be used in a general sense, or the prefixes *fluoro-*, *chloro-*, *bromo-*, or *iodo-* can be used for specific halogen substitutions. Halogen elements can cross-link to form diatomic molecules with polar covalent single bonds.

Chlorine (Cl_2) was the first halogen to be discovered in 1774, followed by iodine (I_2), bromine (Br_2), fluorine (F_2), and astatine (At, discovered last in 1940). The name "halogen" is derived from the Greek roots hal- ("salt") and -gen ("to form"). Together these words combine to mean "salt former", referencing the fact that halogens form salts when they react with metals. *Halite* is the mineral name for rock salt, a natural mineral consisting essentially of sodium chloride (NaCl). Lastly, the halogens are also relevant in daily life, whether it be the fluoride that goes into toothpaste, the chlorine that disinfects drinking water, or the iodine that facilitates the production of thyroid hormones in one's body.

Elements

Fluorine - Fluorine has an atomic number of 9 and is denoted by the symbol F. Elemental fluorine was first discovered in 1886 by isolating it from hydrofluoric acid. Fluorine exists as a diatomic molecule in its free state (F_2) and is the most abundant halogen found in the Earth's crust. Fluorine is the most electronegative element in the periodic table. It appears as a pale yellow gas at room temperature. Fluorine also has a relatively small atomic radius. Its oxidation state is always -1 except in its elemental, diatomic state (in which its oxidation state is zero). Fluorine is extremely reactive and reacts directly with all elements except helium (He), neon (Ne) and argon (Ar). In H_2O solution, hydrofluoric acid (HF) is a weak acid. Although fluorine is highly electronegative, its electronegativity does not determine its acidity; HF is a weak acid due to the fact that the fluoride ion is basic (pH>7). In addition, fluorine produces very powerful oxidants. For example, fluorine can react with the noble gas xenon and form the strong oxidizing agent Xenon Difluoride (XeF_2). There are many uses for fluorine, which will be discussed later.

Chlorine - Chlorine has the atomic number 17 and the chemical symbol Cl. Chlorine was discovered in 1774 by extracting it from hydrochloric acid. In its elemental state, it forms the diatomic molecule Cl_2. Chlorine exhibits multiple oxidation states, such as -1, +1, +3, +5, and +7. At room temperature it appears as a light green gas. Since the bond that forms between the two chlorine atoms is weak, the Cl_2 molecule is very reactive. Chlorine reacts with metals to produce salts called chlorides. Chloride ions are the most abundant ions that dissolve in the ocean. Chlorine also has two isotopes: ^{35}Cl and ^{37}Cl. Sodium chloride is the most prevalent compound of the chlorides.

Bromine - Bromine has an atomic number of 35 with a symbol of Br. It was first discovered in 1826. In its elemental form, it is the diatomic molecule Br_2. At room temperature, bromine is a reddish- brown liquid. Its oxidation states vary from -1, +1, 3, 4 and 5. Bromine is more reactive than iodine, but not as reactive as chlorine. Also, bromine has two isotopes: ^{79}Br and ^{81}Br. Bromine consists of bromide salts, which have been found in the sea. The world production of bromide has increased significantly over the years, due to its accessibility and longer existence. Like all of the other halogens, bromine is an oxidizing agent, and is very toxic.

Iodine - Iodine has the atomic number 53 and symbol I. Iodine has oxidation states -1, +1, +5 and +7. Iodine exists as a diatomic molecule, I_2, in its elemental state. At room temperature, it appears as a violet solid. Iodine has one stable isotope: ^{127}I. It was first discovered in 1811 through the use of seaweed and sulfuric acid. Currently, iodide ions can be isolated in seawater. Although iodine is not very soluble in water, the solubility may increase if particular iodides are mixed into the solution. Iodine has many important roles in life, including thyroid hormone production. This will be discussed in Part VI of the text.

Astatine - Astatine is a radioactive element with an atomic number of 85 and symbol At. Its possible oxidation states include: -1, +1, +3, +5, and +7. It is the only halogen that is not a diatomic molecule, and it appears as a black, metallic solid at room temperature. Astatine is a very rare element, so there is not that much known about this element. In addition, astatine has a very short radioactive half-life, no longer than a couple of hours. It was discovered in 1940 by synthesis. Also, it is thought that astatine is similar to iodine. However, these two elements are assumed to differ in their metallic character.

Table 1.1: Electron configurations of the halogens.

Halogen	Electronic Configuration
Fluorine	$1s^2\ 2s^2\ 2p^5$
Chlorine	$[Ne]3s^2\ 3p^5$
Bromine	$[Ar]3d^{10}\ 4s^2\ 4p^5$
Iodine	$[Kr]4d^{10}\ 5s^2\ 5p^5$
Astatine	$[Xe]4f^{14}\ 5d^{10}\ 6s^2\ 6p^5$

Periodic Trends

The periodic trends observed in the halogen group:

Melting and Boiling Points (increase down the group)

The melting and boiling points increase down the group because of the van der Waals forces. The size of the molecules increases down the group. This increase in size means an increase in the strength of the van der Waals forces.

$$F < Cl < Br < I < At$$

Table 1.2: Melting and Boiling Points of Halogens

Halogen	Melting Point (˚C)	Boiling Point (˚C)
Fluorine	-220	-188
Chlorine	-101	-35
Bromine	-7.2	58.8
Iodine	114	184
Astatine	302	337

Atomic Radius (increases down the group)

The size of the nucleus increases down a group (F < Cl < Br < I < At) because the numbers of protons and neutrons increase. In addition, more energy levels are added with each period. This results in a larger orbital, and therefore a longer atomic radius.

Table 1.3: Atomic Radii of Halogens

Halogen	Covalent Radius (pm)	Ionic (X-) radius (pm)
Fluorine	71	133
Chlorine	99	181
Bromine	114	196
Iodine	133	220
Astatine	150	

Ionization Energy (decreases down the group)

If the outer valence electrons are not near the nucleus, it does not take as much energy to remove them. Therefore, the energy required to pull off the outermost electron is not as high for the elements at the bottom of the group since there are more energy levels. Also, the high ionization energy makes the element appear non-metallic. Iodine and astatine display metallic properties, so ionization energy decreases down the group (At < I < Br < Cl < F).

Table 1.4 Ionization Energy of Halogens

Halogen	First Ionization Energy (kJ/mol)
Fluorine	1681
Chlorine	1251
Bromine	1140
Iodine	1008
Astatine	890±40

Electronegativity (decreases down the group)

The number of valence electrons in an atom increases down the group due to the increase in energy levels at progressively lower levels. The electrons are progressively further from the nucleus; therefore, the nucleus and the electrons are not as attracted to each other. An increase in shielding is observed. Electronegativity therefore decreases down the group (At < I < Br < Cl < F).

Table 1.5: Electronegativity of Halogens

Halogen	Electronegativity
Fluorine	4.0
Chlorine	3.0
Bromine	2.8
Iodine	2.5
Astatine	2.2

Electron Affinity (decreases down the group)

Since the atomic size increases down the group, electron affinity generally decreases (At < I < Br < **F** < Cl). An electron will not be as attracted to the nucleus, resulting in a low electron affinity. However, fluorine has a lower electron affinity than chlorine. This can be explained by the small size of fluorine, compared to chlorine.

Table 1.6: Electron Affinity of Halogens

Halogen	Electron Affinity (kJ/mol)
Fluorine	-328.0
Chlorine	-349.0
Bromine	-324.6
Iodine	-295.2
Astatine	-270.1

Reactivity of Elements (decreases down the group)

The reactivities of the halogens decrease down the group (At < I < Br < Cl < F). This is due to the fact that the atomic radius increases in size with an increase of electronic energy levels. This lessens the attraction for valence electrons of other atoms, decreasing reactivity. This decrease also occurs because electronegativity decreases down a group; therefore, there is less electron "pulling." In addition, there is a decrease in oxidizing ability down the group.

Hydrogen Halides and Halogen Oxoacids

Hydrogen Halides

A halide is formed when a halogen reacts with another, less electronegative element to form a binary compound. Hydrogen, for example, reacts with halogens to form halides of the form HX:

- Hydrogen Fluoride: HF
- Hydrogen Chloride: HCl
- Hydrogen Bromide: HBr
- Hydrogen Iodide: HI

Hydrogen halides readily dissolve in water to form hydrohalic (*hydrofluoric*, *hydrochloric*, *hydrobromic*, *hydroiodic*) acids. The properties of these acids are given below:

- The acids are formed by the following reaction: $HX\ (aq) + H_2O\ (l) \rightarrow X^-\ (aq) + H_3O^+\ (aq)$
- All hydrogen halides form strong acids, except HF
- The acidity of the hydrohalic acids increases as follows: HF < HCl < HBr < HI

Hydrofluoric acid can etch glass and certain inorganic fluorides over a long period of time.

It may seem counterintuitive to say that HF is the weakest hydrohalic acid because fluorine has the highest electronegativity. However, the H-F bond is very strong; if the H-X bond is strong, the resulting acid is weak. A strong bond is determined by a short bond length and a large bond dissociation energy. Of all the hydrogen halides, HF has the shortest bond length and largest bond dissociation energy.

Halogen Oxoacids

A halogen oxoacid is an acid with hydrogen, oxygen, and halogen atoms. The acidity of an oxoacid can be determined through analysis of the compound's structure. The halogen oxoacids are given below:

- Hypochlorous Acid: HOCl
- Chlorous Acid: $HClO_2$
- Chloric Acid: $HClO_3$
- Perchloric Acid: $HClO_4$
- Hypobromous Acid: HOBr
- Bromic Acid: $HBrO_3$
- Perbromic Acid: $HBrO_4$
- Hypoiodous Acid: HOI
- Iodic Acid: HIO_3

- Metaperiodic Acid: HIO_4; H_5IO_6

In each of these acids, the proton is bonded to an oxygen atom; therefore, comparing proton bond lengths is not useful in this case. Instead, electronegativity is the dominant factor in the oxoacid's acidity. Acidic strength increases with more oxygen atoms bound to the central atom.

States of Matter at Room Temperature

Table 1.7: States of Matter and Appearance of Halogens

States of Matter (at Room Temperature)	Halogen	Appearance
Solid	Iodine	Violet
	Astatine	Black/Metallic [Assumed]
Liquid	Bromine	Reddish-Brown
Gas	Fluorine	Pale Yellow-Brown
	Chlorine	Pale Green

Explanation for Appearance

The halogens' colors are results of the absorption of visible light by the molecules, which causes electronic excitation. Fluorine absorbs violet light, and therefore appears light yellow. Iodine, on the other hand, absorbs yellow light and appears violet (yellow and violet are complementary colors, which can be determined using a color wheel). The colors of the halogens grow darker down the group:

- Fluorine → pale yellow/brown
  - http://www.daviddarling.info/images/fluorine.jpg
- Chlorine → pale green
  - http://amazingrust.com/Experiments/how_to/Images/Chlorine_gas.jpg
- Bromine → red-brown
  - www.crscientific.com/brominecell4.jpg
- Iodine → violet
  - genchem.chem.wisc.edu/lab/PTL...ments/I/I.jpeg
- Astatine* → black/metallic
  - www4.msu.ac.th/satit/studentP...t/astatine.jpg

In closed containers, liquid bromine and solid iodine are in equilibrium with their vapors, which can often be seen as colored gases. Although the color for astatine is unknown, it is assumed that astatine must be darker than iodine's violet (i.e., black) based on the preceding trend.

Oxidation States of Halogens in Compounds

As a general rule, halogens usually have an oxidation state of -1. However, if the halogen is bonded to oxygen or to another halogen, it can adopt different states: the -2 rule for oxygen takes precedence over this rule; in the case of two different halogens bonded together, the more electronegative atom takes precedence and adopts the -1 oxidation state.

Example 1.1: Iodine Chloride (ICl)

Chlorine has an oxidation state of -1, and iodine will have an oxidation of +1. Chlorine is more electronegative than iodine, therefore giving it the -1 oxidation state.

Example 1.2: Perbromic acid ($HBrO_4$)

Oxygen has a total oxidation state of -8 (-2 charge x 4 atoms= -8 total charge). Hydrogen has a total oxidation state of +1. Adding both of these values together, the total oxidation state of the compound so far is -7. Since the final oxidation state of the compound must be 0, bromine's oxidation state is +7.

A third exception to the rule is this: if a halogen exists in its elemental form (X_2), its oxidation state is zero.

Table 1.8: Oxidation States of Halogens

Halogen	Oxidation States in Compounds
Fluorine	(always) -1*
Chlorine	-1, +1, +3, +5, +7
Bromine	-1, +1, +3, +4, +5
Iodine	-1, +1,+5, +7
Astatine	-1, +1, +3, +5, +7

Example 1.3: Fluorine

Why does fluorine always have an oxidation state of -1 in its compounds?

Solution

Electronegativity increases across a period, and decreases down a group. Therefore, fluorine has the highest electronegativity of all of the elements, indicated by its position on the periodic table. Its electron configuration is $1s^2\ 2s^2\ 2p^5$. If fluorine gains one more electron, the outermost p orbitals are completely filled (resulting in a full octet). Because fluorine has a high electronegativity, it can easily remove the desired electron from a nearby atom. Fluorine is then isoelectronic with a noble gas (with eight valence electrons); all its outermost orbitals are filled. Fluorine is much more stable in this state.

Applications of Halogens

Fluorine: Although fluorine is very reactive, it serves many industrial purposes. For example, it is a key component of the plastic *polytetrafluoroethylene* (called *Teflon-TFE* by the DuPont company) and certain other polymers, often referred to as fluoropolymers. Chlorofluorocarbons (CFCs) are organic chemicals that were used as refrigerants and propellants in aerosols before growing concerns about their possible environmental impact led to their discontinued use. Hydrochlorofluorocarbons (HFCs) are now used instead. Fluoride is also added to toothpaste and drinking water to help reduce tooth decay. Fluorine also exists in the clay used in some ceramics. Fluorine is associated with generating nuclear power as well. In addition, it is used to produce fluoroquinolones, which are antibiotics. Below is a list of some of fluorine's important inorganic compounds.

Table 1.9: Important Inorganic Compounds of Fluorine

Compound	Uses
Na_3AlF_6	Manufacture of aluminum
BF_3	Catalyst
CaF_2	Optical components, manufacture of HF, metallurgical flux
ClF_3	Fluorinating agent, reprocessing nuclear fuels
HF	Manufacture of F_2, AlF_3, Na_3AlF_6, and fluorocarbons
LiF	Ceramics manufacture, welding, and soldering
NaF	Fluoridating water, dental prophylaxis, insecticide
SF_6	Insulating gas for high-voltage electrical equipment
SnF_2	Manufacture of toothpaste
UF_6	Manufacture of uranium fuel for nuclear reactors

Chlorine: Chlorine has many industrial uses. It is used to disinfect drinking water and swimming pools. Sodium hypochlorite (NaClO) is the main component of bleach. Hydrochloric acid, sometimes called muriatic acid, is a commonly used acid in industry and laboratories. Chlorine is also present in polyvinyl chloride (PVC) and several other polymers. PVC is used in wire insulation, pipes, and electronics. In addition, chlorine is very useful in the pharmaceutical industry. Medicinal products containing chlorine are used to treat infections, allergies, and diabetes. The neutralized form of hydrochloride is a component of many medications. Chlorine is also used to sterilize hospital machinery and limit infection growth. In agriculture, chlorine is a component of many commercial pesticides: DDT (dichlorodiphenyltrichloroethane) was used as an agricultural insecticide, but its use was discontinued.

Bromine: Bromine is used in flame retardants because of its fire-resistant properties. It also found in the pesticide methyl bromide, which facilitates the storage of crops and eliminates the spread of bacteria. However, the excessive use of methyl bromide has been discontinued due to its impact on the ozone layer. Bromine is involved in gasoline production as well. Other uses of bromine include the production of photography film, the content in fire extinguishers, and drugs treating pneumonia and Alzheimer's disease.

Iodine: Iodine is important in the proper functioning of the thyroid gland of the body. If the body does not receive adequate iodine, a goiter (enlarged thyroid gland) will form. Table salt now contains iodine to help promote proper functioning of the thyroid hormones. Iodine is also used as an antiseptic. Solutions used to clean open wounds likely contain iodine, and it is commonly found in disinfectant sprays. In addition, silver iodide is important for photography development.

Astatine: Because astatine is radioactive and rare, there are no proven uses for this halogen element. However, there is speculation that this element could aid iodine in regulating the thyroid hormones. Also, ^{211}At has been used in mice to aid the study of cancer.

VII. Outside Links

- Grube, Karl; Leffler, Amos J. "Synthesis of metal halides (ML)." *J. Chem. Educ.* **1993**, *70*, A204.
- This video provides information about some of the physical properties of chlorine, bromine, and iodine: http://www.youtube.com/watch?v=yP0U5rGWqdg
- The following video compares four halogens: fluorine, chlorine, bromine and iodine in terms of chemical reactions and physical properties. http://www.youtube.com/watch?v=u2ogMUDBaf4
- Color wheel referred to in the text: http://www.wou.edu/las/physci/ch462/c-wheel.gif
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Practice Problems

1. Why does fluorine always have an oxidation state of -1 in its compounds?
2. Find the oxidation state of the halogen in each problem:
    a. HOCl
    b. KIO_3
    c. F_2
3. What are three uses of chlorine?
4. Which element(s) exist(s) as a solid at room temperature?
5. Do the following increase or decrease down the group of halogens?
    a. boiling point and melting point
    b. electronegativity
    c. ionization energy

Answers

1. Electronegativity increases across a period, and decreases down a group. Therefore, fluorine has the highest electronegativity out of all of the elements. Because fluorine has seven valence electrons, it only needs one more electron to acheive a noble gas configuration (eight valence electrons). Therefore, it will be more likely to pull off an electron from a nearby atom.
2. disinfecting water, pesticides, and medicinal products
3. a. +1 (Hydrogen has an oxidation state of +1, and oxygen has an oxidation state of -2. Therefore, chlorine must have an oxidation state of +1 so that the total charge can be zero)
    b. +5 (Potassium's oxidation state is +1. Oxygen has an oxidation state of -2, so for this compound it is -6 (-2 charge x 3 atoms= -6). Since the total oxidation state has to be zero, iodine's oxidation state must be +5).
    c. 0 (Elemental forms always have an oxidation state of 0.)
4. iodine and astatine
5. a. increases
    b. decreases
    c. decreases

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2. Petrucci, Ralph H. Genereal Chemistry: Principles and Modern Applications. 9th Ed. New Jersey: Pearson Education Inc, 2007. 920-928.
3. Verma, N.K., B. Kapila, and S.K. Khanna. Comprehensive Chemistry XII. New Delhi: Laxmi Publications, 2007. 718-30.

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7.10.1.3: Halogen Group (Group 17) Trends

1. All elements are diatomic and molecular and the boiling and melting points increase as a result of the increasing van der Waals interactions between diatomic molecules for the heavier elements.

2. The elements are typical non-metals in their physical and chemical properties. They form anionic compounds based on X^- (X = halogen), which is associated with a complete octet.

> The ionic compounds MX become progressively less ionic as the relative atomic mass of X increases, because of the decreasing electronegativity of the halogens. Iodine has the greatest tendency to form cationic species, *e.g.*, I_2^+, I_5^+, because it has the lowest ionization energy. The cation Br_2^+ is known in $Br_2^+Sb_3F_{16}^-$, and Br_5^+ has been reported.

3. The atoms also form strong covalent bonds with other non-metals. The mean bond enthalpies for E-X bonds are particularly large for fluorine and therefore a wide range of molecular fluorides are known; fluorine is particularly effective at bringing out the highest valencies of the non-metals and highest oxidation states of the metals.

4. The oxidizing ability of the halogens decreases markedly down the group: $F_2 > Cl_2 > Br_2 > I_2$, and only iodine is oxidized by nitric acid.

5. The stabilities of the hydrogen halides decrease down the group, but their acid strengths increase.

6. Only H-F forms strong hydrogen bonds and this is reflected in the boiling and melting points of the hydrogen halides.

7. The halogens form many interhalogen compounds with the less electronegative halogen surrounded by the more electronegative halogens. Neutral, anionic, and cationic interhalogen compounds are known. ICl and IBr are widely used in organic synthesis and are commercially available.

> The most extensive series of compounds exists for iodine, *e.g.*, IF_7, IF_5, ICl_4^-, ICl_2^-.Fluorine does not form any interhalogen compounds where it occupies the central position within the molecule.

8. Oxygen fluorides are extremely strong and reactive oxidants and have been explored as potential rocket fuels; the oxides become less reactive down the column and more numerous. Iodine forms a particularly wide range of oxides.

9. The perhalates, EO_4^-, are only known for Cl, Br, and I. They exhibit an alternation in their oxidizing abilities, and the perbromates are particularly strong oxidizing agents.

10. In the highest oxidation state (+7) the relative oxidizing ability is:

> Br> I > Cl

and results in the formation of the corresponding +5 oxoanions,

> $ClO_4^- + 2e^- = ClO_3^-$ $E° = 1.20$ V
> $BrO_4^- + 2e^- = BrO_3^-$ $E° = 1.85$ V
> $IO_4^- + 2e^- = IO_3^-$ $E° = 1.63$ V

The hypohalite ions disproportionate according to the equation:

> $2XO^- = 2X^- + XO_3^-$

The equilibrium constants are 10^{27} for ClO^-/Cl^- :(the reaction is slow at room temperature), 10^{15} for BrO^-/Br^-, and $10^{20}$for IO^-/I^-. HOF has been prepared from ice + F_2 but is very reactive, decomposing to HF + O_2.

Contributors and Attributions

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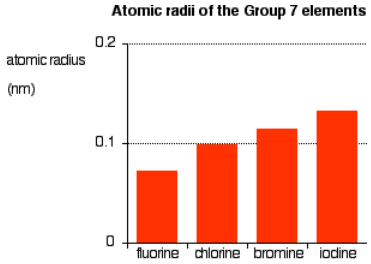
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7.10.1.4: Physical Properties of the Group 17 Elements

This page discusses the trends in some atomic and physical properties of the Group 17 elements (the halogens): fluorine, chlorine, bromine and iodine. Sections below describe the trends in atomic radius, electronegativity, electron affinity, melting and boiling points, and solubility. There is also a section on the bond enthalpies (and strengths) of halogen-halogen bonds (for example, the Cl-Cl bond) and of hydrogen-halogen bonds (e.g., the H-Cl bond).

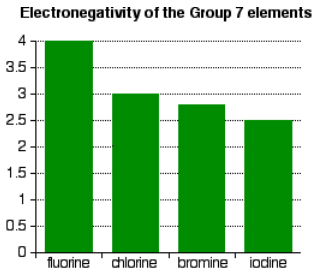
Trends in Atomic Radius

You can see that the atomic radius increases as you go down the group.

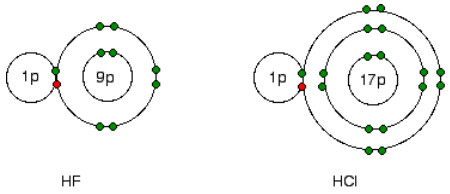


The radius of an atom is governed by

- Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons. It is usually measured on the Pauling scale, on which the most electronegative element (fluorine) is given an electronegativity of 4.0.



As shown in the figure above, electronegativity decreases from fluorine to iodine; the atoms become less effective at attracting bonding pairs of electrons as they grow larger. This can be visualized using dots-and-crosses diagrams for hydrogen fluoride and hydrogen chloride.



The bonding electrons between the hydrogen and the halogen experience the same net charge of +7 from either the fluorine or the chlorine. However, in the chlorine case, the nucleus is further away from the bonding pair. Therefore, electrons are not as strongly attracted to the chlorine nucleus as they are to the fluorine nucleus.

The stronger attraction to the closer fluorine nucleus makes fluorine more electronegative.

Summarizing the trend down the group

As the halogen atoms get larger, any bonding pair is farther and farther away from the halogen nucleus, and so is less strongly attracted towards it. Hence, the elements become less electronegative as you go down the group.

Contributors and Attributions

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SECTION OVERVIEW

7.10.2: Chemical Properties of the Halogens

Covers the halogens in Group 17: fluorine (F), chlorine (Cl), bromine (Br) and iodine (I). Includes trends in atomic and physical properties, the redox properties of the halogens and their ions, the acidity of the hydrogen halides, and the tests for the halide ions.

Topic hierarchy

7.10.2.1: Halide Ions as Reducing Agents

7.10.2.2: Halogens as Oxidizing Agents

7.10.2.3: Interhalogens

7.10.2.4: More Reactions of Halogens

7.10.2.5: Oxidizing Ability of the Group 17 Elements

7.10.2.6: Testing for Halide Ions

7.10.2.7: The Acidity of the Hydrogen Halides

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7.10.2.1: Halide Ions as Reducing Agents

This page examines the redox reactions involving halide ions and concentrated sulfuric acid, using these reactions to discuss the trend in reducing ability of the ions from fluoride to iodide. Two types of reactions might occur when concentrated sulfuric acid is added to a solid ionic halide like sodium fluoride, chloride, bromide or iodide. The concentrated sulfuric acid can act as both an acid and an oxidizing agent.

Concentrated sulfuric acid acting as an acid

Concentrated sulfuric acid transfers a proton to the halide ion to produce a gaseous hydrogen halide, which immediately escapes from the system. If the hydrogen halide is exposed to moist air, steam fumes are formed. For example, concentrated sulfuric acid reacts with solid sodium chloride at low temperatures to produce hydrogen chloride and sodium bisulfate, as in the following equation:

$$NaCl + H_2SO_4 \rightarrow HCl + NaHSO_4$$

All the halide ions behave similarly.

Concentrated sulfuric acid acting as an oxidizing agent

With fluoride or chloride

Concentrated sulfuric acid is not a strong enough oxidizing agent to oxidize fluoride or chloride. In those cases, only the steamy fumes of the hydrogen halide—hydrogen fluoride or hydrogen chloride—are produced. In terms of the halide ions, fluoride and chloride are not strong enough reducing agents to reduce the sulfuric acid. This is not the case for bromides and iodides.

With bromide

Bromide is a strong enough reducing agent to reduce sulfuric acid. Bromide is oxidized to bromine in the process, as in the half-equation below:

$$2Br^- \rightarrow Br_2 + 2e^-$$

Bromide reduces sulfuric acid to sulfur dioxide gas, decreasing the oxidation state of sulfur from +6 to +4. The half-equation for this transition is as follows:

$$H_2SO_4 + 2H^+ + 2e^- \rightarrow SO_2 + 2H_2O$$

These two half-equations can be combined into the overall ionic equation for the reaction:

$$H_2SO_4 + 2H^+ + 2Br^- \rightarrow Br_2 + SO_2 + 2H_2O$$

In practice, this reaction is confirmed by the steamy fumes of hydrogen bromide contaminated with the brown color of bromine vapor. The sulfur dioxide is a colorless gas, so its presence cannot be directly observed.

With Iodide

Iodide is a stronger reducing agent than bromide, and it is oxidized to iodine by the sulfuric acid:

$$2I^- \rightarrow I_2 + 2e^-$$

The reduction of the sulfuric acid is more complicated than with bromide. Iodide is powerful enough to reduce it in three steps:

- sulfuric acid to sulfur dioxide (sulfur oxidation state = +4)
- sulfur dioxide to elemental sulfur (oxidation state = 0)
- sulfur to hydrogen sulfide (sulfur oxidation state = -2).

The most abundant product is hydrogen sulfide. The half-equation for its formation is as follows:

$$H_2SO_4 + 8H^+ + 8e^- \rightarrow H_2S + 4H_2O$$

Combining these two half-equations gives the following net ionic equation:

$$H_2SO_4 + 8H^+ + 8I^- \rightarrow 4I_2 + H_2S + 4H_2O$$

This is confirmed by a trace of steamy fumes of hydrogen iodide and a large amount of iodine. The reaction is exothermic: purple iodine vapor is formed, with dark gray solid iodine condensing around the top of the reaction vessel. There is also a red color where the iodine comes into contact with solid iodide salts. The red color is due to the I_3^- ion formed by reaction between I_2 molecules and I^- ions. Hydrogen sulfide gas can be detected by its "rotten egg" smell, but this gas is intensely poisonous.

Summary of the trend in reducing ability

- Fluoride and chloride cannot reduce concentrated sulfuric acid.
- Bromide reduces sulfuric acid to sulfur dioxide. In the process, bromide ions are oxidized to bromine.
- Iodide reduces sulfuric acid to a mixture of products including hydrogen sulfide. Iodide ions are oxidized to iodine.
- The reducing ability of halide ions increases down the group.

Explaining the trend

An over-simplified explanation

The following explanation is only (partially) accurate if fluoride is neglected. When a halide ion acts as a reducing agent, it transfers electrons to something else. That means that the halide ion itself loses electrons. The larger the halide ion, the farther the outer electrons are from the nucleus, and the more they are shielded by inner electrons. It therefore gets easier for the halide ions to lose electrons down the group because there is less attraction between the outer electrons and the nucleus. This argument seems valid, but it is flawed. The energetics of the change must be examined.

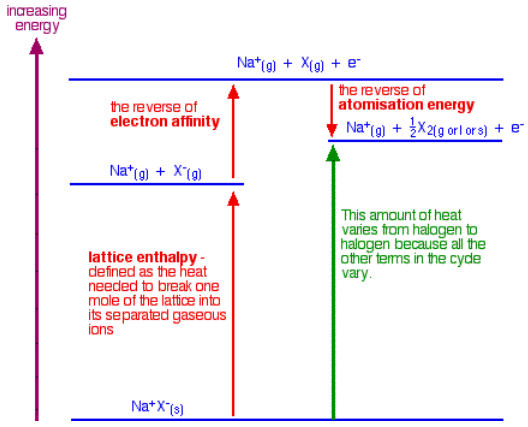
A more detailed explanation

Enthalpy change variation between halogens

The amount of heat evolved or absorbed when a solid halide (like sodium chloride) is converted into an elemental halogen must be considered. Taking sodium chloride as an example, the following energetic quantities are important:

- The energy required to break the attractions between the ions in the sodium chloride (the lattice enthalpy).
- The energy required to remove the electron from the chloride ion. This is the reverse of the electron affinity of the chlorine (the electron affinity can be acquired from a data table and negated).
- The energy recovered when the chlorine atoms convert to diatomic chlorine. Energy is released when these bonds are formed. Chlorine is simple because it is a gas. In bromine and iodine, heat is also released during condensation to a liquid or a solid, respectively. To account for this, it is simpler to think in terms of atomization energy rather than bond energy. The value of interest is the reverse of atomization energy.

Atomization energy is the energy needed to produce 1 mole of isolated gaseous atoms starting from an element in its standard state (gas for chlorine, and liquid for bromine, for example - both of them as X_2). The figure below shows how this information fits together:



The enthalpy change shown by the green arrow in the diagram for each of the halogens must be compared. The diagram shows that the overall change involving the halide ions is endothermic (the green arrow is pointing up toward a higher energy).

This is not the total enthalpy change for the whole reaction. Heat is emitted when the changes involving the sulfuric acid occur. That is the same irrespective of the halogen in question. The total enthalpy change is the sum of the enthalpy changes for the halide ion half-reaction and the sulfuric acid half-reaction.

The table below shows the energy changes that vary from halogen to halogen. The process is assumed to start from the solid sodium halide. The values for the lattice enthalpies for other solid halides would be different, but the pattern would be the same.

	heat needed to break up NaX lattice (kJ mol^{-1})	heat needed to remove electron from halide ion (kJ mol^{-1})	heat released in forming halogen molecules (kJ mol^{-1})	sum of these (kJ mol-1)
F	+902	+328	-79	+1151
Cl	+771	+349	-121	+999
Br	+733	+324	-112	+945
I	+684	+295	-107	+872

The overall enthalpy change for the halide half-reaction:

The sum of the enthalpy changes, in the final column, is decreasingly endothermic down the group. The total change in enthalpy (including the sulfuric acid) is also less positive.

The amount of heat produced in the half-reaction involving the sulfuric acid must be great enough to make the reactions with the bromide or iodide feasible, but not enough to compensate for the more positive values produced by the fluoride and chloride half-reactions.

Exploring the changes in the various energy terms

In this section, the individual energy terms in the table that are most important in making the halogen half-reaction less endothermic down the group are determined.

Chlorine to iodine

From chlorine to iodine, the lattice enthalpy changes most, decreasing by 87 kJ mol^{-1}. By contrast, the energy required to remove the electron decreases by only 54 kJ mol^{-1}. Both of these terms matter, but the decrease in lattice enthalpy is the more significant. This quantity decreases because the ions are getting larger. That means that they are farther away from each other, and so the attractions between positive and negative ions in the solid lattice are lessened.

The simplified explanation mentioned earlier is misleading because it concentrates on the less-important decrease in the amount of energy needed to remove the electron from the ion.

Fluorine

Fluoride ions are very difficult to oxidize to fluorine. The table above shows that this has nothing to do with the amount of energy required to remove an electron from a fluoride ion. It actually takes less energy to remove an electron from a fluoride ion than from a chloride ion. The generalization that an electron becomes easier to remove as the ion becomes larger does not apply here.

Fluoride ions are so small that the electrons experience strong repulsion from each other. This outweighs the effect of their closeness to the nucleus and makes them easier to remove than the simplified argument predicts.

There are two important reasons why fluoride ions are so difficult to oxidize. The first is the comparatively high lattice enthalpy of the solid fluoride. This is due to the small size of the fluoride ion, which means that the positive and negative ions are very close together and therefore strongly attracted to each other. The other factor is the small amount of heat that is released when the

fluorine atoms combine to make fluorine molecules (see the table above). This is due to the low bond enthalpy of the F-F bond. The reason for this low bond enthalpy is discussed on a separate page.

What if the halide ions were in solution rather than in a solid?

This discussion has focused on the energetics of the process starting from solid halide ions because that is the standard procedure when using concentrated sulfuric acid. Halides could also be oxidized in solution with another oxidizing agent.

The trend is exactly the same. Fluoride is difficult to oxidize and it becomes easier down the group toward iodide; in other words, fluoride ions are not good reducing agents, but iodide ions are.

The explanation starts from the hydrated ions in solution rather than solid ions. In a sense, this has already been done on another page. Fluorine is a very powerful oxidizing agent because it very readily forms its negative ion in solution. It is therefore energetically difficult to reverse the process. By contrast, for energetic reasons, iodine is relatively reluctant to form its negative ion in solution. Therefore, it is relatively easy for it to revert back to iodine.

Contributors and Attributions

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7.10.2.2: Halogens as Oxidizing Agents

This page examines the trend in oxidizing ability of the Group 17 elements (the halogens): fluorine, chlorine, bromine and iodine. It considers the ability of one halogen to oxidize the ions of another, and how this changes down the group.

Basic facts

Consider a situation in which one halogen (chlorine, for example) is reacted with the ions of another (iodide, perhaps) from a salt solution. In the chlorine and iodide ion case, the reaction is as follows:

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$$

- The iodide ions lose electrons to form iodine molecules. In other words, they are oxidized.
- The chlorine molecules gain electrons to form chloride ions— they are reduced.

This is therefore a redox reaction in which chlorine acts as an oxidizing agent.

Fluorine

Fluorine must be excluded from this discussion because its oxidizing abilities are too strong. Fluorine oxidizes water to oxygen, as in the equation below, and so it is impossible to carry out reactions with it in aqueous solution.

$$2F_2 + 2H_2O \rightarrow 4HF + O_2$$

Chlorine, Bromine and Iodine

In each case, a halogen higher in the group can oxidize the ions of one lower down. For example, chlorine can oxidize bromide ions to bromine:

$$Cl_2 + 2Br^- \rightarrow 2Cl^- + Br_2$$

The bromine forms an orange solution. As shown below, chlorine can also oxidize iodide ions to iodine:

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$$

The iodine appears either as a red solution if little chlorine is used, or as a dark gray precipitate if the chlorine is in excess.

Bromine can only oxidize iodide ions, and is not a strong enough oxidizing agent to convert chloride ions into chlorine. A red solution of iodine is formed (see the note above) until the bromine is in excess. Then a dark gray precipitate is formed.

$$Br_2 + 2I^- \rightarrow 2Br^- + I_2$$

Iodine won't oxidize any of the other halide ions, except possibly the extremely radioactive and rare astatide ions.

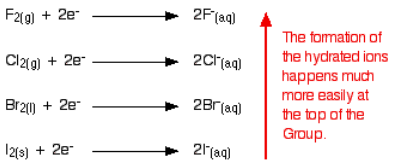
To summarize

- Oxidation is the loss of electrons. Each of the elements (for example, chlorine) could potentially take electrons from something else and are subsequently ionized (e.g., Cl^-). This means that they are all potential oxidizing agents.
- Fluorine is such a powerful oxidizing agent that solution reactions are unfeasible.
- Chlorine has the ability to take electrons from both bromide ions and iodide ions. Bromine and iodine cannot reclaim those electrons from the chloride ions formed.
- This indicates that chlorine is a more powerful oxidizing agent than either bromine or iodine.
- Similarly, bromine is a more powerful oxidizing agent than iodine. Bromine can remove electrons from iodide ions, producing iodine; iodine cannot reclaim those electrons from the resulting bromide ions.

In short, oxidizing ability decreases down the group.

Explaining the trend

Whenever one of the halogens is involved in oxidizing a species in solution, the halogen end is reduced to a halide ion associated with water molecules. The following figure illustrates this process:



Down the group, the ease with which these hydrated ions are formed decreases; the halogens become less effective as oxidizing agents, taking electrons from something else less readily. The reason that the hydrated ions form less readily down the group is due to several complicated factors. Unfortunately, this explanation is often over-simplified, giving a faulty and misleading explanation. The wrong explanation is dealt with here before a proper explanation is given.

The Incorrect Explanation

The following explanation is normally given for the trend in oxidizing ability of chlorine, bromine and iodine. The ease of ionization depends on how strongly the new electrons are attracted. As the atoms get larger, the new electrons are further from the nucleus and increasingly shielded by the inner electrons (offsetting the effect of the greater nuclear charge). The larger atoms are therefore less effective at attracting new electrons and forming ions. This is equivalent to saying electron affinity decreases down the group. Electron affinity is described in detail on another page.

The problem with this argument is that it does not include fluorine. Fluorine's tendency to form a hydrated ion is much higher than that of chlorine. However, fluorine's electron affinity is less than that of chlorine. This contradicts the above argument. This problem stems from examining a single part of a very complicated process. The argument about atoms accepting electrons applies only to isolated atoms in the gas state picking up electrons to form isolated ions, also in the gas state. The argument must be generalized.

In reality:

- The halogen starts as a diatomic molecule, X_2. This may be a gas, liquid or solid at room temperature, depending on the halogen.
- The diatomic molecule must split into individual atoms (atomization)
- Each atom gains an electron (electron affinity; this is the element of the process of interest in the faulty explanation.)
- The isolated ions are surrounded by water molecules; hydrated ions are formed (hydration).

The Correct Explanation

The table below shows the energy involved in each of these changes for atomization energy, electron affinity, and hydration enthalpy (hydration energy):

	atomization energy (kJ mol^{-1})	electron affinity (kJ mol^{-1})	hydration enthalpy (kJ mol^{-1})	overall (kJ mol^{-1})
F	+79	-328	-506	-755
Cl	+121	-349	-364	-592
Br	+112	-324	-335	-547
I	+107	-295	-293	-481

Consider first the fifth column, which shows the overall heat evolved, the sum of the energies in the previous three columns.

The amount of heat evolved decreases quite dramatically from the top to the bottom of the group, with the biggest decrease between fluorine and chlorine. Fluorine generates a large amount of heat when it forms its hydrated ion, chlorine a lesser amount, and so on down the group.

The first electron affinity is defined as the energy released when 1 mole of gaseous atoms each acquire an electron to form 1 mole of gaseous 1- ions, as in the following equation: In symbol terms:

$$X(g) + e^- \rightarrow X^-(g)$$

The fifth column measures the energy released when 1 mole of gaseous ions dissolves in water to produce hydrated ions, as in the following equation, which is not equivalent to that above:

$$X^-(g) \rightarrow X^-(aq)$$

Why is fluorine a stronger oxidizing agent than chlorine?

There are two main factors. First, the atomization energy of fluorine is abnormally low. This reflects the low bond enthalpy of fluorine.

The main reason, however, is the very high hydration enthalpy of the fluoride ion. That is because fluoride is very small. There is a very strong attraction between fluoride ions and water molecules. The stronger the attraction, the more heat is evolved when the hydrated ions are formed.

Why does oxidizing ability decrease from chlorine to bromine to iodine?

The decrease in atomization energy between these three elements is relatively small, and would tend to make the overall change more negative down the group. It is helpful to look at the changes in electron affinity and hydration enthalpy down the group. Using the figures from the previous table:

	change in electron affinity (kJ mol^{-1})	change in hydration enthalpy (kJ mol^{-1})
Cl to Br	+25	+29
Br to I	+29	+42

Both of these effects contribute, but the more important factor—the one that changes the most—is the change in the hydration enthalpy. Down the group, the ions become less attractive to water molecules as they get larger. Although the ease with which an atom attracts an electron matters, it is not as important as the hydration enthalpy of the negative ion formed.

The faulty explanation is incorrect even if restricted to chlorine, bromine and iodine:

- This is the energy needed to produce 1 mole of isolated gaseous atoms starting from an element in its standard state (gas for chlorine, and liquid for bromine, for example, both of the form X_2).
- For a gas like chlorine, this is simply half of the bond enthalpy (because breaking a Cl-Cl bond produces 2 chlorine atoms, not 1). For a liquid like bromine or a solid like iodine, it also includes the energy that is needed to convert them into gases.

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7.10.2.3: Interhalogens

The halogens react with each other to form interhalogen compounds. The general formula of most interhalogen compounds is XY_n, where n = 1, 3, 5 or 7, and X is the less electronegative of the two halogens. The compounds which are formed by the union of two different halogens are called interhalogen compounds. There are never more than two types of halogen atoms in an **interhalogen** molecule. These are of four general types:

1. AX- type : ClF, BrF, BrCl, ICl, IBr,
2. AX_3-type: ClF_3, BrF_3, $(ICl_3)_2$,
3. AX_5-type: ClF_5, BrF_5, IF_5,
4. AX_7-type: IF_7.

The interhalogen compounds of type AX and AX_3 are formed between halogens having a very low electronegativity difference (e.g., ClF, ClF_3). The interhalogen compounds of type AX_5 and AX_7 are formed by larger atoms having a low electronegativity with the smaller atoms having a high electronegativity. This is because it is possible to fit a greater number of smaller atoms around a larger one (e.g., BrF_5, IF_7).

Interhalogens are all prone to hydrolysis and ionize to give rise to polyatomic ions. The interhalogens are generally more reactive than halogens except for F. This is because A-X bonds in interhalogens are weaker than the X-X bonds in dihalogen molecules. Reactions of interhalogens are similar to those of halogens. Hydrolysis of interhalogen compounds gives a halogen acid and an oxy-acid.

Nomenclature

To name an interhalogen compound, the less electronegative element is placed on to the left in formulas and naming is straightforward.

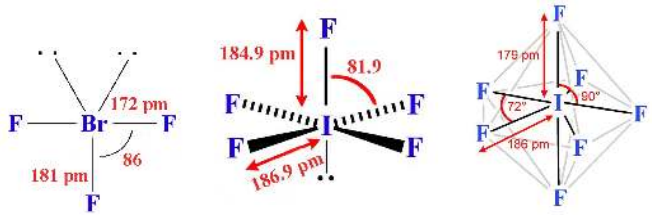
Properties

Some properties of interhalogen compounds are listed below. They are all prepared by direct combination of the elements, although since in some cases more than one product is possible, the conditions may be varied by altering the temperature and relative proportions. For example, under the same conditions, difluorine reacts with dichlorine to give ClF, with dibromine to give BrF_3, but with diiodine to give IF_5.

Compound	ClF	BrF	BrCl	ICl	IBr	ClF_3	BrF_3	IF_3	I_2Cl_6	ClF_5	BrF_5	IF_5	IF_7
Appearance at 298K	Colorless gas	Pale brown gas	impure	Red solid	Black solid	Colorless gas	Yellow liquid	Yellow solid	Orange solid	Colorless gas	Colorless liquid	Colorless liquid	Colorless gas
Stereochemistry	linear	linear	linear	linear	linear	T-shaped	T-shaped	T-shaped	planar	square-based pyramid	square-based pyramid	square-based pyramid	pentagonal bipyramid
Melting point /K	117	~240	dissoc.	300(a)	313	197	282	245 (dec)	337 (sub)	170	212.5	282.5	278 (sub)
Boiling point /K	173	~293	~278	~373	389	285	399	-	-	260	314	373	-
$\Delta_f H°(298\ K)$ /kJ mol^{-1}	-50.3	-58.5	14.6	-23.8	-10.5	-163.2	-300.8	~-500	-89.3	-255	-458.6	-864.8	-962
Dipole moment for gas-phase molecule /D	0.89	1.42	0.52	1.24	0.73	0.6	1.19	-	0	-	1.51	2.18	0
Bond distances in gas-phase molecules except for IF_3 and I_2Cl_6 / pm	163	176	214	232	248.5	160 (eq), 170 (ax)	172 (eq), 181 (ax)	187 (eq), 198 (ax)	238 (terminal) 268 (bridge)	172 (basal), 162 (apical)	178 (basal), 168 (apical)	187 (basal), 185 (apical)	186 (eq), 179 (ax)

Structures

The structures found for the various interhalogens conform to what would be expected based on the VSEPR model. For XY_3 the shape can be described as T-shaped with 2 lone pairs sitting in two of the equatorial positions of a trigonal bipyramid. For XY_5 the shape is a square pyramid with the unpaired electrons sitting in an axial position of an octahedron, and XY_7 is a pentagonal bipyramid.



XY diatomic interhalogens

The interhalogens with formula XY have physical properties intermediate between those of the two parent halogens. The covalent bond between the two atoms has some ionic character, with the larger element, X, becoming oxidized and having a partial positive charge. Most combinations of F, Cl, Br and I are known, but not all are stable.

- Chlorine monofluoride (ClF), the lightest interhalogen, is a colorless gas with a boiling point of 173 °K.
- Bromine monofluoride (BrF) has not been obtained in the pure form - it dissociates into the trifluoride and free bromine. Similarly, iodine monofluoride is unstable - iodine reacts with fluorine to form a pentafluoride.
- Iodine monofluoride (IF) is unstable and disproportionates rapidly and irreversibly at room temperature:

$$5\,\mathrm{IF} \longrightarrow 2\,\mathrm{I_2} + \mathrm{IF_5}$$

  . However, its molecular properties have been determined by spectroscopy: the iodine-fluorine distance is 190.9 pm and the I-F bond dissociation energy is around 277 kJ mol^{-1}. $\Delta H_f°$ = -95.4 kJ mol^{-1} and $\Delta G_f°$ = -117.6 kJ mol^{-1}, both at 298 K.

  IF can be generated by the following reactions:
  $I_2 + F_2 \rightarrow 2IF$ at -45 °C in CCl_3F;
  $I_2 + IF_3 \rightarrow 3IF$ at -78 °C in CCl_3F;
  $I_2 + AgF \rightarrow IF + AgI$ at 0 °C.
- Bromine monochloride (BrCl) is an unstable red-brown gas with a boiling point of 5 °C.
- Iodine monochloride (ICl) consists of red transparent crystals which melt at 27.2 °C to form a choking brownish liquid (similar in appearance and weight to bromine). It reacts with HCl to form the strong acid $HICl_2$. The crystal structure of iodine monochloride consists of puckered zig-zag chains, with strong interactions between the chains.
- Iodine monobromide (IBr) is made by direct combination of the elements to form a dark red crystalline solid. It melts at 42 °C and boils at 116 °C to form a partially dissociated vapor.

XY_3 interhalogens

- Chlorine trifluoride (ClF_3) is a colorless gas that condenses to a green liquid and freezes to a white solid. It is made by reacting chlorine with an excess of fluorine at 250° C in a nickel tube. It reacts more violently than fluorine, often explosively. The molecule is planar and T-shaped.
- Bromine trifluoride (BrF_3) is a yellow-green liquid that conducts electricity - it ionizes to form $[BrF_2^+] + [BrF_4^-]$. It reacts with many metals and metal oxides to form similar ionized entities; with some others it forms the metal fluoride plus free bromine and oxygen. It is used in organic chemistry as a fluorinating agent. It has the same molecular shape as chlorine trifluoride.
- Iodine trifluoride (IF_3) is a yellow solid which decomposes above -28 °C. It can be synthesized from the elements, but care must be taken to avoid the formation of IF_5. F_2 attacks I_2 to yield IF_3 at -45 °C in CCl_3F. Alternatively, at low temperatures, the fluorination reaction $I_2 + 3XeF_2 \rightarrow 2IF_3 + 3Xe$ can be used. Not much is known about iodine trifluoride as it is so unstable.
- Iodine trichloride (ICl_3) forms lemon yellow crystals which can be melted under pressure to a brown liquid. It can be made from the elements at low temperature, or from iodine pentoxide and hydrogen chloride. It reacts with many metal chlorides to form tetrachloriodides, and hydrolyses in water. The molecule is a planar dimer, with each iodine atom surrounded by four chlorine atoms. In the melt it is conductive, which may indicate dissociation:

$$\mathrm{I_2Cl_6} \longrightarrow \mathrm{ICl_2^+} + \mathrm{ICl_4^-}$$

Chlorine trifluoride, ClF_3, was first reported in 1931; it is primarily used for the manufacture of uranium hexafluoride, UF_6, as part of nuclear fuel processing and reprocessing by the reaction:

$$U + 3\,ClF_3 \longrightarrow UF_6 + 3\,ClF$$

U isotope separation is difficult because the two isotopes have very nearly identical chemical properties, and can only be separated gradually using small mass differences. (^{235}U is only 1.26% lighter than ^{238}U.) A cascade of identical stages produces successively higher concentrations of ^{235}U. Each stage passes a slightly more concentrated product to the next stage and returns a slightly less concentrated residue to the previous stage.

There are currently two generic commercial methods employed internationally for enrichment: gaseous diffusion (referred to as first generation) and gas centrifuge (second generation), which consumes only 6% as much energy as gaseous diffusion. These both make use of the volatility of UF_6.

ClF_3 has been investigated as a high-performance storable oxidizer in rocket propellant systems. Handling concerns, however, prevented its use.

ClF_3 is Hypergolic

Hypergolic means explodes on contact with no need for any activator. One observer made the following comment about ClF_3:

> "It is, of course, extremely toxic, but that's the least of the problem. It is hypergolic* with every known fuel, and so rapidly hypergolic that no ignition delay has ever been measured. It is also hypergolic with such things as cloth, wood, and test engineers, not to mention asbestos, sand, and water with which it reacts explosively. It can be kept in some of the ordinary structural metals-steel, copper, aluminium, etc.-because of the formation of a thin film of insoluble metal fluoride which protects the bulk of the metal, just as the invisible coat of oxide on aluminium keeps it from burning up in the atmosphere. If, however, this coat is melted or scrubbed off, and has no chance to reform, the operator is confronted with the problem of coping with a metal-fluorine fire. For dealing with this situation, I have always recommended a good pair of running shoes."

It is believed that prior to and during World War II, ClF_3 code named N-stoff ("substance N") was being stockpiled in Germany for use as a potential incendiary weapon and poison gas. The plant was captured by the Russians in 1944, but there is no evidence that the gas was actually ever used during the war.

XY_5 interhalogens

- Chlorine pentafluoride (ClF_5) is a colorless gas, made by reacting chlorine trifluoride with fluorine at high temperatures and high pressures. It reacts violently with water and most metals and nonmetals.
- Bromine pentafluoride (BrF_5) is a colorless fuming liquid, made by reacting bromine trifluoride with fluorine at 200° C. It is physically stable, but reacts violently with water and most metals and nonmetals.
- Iodine pentafluoride (IF_5) is a colorless liquid, made by reacting iodine pentoxide with fluorine, or iodine with silver fluoride. It is highly reactive, even slowly with glass. It reacts with elements, oxides and carbon halides. The molecule has the form of a tetragonal pyramid.
- Primary amines react with iodine pentafluoride to form nitriles after hydrolysis with water.

$$R - CH_2 - NH_2 \rightarrow R - CN$$

XY_7 interhalogens

- Iodine heptafluoride (IF_7) is a colorless gas. It is made by reacting the pentafluoride with fluorine. IF_7 is chemically inert, having no lone pair of electrons in the valency shell; in this it resembles sulfur hexafluoride. The molecule is a pentagonal bipyramid. This compound is the only interhalogen compound possible where the larger atom is carrying seven of the smaller atoms.
- All attempts to form bromine heptafluoride have met with failure; instead, bromine pentafluoride and fluorine gas are produced.

Diatomic Interhalogens (AX)

The interhalogens of form XY have physical properties intermediate between those of the two parent halogens. The covalent bond between the two atoms has some ionic character, the less electronegative element, X, being oxidized and having a partial positive charge. Most combinations of F, Cl, Br and I are known, but not all are stable.

- **Chlorine monofluoride (ClF)**: The lightest interhalogen compound, ClF is a colorless gas with a normal boiling point of -100 °C.
- **Bromine monofluoride (BrF)**: BrF has not been obtained in a pure form; it dissociates into the trifluoride and free bromine.
- **Iodine monofluoride (IF):** IF is unstable and decomposes at 0 C, disproportionating into elemental iodine and iodine pentafluoride.
- **Bromine monochloride (BrCl):** A red-brown gas with a boiling point of 5 °C.
- **Iodine monochloride (ICl):** Red transparent crystals which melt at 27.2 °C to form a choking brownish liquid (similar in appearance and weight to bromine). It reacts with HCl to form the strong acid $HICl_2$. The crystal structure of iodine monochloride consists of puckered zig-zag chains, with strong interactions between the chains.
- **Iodine monobromide (IBr)**: Made by direct combination of the elements to form a dark red crystalline solid. It melts at 42 °C and boils at 116 °C to form a partially dissociated vapor.

Tetra-atomic Interhalogens (AX_3)

- **Chlorine trifluoride (ClF_3)** is a colorless gas which condenses to a green liquid and freezes to a white solid. It is made by reacting chlorine with an excess of fluorine at 250 °C in a nickel tube. It reacts more violently than fluorine, often explosively. The molecule is planar and T-shaped. It is used in the manufacture of uranium hexafluoride.
- **Bromine trifluoride (BrF_3)** is a yellow-green liquid which conducts electricity and ionizes to form $[BrF_2^+] + [BrF_4^-]$. It reacts with many metals and metal oxides to form similar ionized entities; with some others it forms the metal fluoride plus free bromine and oxygen. It is used in organic chemistry as a fluorinating agent. It has the same molecular shape as chlorine trifluoride.
- **Iodine trifluoride (IF_3)** is a yellow solid which decomposes above -28 °C. It can be synthesized from the elements, but care must be taken to avoid the formation of IF_5. F_2 attacks I_2 to yield IF_3 at -45 °C in CCl_3F. Alternatively, at low temperatures, the fluorination reaction $I_2 + 3XeF_2 \rightarrow 2IF_3 + 3Xe$ can be used. Not much is known about iodine trifluoride as it is so unstable.
- **Iodine trichloride (ICl_3)** forms lemon yellow crystals which can be melted under pressure to a brown liquid. It can be made from the elements at low temperature, or from iodine pentoxide and hydrogen chloride. It reacts with many metal chlorides to form tetrachloriodides, and hydrolyses in water. The molecule is a planar dimer, with each iodine atom surrounded by four chlorine atoms.

Hexa-atomic Interhalogens (AX_5)

- **Chlorine pentafluoride (ClF_5)** is a colorless gas, made by reacting chlorine trifluoride with fluorine at high temperatures and high pressures. It reacts violently with water and most metals and nonmetals.
- **Bromine pentafluoride (BrF_5)** is a colorless fuming liquid, made by reacting bromine trifluoride with fluorine at 200Å C. It is physically stable, but reacts violently with water and most metals and nonmetals.
- **Iodine pentafluoride (IF_5)** is a colorless liquid, made by reacting iodine pentoxide with fluorine, or iodine with silver fluoride. It is highly reactive, even slowly with glass. It reacts with elements, oxides and carbon halides.The molecule has the form of a tetragonal pyramid.

Octa-atomic interhalogens (AX_7)

- **Iodine heptafluoride (IF_7)** is a colourless gas. It is made by reacting the pentafluoride with fluorine. IF_7 is chemically inert, having no lone pair of electrons in the valency shell; in this it resembles sulfur hexafluoride. The molecule is a pentagonal bipyramid. This compound is the only interhalogen compound possible where the larger atom is carrying seven of the smaller atoms
- All attempts to form **bromine heptafluoride** (BrF_7) have failed and instead produce bromine pentafluoride (BrF_5) gas.

Summary

All interhalogens are volatile at room temperature. All are polar due to differences in their electronegativity. These are usually covalent liquids or gases due to small electronegativity differences among them. Some compounds partially ionize in solution. For example:

$$2\,ICl \rightarrow I^+ + ICl_2^-$$

Interhalogen compounds are more reactive than normal halogens, except for fluorine.

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7.10.2.4: More Reactions of Halogens

This page describes reactions of the halogens that do not fall under the other categories in other pages in this section. All the reactions described here are redox reactions.

Reactions with hydrogen

The following examples illustrate the decrease in reactivity of the halogens down Group 7.

Fluorine combines explosively with hydrogen even under cold, dark conditions, evolving hydrogen fluoride gas.

A mixture of chlorine and hydrogen explodes if exposed to sunlight or a flame, producing hydrogen chloride gas. This reaction can be controlled by lighting a jet of hydrogen and then lowering it into a gas jar of chlorine. The hydrogen burns at a slower, constant rate, and hydrogen chloride gas is formed as before.

Bromine vapor and hydrogen combine with a mild explosion when ignited. Hydrogen bromide gas is formed.

Iodine and hydrogen combine only partially even on constant heating. An equilibrium exists between the hydrogen and the iodine and hydrogen iodide gas.

Each of these reactions has an equation of the form:

$$H_2 + X_2 \rightarrow 2HX$$

A minor exception is made for iodine: the single arrow is replaced with a reversible sign.

Reactions with phosphorus

Care must be taken when analyzing the rates of these reactions; analogous reactions must be compared. For example, it is nonsensical to compare the rate at which phosphorus reacts with gaseous chlorine with the rate at which it reacts with liquid bromine. There is more contact between phosphorus and liquid bromine than between phosphorus and gaseous chlorine.

The formation of trihalides, PX_3

All halogens react with phosphorus to form, in the first instance, phosphorus(III) halides of the form PX_3.

There are two common forms of phosphorus: white phosphorus (sometimes called yellow phosphorus) and red phosphorus. White phosphorus is more reactive than red phosphorus. This video on YouTube shows the reaction between red phosphorus and bromine. This is a violent reaction under cold conditions, and white phosphorus behaves even more dramatically.

When writing the equations for these reactions, it is important to remember that white phosphorus is molecular, consisting of P_4 molecules, whereas red phosphorus is polymeric, indicated by the symbol P. The reaction for white phosphorus and bromine is as follows:

$$P_4 + 6Br_2 \rightarrow 4PBr_3$$

The red phosphorus equation is shown below:

$$2P + 3Br_2 \rightarrow 2PBr_3$$

The formation of pentahalides, PX_5

In excess chlorine or bromine, phosphorus reacts to form phosphorus(V) chloride or bromide. Most simply, using white phosphorus:

$$P_4 + 10Cl_2 \rightarrow 4PCl_5$$

The reaction between phosphorus(III) chloride and phosphorus(V) chloride is reversible:

$$PCl_3 + Cl_2 \rightleftharpoons PCl_5$$

An excess of chlorine pushes this equilibrium to the right. Phosphorus does not form a pentaiodide, in contrast; this is likely because five large iodine atoms cannot physically fit around the central phosphorus atom.

Reactions with sodium

All halogens react with sodium to produce sodium halides. A common reaction between hot sodium and chlorine gas produces a bright orange flame and white sodium chloride.

$$2Na + Cl_2 \rightarrow 2NaCl$$

Hot sodium will also burn in bromine or iodine vapor to produce sodium bromide or sodium iodide. Each of these reactions produces an orange flame and a white solid.

Reactions with iron

With the exception of iodine, iron burns in halogen vapor, forming iron(III) halides. Iodine is less reactive, and produces iron(II) iodide.

Fluorine

Cold iron wool burns in cold fluorine to give iron(III) fluoride. Anhydrous iron(III) fluoride is described as either white or pale green. A standard inorganic chemistry textbook by Cotton and Wilkinson describes it as white. The reaction is given below:

$$2Fe + 3F_2 \rightarrow 2FeF_3$$

This is a rapid reaction, in which the iron burns and is oxidized to an iron(III) compound—in other words, from an oxidation state of zero in the elemental metal to an oxidation state of +3 in the iron(III) compound.

Chlorine

Chlorine gas in contact with hot iron forms iron(III) chloride. Anhydrous iron(III) chloride forms black crystals; any trace of water present in the apparatus or in the chlorine reacts with the crystals, turning them reddish-brown. The equation for this reaction is given below:

$$2Fe + 3Cl_2 \rightarrow 2FeCl_3$$

The iron is again oxidized from a state of zero to +3.

Bromine

Bromine vapor passed over hot iron triggers a similar, slightly less vigorous reaction, shown below; iron(III) bromide is produced. Anhydrous iron(III) bromide usually appears as a reddish-brown solid.

$$2Fe + 3Br_2 \rightarrow 2FeBr_3$$

In this reaction the iron is again oxidized to a +3 state.

Iodine

The reaction between hot iron and iodine vapor produces gray iron(II) iodide, and is much less vigorous. This reaction, the equation for which is given below, is difficult to carry out because the product is always contaminated with iodine.

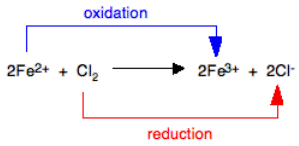
$$Fe + 2I_2 \rightarrow FeI_2$$

Iodine is only capable of oxidizing iron to the +2 oxidation state.

Reactions with solutions containing iron(II) ions

Only the reactions of chlorine, bromine, and iodine can be considered. Aqueous fluorine is very reactive with water. Chlorine and bromine are strong enough oxidizing agents to oxidize iron(II) ions to iron(III) ions. In the process, chlorine is reduced to chloride ions, bromine to bromide ions.

This process is easiest to visualize with ionic equations:



For the bromine equation, Br is substituted for Cl.

The pale green solution containing the iron(II) ions turns into a yellow or orange solution containing iron(III) ions. Iodine is not a strong enough oxidizing agent to oxidize iron(II) ions, so there is no reaction. In fact, the reverse reaction proceeds. Iron(III) ions are strong enough oxidizing agents to oxidize iodide ions to iodine as shown:

$$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$$

Reactions with sodium hydroxide solution

Once again, only chlorine, bromine, and iodine are considered.

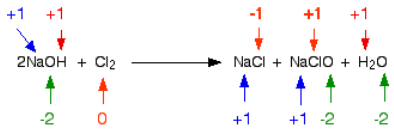
The reaction of chlorine with cold sodium hydroxide solution

Chlorine and cold, dilute sodium hydroxide react as follows:

$$2NaOH + Cl_2 \rightarrow NaCl + NaClO + H_2O$$

NaClO (sometimes written as NaOCl) symbolizes sodium chlorate(I). The traditional name for this compound is sodium hypochlorite; the solution on the product side of the equation is commonly sold as bleach.

Consider this reaction in terms of oxidation states. Chlorine displays an obvious state change from its elemental form to ionic compounds. The oxidation numbers for each element are shown below:



Chlorine is the only element that changes oxidation state—it is both oxidized and reduced. One atom is reduced because its oxidation state has decreased; the other is oxidized. This is a good example of a disproportionation reaction, a reaction in which a single substance is both oxidized and reduced.

The reaction of chlorine with hot sodium hydroxide solution

Chlorine reacts with hot, concentrated sodium hydroxide as follows:

$$6NaOH + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$$

The product formed is sodium chlorate(V) - $NaClO_3$. As before, the oxidation states of each element are calculated. Once again, the only change is in chlorine, from 0 in the chlorine molecules on the reactant side to -1 (in the NaCl) and +5 (in the $NaClO_3$). This is another example of a disproportionation reaction.

Balancing equations for these reactions

The first equation is simple to balance. The second one is more difficult; oxidation states are used to derive it.

The two main products of the reaction are NaCl and $NaClO_3$, so the reaction can be tentatively written as follows:

$$NaOH + Cl_2 \rightarrow NaCl + NaClO_3 + ?$$

In its conversion to NaCl, the oxidation state of the chlorine decreases from 0 to -1. When converted to $NaClO_3$, it increases from 0 to +5. The positive and negative oxidation state changes must cancel out, so for every $NaClO_3$ formed, there must be 5 NaCl:

$$NaOH + Cl_2 \rightarrow 5NaCl + NaClO_3 + ?$$

Now it is a simple task to balance the sodium and the chlorine atoms, after which there are enough hydrogen and oxygen atoms to make $3H_2O$.

The reactions involving bromine and iodine

These are essentially similar to that of chlorine; the difference lies in the reaction temperatures. The tendency to form the ion with the halogen in the +5 oxidation state increases rapidly down the group.

Bromine and sodium hydroxide solution

For bromine, the formation of the sodium bromate(V) happens at around room temperature. Sodium bromate(I) must be formed at about 0°C.

Iodine and sodium hydroxide solution

In this case, sodium iodate(V) is formed at any temperature. Cotton and Wilkinson (Advanced Inorganic Chemistry 3rd edition page 477) say that the iodate(I) ion is unknown in solution.

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7.10.2.5: Oxidizing Ability of the Group 17 Elements

Consider a reaction between one halogen—chlorine, for example—and the ions of another—iodide, in this case. The iodide ions are dissolved from a salt such as sodium iodide or potassium iodide. The sodium or potassium ions are spectator ions and therefore irrelevant to the reaction, which proceeds as follows:

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$$

- The iodide ions lose electrons to form iodine molecules; they are oxidized.
- The chlorine molecules gain electrons to form chloride ions. They are reduced.

This is a redox reaction in which chlorine is acting as an oxidizing agent. The driving force force this reaction is straightforward to identify from the table of Standard Reduction Potentials (Table P2).

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7.10.2.6: Testing for Halide Ions

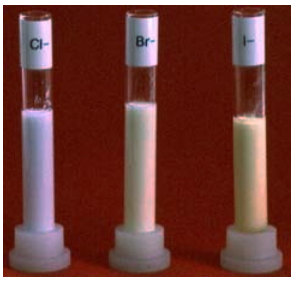
This page discusses the tests for halide ions (fluoride, chloride, bromide and iodide) using silver nitrate and ammonia.

Using silver nitrate solution

This test is carried out in a solution of halide ions. The solution is acidified by adding dilute nitric acid. The nitric acid reacts with, and removes, other ions that might also form precipitates with silver nitrate. Silver nitrate solution is then added, and the halide can be identified from the following products:

ion present	observation
F^-	no precipitate
Cl^-	white precipitate
Br^-	very pale cream precipitate
I^-	very pale yellow precipitate

The chloride, bromide and iodide precipitates are shown in the photograph:



The chloride precipitate is easily identified, but the other two are quite similar to each other. They can only be differentiated in a side-by-side comparison. All the precipitates change color if they are exposed to light, taking on gray or purple tints. The absence of a precipitate with fluoride ions is unhelpful unless it is known that a halogen is present; otherwise, it indicates that there is no chloride, bromide, or iodide.

The chemistry of the test

The precipitates are insoluble silver halides: silver chloride, silver bromide or silver iodide. The formation of these is illustrated in the following equations:

$$Ag^+_{aq} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$$

$$Ag^+_{aq} + Br^-_{(aq)} \rightarrow AgBr_{(s)}$$

$$Ag^+_{aq} + I^-_{(aq)} \rightarrow AgI_{(s)}$$

Silver fluoride is soluble, so no precipitate is formed.

$$Ag^+_{aq} + F^-_{(aq)} \rightarrow Ag^+_{aq} + F^-_{(aq)}$$

Confirming the precipitate using ammonia solution

Ammonia solution is added to the precipitates.

original precipitate	Observation
AgCl	precipitate dissolves to give a colorless solution
AgBr	precipitate is almost unchanged using dilute ammonia solution, but dissolves in concentrated ammonia solution to give a colorless solution
AgI	precipitate is insoluble in ammonia solution of any concentration

There are no absolutely insoluble ionic compounds. A precipitate forms if the concentrations of the ions in solution in water exceed a certain value, unique to every compound. This value is known as the solubility product. For the silver halides, the solubility product is given by the expression:

$$K_{sp} = [Ag^+][X^-]$$

The square brackets indicate molar concentrations, with units of mol L^{-1}.

- If the product of the concentrations of ions is less than the solubility product, no precipitate is formed.
- If the product of the concentrations exceeds this value, a precipitate is formed.

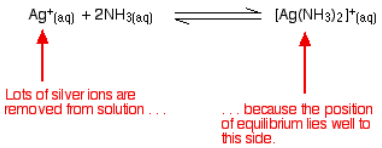
Essentially, the product of the ionic concentrations is never greater than the solubility product value. Enough solid is always precipitated to lower the ionic product to the solubility product. The table below lists solubility products from silver chloride to silver iodide (a solubility product for silver fluoride cannot be reported because it is too soluble).

	K_{sp} (mol^2dm^{-6})
AgCl	1.8×10^{-10}
AgBr	7.7×10^{-13}
AgI	8.3×10^{-17}

The compounds are all quite insoluble, but become even less so down the group.

The purpose of ammonia

The ammonia combines with silver ions to produce a complex ion called the diamminesilver(I) ion, $[Ag(NH_3)_2]^+$. This is a reversible reaction, but the complex is very stable, and the position of equilibrium lies well to the right. The equation for this reaction is given below:



A solution in contact with one of the silver halide precipitates contains a very small concentration of dissolved silver ions. The effect of adding the ammonia is to lower this concentration still further. If the adjusted silver ion concentration multiplied by the halide ion concentration is less than the solubility product, some precipitate dissolves to restore equilibrium.

This occurs with silver chloride, and with silver bromide if the ammonia is concentrated. The more concentrated ammonia pushes the equilibrium even further to the right, lowering the silver ion concentration even more.

The silver iodide is so insoluble that ammonia cannot lower the silver ion concentration enough for the precipitate to dissolve.

An alternative test using concentrated sulfuric acid

Adding concentrated sulfuric acid to a solid sample of one of the halides gives the following results:

ion present	observation
F^-	steamy acidic fumes (of HF)
Cl^-	steamy acidic fumes (of HCl)
Br^-	steamy acidic fumes (of HBr) contaminated with brown bromine vapor
I^-	some HI fumes with large amounts of purple iodine vapor and a red compound in the reaction vessel

The only possible confusion is between a fluoride and a chloride—they behave identically under these conditions. They can be distinguished by dissolving the original solid in water and then testing with silver nitrate solution. The chloride gives a white precipitate; the fluoride produces none.

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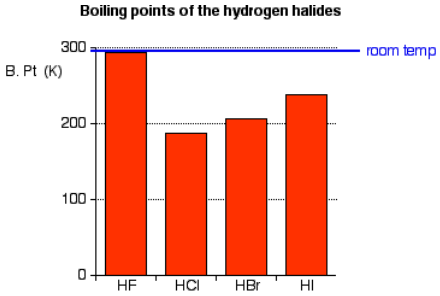
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7.10.2.7: The Acidity of the Hydrogen Halides

This page discusses the acidity of the hydrogen halides: hydrogen fluoride, hydrogen chloride, hydrogen bromide and hydrogen iodide. It begins by describing their physical properties and synthesis and then explains what happens when they react with water to make acids such as hydrofluoric acid and hydrochloric acid.

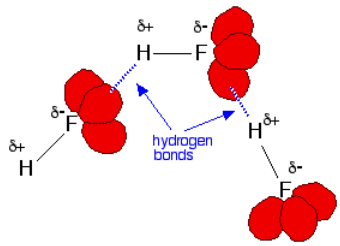
Physical properties

The hydrogen halides are colorless gases at room temperature, producing steamy fumes in moist air. The boiling points of these compounds are shown in the figure below:



Hydrogen fluoride has an abnormally high boiling point for a molecule of its size (293 K or 20°C), and can condense under cool conditions. This is due to the fact that hydrogen fluoride can form hydrogen bonds. Because fluorine is the most electronegative of all the elements, the fluorine-hydrogen bond is highly polarized. The hydrogen atom carries a high partial positive charge (δ+); the fluorine is fairly negatively charged (δ-).

In addition, each fluorine atom has 3 lone pairs of electrons. Fluorine's outer electrons are at the n=2 level, and the lone pairs represent small, highly charged regions of space. Hydrogen bonds form between the δ+ hydrogen on one HF molecule and a lone pair on the fluorine of another one.The figure below illustrates this association:



The other hydrogen halides do not form hydrogen bonds because the larger halogens are not as electronegative as fluorine; therefore, the bonds are less polar. In addition, their lone pairs are at higher energy levels, so the halogen does not carry such an intensely concentrated negative charge; therefore, other hydrogen atoms are not attracted as strongly.

Making hydrogen halides

There are several ways of synthesizing hydrogen halides; the method considered here is the reaction between an ionic halide, like sodium chloride, and an acid like concentrated phosphoric(V) acid, H_3PO_4, or concentrated sulfuric acid.

Making hydrogen chloride

When concentrated sulfuric acid is added to sodium chloride under cold conditions, the acid donates a proton to a chloride ion, forming hydrogen chloride. In the gas phase, it immediately escapes from the system.

$$Cl^- + H_2SO_4 \rightarrow HCl + HSO_4^-$$

The full equation for the reaction is:

$$NaCl + H_2SO_4 \rightarrow HCl + NaHSO_4$$

Sodium bisulfate is also formed in the reaction. Concentrated phosphoric(V) acid reacts similarly, according to the following equation:

$$Cl^- + H_3PO_4 \rightarrow HCl + H_2PO_4^-$$

The full ionic equation showing the formation of the salt, sodium biphosphate(V), is given below:

$$NaCl + H_3PO_4 \rightarrow HCl + NaH_2PO_4$$

Making other hydrogen halides

All hydrogen halides can be formed by the same method, using concentrated phosphoric(V) acid.

Concentrated sulfuric acid, however, behaves differently. Hydrogen fluoride can be made with sulfuric acid, but hydrogen bromide and hydrogen iodide cannot.

The problem is that concentrated sulfuric acid is an oxidizing agent, and as well as producing hydrogen bromide or hydrogen iodide, some of the halide ions are oxidized to bromine or iodine. Phosphoric acid does not have this ability because it is not an oxidant.

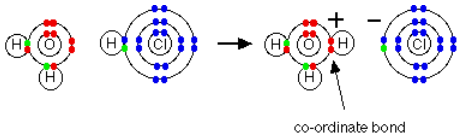
The acidity of the hydrogen halides

Hydrogen chloride as an acid

By the Bronsted-Lowry definition of an acid as a proton donor, hydrogen chloride is an acid because it transfers protons to other species. Consider its reaction with water.

Hydrogen chloride gas is soluble in water; its solvated form is hydrochloric acid. Hydrogen chloride fumes in moist air are caused by hydrogen chloride reacting with water vapor in the air to produce a cloud of concentrated hydrochloric acid.

A proton is donated from the hydrogen chloride to one of the lone pairs on a water molecule.



A coordinate (dative covalent) bond is formed between the oxygen and the transferred proton.

The equation for the reaction is the following:

$$H_2O + HCl \rightarrow H_3O^+ + Cl^-$$

The H_3O^+ ion is the hydroxonium ion (also known as the hydronium ion or the oxonium ion). This is the normal form of protons in water; sometimes it is shortened to the proton form, $H^+(aq)$, for brevity.

When hydrogen chloride dissolves in water (to produce hydrochloric acid), almost all the hydrogen chloride molecules react in this way. Hydrochloric acid is therefore a strong acid. An acid is strong if it is fully ionized in solution.

Hydrobromic acid and hydriodic acid as strong acids

Hydrogen bromide and hydrogen iodide dissolve in (and react with) water in exactly the same way as hydrogen chloride does. Hydrogen bromide forms hydrobromic acid; hydrogen iodide gives hydriodic acid. Both of these are also strong acids.

Hydrofluoric acid as an exception

By contrast, although hydrogen fluoride dissolves freely in water, hydrofluoric acid is only a weak acid; it is similar in strength to organic acids like methanoic acid. The complicated reason for this is discussed below.

The bond enthalpy of the H-F bond

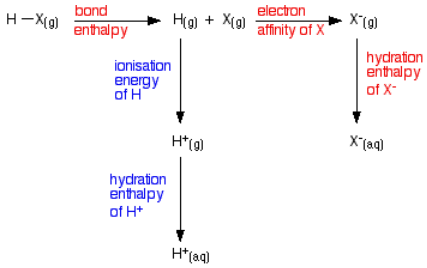
Because the fluorine atom is so small, the bond enthalpy (bond energy) of the hydrogen-fluorine bond is very high. The chart below gives values for all the hydrogen-halogen bond enthalpies:

	bond enthalpy (kJ mol^{-1})
H-F	+562
H-Cl	+431
H-Br	+366
H-I	+299

In order for ions to form when the hydrogen fluoride reacts with water, the H-F bond must be broken. It would seem reasonable to say that the relative reluctance of hydrogen fluoride to react with water is due to the large amount of energy needed to break that bond, but this explanation does not hold.

The energetics of the process from HX(g) to X^-(aq)

The energetics of this sequence are of interest:



All of these terms are involved in the overall enthalpy change as you convert $HX_{(g)}$ into its ions in water.

However, the terms involving the hydrogen are the same for every hydrogen halide. Only the values for the red terms in the diagram need be considered. The values are tabulated below:

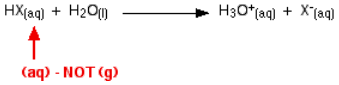
	bond enthalpy of HX (kJ mol^{-1})	electron affinity of X (kJ mol^{-1})	hydration enthalpy of X^- (kJ mol^{-1})	sum of these (kJ mol^{-1})
HF	+562	-328	-506	-272
HCl	+431	-349	-364	-282
HBr	+366	-324	-335	-293
HI	+299	-295	-293	-289

There is virtually no difference in the total HF and HCl values.

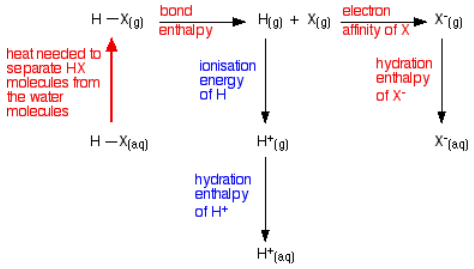
The large bond enthalpy of the H-F bond is offset by the large hydration enthalpy of the fluoride ion. There is a very strong attraction between the very small fluoride ion and the water molecules. This releases a lot of heat (the hydration enthalpy) when the fluoride ion becomes wrapped in water molecules.

Other attractions in the system

The energy terms considered previously have concerned HX molecules in the gas phase. To reach a more correct explanation, the molecules must first be considered as unreacted aqueous HX molecules. The equation for this is given below:



The equation is incorporated into an improved energy cycle as follows:



Unfortunately, values for the first step in the reaction are not readily available. However, in each case, the initial separation of the HX from water molecules is endothermic. Energy is required to break the intermolecular attractions between the HX molecules and water.

That energy is much greater for hydrogen fluoride because it forms hydrogen bonds with water. The other hydrogen halides experience only the weaker van der Waals dispersion forces or dipole-dipole attractions.

The overall enthalpy changes (including all the stages in the energy cycle) for the reactions are given in the table below:

$$HX(aq) + H_2O(l) \rightarrow H_3O^+(aq) + X^-(aq)$$

	enthalpy change (kJ mol^{-1})
HF	-13
HCl	-59
HBr	-63
H-I	-57

The enthalpy change for HF is much smaller in magnitude than that for the other three hydrogen halides, but it is still negative exothermic change. Therefore, more information is needed to explain why HF is a weak acid.

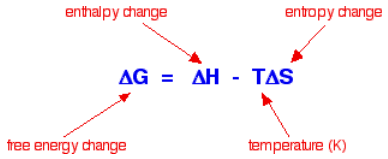
Entropy and free energy considerations

The free energy change, not the enthalpy change, determines the extent and direction of a reaction.

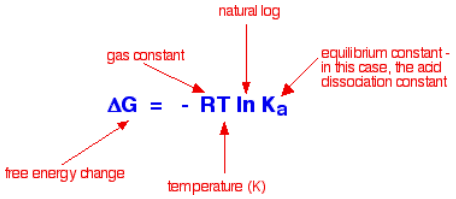
Free energy change is calculated from the enthalpy change, the temperature of the reaction and the entropy change during the reaction.

For simplicity, entropy can be thought of as a measure of the amount of disorder in a system. Entropy is given the symbol **S**. If a system becomes more disordered, then its entropy increases. If it becomes more ordered, its entropy decreases.

The key equation is given below:



In simple terms, for a reaction to happen, the free energy change must be negative. But more accurately, the free energy change can be used to calculate a value for the equilibrium constant for a reaction using the following expression:



The term K_a is the equilibrium constant for the reaction below:

$$HX(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + X^-(aq)$$

The values for TΔS (needed to calculate ΔG) for the four reactions at a temperature of 298 K are tabulated below:

	$T_\Delta S$ (kJ mol^{-1})
HF	-29
HCl	-13
HBr	-4
H-I	+4

Notice that at the top of the group, the systems become more ordered when the HX reacts with the water. The entropy of the system (the amount of disorder) decreases, particularly for the hydrogen fluoride.

The reason for this is that the very strong attraction between H_3O^+ and $F^-_{(aq)}$ imposes a lot of order on the system, as does the attraction between the water molecules and the various ions present. These attractions are each greatest for the small fluoride ions.

The total effect on the free energy change, and therefore the value of the equilibrium constant, can now be considered. These values are calculated in the following table:

	$_\Delta H$ (kJ mol^{-1})	$T_\Delta S$ (kJ mol^{-1})	$_\Delta G$ (kJ mol^{-1})	K_a (mol dm^{-3})
HF	-13	-29	+16	1.6×10^{-3}
HCl	-59	-13	-46	1.2×10^{8}
HBr	-63	-4	-59	2.2×10^{10}
HI	-57	+4	-61	5.0×10^{10}

The values for these estimated equilibrium constants for HCl, HBr and HI are so high that the reaction can be considered "one-way". The ionization is virtually 100% complete. These are all strong acids, increasing in strength down the group.

By contrast, the estimated K_a for hydrofluoric acid is small. Hydrofluoric acid only ionizes to a limited extent in water. Therefore, it is a weak acid.

The estimated value for HF in the table can be compared to the experimental value:

- Experimental value: 5.6×10^{-4} mol dm^{-3}
- Estimated value: 1.6×10^{-3} mol dm^{-3}

These values differ by an order of magnitude, but because of the logarithmic relationship between the free energy and the equilibrium constant, a very small change in ΔG has a very large effect on K_a.

To have the values in close agreement, ΔG would have to increase from +16 to +18.5 kJ mol^{-1}. Given the uncertainty in the values used to calculate ΔG, the difference between the calculated value and the experimental value could easily fall within this range.

Summary: Why is hydrofluoric acid a weak acid?

The two main factors are:

- Entropy decreases dramatically when the hydrogen fluoride reacts with water. This is particularly noticeable with hydrogen fluoride because the attraction of the small fluoride ions produced imposes significant order on the surrounding water molecules and nearby hydronium ions. The effect decreases with larger halide ions.

- Very strong hydrogen bonding exists between the hydrogen fluoride molecules and water molecules. This costs a large amount of energy to break. This effect does not occur in the other hydrogen halides.

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7.10.3: Chemistry of Fluorine (Z=9)

Fluorine (F) is the first element in the Halogen group (group 17) in the periodic table. Its atomic number is 9 and its atomic weight is 19, and it's a gas at room temperature. It is the most electronegative element, given that it is the top element in the Halogen Group, and therefore is very reactive. It is a nonmetal, and is one of the few elements that can form diatomic molecules (F_2). It has 5 valence electrons in the 2p level. Its electron configuration is $1s^2 2s^2 2p^5$. It will usually form the anion F^- since it is extremely electronegative and a strong oxidizing agent. Fluorine is a Lewis acid in weak acid, which means that it accepts electrons when reacting. Fluorine has many isotopes, but the only stable one found in nature is F-19.

Quick Reference Table

Symbol	F
Atomic Number	9
Group	17 (Halogens)
Electron Configuration	$1s^2 2s^2 2p^5$
Atomic Weight	18.998 g
Density	1.7 g/L
Melting Point	-219.62°C
Boiling Point	-188.12°C
Critical Point	144.13K, 5.172 MPa
Oxidation States	-1
Electronegativity	3.98
Stable Isotopes	F-19

Brief History

In the late 1600's minerals which we now know contain fluorine were used in etching glass. The discovery of the element was prompted by the search for the chemical substance which was able to attack glass (it is HF, a weak acid). The early history of the isolation and work with fluorine and hydrogen fluoride is filled with accidents since both are extremely dangerous. Eventually, electrolysis of a mixture of KF and HF (carefully ensuring that the resulting hydrogen and fluorine would not come in contact) in a platinum apparatus yielded the element.



Figure 1: Image courtesy of Wikipedia

Fluorine was discovered in 1530 by Georgius Agricola. He originally found it in the compound Fluorspar, which was used to promote the fusion of metals. It was used in this application until 1670, when Schwanhard discovered its usefulness in etching glass. Pure fluorine (from the Latin fluere, for "flow") was not isolated until 1886 by Henri Moissan, burning and even killing many scientists along the way. It has many uses today; a particular one was being used in the Manhattan project to help create the first nuclear bomb.

Electronegativity of Fluorine

Fluorine is the most electronegative element on the periodic table, which means that it is a very strong oxidizing agent and accepts other elements' electrons. Fluorine's atomic electron configuration is $1s^2 2s^2 2p^5$ (see Figure 2).

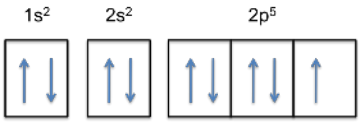


Figure 2: Electronic configuration of fluorine

Fluorine is the most electronegative element because it has 5 electrons in its 2p shell. The optimal electron configuration of the 2p orbital contains 6 electrons, so since fluorine is so close to ideal electron configuration, the electrons are held very tightly to the nucleus. The high electronegativity of fluorine explains its small radius because the positive protons have a very strong attraction to the negative electrons, holding them closer to the nucleus than the bigger and less electronegative elements do.

Reactions of Fluorine

Because of its reactivity, elemental fluorine is never found in nature, and no other chemical element can displace fluorine from its compounds. Fluorine bonds with almost any element, both metals and nonmetals, because it is a very strong oxidizing agent. It is very unstable and reactive since it is so close to its ideal electron configuration. It forms covalent bonds with nonmetals, and since it is the most electronegative element, is always going to be the element that is reduced. It can also form a diatomic element with itself (F_2), or covalent bonds where it oxidizes other halogens (ClF, ClF_3, ClF_5). It will react explosively with many elements and compounds such as hydrogen and water. Elemental fluorine is slightly basic, which means that when it reacts with water it forms OH^-.

$$2F_2 + 2H_2O \rightarrow O_2 + 4HF \tag{1}$$

When combined with hydrogen, fluorine forms hydrofluoric acid (HF), which is a weak acid. This acid is very dangerous and when dissociated can cause severe damage to the body because while it may not be painful initially, it passes through tissues quickly and can cause deep burns that interfere with nerve function.

$$HF + H_2O \rightarrow H_3O^+ + F^- \tag{2}$$

There are also some organic compounds made of fluorine, ranging from nontoxic to highly toxic. Fluorine forms covalent bonds with carbon, which sometimes form into stable aromatic rings. When carbon reacts with fluorine, the reaction is complex and forms a mixture of CF_4, C_2F_6, and C_5F_{12}.

$$C_{(s)} + F_{2(g)} \rightarrow CF_{4(g)} + C_2F_6 + C_5F_{12} \tag{3}$$

Fluorine reacts with oxygen to form OF_2 because fluorine is more electronegative than oxygen. The reaction goes:

$$2F_2 + O_2 \rightarrow 2OF_2 \tag{4}$$

Fluorine is so electronegative that sometimes it will even form molecules with noble gases like Xenon, such as the molecule xenon difluoride, XeF_2.

$$Xe + F_2 \rightarrow XeF_2 \tag{5}$$

Fluorine also forms strong ionic compounds with metals. Some common ionic reactions of fluorine are:

$$F_2 + 2NaOH \rightarrow O_2 + 2NaF + H_2 \tag{6}$$

$$4F_2 + HCl + H_2O \rightarrow 3HF + OF_2 + ClF_3 \tag{7}$$

$$F_2 + 2HNO_3 \rightarrow 2NO_3F + H_2 \tag{8}$$

Applications of Fluorine

Compounds of fluorine are present in fluoridated toothpaste and in many municipal water systems, where they help to prevent tooth decay. And, of course, fluorocarbons such as Teflon have made a major impact on life in the 20th century. There are many

applications of fluorine:

- Rocket fuels
- Polymer and plastics production
- Teflon and tefzel production
- When combined with oxygen, used as a refrigerator cooler
- Hydrofluoric acid used for glass etching
- Purify public water supplies
- Uranium production
- Air conditioning

Sources

Fluorine can either be found in nature or produced in a lab. To make it in a lab, compounds like potassium fluoride are put through electrolysis with hydrofluoric acid to create pure Fluorine and other compounds. It can be carried out with a variety of compounds, usually ionic ones involving fluorine and a metal. Fluorine can also be found in nature in various minerals and compounds. The two main compounds it can be found in are Fluorspar (CaF_2) and Cryolite (Na_3AlF_6).

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Problems

(Highlight to view answers)

1. Q. What is the electron configuration of fluorine? of F^-?

A.

2. Q. Is fluorine usually oxidized or reduced? explain.

A.

3. Q. What are some common uses of fluorine?

A.

4. Q. Does fluorine form compounds with nonmetals? if so, give two examples, one of them being of an oxide.

A.

5. Q. What group is fluorine in? (include name of group and number)

A.

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7.10.4: Chemistry of Chlorine (Z=17)

Chlorine is a halogen in group 17 and period 3. It is very reactive and is widely used for many purposes, such as as a disinfectant. Due to its high reactivity, it is commonly found in nature bonded to many different elements.

Chlorine, which is similar to fluorine but not as reactive, was prepared by Sheele in the late 1700's and shown to be an element by Davy in 1810. It is a greenish-yellow gas with a disagreeable odor (you can detect it near poorly balanced swimming pools). Its name comes from the Greek word chloros, meaning greenish-yellow. In high concentration it is quite toxic and was used in World War I as a poison gas.

Properties

Atomic Number	17
Atomic Weight	35.457
Electron Configuration	$[Na]3s^23p^5$
1st Ionization Energy	1251 kJ/mol
Ionic Radius	181 pm
Density (Dry Gas)	3.2 g/L
Melting Point	-101°C
Boiling Point	-34.05°C
Specific Heat	0.23 g cal/g/°C
Heat of Vaporization	68 g cal/g
Heat of Fusion	22 g cal/g
Critical Temperature	114°C
Standard Electron Potential $Cl_2 + 2e^- \rightarrow 2Cl^-$	1.358V

At room temperature, pure chlorine is a yellow-green gas. Chlorine is easily reduced, making it a good oxidation agent. By itself, it is not combustible, but many of its reactions with different compounds are exothermic and produce heat. Because chlorine is so highly reactive, it is found in nature in a combined state with other elements, such as NaCl (common salt) or KCl (sylvite). It forms strong ionic bonds with metal ions.

Like fluorine and the other members of the halogen family, chlorine is diatomic in nature, occurring as Cl_2 rather than Cl. It forms -1 ions in ionic compounds with most metals. Perhaps the best known compound of that type is sodium chloride, common table salt (NaCl).

Small amounts of chlorine can be produced in the lab by oxidizing HCl with MnO_2. On an industrial scale, chlorine is produced by electrolysis of brines or even sea water. Sodium hydroxide (also in high demand) is a by-product of the process.

In addition to the ionic compounds that chlorine forms with metals, it also forms molecular compounds with non-metals such as sulfur and oxygen. There are four different oxides of the element. Hydrogen chloride gas (from which we get hydrochloric acid) is an important industrial product.

Reactions with Water

Usually, reactions of chlorine with water are for disinfection purposes. Chlorine is only slightly soluble in water, with its maximum solubility occurring at 49° F. After that, its solubility decreases until 212° F. At temperatures below that range, it forms crystalline hydrates (usually Cl_2) and becomes insoluble. Between that range, it usually forms hypochlorous acid ($HOCl$). This is the primary reaction used for water/wastewater disinfection and bleaching.

$$Cl_2 + H_2O \rightarrow HOCl + HCl$$

At the boiling temperature of water, chlorine decomposes water:

$$2Cl_2 + 2H_2O \rightarrow 4HCl + O_2$$

Reactions with Oxygen

Although chlorine usually has a -1 oxidation state, it can have oxidation states of +1, +3, +4, or +7 in certain compounds, such as when it forms *oxoacids* with the alkali metals.

Oxidation State	Compound
+1	NaClO
+3	$NaClO_2$
+5	$NaClO_3$
+7	$NaClO_4$

Reactions with Hydrogen

When H_2 and Cl_2 are exposed to sunlight or high temperatures, they react quickly and violently in a spontaneous reaction. Otherwise, the reaction proceeds slowly.

$$H_2 + Cl_2 \rightarrow 2HCl$$

HCl can also be produced by reacting chlorine with compounds containing hydrogen, such as hydrogen sulfide

Reactions with Halogens

Chlorine, like many of the other halogens, can form interhalogen compounds (examples include BrCl, ICl, ICl_2). The heavier element in one of these compounds acts as the central atom. For chlorine, this occurs when it is bonded to fluorine in ClF, ClF_3, and ClF_5.

Reactions with Metals

Chlorine reacts with most metals and forms metal chlorides, with most of these compounds being soluble in water. Examples of insoluble compounds include $AgCl$ and $PbCl_2$. Gaseous or liquid chlorine usually does not have an effect on metals such as iron, copper, platinum, silver, and steel at temperatures below 230°F. At high temperatures, however, it reacts rapidly with many of the metals, especially if the metal is in a form that has a high surface area (such as when powdered or made into wires).

Example: Oxidizing Iron

Chlorine can oxidize iron:

$$Cl_2 + Fe \rightarrow FeCl_2$$

Half Reactions:

$$Fe \rightarrow Fe^{+2} + 2e^-$$

$$Cl_2 + 2e^- \rightarrow 2Cl^-$$

Isotopes

^{35}Cl and ^{37}Cl are the two natural, stable isotopes of chlorine. ^{36}Cl, a radioactive isotope, occurs only in trace amounts as a result of cosmic rays in the atmosphere. Chlorine is usually a mixture of 75% ^{35}Cl and 25% ^{37}Cl. Besides these isotopes, the other isotopes must be artificially produced. A table containing some common isotopes is found below:

Isotope	Atomic Mass	Half-Life
^{33}Cl	32.986	2.8 seconds
^{34}Cl	33.983	33 minutes
^{35}Cl	34.979	Stable (∞)
^{36}Cl	35.978	400,000 years
^{37}Cl	35.976	Stable (∞)
^{38}Cl	37.981	39 Minutes

Production and Uses

Chlorine is a widely used chemical with many applications.

Water Treatment

Chlorine is used in the disinfection (removal of harmful microorganisms) of water and wastewater. In the United States, it is almost exclusively used. Chlorine was first used to disinfect drinking water in 1908, using sodium hypochlorite (NaOCl):

$$NaOCl + H_2O \rightarrow HOCl + NaOH$$

Following widespread use of sodium hypochlorite to disinfect water, diseases caused by unclean water decreased greatly. Compared to other methods, it is effective at lower concentrations and is inexpensive.

Polyvinyl Chloride (PVC)

Polyvinyl chloride is a plastic which is widely manufactured throughout the globe, and is responsible for nearly a third of the world's use of chlorine. It is usually manufactured by first taking EDC (ethylene dichloride) and then making it into a vinyl chloride, the basic unit for PVC. From then on, vinyl chloride monomers are linked together to form a polymer. PVC becomes malleable at high temperatures, making it flexible and ideal for many purposes from pipes to clothing. However, PVC is toxic. When in gaseous form and inhaled, it can cause damage to the lungs, the body's blood circulation, and the nervous system. The production of PVC has many regulations surrounding it due to the many harmful effects that the plastic itself and the intermediates involved have on the environment and on human health.

Paper Bleaching

Paper is one of the most widely consumed products in the world. Before wood is made into a paper product, however, it must be turned into pulp (separated fibrous material). This pulp has a color that ranges from light to dark brown. Chlorine is used to bleach the pulp to turn it into a bright, white color, which makes it desirable for consumers. The process usually involves a number of steps, depending on the nature of the pulp.

Problems

1) Solve and balance the following equations

a. $H_2S + Cl_2 + H_2O \rightarrow$
b. $Sb + Cl_2 + H_2O \rightarrow$

2) Write the electron configuration for chlorine.

3) What is the molecular geometry of the following? (See Valence Bond Theory)

a. ClO_2

b. ClF_5

4) What are the naturally occurring chlorine isotopes?

5) When does chlorine have an oxidation state of +5?

Answers

1) Solve and balance the following equations:

a. $H_2S + 4Cl_2 + 4H_20$ --> $H_2S0_4 + 8HCl$
b. $2Sb + 3Cl_2$ --> $2SbCl_3$

2) The electron configuration of chlorine is: $1s^22s^22p^63s^23p^5$

3) What is the molecular geometry of the following?

a. ClO_2 -Bent or angular; the Cl is bonded to two ligands, has one lone pair and one unpaired electron.
b. ClF_5 -Square pyramid; the Cl is bonded to five ligands and has one lone pair.

4) The naturally occurring chlorine isotopes are chlorine-35 and chlorine-37. While chlorine-36 does occur naturally, it is radioactive and unstable.

5) Chlorine has an oxidation state of +5 when it reacts with oxoacids with the Alkali Metals.

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7.10.4.1: The Manufacture of Chlorine

This page describes the manufacture of chlorine by the electrolysis of sodium chloride solution using a diaphragm cell and a membrane cell. Both cells rely on the same underlying chemistry, but differ in detail.

Background chemistry

Chlorine is manufactured by electrolyzing sodium chloride solution. This process generates three useful substances: chlorine, sodium hydroxide, and hydrogen.

The chemistry of the electrolysis process

Sodium chloride solution contains the following:

- sodium ions
- chloride ions
- protons (from the water)
- hydroxide ions (from the water)

The protons and hydroxide ions come from the equilibrium:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \tag{7.10.4.1.1}$$

At any time, the concentration of protons or hydroxide ions is very small; the position of equilibrium lies well to the left.

At the anode

The negative ions, chloride and hydroxide, are attracted to the positively charged anode. It is easier to oxidize hydroxide ions to oxygen than to oxidize chloride ions to chlorine, but there are far more chloride ions arriving at the anode than hydroxide ions.

The major reaction at the anode is therefore:

$$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^- \tag{7.10.4.1.2}$$

Two chloride ions each give up an electron to the anode, and the atoms produced combine into chlorine gas. The chlorine is, however, contaminated with small amounts of oxygen because of a reaction involving hydroxide ions, which also give up electrons:

$$4OH^-_{(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)} + 4e^- \tag{7.10.4.1.3}$$

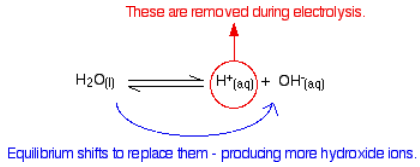
The chlorine must be purified by removing this oxygen.

At the cathode

Sodium ions and protons (from the water) are attracted to the negative cathode. It is much easier for a proton to pick up an electron than for a sodium ion to do so. Therefore, the following reaction occurs:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \tag{7.10.4.1.4}$$

As protons convert into hydrogen gas, the equilibrium below shifts to the right to replace them:



The net effect of this process is a buildup of sodium ions and newly-produced hydroxide ions at the cathode. In other words, sodium hydroxide solution is formed.

The necessity of keeping all products separate

If chlorine comes into contact with hydrogen, it produces a mixture that explodes violently on exposure to sunlight or heat, producing hydrogen chloride gas. Clearly these gases must remain separated. However, chlorine also reacts with sodium hydroxide solution to produce a mixture of sodium chloride and sodium chlorate(I), also known as sodium hypochlorite; this mixture is commonly sold as bleach. In addition, when the desired products are chlorine and sodium hydroxide rather than bleach, chlorine and sodium hydroxide must also be kept apart. The diaphragm and membrane cells are designed to keep all the products separate.

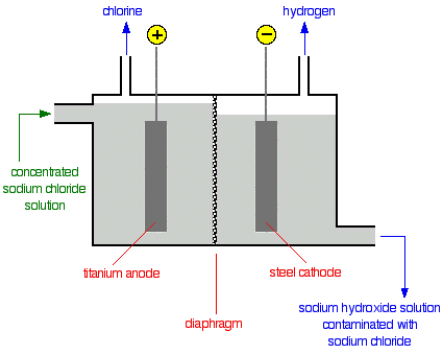


Figure 1: The diaphragm cell

The diaphragm

The diaphragm is made of a porous mixture of asbestos and polymers. The solution can seep through it from the anode compartment into the cathode compartment. Notice that there is a higher level of liquid on the anode side. This ensures that the liquid always flows from left to right, preventing any of the sodium hydroxide solution from coming into contact with chlorine products.

Production of chlorine at the anode

Chlorine is produced at the titanium anode according to the following equation:

$$2Cl^-(aq) - 2e^- \rightarrow Cl_2(g)$$

The product is contaminated with some oxygen because of the reaction below:

$$4OH^-(aq) - 4e^- \rightarrow 2H_2O(l) + O_2(g)$$

The chlorine is purified by liquefaction under pressure. The oxygen remains a gas when compressed at ordinary temperatures.

Production of hydrogen at the cathode

Hydrogen is produced at the steel cathode by the following process:

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

Production of the sodium hydroxide

A dilute solution of sodium hydroxide solution is also produced at the cathode (see above for the explanation of what happens at the cathode). It is highly contaminated with unreacted sodium chloride.

The sodium hydroxide solution leaving the cell is concentrated by evaporation. During this process, most of the sodium chloride crystallizes out as solid salt. The salt can be separated, dissolved in water, and passed through the cell again. Even after concentration, sodium hydroxide still contains a small percentage of sodium chloride.

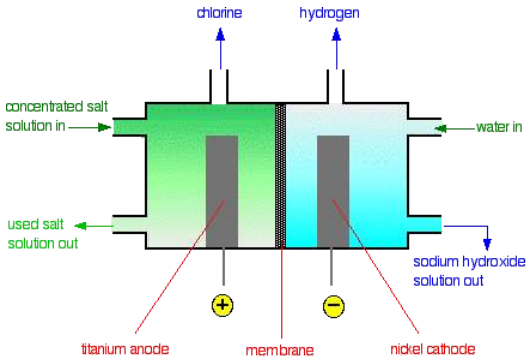


Figure 2: The membrane cell

The membrane

The membrane is made from a polymer that only allows the diffusion of positive ions. That means that only the sodium ions can pass through the membrane; the chloride ions are blocked. The advantage of this is that the sodium hydroxide formed in the right-hand compartment is never contaminated with sodium chloride. The sodium chloride solution must be pure. If it contains any other metal ions, these can also pass through the membrane and so contaminate the sodium hydroxide solution.

Production of chlorine

Chlorine is produced at the titanium anode according to the following equation:

$$2Cl^-(aq) + 2e^- \rightarrow Cl_2(g)$$

It is contaminated with some oxygen because of the parallel reaction below:

$$4OH^-(aq) + 4e^- \rightarrow 2H_2O(l) + O_2$$

The chlorine is purified by liquefaction under pressure. The oxygen remains in the gas phase when compressed at normal temperatures.

Production of hydrogen

Hydrogen is produced at the nickel cathode as follows:

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

Production of sodium hydroxide

An approximately 30% solution of sodium hydroxide solution is also produced at the cathode (see the background chemistry section for an explanation of what happens at the cathode).

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7.10.5: Chemistry of Bromine (Z=35)

Bromine is a reddish-brown fuming liquid at room temperature with a very disagreeable chlorine-like smell. In fact its name is derived from the Greek bromos or "stench". It was first isolated in pure form by Balard in 1826. It is the only non-metal that is a liquid at normal room conditions. Bromine on the skin causes painful burns that heal very slowly. It is an element to be treated with the utmost respect in the laboratory.

Most bromine is produced by displacement from ordinary sea water. Chlorine (which is more active) is generally used to dislodge the bromine from various compounds in the water. Before leaded gasolines were removed from the market, bromine was used in an additive to help prevent engine "knocking". Production now is chiefly devoted to dyes, disinfectants and photographic chemicals.

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7.10.6: Chemistry of Iodine (Z=53)

Elemental iodine is a dark grey solid with a faint metallic luster. When heated at ordinary air pressures it sublimes to a violet gas. The name iodine is taken from the Greek ioeides which means "violet colored". It was discovered in 1811 by Courtois.

Commercially iodine is recovered from seaweed and brines. It is an important trace element in the human diet, required for proper function of the thyroid gland. Thus iodine is added to table salt ("iodized") to insure against iodine deficiencies. Radioactive isotopes of iodine are used in medical tracer work involving the thyroid and also to treat diseases of that gland.

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7.10.7: Chemistry of Astatine (Z=85)

Astatine was formerly known as alabamine. It has no stable isotopes and was first synthetically produced (1940) at the University of California.

Name: Astatine
Symbol: At
Atomic Number: 85
Atomic Mass: (210.0) amu
Melting Point: 302.0 °C (575.15 K, 575.6 °F)
Boiling Point: 337.0 °C (610.15 K, 638.6 °F)
Number of Protons/Electrons: 85
Number of Neutrons: 125
Classification: Halogen
Crystal Structure: Unknown
Density @ 293 K: Unknown
Color: Unknown
Date of Discovery: 1940
Discoverer: D.R. Corson
Name Origin: From the Greek word *astatos* (unstable)
Uses: No uses known
Obtained From: Man-made
Oxidation Number: -1, +5

Astatine is the last of the known halogens and was synthesized in 1940 by Corson and others at the University of California. It is radioactive and its name, from the Greek astatos, means "unstable". The element can be produced by bombarding targets made of bismuth-209 with high energy alpha particles (helium nuclei). Astatine 211 is the product and has a half-life of 7.2 hours. The most stable isotope of astatine is 210, which has a half-life of 8.1 hours.

Not much is known about the chemical properties of astatine, but it is expected to react like the other halogens, although much less vigorously, and it should be more metallic than iodine. There should be tiny quantities of astatine in the earth's crust as products of other radioactive decays, but their existence would be short-lived.

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SECTION OVERVIEW

7.11: The Noble Gases

The noble gases (Group 18) are located in the far right of the periodic table and were previously referred to as the "inert gases" due to the fact that their filled valence shells (octets) make them extremely nonreactive. The noble gases were characterized relatively late compared to other element groups.

7.11.1: Properties of Nobel Gases

7.11.1.1: Noble Gas (Group 18) Trends

7.11.2: Reactions of Nobel Gases

7.11.3: Chemistry of Helium (Z=2)

7.11.4: Chemistry of Neon (Z=10)

7.11.5: Chemistry of Argon (Z=18)

7.11.6: Chemistry of Krypton (Z=36)

7.11.7: Chemistry of Xenon (Z=54)

7.11.8: Chemistry of Radon (Z=86)

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7.11.1: Properties of Nobel Gases

The noble gases (Group 18) are located in the far right of the periodic table and were previously referred to as the "inert gases" due to the fact that their filled valence shells (octets) make them extremely nonreactive. The noble gases were characterized relatively late compared to other element groups.

The History

The first person to discover the noble gases was Henry Cavendish in the late 180th century. Cavendish distinguished these elements by chemically removing all oxygen and nitrogen from a container of air. The nitrogen was oxidized to NO_2 by electric discharges and absorbed by a sodium hydroxide solution. The remaining oxygen was then removed from the mixture with an absorber. The experiment revealed that 1/120 of the gas volume remained un-reacted in the receptacle. The second person to isolate, but not typify, them was William Francis (1855-1925). Francis noted the formation of gas while dissolving uranium minerals in acid.

Argon

In 1894, John William Strutt discovered that chemically-obtained pure nitrogen was less dense than the nitrogen isolated from air samples. From this breakthrough, he concluded that another, unknown gas was present in the air. With the aid of William Ramsay, Strutt managed to replicate and modify Cavendish's experiment to better understand the inert component of air in his original experiment. The researchers' procedure differed from the Cavendish procedure: they removed the oxygen by reacting it with copper, and removed the nitrogen in a reaction with magnesium. The remaining gas was properly characterized and the new element was named "argon," which originates from the Greek word for "inert."

Helium

Helium was first discovered in 1868, manifesting itself in the solar spectrum as a bright yellow line with a wavelength of 587.49 nanometers. This discovery was made by Pierre Jansen. Jansen initially assumed it was a sodium line. However, later studies by Sir William Ramsay (who isolated helium on Earth by treating a variety of rare elements with acids) confirmed that the bright yellow line from his experiment matched up with that in the spectrum of the sun. From this, British physicist William Crookes identified the element as helium.

Neon, Krypton, Xenon

These three noble gases were discovered by Morris W. Travers and Sir William Ramsay in 1898. Ramsay discovered neon by chilling a sample of the air to a liquid phase, warming the liquid, and capturing the gases as they boiled off. Krypton and xenon were also discovered through this process.

Radon

In 1900, while studying the decay chain of radium, Friedrich Earns Dorn discovered the last gas in Group 18: radon. In his experiments, Dorn noticed that radium compounds emanated radioactive gas. This gas was originally named niton after the Latin word for shining, "nitens". In 1923, the International Committee for Chemical Elements and International Union of Pure Applied Chemistry (IUPAC) decided to name the element radon. All isotopes of radon are radioactive. Radon-222 has the longest half-life at less than 4 days, and is an alpha-decay product of Radium-226 (part of the U-238 to Pb-206 radioactive decay chain).

The Electron Configurations for Noble Gases

- **Helium** $1s^2$
- **Neon** [He] $2s^2\ 2p^6$
- **Argon** [Ne] $3s^2\ 3p^6$
- **Krypton** [Ar] $3d^{10}\ 4s^2\ 4p^6$
- **Xenon** [Kr] $4d^{10}\ 5s^2\ 5p^6$
- **Radon** [Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^6$

Table 1: Trends within Group 18

	Atomic #	Atomic mass	Boiling point (K)	Melting point (K)	1st Ionization ($E/kJ\ mol^{-1}$)	Density (g/dm^3)	Atomic radius (pm)
He	2	4.003	4.216	0.95	2372.3	0.1786	31
Ne	10	20.18	27.1	24.7	2080.6	0.9002	38
Ar	18	39.948	87.29	83.6	1520.4	1.7818	71
Kr	36	83.3	120.85	115.8	1350.7	3.708	88
Xe	54	131.29	166.1	161.7	1170.4	5.851	108
Rn	86	222.1	211.5	202.2	1037.1	9.97	120

The Atomic and Physical Properties

- Atomic mass, boiling point, and atomic radii **INCREASE** down a group in the periodic table.
- The first ionization energy **DECREASES** down a group in the periodic table.
- The noble gases have the largest ionization energies, reflecting their chemical inertness.
- Down Group 18, atomic radius and interatomic forces **INCREASE** resulting in an **INCREASED** melting point, boiling point, enthalpy of vaporization, and solubility.
- The **INCREASE** in density down the group is correlated with the **INCREASE** in atomic mass.
- Because the atoms **INCREASE** in atomic size down the group, the electron clouds of these non polar atoms become increasingly polarized, which leads to weak van Der Waals forces among the atoms. Thus, the formation of liquids and solids is more easily attainable for these heavier elements because of their melting and boiling points.
- Because noble gases' outer shells are full, they are extremely stable, tending not to form chemical bonds and having a small tendency to gain or lose electrons.
- Under standard conditions all members of the noble gas group behave similarly.
- All are monotomic gases under standard conditions.
- Noble gas atoms, like the atoms in other groups, **INCREASE** steadily in atomic radius from one period to the next due to the **INCREASING** number of electrons.
- The size of the atom is positively correlated to several properties of noble gases. The ionization potential **DECREASES** with an **INCREASING** radius, because the valence electrons in the larger noble gases are further away from the nucleus; they are therefore held less tightly by the atom.
- The attractive force **INCREASES** with the size of the atom as a result of an **INCREASE** in polarizability and thus a **DECREASE** in ionization potential.
- Overall, noble gases have weak interatomic forces, and therefore very low boiling and melting points compared with elements of other groups.

For covalently-bonded diatomic and polyatomic gases, heat capacity arises from possible translational, rotational, and vibrational motions. Because monatomic gases have no bonds, they cannot absorb heat as bond vibrations. Because the center of mass of monatomic gases is at the nucleus of the atom, and the mass of the electrons is negligible compared to the nucleus, the kinetic energy due to rotation is negligible compared to the kinetic energy of translation (unlike in di- or polyatomic molecules where rotation of nuclei around the center of mass of the molecule contributes significantly to the heat capacity). Therefore, the internal energy per mole of a monatomic noble gas equals its translational contribution, $\frac{3}{2}RT$, where R is the universal gas constant and T is the absolute temperature.

For monatomic gases at a given temperature, the average kinetic energy due to translation is practically equal regardless of the element. Therefore at a given temperature, the heavier the atom, the more slowly its gaseous atoms move. The mean velocity of a monatomic gas decreases with increasing molecular mass, and given the simplified heat capacity situation, noble gaseous thermal conductivity decreases with increasing molecular mass.

Applications of Noble Gases

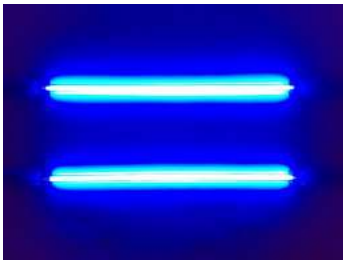
Helium

Helium is used as a component of breathing gases due to its low solubility in fluids or lipids. This is important because other gases are absorbed by the blood and body tissues when under pressure during scuba diving. Because of its reduced solubility, little helium is taken into cell membranes; when it replaces part of the breathing mixture, helium causes a decrease in the narcotic effect of the gas at far depths. The reduced amount of dissolved gas in the body means fewer gas bubbles form, decreasing the pressure of the ascent. **Helium** and **Argon** are used to shield welding arcs and the surrounding base metal from the atmosphere.

Helium is used in very low temperature cryogenics, particularly for maintaining superconductors (useful for creating strong magnetic fields) at a very low temperatures. Helium is also the most common carrier gas in gas chromatography.

Neon

Neon has many common and familiar applications: neon lights, fog lights, TV cine-scopes, lasers, voltage detectors, luminous warnings, and advertising signs. The most popular application of neon is the neon tubing used in advertising and elaborate decorations. These tubes are filled with neon and helium or argon under low pressure and submitted to electrical discharges. The color of emitted light is depends on the composition of the gaseous mixture and on the color of the glass of the tube. Pure Neon within a colorless tube absorbs red light and reflects blue light, as shown in the figure below. This reflected light is known as fluorescent light.



One of the many colors of neon lights.

Argon

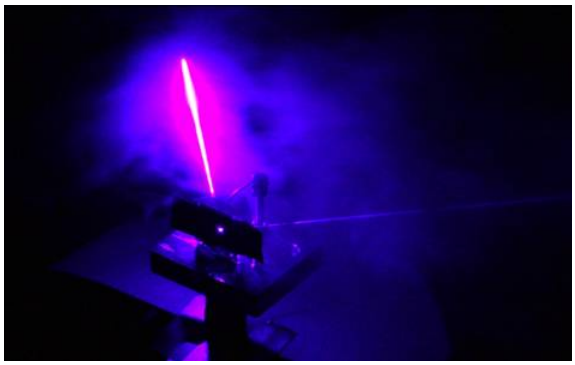
Argon has a large number of applications in electronics, lighting, glass, and metal fabrications. Argon is used in electronics to provide a protective heat transfer medium for ultra-pure silicon crystal semiconductors and for growing germanium. Argon can also fill fluorescent and incandescent light bulbs, creating the blue light found in "neon lamps." By utilizing argon's low thermal conductivity, window manufacturers provide a gas barrier needed to produce double-pane insulated windows. This insulation barrier improves the windows' energy efficiencies. Argon also creates an inert gas shield during welding, flushes out melted metals to eliminate porosity in casting, and provides an oxygen- and nitrogen-free environment for annealing and rolling metals and alloys.



Argon plasma light bulb.

Krypton

Similarly to argon, krypton can be found in energy efficient windows. Because of its superior thermal efficiency, krypton is sometimes chosen over argon for insulation. It is estimated that 30% of energy efficient windows sold in Germany and England are filled with krypton; approximately 1.8 liters of krypton are used in these countries. Krypton is also found in fuel sources, lasers and headlights. In lasers, krypton functions as a control for a desired optic wavelength. It is usually mixed with a halogen (most likely fluorine) to produce excimer lasers. Halogen sealed beam headlights containing krypton produce up to double the light output of standard headlights. In addition, Krypton is used for high performance light bulbs, which have higher color temperatures and efficiency because the krypton reduces the rate of evaporation of the filament.



Krypton laser.

Xenon

Xenon has various applications in incandescent lighting, x-ray development, plasma display panels (PDPs), and more. Incandescent lighting uses xenon because less energy can be used to obtain the same light output as a normal incandescent lamp. Xenon has also made it possible to obtain better x-rays with reduced amounts of radiation. When mixed with oxygen, it can enhance the contrast in CT imaging. These applications have had great impact on the health care industries. Plasma display panels (PDPs) using xenon as one of the fill gases may one day replace the large picture tubes in television and computer screens.

Nuclear fission products may include several radioactive isotopes of xenon, which absorb neutrons in nuclear reactor cores. The formation and elimination of radioactive xenon decay products are factors in nuclear reactor control.

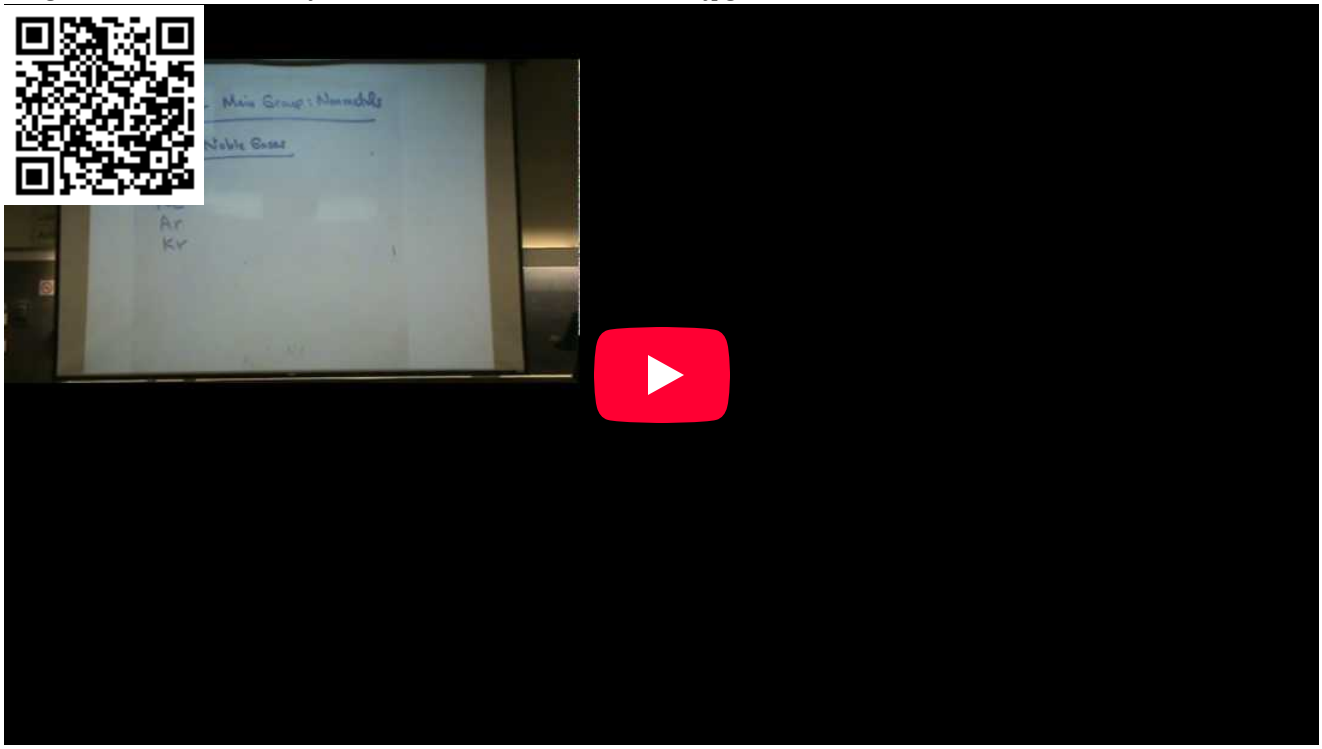
Radon

Radon is reported as the second most frequent cause of lung cancer, after cigarette smoking. However, it also has beneficial applications in radiotherapy, arthritis treatment, and bathing. In radiotherapy, radon has been used in implantable seeds, made of glass or gold, primarily used to treat cancers. It has been said that exposure to radon mitigates auto-immune diseases such as arthritis. Some arthritis sufferers have sought limited exposure to radioactive mine water and radon to relieve their pain. "Radon Spas" such as Bad Gastern in Austria and Onsen in Japan offer a therapy in which people sit for minutes to hours in a high-radon atmosphere, believing that low doses of radiation will boost up their energy.

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- Wikipedia article on XeF_6: en.Wikipedia.org/wiki/XeF6
- Wikipedia article on XeO_4: en.Wikipedia.org/wiki/XeO4
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- Image of Helium: http://www.flw.com/datatools/periodic/e_model/2.gif
- Image of Neon: http://creationwiki.org/pool/images/thumb/4/41/Electron_shell_Neon.png/112px-Electron_shell_Neon.png
- Image of Argon: http://www.flw.com/datatools/periodic/002.php?id=18
- Image of Krypton: http://www.flw.com/datatools/periodic/e_model/36.gif
- Image of Xenon: http://www.flw.com/datatools/periodic/e_model/54.gif
- Image of Radon: http://www.flw.com/datatools/periodic/002.php?id=86
- Image of XeF_6: http://www.faidherbe.org/site/cours/dupuis/images4/xef6.gif
- Image of helium balloons:http://www.carondelet.pvt.k12.ca.us/PeriodicTable/He/helium%20pic3.jpg
- Image of neon light:http://www.neonsdirect.co.uk/images/blue-neon-lights.jpg
- Image of argon plasma light bulb: http://www.vk2zay.net/article/file/17
- Image of krypton laser: www.ucd.ie/physics/preston/re...biophysics.jpg
- Image of xenon headlights: www.bmw.com/com/en/newvehicle...s_bi_xenon.jpg
- Image of radon bath:www.sibyllenbad.de/cms/medien...264-sb_199.jpg
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7.11.1.1: Noble Gas (Group 18) Trends

1. All elements exist in the atomic form and are highly stable.
2. Xe can form a few complexes due to it's modest electronegativity (2.6)
3. The large size of Xe provides coordinative unsaturation to form coordination numbers up to 8, [XeF8]2-.
4. Kinetic inertness seen in C, N, O, F, P, S, Se, Cl, Br, I is now seen in Xe and Kr so that Xe oxidation states range from 0, [Xe], to +VIII, [Kr].
5. Alternating oxidation states remain stable as in the halogens.
6. Stereochemcially active lone pair in every oxidation state except VIII.
7. Similar to N, the highest oxidation state (VIII) is only accessible is p bonding occurs to decrease the electron density on Xe.
8. Xenon oxides are acidic, xenon hydrides are non-existent, and only xenon fluorides can be used to form other xenon halogen complexes.

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7.11.2: Reactions of Nobel Gases

The noble gases (Group 18) are located in the far right of the periodic table and were previously referred to as the "inert gases" due to the fact that their filled valence shells (octets) make them extremely nonreactive.

The Chemical Properties

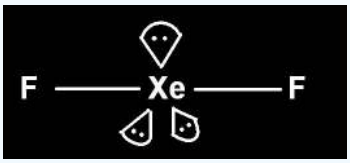
Noble gases are odorless, colorless, nonflammable, and monotonic gases that have low chemical reactivity.

Atomic Number	Element	Number of Electrons/Shell
2	Helium	2
10	Neon	2,8
18	Argon	2,8,8
36	Krypton	2,8,18,8
54	Xenon	2,8,18,18,8
86	Radon	2,8,18,32,18,8

The full valence electron shells of these atoms make noble gases extremely stable and unlikely to form chemical bonds because they have little tendency to gain or lose electrons. Although noble gases do not normally react with other elements to form compounds, there are some exceptions. Xe may form compounds with fluoride and oxide.

Example 1: Xenon Fluorides

Xenon Difluoride ($XeF2$)



- Dense white crystallized solid
- Powerful fluorinating agent
- Covalent inorganic fluorides
- Stable xenon compound
- Decomposes on contact with light or water vapor
- Linear geometry
- Moisture sensitive
- Low vapor pressure

Xenon Tetrafluoride (XeF_4)

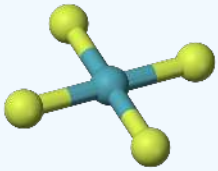




Figure: On Oct. 2, 1963, Argonne announced the creation of xenon tetrafluoride, the first simple compound of xenon, a noble gas widely thought to be chemically inert.

- Colorless Crystals
- Square planar geometry
- Discovered in 1963

Xenon Hexafluoride (XeF_6)

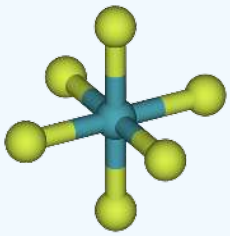
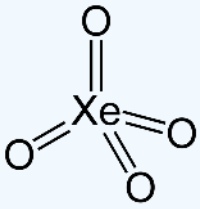


Figure used with permission from Wikipedia.

- Strongest fluorinating agent
- Colorless solid
- Highest coordination of the three binary fluorides of xenon (XeF_2 and XeF_4)
- Formation is exergonic, and the compound is stable at normal temperatures
- Readily sublimes into intense yellow vapors
- Structure lacks perfect octahedral symmetry

Example 2: Xenon Oxide

Xenon Tetroxide (XeO_4)



- Yellow crystalline solid
- Relatively stable
- Oxygen is the only element that can bring xenon up to its highest oxidation state of +8

Two other short-lived xenon compounds with an oxidation state of +8, XeO_3F_2 and XeO_2F_4, are produced in the reaction of xenon tetroxide with xenon hexafluoride.

Example 3: Radon Compounds

Radon difluoride (RnF_2) is one of the few reported compounds of radon. Radon reacts readily with fluorine to form a solid compound, but this decomposes on attempted vaporization and its exact composition is uncertain. The usefulness of radon compounds is limited because of the noble gas's radioactivity. The longest-lived isotope, ^{222}Ra, has a half-life of only 3.82 days.

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7.11.3: Chemistry of Helium (Z=2)

Helium is at the top of the noble gas group (which also contains neon, argon, krypton, xenon, and radon) and is the least reactive element. Helium has many interesting characteristics, such as making balloons float and raising the pitch of one's voice; these applications are discussed below.

Introduction

Helium is the second most abundant element in the universe, next to hydrogen. Helium is colorless, odorless, and tasteless. It has a very low boiling point, and is monatomic. Helium is small and extremely light, and is the least reactive of all elements; it does not react with any other elements or ions, so there are no helium-bearing minerals in nature. Helium was first observed by studying the sun, and was named after the Greek word for the sun, *Helios*.

Physical Properties	
Color	Colorless
Phase at Room Temperature	Gas
Density	0.0002 g/cm^3
Boiling Point	4.2 K
Heat of Vaporization	0.1 kJ/mol
Thermal Conductivity	0.15 J/m sec K
Source	Natural gas

Atomic Properties	
Electron Configuration	1s^2
Number of Isotopes	7 (2 liquid)
Electron Affinity	0 kJ/mol
First Ionization Energy	2372.3 kJ/mol
Second Ionization Energy	5250.3 kJ/mol
Polarizability	0.198 Å^3
Atomic Weight	4.003
Atomic Volume	27.2 cm^3/mol
Atomic Radius	31 pm

Abundance	
In Earth's Crust	8x10^{-3}
In Earth's Ocean	7×10^{-6}
In Human Body	0%

Occurrence and production

Helium is one of the most abundant elements in the universe. Large quantities are produced in the energy-producing fusion reactions in stars. Previously, helium was rarely used, because only .0004% of Earth's atmosphere is helium—that equates to one

helium molecule for every 200,000 air molecules, including oxygen, hydrogen, and nitrogen. However, the discovery of helium-rich wells in Texas, Russia, Poland, Algeria, China, and Canada has made helium more accessible.

Helium is produced in minerals through radioactive decay. Helium is extracted from natural gas deposits, which often contain as much as 10% helium. These natural gas reserves are the only industrially-available source of helium. The total world helium resources theoretically add up to 25.2 billion cubic meters; the United States contains 11.1 billion cubic meters. The extracted gas is subjected to chemical pre-purification, using an alkaline wash to remove carbon dioxide and hydrogen sulfide. The remaining gas is cooled to -200°C, where all materials, except helium gas, are liquefied.

History

Helium was first discovered in 1868 by the French astronomer P. J. C. Jenssen, who was studying the chromosphere of the Sun during a solar eclipse. He used a spectrometer to resolve the light into its spectrum, in which each color represents a different gaseous element. He observed a new yellow light, concluding that it indicated the presence of an element not previously known. In 1895, the existence of helium on Earth was proved by Sir William Ramsay. Heating cleveite (a radioactive mineral) released an inert gas, which was found to be helium; this helium is a by-product of the natural decay of radioactive elements. The chemists Norman Lockyer and Edward Frankland confirmed helium as an element and named it after *helios*, the Greek word for the Sun.

Applications and hazards

Helium has a number of applications due to its inert nature. Liquefied helium has cryogenic properties, and is used to freeze biological materials for long term storage and later use. Twenty percent of industrial helium use is in wielding and industrial applications. Helium protects the heated parts of metals such as aluminum and titanium from air. Mixtures of helium and oxygen are used in tanks for underwater breathing devices: due to its low density, helium gas allows oxygen to stream easily through the lungs. Because helium remains a gas, even at temperatures low enough to liquefy hydrogen, it is used as pressure gas to move liquid hydrogen into rocket engines. Its inert nature also makes helium useful for cooling nuclear power plants.

The most commonly known characteristic of helium is that it is lighter than air. It can levitate balloons during parties and fly blimps over sports stadiums. Helium has 92% of the lifting power of hydrogen; however, it is safer to use because it is noncombustible and has lower rate of diffusion than that of hydrogen gas. The famous Hindenburg disaster is an example of the hazards of using combustible gas like hydrogen. Because helium was previously very expensive only available from natural gas reserves in U.S., Nazi Germany had only hydrogen gas at its disposal. The consequences were devastating, as shown below:



Currently, helium is found in other natural gas reserves around the world. The cost of helium has decreased from $\$2500/ft^3$ in 1915 to $\$0.15/ft^3$ in 1989. Helium is what keeps the Goodyear blimps afloat over stadiums.



Helium is often inhaled from balloons to produce a high, squeaky voice. This practice can be very harmful. Inhaling helium can lead to loss of consciousness and cerebral arterial gas embolism, which can temporarily lead to complete blindness. This occurs when blood vessels in the lungs rupture, allowing the gas to gain access to the pulmonary vasculature and subsequently the brain.

Characteristics

Gas and plasma phases

Helium is naturally found in the gas state. Helium is the second least reactive element and noble gas (after neon). Its low atomic mass, thermal conductivity, specific heat, and sound speed are greatest after hydrogen. Due to the small size of helium atoms, the diffusion rate through solids is three times greater than that of air and 65% greater than that of hydrogen. The element is inert, monatomic in standard conditions, and the least water soluble gas.

At normal ambient temperatures, helium has a negative Joule Thomson coefficient. Thus, upon free expansion, helium naturally heats up. However, below its Joule Thomson inversion temperature (32-50 K at 1 atm), it cools when allowed to freely expand. Once cooled, helium can be liquefied through expansion cooling. Helium is commonly found throughout the universe as plasma, a state in which electrons are not bound to nuclei. Plasmas have high electrical conductivities and are highly influenced by magnetic and electric fields.

Solid and liquid phases

Helium is the only element that cannot be solidified by lowering the temperature at ordinary pressures; this must be accompanied by a pressure increase. The volume of solid helium, ^{3}He and ^{4}He, can be decreased by more than 30% by applying pressure. Solid helium has a projected density of 0.187 ± 0.009 g/mL at 0 K and 25 bar. Solid helium also has a sharp melting point and a crystalline structure. There are two forms of liquid helium: $He^{4}I$ and $He^{4}II$.

Helium I

Helium I is formed when temperature falls below 4.22 K and above the lambda point of 2.1768 K. It is a clear liquid that boils when heat is applied and contracts when temperature is lowered. Below the lambda point, helium does not boil, but expands. Helium I has a gas-like index of refraction of 1.026 which makes its surface difficult to see. It has a very low viscosity and a density 1/8th that of water. This property can be explained with quantum mechanics. Both helium I and II are quantum fluids, displaying atomic properties on a macroscopic scale due to the fact that the boiling point of helium is so close to absolute zero.

Helium II

At 2.174 K, helium I forms into helium II. Its properties are very unusual, and the substance is described as superfluid. Superfluid is a quantum-mechanical state of matter; the two-fluid model for helium II explains why one portion of helium atoms exists in a ground state, flowing with zero viscosity, and another portion is in an excited state, behaving like an ordinary fluid. The viscosity of $He^{4}II$ is so low that there is no internal friction.

$He^{4}II$ can conduct heat 300 times more effectively than silver, making it the best heat conductor known. Its thermal conductivity is a million times that of helium I and several hundred times that of copper. The conductivity and viscosity of helium II do not obey classical rules, but are consistent with the rules of quantum mechanics. When temperature is lowered, helium II expands in volume. It cannot be boiled, but evaporates directly to gas when heated.

In this superfluid state, liquid helium can flow through thin capillaries or cracks much faster than helium gas. It also exhibits a creeping effect, moving along the surface seemingly against gravity. Helium II creeps along the sides of a open vessel until it reaches a warmer region where it evaporates. As a result of the creeping behavior and the ability to leak rapidly through tiny openings, helium II is very difficult to confine. Helium II also exhibits a fountain effect. Suppose a chamber allows a reservoir of

helium II to filter superfluid and non-superfluid helium. When the interior of the container is heated, superfluid helium converts to non-superfluid helium to maintain equilibrium. This creates intense pressure on the superfluid helium, causing the liquid to fountain out of the container.

Isotopes

Helium has eight known isotopes but only two are stable: ^{3}He and ^{4}He. ^{3}He is found in only very small quantities compared to ^{4}He. It is produced in trace amounts by the beta decay of tritium. This form is found in abundance in stars, as a product of nuclear fusion. Extraplanetary materials have trace amounts of ^{3}He from solar winds. ^{4}He is produced by the alpha decay of heavier radioactive elements on Earth. It is an unusually stable isotope because its nucleons are arranged in complete shells.

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Outside Links

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- http://chemistry.wikia.com/wiki/Helium
- en.Wikipedia.org/wiki/Goodyear_Blimp

Problems

1. What happens when a lit cigarette is thrown at a leaking, high-pressured helium cylinder?

    a). nothing

    b). the cigarette is incinerated before touching the cylinder

    c). the cylinder explodes

    d). the cylinder becomes a flame thrower

2. How many isotopes of helium are known? _____
3. (Helium gas, or helium II liquid) leaks faster than the other when stored in a opened cylinder (at STP).
4. What happens when a section of divided petri dish is filled with helium II at 2.173K?

    a). It starts boiling.

    b). It starts "creeping" over the divider, soon filling up the other sections of the dish.

    c). It evaporates and soon leaves the dish.

    d.) It solidifies and expands, breaking the dividers of the petri dish, and filling up the whole dish.

5. Helium was first discovered through _____.

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7.11.4: Chemistry of Neon (Z=10)

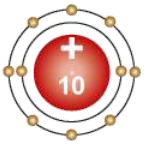


Figure 1: Electron Diagram of Neon. Image courtesy of xxx

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7.11.5: Chemistry of Argon (Z=18)

Argon is it is colorless, tasteless and odorless noble gas that is located in Group 18 on the Periodic Table. It was discovered by Henry Cavendish in 1785 and was named Argon, which is derived from the Greek word "argos" meaning inactive. Cavendish formed oxides of nitrogen by passing electric currents through air, then dissolved them in water to get nitric acid, but was unable to get all of the air to react. He suspected that there was a then unidentified gas component of air; Ramsay and Rayleigh went on to isolate this component in 1894, and the new found element was thus named Argon.

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7.11.6: Chemistry of Krypton (Z=36)

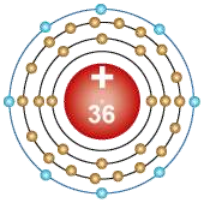
Krypton is one of the six Noble Gas elements (Group 18), which are widely known for their relative "inertness" and difficulty in forming chemical compounds with any other elements, due to these elements having full valence shells. Contrary to original thinking, however, Krypton has been made to react with the highly electronegative elements and is used in lighting and other commercial purposes.

Facts



- Element number: 36
- Electron configuration: $[Ar]3d^{10}4s^{2}4p^{6}$
- Atomic weight: 83.798g/mol
- Color: colorless, odorless, tasteless
- Light: large number of spectral lines, strongest being green and yellow/ whitish emission
- Solidified: white and crystalline/ face-centered cubic crystal structure
- Melting point: 115.79K
- Boiling point: 119.92K
- Critical point: 209.41K
- Specific heat capacity: 20.786 J/mol K
- 0.000108-0.000114% of atmosphere
- 6 Stable isotopes
- Produced by breakdown of uranium and plutonium in the earth's crust at a very small %

The Origin and History



Krypton is found in the Group 18 elements, otherwise known as the Noble Gases. In 1785, Henry Cavendish suggested that air contained nonreactive gases after he was unsuccessful in getting a sample of air to react. A century later, British chemists John Rayleigh and William Ramsey began to isolate these inert gases (beginning with Argon) and seperated them in their own group on the periodic table since each of these elements had full electron valence shells. One of these gases, Krypton, was discovered along with Neon and Xenon by Rayleigh and fellow chemist Morris Travers in 1898 in a residue left from evaporating almost all components of liquid air. The name Krypton is derived from the Greek word "kryptos", meaning "hidden". However, the inert quality of these gases was disproved when Xenon compounds were created in 1962 and a Krypton compound (KrF2) was synthesized successfully a year later. This proved that this group of gases is not necessarily inert. Although both Kr and Xe have full valence shells, they are both the most easily ionized of the group. It simply took an element of high electronegativity, in this case Fluorine, to force Xe and Kr to react under high temperatures.

Isolation

It ranks sixth in abundance in the atmosphere. As with the other noble gases, krypton is isolated from the air by liquefaction.

Compounds & Isotopes

Although Krypton is naturally chemically nonreactive, krypton difluoride was synthesized in 1963.

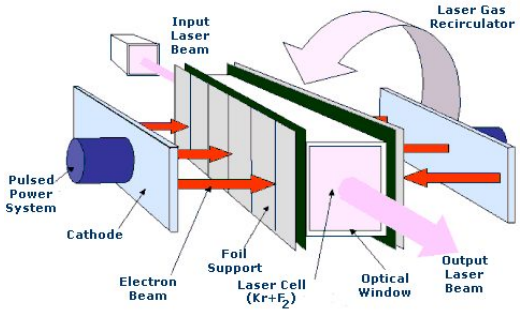
$$Kr_{(g)} + F_{2(g)} \rightarrow KrF_{2(g)}$$

It has also been discovered that Krypton can bond with other atoms besides Fluorine, however such compounds are much more unstable than krypton difluoride. For example, KrF_2 can bond with nitrogen when it reacts with $[HC{\equiv}NH]^{+}[AsF_{-6}]$ under -50°C to form $[HC{\equiv}N–Kr–F]^{+}$. There have been other reports of successfully synthesizing additional Krypton compounds, but none have been verified. Krypton has 6 stable isotopes: ^{78}Kr, ^{80}Kr, ^{82}Kr, ^{83}Kr, ^{84}Kr, and ^{86}Kr. There are a total of 31 isotopes of Krypton, and the only isotope besides the six given that occur naturally is ^{81}Kr which is a product of atmospheric reactions between the other natural isotopes.

Applications

Krypton gas is used in various kinds of lights, from small bright flashlight bulbs to special strobe lights for airport runways. Due to Krypton's large number of spectral lines, it's ionized gas is white, which is why light bulbs that are krypton based are used in photography and studio lighting in the film industry. In neon lights, Krypton reacts with other gases to produce a bright yellow light as well. The isotope ^{85}Kr can also be used in combination with phosphors to produce materials that shine in the dark due to the fact that this particular isotope of Krypton reflects off of phosphors. Krypton is also used in lasers as a control for a desired wavelength, especially in red lasers because Krypton has a much higher light density in the red spectral region than other gases such as Neon, which is why krypton-based lasers are used to produce red light in laser-light shows.

Perhaps one of the most significant uses of Krypton is in the krypton-fluoride laser which is used in nuclear fusion energy research.



other.nrl.navy.mil/LaserFusio...ercreation.htm

Isotopes of Krypton

Yet another important application of Krypton, specifically ^{83}Kr, is in Magnetic Resonance Imaging (MRI), which is used instead of other gases because of its high spin and smaller/less polar electron cloud compared to other noble gases such as Xenon. It is used to distinguish hydrophobic and hydrophillic regions containing an airway.

An international agreement was made in 1960 to base the length of the meter on the wavelength of light emitted by ^{86}Kr (605.78 nm). However, this was changed in 1983 when the International Bureau of Weights and Measures determined the meter to be the distance that light travels in a vacuum in 1/299,792,458 s.

Problems

1. How is the element Krypton isolated?
2. Why can fluorine react with Krypton to form a compound?
3. What is the electron configuration of Krypton?
4. What colors are most pronounced in the Krypton spectral emission?
5. How many stable isotopes of Krypton are there?

Solutions

1. By evaporating the componnts of liquid air.
2. Because fluorine is highly electronegative and Krypton is readily ionizable.
3. $[Ar]3d^{10}4s^{2}4p^{6}$
4. Green and yellow
5. 6

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7.11.7: Chemistry of Xenon (Z=54)

Xenon is an element under the Noble gases group and is on period 7 of the periodic table. This element is most notable for its bright luminescence in light bulbs. Xenon is unique for being the first noble gas element to be synthesized into a compound.

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7.11.8: Chemistry of Radon (Z=86)

Radon is a colorless, odorless gas, the primary source of indoor air pollution. It sinks in air because it has a high density as is therefore often found in the basements of homes, particularly in areas where with a lot of shale and boulders in the soil. Radon results from the radioactive decay of radium in the soil, and it further decays to produce radioactive daughters including polonium and lead. Radon gas, along with decay products that can attach to dust and airborne particles, enters the lungs and decays, producing alpha and beta radiation that damages DNA and causes lung cancer.

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CHAPTER OVERVIEW

8: Introduction to Solid State Chemistry

Introduction to Solid State Chemistry is a first-year single-semester college course on the principles of chemistry. This unique and popular course satisfies MIT's general chemistry degree requirement, with an emphasis on solid-state materials and their application to engineering systems.

- 8.1: The Nature of Crystalline Solids
  - 8.1.1: Crystal Structures of Metals
  - 8.1.2: Ionic and Covalent Solids - Structures
    - 8.1.2.1: Prelude to Ionic and Covalent Solids - Structures
    - 8.1.2.2: Close-packing and Interstitial Sites
    - 8.1.2.3: Structures Related to NaCl and NiAs
    - 8.1.2.4: Tetrahedral Structures
    - 8.1.2.5: Layered Structures and Intercalation Reactions
    - 8.1.2.6: Bonding in TiS_2, MoS_2, and Pyrite Structures
    - 8.1.2.7: Spinel, Perovskite, and Rutile Structures
    - 8.1.2.8: Discussion Questions
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- 8.2: Bonding in Metals, Semiconductors and Insulators – Band Structure
  - 8.2.1: Prelude to Electronic Properties of Materials - Superconductors and Semiconductors
  - 8.2.2: Periodic Trends- Metals, Semiconductors, and Insulators
  - 8.2.3: Bonding in Metals
  - 8.2.4: Conduction in Metals
  - 8.2.5: Superconductors
  - 8.2.6: Semiconductors- Band Gaps, Colors, Conductivity and Doping
  - 8.2.7: Semiconductor p-n Junctions
  - 8.2.8: Diodes, LEDs and Solar Cells
- 8.3: X-rays and X-ray Diffraction
- 8.4: The Imperfect Solid State
- 8.5: Glasses
- 8.6: Phase Equilibria and Phase Diagrams

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8.1: The Nature of Crystalline Solids

In an assembly of atoms or molecules a solid phase is formed whenever the interatomic (intermolecular) attractive forces significantly exceed the disruptive thermal forces and thus restrict the mobility of atoms, forcing them into more-or-less fixed positions. From energy considerations it is evident (as discussed in LN-2) that in such solids the atoms or molecules will always attempt to assume highly ordered structures which are characterized by *symmetry*. Depending on the nature of the acting interatomic forces, all solids may be subdivided into:

a. Ionic solids (NaCl)
b. Covalent solids (Diamond)
c. Metallic solids (Fe, Ni, etc.)
d. Van der Waals solids (ice, solid He)

Solids as we encounter them in nature may or may not reflect the internally ordered arrangement in their appearance. We find, for example, well-formed quartz crystals, garnets, diamonds and snowflakes which are all characterized by flat bounding planes which intersect at characteristic angles. On the other hand, we also observe rounded stones and man-made cast solid objects with no external evidence of internal order (fig. 1).

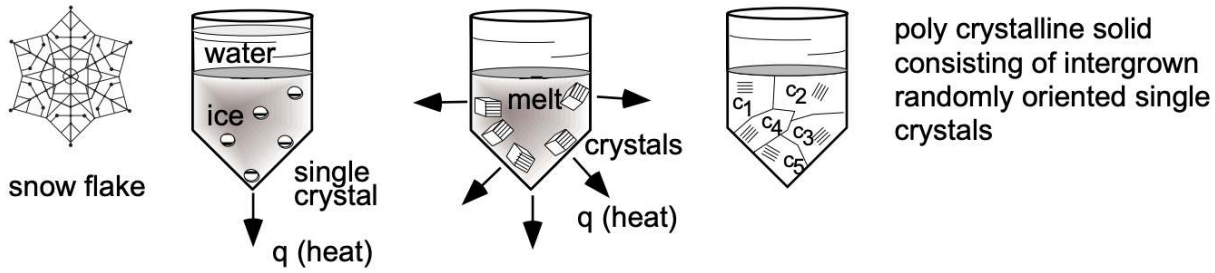


Figure 1 Crystals, internal order and external appearance

To understand the external appearance of the solid state it is necessary to consider the formation of solids from different *phases*. Solids, for example, are formed upon cooling of liquids (melts) - by freezing or solidification; this solidification process normally proceeds in total confinement and the resulting “cast” structure will have an external appearance which reflects in detail the confining geometry (and not the internal order). Moreover, depending on solidification conditions, the solid body may be either a *single crystal* or *polycrystalline*. Polycrystalline solids (in excess of 95% of the solid state encountered) may be thought of as an assembly of microscopic single crystals with random orientation held together like a maze structure by the interwoven irregular shapes of the individual crystals.

A typical example of an "unconfined" phase transformation is the formation of snowflakes where the external boundaries of the solid have assumed *crystalline* appearance, reflecting in detail the internally ordered molecular (H_2O) arrangement. Another unconfined formation of a solid is precipitation from solution (sugar crystals, $CuSO_4$ and the like). Similarly, the formation of crystals from the vapor phase leads to bodies which externally reflect elements of internal order.

CRYSTAL STRUCTURE

From the earlier discussion it should be apparent that, when strong interatomic forces exist, atoms tend to pack closely together - the closeness of packing being particularly pronounced in the solid state. In this case atoms can be regarded as hard spheres and the problem of close packing can be treated as one in which the whole assembly has a tendency toward efficient packing. A little thought or a few simple experiments with ping-pong balls quickly convince us that regular arrangements of the spheres generally lead to more compact assemblies than irregular arrangements (fig. 2). The same principle applies to arrangement of atoms in the solid state. Where strong attractive forces are exerted we find that the atoms or molecules concerned arrange themselves in a regular three-dimensional pattern. It is this regularity which is the basis of crystallinity in materials: i.e., *a crystal structure is nothing more than an orderly array of atoms or molecules.* This definition of a crystal is distinct from the popular concept based on observation of external symmetry of crystals, often seen during the study of elementary chemistry, in which some crystals appear cubic, others needle-shaped and so on. The regular external shape is obtained only when the conditions of crystallization are

favorable to development of flat, geometric faces. In most instances, particularly with metals, these conditions are absent, and the crystals have irregular surfaces even though the internal arrangement is perfectly geometric.

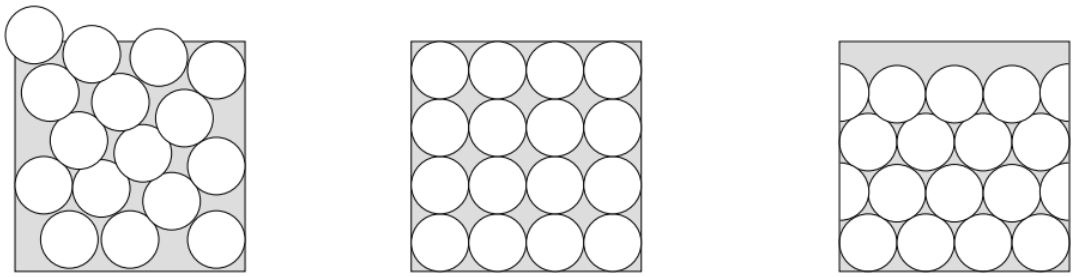


Figure 2 The packing density of ordered systems.

Atomic arrays in crystals are conveniently described with respect to a three-dimensional net of straight lines. Consider a lattice of lines, as in fig. 3, dividing space into equal-sized prisms which stand side-by-side with all faces in contact, thereby filling all space and leaving no voids. The intersections of these lines are points of a **space lattice**, i.e., a *geometrical abstraction* which is useful as a reference in describing and correlating symmetry of actual crystals. These lattice points are of fundamental importance in describing crystals for they may be the positions occupied by individual atoms in crystals or they may be points about which several atoms are clustered. Since prisms of many different shapes can be drawn through the points of a space lattice to partition it into cells, the manner in which the network of reference lines is drawn is arbitrary. It is not necessary that the lines be drawn so that atoms lie only at corners of unit prisms. In fact, it is more convenient to describe some crystals with respect to prisms in which atoms lie at prism centers or at the centers of prism faces as well as at prism corners.

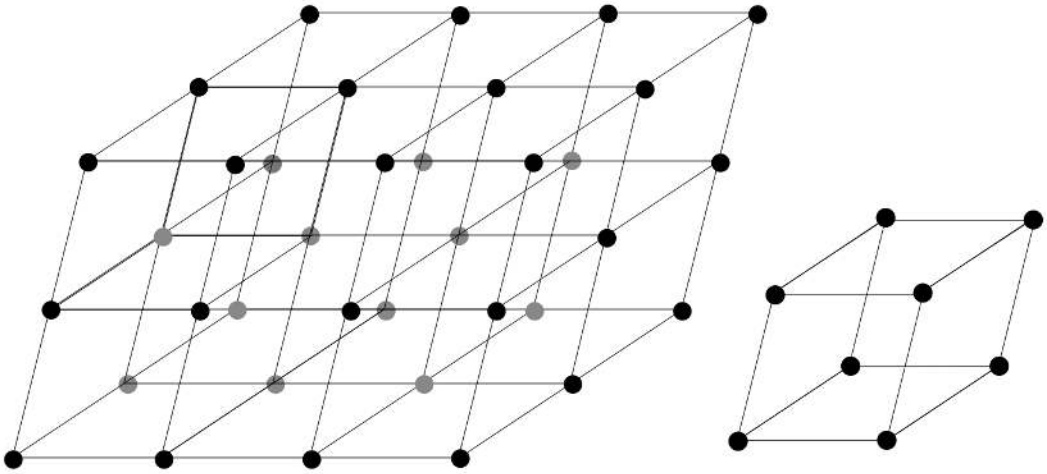


Figure 3 The space lattice

An important characteristic of a space lattice is that every point has identical surroundings: the grouping of lattice points about any given point is identical to the grouping about any other point in the lattice. In other words, if we could move about in the lattice, we would not be able to distinguish one point from another because rows and planes near each point would be identical. If we were to wander among the atoms of a solid metal or chemical compound, we would find the view from any lattice point exactly the same as that from any other.

There are fourteen space lattices (fig. 4). That is, no more than fourteen ways can be found in which points can be arranged in space so that each point has identical surroundings. Of course, there are many more than fourteen ways in which atoms can be arranged in actual crystals; thus there are a great number of crystal *structures*. Too often the term “lattice” is loosely used as a synonym for “structure”, an incorrect practice which is frequently confusing. The distinction can be clearly seen if we remember that a space lattice is an array of points in space. It is a geometrical abstraction which is useful only as a reference in describing and correlating symmetry of actual crystals. A crystal structure, however, is the arrangement of atoms or molecules which actually exists in a crystal. It is a dynamic, rather than a static, arrangement and is subject to many imperfections. Although any crystal structure has an inherent symmetry which corresponds to one of the fourteen space lattices, one, two or several atoms or molecules

in the crystal structure may be associated with each point of the space lattice. This symmetry can be maintained with an infinite number of different actual arrangements of atoms - making possible an endless number of crystal structures.

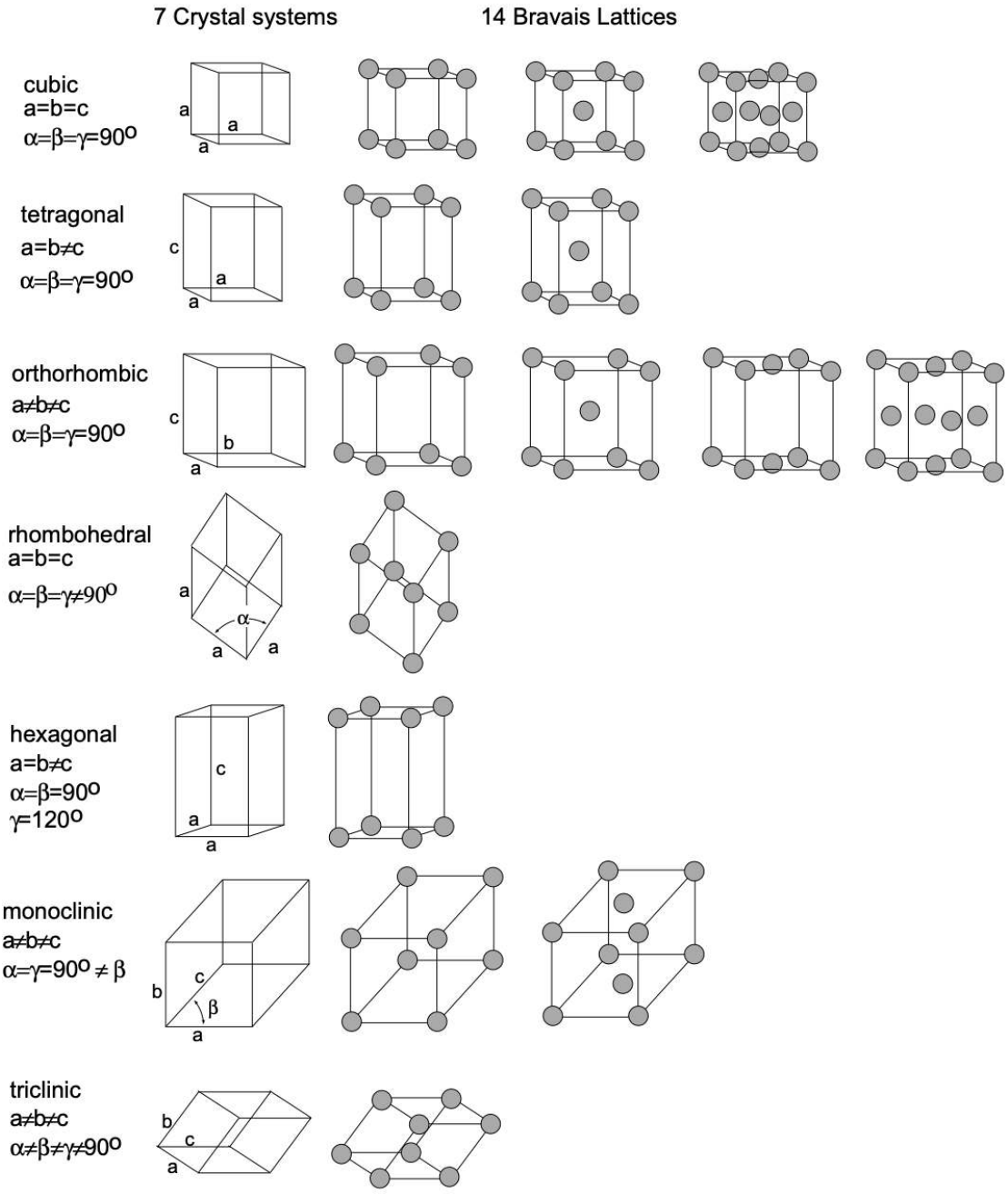


Figure 4 The 7 crystal systems and the 14 Bravais lattices

To specify a given arrangement of points in a space lattice, it is customary to identify a unit cell with a set of coordinate axes, chosen to have an origin at one of the lattice points (fig. 5). In a cubic lattice, for example, we choose three axes of equal length that are mutually perpendicular and form three edges of a cube. Each space lattice has some convenient set of axes, but they are not necessarily equal in length or orthogonal. Seven different systems of axes are used in crystallography, each possessing certain characteristics as to equality of angles and equality of lengths. These seven crystal systems are tabulated in Table I (to be considered in conjunction with fig. 4).

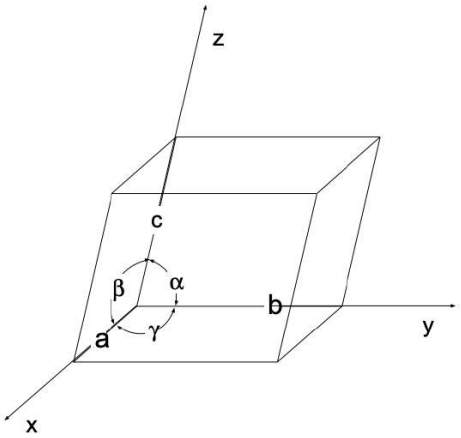


Figure 5 Specification of Unit Cell parameters

Table I. The Seven Crystal Systems

System	Parameters	Interaxial Angles
	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$
Triclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \neq \beta$
Monoclinic	$a \neq b \neq c$	$\alpha = \beta = \gamma$
Orthorhombic	$a = b \neq c$	$\alpha = \beta = \gamma$
Tetragonal	$a = b = c$	$\alpha = \beta = \gamma = 90°$
Cubic	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$
Hexagonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$
Rhombohedral	$a = ch$	

The network of lines through the points of a space lattice (fig. 3) divides it into *unit cells* (see also fig. 4). Each unit cell in a space lattice is identical in size, shape and orientation to every other unit cell. It is the building block from which the crystal is constructed by repetition in three dimensions. The unit cells of the fourteen space lattices are shown in fig. 4. All crystal structures are based on these fourteen arrangements.

The body-centered cubic, face-centered cubic and hexagonal lattices are common and of prime importance in metals. Some of the metals associated with nuclear applications, such as uranium and plutonium, have crystal structures which are more complicated than these three relatively simple types. In general, crystalline ceramics also are more complex.

CELLS VS PRIMITIVE CELLS

In the literature we often find reference to **unit cells** and to **primitive cells**. The primitive cell may be defined as a geometrical shape which, when repeated indefinitely in three dimensions, will fill all space and is the equivalent of one atom. The unit cell differs from the primitive cell in that it is not restricted to being the equivalent of one atom. In some cases the two coincide. For instance, in fig. 4 all fourteen space lattices are shown by their unit cells. Of these fourteen, only seven (which are those?) are also primitive cells.

Primitive cells are drawn with lattice points at all corners, and each primitive cell contains the equivalent of one atom. For instance, a simple cubic unit cell has an atom at each corner. However, at any of these given corners, this atom must be shared with seven other identical cubes which fill the volume surrounding this point. Thus there is effectively only 1/8 of the atom which can be assigned to that particular unit cell. Since there are eight corners in a cube, there is the equivalent of one atom, and thus the primitive cell and unit cell coincide.

Continuing, consider the *body-centered cubic* (BCC) lattice. In this case there is one atom at the center of the cube and one atom contributed by the eight corners. This cell, then, has two atoms and, to avoid confusion, should be termed a unit cell. In the *face-centered cubic* lattice there are six face atoms, but each face atom is shared by two cells. Consequently, each face contributes 1/2 an atom. The faces thus contribute three atoms and the corners one, for a total of four atoms in the unit cell. The face-centered cubic structure (FCC) can also be considered as four interpenetrating simple cubic cells.

In the study of crystals the primitive cell has limited use because the unit cell more clearly demonstrates the symmetrical features of a lattice. In other words, the unit cell can usually be visualized readily whereas the primitive cell cannot. For example, the cubic nature of the face-centered cubic lattice is immediately apparent in the unit cell, but it is not nearly so obvious in the rhombohedral primitive cell.

PACKING OF ATOMS

A crystal structure is a regular array of atoms arranged on one of the fourteen space lattices. The least complicated crystal structures are those having a single atom at each lattice point. Polonium has the simplest structure, being simple cubic. In normal metals, the atoms (or positive ions) are held together by a cloud of free electrons so that each atom tends to be attracted equally and indiscriminately to all its geometrically nearest neighbors by the free electrons passing between them. This condition fosters the formation of closely packed structures of the types which can be demonstrated by efficiently packing uniformly-sized spheres into a given volume.

You can gain a better grasp of packing by conducting an experiment as follows. Assume we have a quantity of small spheres which we are required to efficiently pack into a box (a ‘two-dimensional’ approach can be made using a handful of pennies). After some shuffling, it is obvious that the closest possible packing is obtained when the spheres are in contact and their centers occupy positions which correspond to the apices of equilateral triangles (fig. 6). It is also evident that there are two sets of triangles – one set with vertices pointing away from the observer (points up) and the other set with vertices pointing toward the observer (points down).

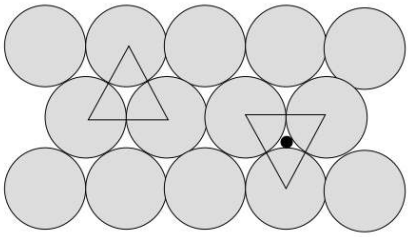


Figure 6 Close packed atomic arrangements

When a second layer is added, there is closest-packing if the spheres in this new layer rest in the hollows formed by the spheres of the first layer. The centers of the spheres in the second layer will lie above the centers of the points-up triangles or above the centers of the points-down triangles, but not both simultaneously. Which set is used is immaterial. For our discussion, however, assume the second layer is centered on the points-up triangles.

When we start adding a third layer, the spheres will again rest in the hollows formed by the spheres in the second layer. And again we have the option of placing the third layer on the points-up or on the points-down triangles. If we center the third layer on the points-down triangles, we find the third layer is directly above the first layer. If additional layers are added using an alternate stacking sequence (i.e., alternately centering the layers on the points-up and the points-down triangles), the sequence can be written as ABABABAB. . . This arrangement of spheres, translated to an arrangement of atoms, is the hexagonal close-packed (HCP) structure - very important, but not discussed in detail here.

Many elements having covalent bonding form arrangements in which the coordination number is (8–N), where N is the number of valence electrons. What, then, is the coordination number of the HCP structure just demonstrated? The geometry of the structure shows that any one atom has twelve equidistant neighbors. It is apparent that if, in any layer, a given sphere is placed in the adjoining layer, it fits in the hollow formed by three spheres and consequently is tangent to three spheres in the adjoining layer. Thus any given atom in the HCP structure is tangent to twelve other atoms – six in its own layer and three each in two adjoining layers.

When the third layer of spheres was added in the above discussion, we assumed this layer was centered on the points-down triangles of the second layer. What happens if the centers of the points-up triangles of the second layer are used instead? The distribution of spheres in the third layer is the same as in the first two layers, but does not lie directly above either of these two layers. If a fourth layer is added, centered on the points-up triangles of the third layer, we find the fourth layer is directly above the first layer and duplicates it completely. The stacking sequence for this structure can be written as ABCABCABC. . . This

arrangement has the same density of packing and the same coordination number as the HCP structure. However, it is the face-centered cubic (FCC) structure.

The HCP and FCC crystal structures have the same density of packing and the same coordination number. Therefore we might expect the behavior of the two HCP and FCC structures to be very much alike with regard to physical and mechanical properties. This, however, in most instances is not the case.

The maximum density of packing is found only in the HCP and FCC crystal structures. Why the metallic bond does not always produce one or the other of these two densest arrangements of atoms is as yet subject of intensive studies. The BCC unit cell contains two atoms, and the coordination number is eight. There is partial compensation for this in the fact that there are six next-nearest neighbors at distances only slightly greater than that of the eight nearest neighbors. Some characteristics of cubic structures are given in Table II.

An interesting example of the type of crystal structure obtained in covalently bonded elements which obey the (8–N) coordination number rule (where N is the number of valence electrons) is the diamond structure. This structure is found in carbon, germanium, silicon, and tin at low temperatures and in certain compounds. Each atom has four nearest neighbors – a configuration that is variously called diamond cubic, body-centered tetrahedral or tetrahedral cubic.

TABLE II. Characteristics of Cubic Lattices

	Simple	Body-Centered	Face-Centered
Unit Cell Volume	a^3	a^3	a^3
Lattice Points Per Cell	1	2	4
Nearest Neighbor Distance	a	$\frac{a\sqrt{3}}{2}$	$\frac{a}{\sqrt{2}}$
Number of Nearest Neighbors	6	8	12
Second Nearest Neighbor Distance	$a\sqrt{2}$	a	a
Number of Second Neighbors	12	6	6

Many compounds crystallize in variations of cubic forms. Rock salt (NaCl), for example, is typical of many oxides, fluorides, chlorides, hydrides and carbides. It is sometimes considered as simple cubic with alternate Na and Cl atoms on the cube corners. Actually the structure is two interpenetrating FCC lattices – one of Na and the other of Cl – and the corner of one is located at point 1/2, 0, 0 of the other.

Many other oxides, fluorides and some intermetallic compounds have the fluorite (CaF_2) structure. This is FCC with Ca at the cube corners and face centers and F at all quarter points along the cube diagonals.

LATTICE PLANES AND DIRECTIONS

It is desirable to have a system of notation for planes within a crystal or space lattice such that the system specifies orientation without giving position in space. *Miller indices* are used for this purpose. These indices are based on the intercepts of a plane with the three crystal axes - i.e., the three edges of the unit cell. The intercepts are measured in terms of the edge lengths or dimensions of the unit cell which are the unit distances from the origin along the three axes. For instance, the plane that cuts the x-axis at a distance from the origin equal to one-half the x-dimension of the cell is said to have an x-intercept equal to $1/2$, and if it cuts the y-axis at $1/2$ the y-dimension of the cell, the y-intercept is $1/2$, regardless of the relative magnitudes of the x - and y-dimensions. If a plane is parallel to an axis, it intercepts the axis at infinity.

To determine Miller indices (hkl) of a plane, we take the following steps:

1. Find the intercepts on the three axes in multiples or fractions of the edge lengths along each axis.
2. Determine the reciprocals of these numbers.
3. Reduce the reciprocals to the three smallest integers having the same ratio as the reciprocals.
4. Enclose these three integral numbers in parentheses, e.g., (hkl).

A cube has six equivalent faces. If we have a definite orientation and wish to discuss one specific plane of these six, it is possible to specify this plane by using the proper Miller indices. Parentheses are used around the Miller indices to signify a specific plane. On the other hand, it is often advantageous to talk about planes of a “form” – i.e., a family of equivalent planes such as the six faces of

a cube. To do this it is customary to use the Miller indices, but to enclose them in curly brackets (braces). Thus the set of cube faces can be represented as {100} in which

$$\{100\} = (100) + (010) + (001) + (\bar{1}00) + (0\bar{1}0) + (00\bar{1})$$

This notation thus provides a shorthand scheme to avoid writing the indices for all six cube faces.

The utility of the scheme is even more evident in the case of the (110) planes – i.e., the dodecahedral planes (in a cubic system), where

$$\begin{aligned}\{110\} =&(110) + (101) + (011) + (\bar{1}10) + (\bar{1}01) + (0\bar{1}1)\\ &+ (1\bar{1}0) + (10\bar{1}) + (01\bar{1}) + (\bar{1}\bar{1}0) + (\bar{1}0\bar{1}) + (0\bar{1}\bar{1})\end{aligned} \tag{8.1.1}$$

The equivalent form for the orthorhombic system is

$$\begin{aligned}\{110\} &= (110) + (\bar{1}10) + (1\bar{1}0) + (\bar{1}\bar{1}0)\\ \{101\} &= (101) + (\bar{1}01) + (10\bar{1}) + (\bar{1}0\bar{1})\\ \{011\} &= (011) + (0\bar{1}1) + (01\bar{1}) + (0\bar{1}\bar{1})\end{aligned} \tag{8.1.2}$$

The octahedral planes for the cube are

$$\begin{aligned}\{111\} =&(111) + (\bar{1}11) + (1\bar{1}1) + (11\bar{1})\\ &+ (\bar{1}\bar{1}1) + (\bar{1}1\bar{1}) + (1\bar{1}\bar{1}) + (\bar{1}\bar{1}\bar{1})\end{aligned} \tag{8.1.3}$$

Direction indices are defined in a different manner. A line is constructed through the origin of the crystal axis in the direction under consideration and the coordinates of a point on the line are determined in multiples of lattice parameters of the unit cell. The indices of the direction are taken as the smallest integers proportional to these coordinates and are closed in square brackets. For example, suppose the coordinates are $x = 3a, y = b$ and $z = c/2$, then the smallest integers proportional to these three numbers are 6, 2 and 1 and the line has a [621] direction. As further examples, the x-axis has direction indices [100], the y-axis [010] and the z-axis [001]. A face diagonal of the xy face of the unit cell has direction indices [110], and a body diagonal of the cell has direction indices [111]. Negative indices occur if any of the coordinates are negative. For example, the $-y$ axis has indices [010]. A full set of equivalent directions, i.e., directions of a form, are indicated by carets: $\langle uvw \rangle$.

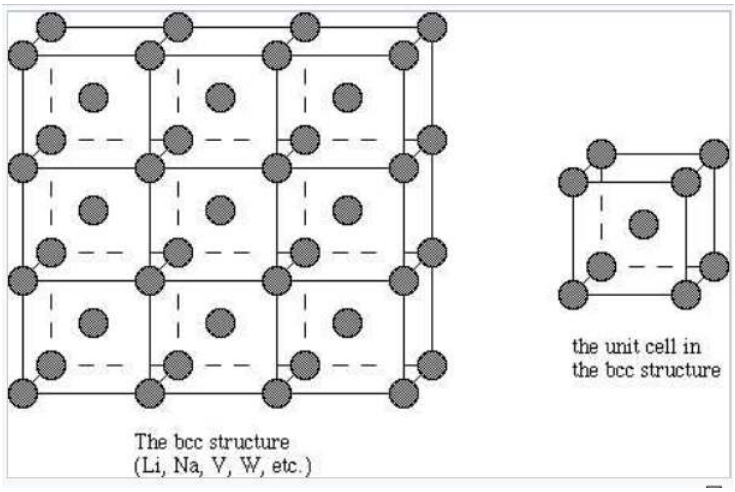
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8.1.1: Crystal Structures of Metals

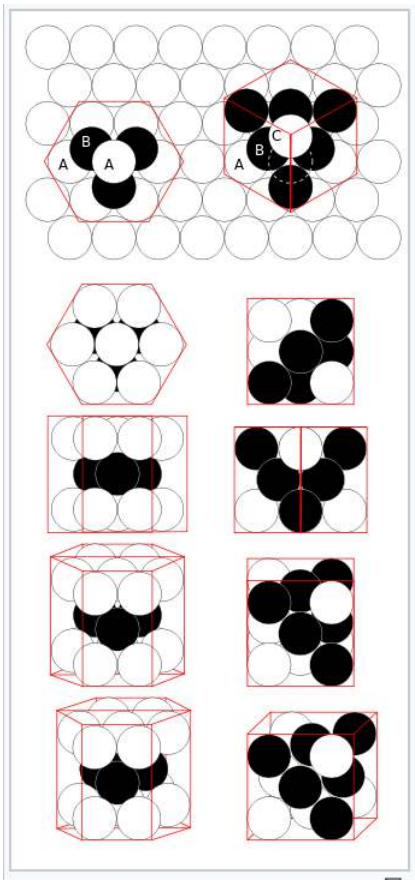
The Crystalline Nature of Metals

All metallic elements (except Cs, Ga, and Hg) are crystalline solids at room temperature. Like ionic solids, metals and alloys have a very strong tendency to crystallize, whether they are made by thermal processing or by other techniques such as solution reduction or electroplating. Metals crystallize readily and it is difficult to form a glassy metal even with very rapid cooling. Molten metals have low viscosity, and the identical (essentially spherical) atoms can pack into a crystal very easily. Glassy metals can be made,

however, by rapidly cooling alloys, particularly if the constituent atoms have different sizes. The different atoms cannot pack in a simple unit cell, sometimes making crystallization slow enough to form a glass.



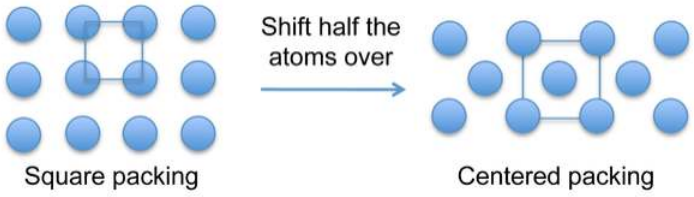
Body-centered cubic



hcp (left) and fcc (right) close-packing of spheres

Crystal structures

Most metals and alloys crystallize in one of three very common structures: body-centered cubic (bcc), hexagonal close packed (hcp), or cubic close packed (ccp, also called face centered cubic, fcc). In all three structures the coordination number of the metal atoms (i.e., the number of equidistant nearest neighbors) is rather high: 8 for bcc, and 12 for hcp and ccp. We can contrast this with the low coordination numbers (i.e., low valences - like 2 for O, 3 for N, or 4 for C) found in nonmetals. In the bcc structure, the nearest neighbors are at the corners of a cube surrounding the metal atom in the center. In the hcp and ccp structures, the atoms pack like stacked cannonballs or billiard balls, in layers with a six-coordinate arrangement. Each atom also has six more nearest neighbors from layers above and below. The stacking sequence is ABCABC... in the ccp lattice and ABAB... in hcp. In both cases, it can be shown that the spheres fill 74% of the volume of the lattice. This is the highest volume fraction that can be filled with a lattice of equal spheres.



Atoms in metallic crystals have a tendency to pack in dense arrangments that fill space efficiently. The simple square packing (above) upon which the simple cubic structure is based is inefficient and thus rare among metallic crystal structures. Body- or face-centered structures fill space more efficiently and more common.

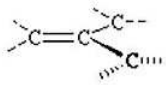
Periodic trends in structure and metallic behavior

Remember where we find the metallic elements in the periodic table - everywhere except the upper right corner. This means that as we go down a group in the p-block (let's say, group IVA, the carbon group, or group VA, the nitrogen group), the properties of the elements gradually change from nonmetals to metalloids to metals. The carbon group nicely illustrates the transition. Starting at the top, the element carbon has two stable allotropes - graphite and diamond. In each one, the valence of carbon atoms is exactly satisfied by making four electron pair bonds to neighboring atoms. In graphite, each carbon has three nearest neighbors, and so there are two single bonds and one double bond. In diamond, there are four nearest neighbors situated at the vertices of a tetrahedron, and so there is a single bond to each one.

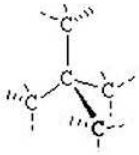
The two elements right under carbon (silicon and germanium) in the periodic table also have the diamond structure (recall that these elements cannot make double bonds to themselves easily, so there is no graphite allotrope for Si or Ge). While diamond is a good insulator, both silicon and germanium are semiconductors (i.e., metalloids). Mechanically, they are hard like diamond. Like carbon, each atom of Si and Ge satisfies its valence of four by making single bonds to four nearest neighbors.

The next element under germanium is tin (Sn). Tin has two allotropes, one with the diamond structure, and one with a slightly distorted bcc structure. The latter has metallic properties (metallic luster, malleability), and conductivity about 10^9 times higher than Si. Finally, lead (Pb), the element under Sn, has the ccp structure, and also is metallic. Note the trends in coordination number and conducting properties:

Element	Structure	Coord. no.	Conductivity
C	graphite, diamond	3, 4	semimetal, insulator
Si	diamond	4	semiconductor
Ge	diamond	4	semiconductor
Sn	diamond, distorted bcc	4, 8	semiconductor, metal
Pb	ccp	12	metal



trigonal bond network in graphite: 1 double bond + 2 single bonds to C



tetrahedral bond network in diamond: 4 single bonds to each C atom

The elements C, Si, and Ge obey the octet rule, and we can easily identify the electron pair bonds in their structures. Sn and Pb, on the other hand, adopt structures with high coordination numbers. They *do not have enough valence electrons* to make electron pair bonds to each neighbor (this is a common feature of metals). What happens in this case is that the valence electrons become "smeared out" or delocalized over all the atoms in the crystal. It is best to think of the bonding in metals as a crystalline arrangement of positively charged cores with a "sea" of shared valence electrons gluing the structure together. Because the electrons are not localized in any particular bond between atoms, they can move in an electric field, which is why metals conduct electricity well. Another way to describe the bonding in metals is nondirectional. That is, an atom's nearest neighbors surround it in every direction, rather than in a few particular directions (like at the corners of a tetrahedron, as we found for diamond). Nonmetals (insulators and semiconductors), on the other hand, have directional bonding. Because the bonding is non-directional and coordination numbers are high, it is relatively easy to deform the coordination sphere (i.e., break or stretch bonds) than it is in the case of a nonmetal. This is why elements like Pb are much more malleable than C, Si, or Ge.

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SECTION OVERVIEW

8.1.2: Ionic and Covalent Solids - Structures

Learning Objectives

- Describe many crystal structures in terms of close-packed frameworks with systematic filling of octahedral and tetrahedral holes.
- Represent crystal structures by drawing them in sections.
- Rationalize, using chemical principles, why certain crystal structures are stable for certain compounds but not for others, as well as why certain structural and bonding motifs are preferred for certain compounds relative to others.
- Predict which crystal structures are most favorable for a given composition based on ionicity and periodic trends.
- Explain structure-dependent properties such as ferroelectricity and magnetic ordering based on crystal structures.
- Understand intercalation reactions in layered and open framework solids.
- Predict the preferred formation of normal or inverse spinels using arguments from transition metal chemistry (e.g. crystal field stabilization energies).

Inorganic solids often have simple crystal structures, and some of these structures are adopted by large families of ionic or covalent compounds. Examples of the most common structures include NaCl, CsCl, NiAs, zincblende, wurtzite, fluorite, perovskite, rutile, and spinel. We will develop these structures systematically from the close packed and non-close packed lattices shown below. Some layered structures, such as $CdCl_2$ and CdI_2, can be thought of as relatives of simple ionic lattices with some atoms "missing."

8.1.2.1: Prelude to Ionic and Covalent Solids - Structures

8.1.2.2: Close-packing and Interstitial Sites

8.1.2.3: Structures Related to NaCl and NiAs

8.1.2.4: Tetrahedral Structures

8.1.2.5: Layered Structures and Intercalation Reactions

8.1.2.6: Bonding in TiS_2, MoS_2, and Pyrite Structures

8.1.2.7: Spinel, Perovskite, and Rutile Structures

8.1.2.8: Discussion Questions

8.1.2.9: References

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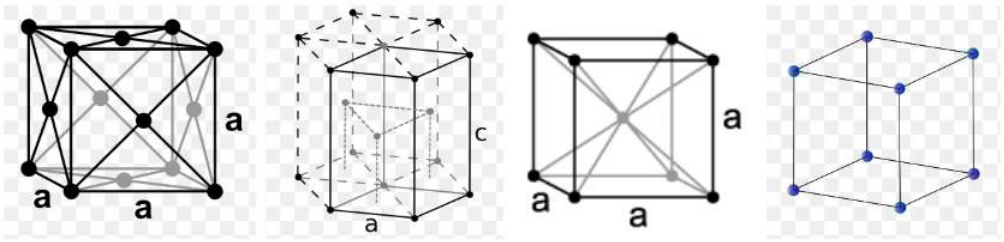
8.1.2.1: Prelude to Ionic and Covalent Solids - Structures

As we noted in our discussion of metal and alloy structures in Chapter 6, there is an intimate connection between the structures and the physical properties of materials. As we "graduate" from simple metal structures based on sphere packings to more complex structures, we find that this is still true. In this chapter we will try to systematize the structures of inorganic solids - metal oxides, halides, sulfides, and related compounds - and develop some rules for which structures to expect based on electronegativity differences, hard-soft acid-base rules, and other periodic trends. We will see that many of these structures are related to the sphere packings that we learned about in Chapter 6.



The morphology of twinned crystals of iron pyrite (FeS_2) is related to the underlying cubic symmetry of the unit cell. Like NaCl, the pyrite crystal structure can be thought of as a face-centered cubic array of anions (S_2^{2-}) with cations (Fe^{2+}) occupying all the octahedral holes.

Inorganic solids often have simple crystal structures, and some of these structures are adopted by large families of ionic or covalent compounds. Examples of the most common structures include NaCl, CsCl, NiAs, zincblende, wurtzite, fluorite, perovskite, rutile, and spinel. We will develop these structures systematically from the close packed and non-close packed lattices shown below. Some layered structures, such as $CdCl_2$ and CdI_2, can be thought of as relatives of simple ionic lattices with some atoms "missing."



Face-centered cubic (fcc) or cubic close-packed (ccp) | Hexagonal close-packed (hcp) | Body-centered cubic | Simple cubic

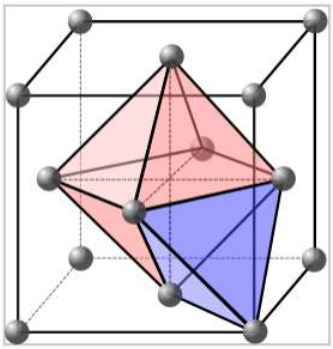
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8.1.2.2: Close-packing and Interstitial Sites

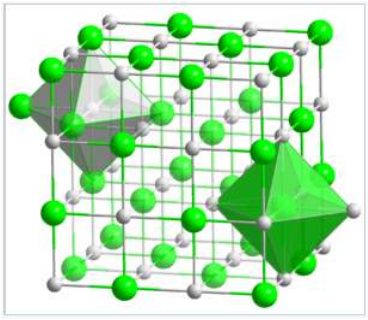
Many common inorganic crystals have structures that are related to cubic close packed (face-centered cubic) or hexagonal close packed sphere packings. These packing lattices contain two types of sites or "holes" that the interstitial atoms fill, and the coordination geometry of these sites is either **tetrahedral** or **octahedral**. An interstitial atom filling a tetrahedral hole is coordinated to four packing atoms, and an atom filling an octahedral hole is coordinated to six packing atoms. In both the hexagonal close packed and cubic close packed lattices, there is one octahedral hole and two tetrahedral holes per packing atom.

Question: Would anions or cations be better as packing atoms?
We might expect that anions, which are often larger than cations, would be better suited to the positions of packing atoms. While this is often true, there are many examples of structures in which cations are the packing atoms, and others in which the distinction is arbitrary. The NaCl structure is a good example of the latter.



One octahedral and one tetrahedral site in a face-centered cubic unit cell. Each cell contains four packing atoms (gray), four octahedral sites (pink), and eight tetrahedral sites (blue).

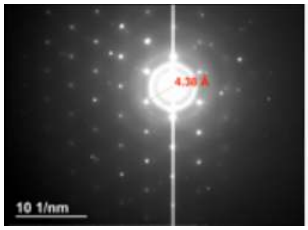
In the NaCl structure, shown on the right, the green spheres are the Cl^- ions and the gray spheres are the Na^+ ions. The octahedral holes in a face-centered cubic lattice can be found at fractional coordinates (1/2 1/2 1/2), (1/2 0 0), (0 1/2 0), and (0 0 1/2). There are four of these holes per cell, and they are filled by the chloride ions. The packing atoms (Na^+) have coordinates (0 0 0), (0 1/2 1/2), (1/2 1/2 0), and (1/2 0 1/2). Note that each of the Na^+ positions is related to a Cl^- position by a translation of (1/2 0 0). Another way of stating this is that the structure consists of **two interpenetrating fcc lattices**, which are related to each other by a translation of half the unit cell along any of the three Cartesian axes. We could have equivalently placed the Cl ions at the fcc lattice points and the Na ions in the octahedral holes by simply translating the origin of the unit cell by (1/2 0 0). Thus the distinction between packing and interstitial atoms in this case is arbitrary.



Crystal structure of NaCl. Both the Na^+ and Cl^- ions are octahedrally coordinated.

NaCl is interesting in that it is a three-dimensional checkerboard, and thus there are no NaCl "molecules" that exist in the structure. When this structure was originally solved (in 1913 by using X-ray diffraction) by W. L. Bragg, his interpretation met resistance by chemists who thought that precise integer stoichiometries were a consequence of the valency of atoms in molecules. The German chemist P. Pfeiffer noted in 1915 that ‘the ordinary notion of valency didn’t seem to apply’, and fourteen years later, the influential chemist H. E. Armstrong still found Bragg’s proposed structure of sodium chloride ‘more than repugnant to the common sense, not

chemical cricket'! Nevertheless, Bragg and his father, W. H. Bragg, persevered and used the then-new technique of X-ray diffraction to determine the structures of a number of other compounds, including diamond, zincblende, calcium fluoride, and other alkali halides. These experiments gave chemists their first real look at the atomic structure of solids, and laid the groundwork for X-ray diffraction experiments that later elucidated the structures of DNA, proteins, and many other compounds. For their work on X-ray diffraction the Braggs received the Nobel prize in Physics in 1915.

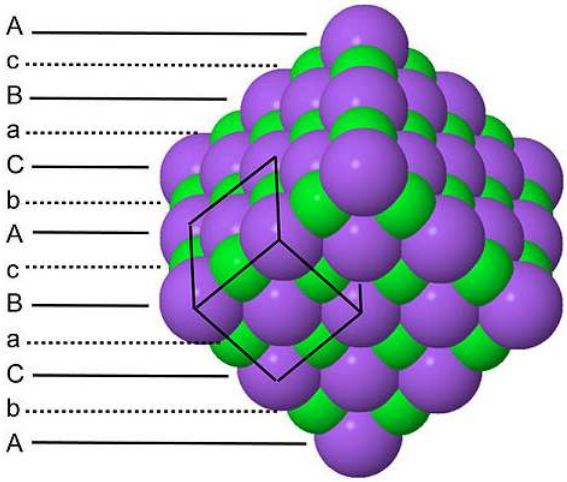


The lattice dimensions and positions of atoms in crystals such as NaCl are inferred from diffraction patterns.

Since each type of atom in the NaCl structure forms a face-centered cubic lattice, there are four Na and four Cl atoms per NaCl unit cell. It is because of this ratio that NaCl has a 1:1 stoichiometry. The shaded green and gray bipyramidal structures in the NaCl lattice show that the Na^+ ions are coordinated to six Cl^- ions, and vice versa. The NaCl structure can be alternatively drawn as a stacking of close-packed layer planes, AcBaCbAcBa... along the body diagonal of the unit cell. Here the uppercase letters represent the packing atoms, and the lower case letters are the interstitial atoms. This layered packing is illustrated below:

NaCl structure

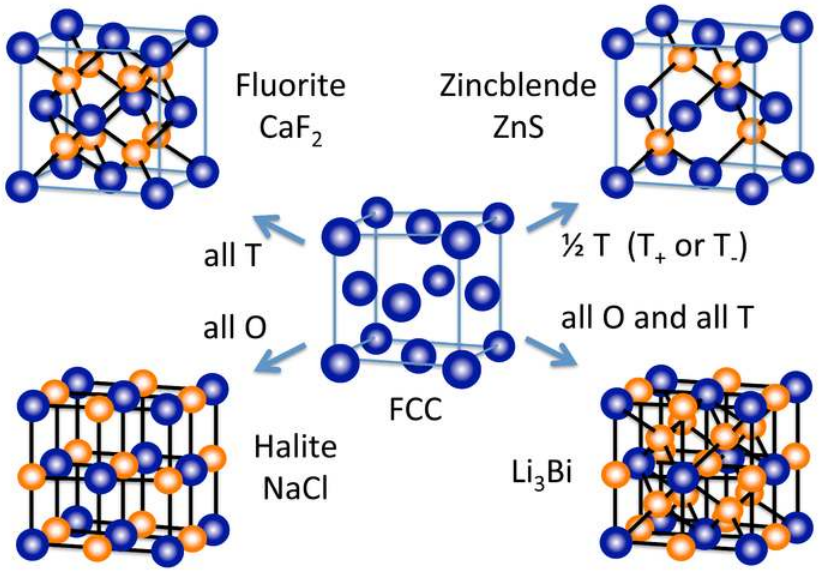
- ---------- A
- - - -c- - - -
- ---------- B
- - - -a- - - -
- ---------- C
- - - -b- - - -
- ---------- A
- - - -c- - - -
- ---------- B
- - - -a- - - -
- ---------- C
- - - -b- - - -
- ---------- A



Note that both the packing atoms and interstitials are stacked in the sequence A-B-C-A-B-C..., in keeping with the fact that each forms a cubic close-packed lattice.

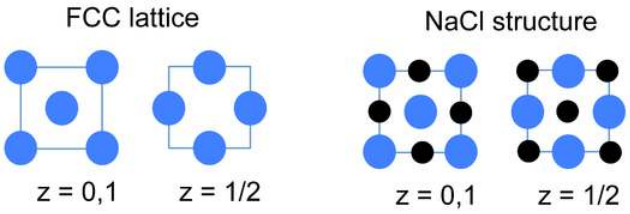
The NaCl structure is fairly common among ionic compounds:

- Alkali Halides (except CsCl, CsBr, and CsI)
- Transition Metal Monoxides (TiO, VO,..., NiO)
- Alkali Earth Oxides and Sulfides (MgO, CaO, BaS... except BeO and MgTe)
- Carbides and Nitrides (TiC, TiN, ZrC, NbC) -these are very stable refractory, interstitial alloys (metallic)



A number of other inorganic crystal structures are formed (at least conceptually) by filling octahedral and/or tetrahedral holes in close-packed lattices. The figure at the right shows some of the most common structures (fluorite, halite, zincblende) as well as a rather rare one (Li_3Bi) that derive from the fcc lattice. From the hcp lattice, we can make the NiAs and wurzite structures, which are the hexagonal relatives of NaCl and zincblende, respectively.

An alternative and very convenient way to represent inorganic crystal structures (especially complex structures such as Li_3Bi) is to draw the unit cell in slices along one of the unit cell axes. This kind of representation is shown at the left for the fcc lattice and the NaCl structure. Since all atoms in these structures have z-coordinates of either 0 or 1/2, only those sections need to be drawn in order to describe the contents of the unit cell. It is a useful exercise to draw some of the fcc compound structures (above) in sections.



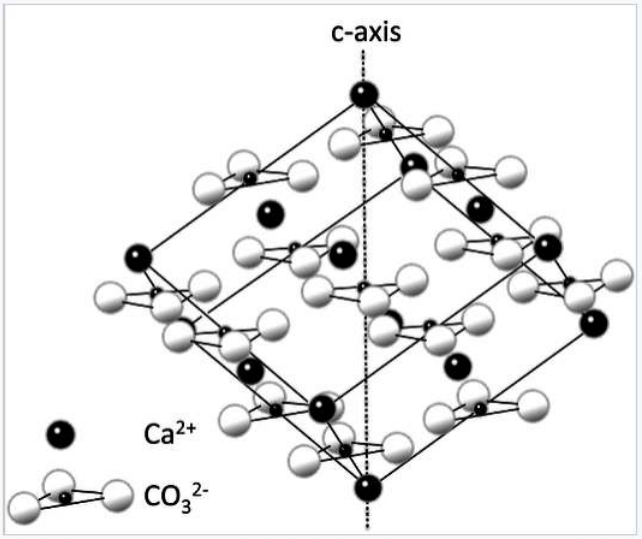
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8.1.2.3: Structures Related to NaCl and NiAs

There are a number of compounds that have structures similar to that of NaCl, but have a lower symmetry (usually imposed by the geometry of the anion) than NaCl itself. These compounds include:

- FeS_2 (pyrite, "fools gold"): S_2^{2-} (disulfide) and Fe^{2+}
- CaC_2 (a salt-like carbide): Ca^{2+} and linear C_2^{2-} anions
- $CaCO_3$ (calcite, limestone, marble): Ca^{2+} and triangular CO_3^{2-}.



The rhombohedral unit cell of the calcite crystal structure. The hexagonal c-axis is shown.

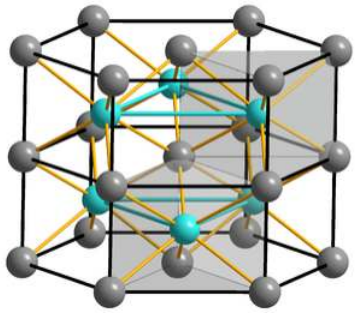
The **calcite** ($CaCO_3$) crystal structure is shown above. Triangular CO_3^{2-} ions fill octahedral holes between the Ca^{2+} ions (black spheres) in a distorted NaCl lattice. As in NaCl, each ion is coordinated by six of the other kind. From this image we can see why the $CaCO_3$ structure has a lower symmetry than that of NaCl. The fourfold rotation symmetry of the NaCl unit cell is lost when the spherical Cl^- ions are replaced by triangular CO_3^{2-} ions. Because of this symmetry lowering, transparent crystals calcite are birefringent, as illustrated below.



Calcite crystals are birefringent, meaning that their refractive indices are different along the two principal crystal directions. This gives rise to the phenomenon of double refraction.

NiAs structure

The NaCl structure can be described a face-centered cubic lattice with all of the octahedral holes filled. What if we start with a hexagonal-close packed lattice rather than a face-centered cubic lattice?



Nickel arsenide crystal structure. The Ni_6As trigonal prisms are shaded gray. One octahedron of six As atoms surrounding a Ni atom is shown in the center of the figure.

This is the structure adopted by **NiAs** and many other transition metal sulfides, phosphides, and arsenides. The cations are shown in gray while the anions are light blue in the figure at the right. The cations are in octahedral coordination, so each cation is coordinated to six anions. The anions are also coordinated to six cations, but they occupy trigonal prismatic sites. In terms of layer stacking, the NiAs structure is AcBcAcBc..., where the A and B sites (the hcp lattice) are occupied by the As atoms, and the c sites, which are eclipsed along the layer stacking axis, are occupied by Ni. Unlike the NaCl structure, where the anion and cation sites are interchangeable, NiAs has unique anion and cation sites. The layer stacking sequence for NiAs is shown below:

- ---------- A
- - - -c- - - -
- ---------- B
- - - -c- - - -
- ---------- A
- - - -c- - - -
- ---------- B
- - - -c- - - -

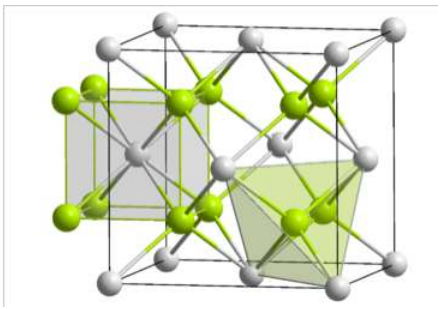
The NiAs structure cannot be adopted by ionic compounds because of the eclipsing cations, because the cation-cation repulsions would be internally destabilizing for an ionic compound. This structure is mainly adopted by covalent and polar covalent MX compounds, typically with "soft" X anions (S, Se, P, As,....) and low-valent transition metal cations. For example, some compounds with the NiAs structure are: MS, MSe, MTe (M=Ti, V, Fe, Co, Ni). Often these are nonstoichiometric or complex stoichiometries with ordered vacancies (Cr_7S_8, Fe_7S_8).

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8.1.2.4: Tetrahedral Structures

In ccp and hcp lattices, there are two tetrahedral holes per packing atom. A stoichiometry of either M_2X or MX_2 gives a structure that fills all tetrahedral sites, while an MX structure fills only half of the sites. An example of an MX_2 structure is **fluorite**, CaF_2, whose structure is shown in the figure at the left. The packing atom in fluorite is Ca^{2+} and the structure is composed of three interpenetrating fcc lattices. It should be noted that the Ca^{2+} ion (gray spheres) as a packing atom defies our "rule" that anions are larger than cations and therefore must be the packing atoms. The fluorite structure is common for ionic MX_2 (MgF_2, ZrO_2, etc.) and M_2X compounds (Li_2O). In contrast, the hcp relative of the fluorite structure is quite rare because of unfavorable close contacts between like-charged ions.



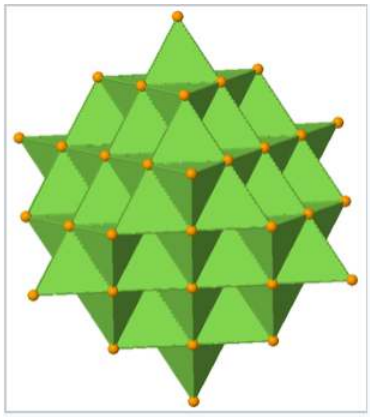
The fluorite (CaF_2) crystal structure showing the coordination environments of the Ca and F atoms

In terms of geometry, Ca^{2+} is in cubic coordination with eight F^- neighbors, and the fluoride ions are tetrahedrally coordinated by four Ca^{2+} ions. The 8:4 coordination geometry is consistent with the 1:2 Ca:F stoichiometry; in all crystal structures the ratio of the coordination numbers is the inverse of the stoichiometric ratio. The three interpenetrating fcc lattices have Ca at 0,0,0 , 1/2,1/2,0 , etc....F at 1/4,1/4,1/4 , 3/4,3/4,1/4 , etc... and F at 3/4,3/4,3/4 , 1/4,1/4/3/4 , etc.

Looking more closely at the tetrahedral sites in fluorite, we see that they fall into two distinct groups: T_+ and T_-. If a tetrahedron is oriented with a vertex pointing upwards along the stacking axis, the site is T_+. Likewise, a tetrahedron with a vertex oriented downward is T_-. The alternation of T_+ and T_- sites allows for efficient packing of ions in the structure. The layer stacking sequence in this structure (including fluoride ions in the T_+ and T_- sites) is:

- ---------- A
- - - -b- - - T_+
- - - -a- - - T_-
- ---------- B
- - - -c- - - T_+
- - - -b- - - T_-
- ---------- C
- - - -a- - - T_+
- - - -c- - - T_-
- ---------- A
- - - -b- - - T_+

- - - -a- - - T_-

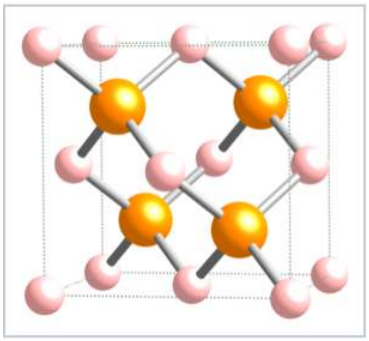


Polyhedral view of the fluorite crystal structure, showing T_+ and T_- Ca_4F tetrahedra. The Ca^{2+} ions are stacked ABCABC... along the body diagonal of the unit cell, which is the vertical direction in this image.

Tetrahedrally bonded compounds with a 1:1 stoichiometry (MX compounds) have only **half** of the tetrahedral sites (either the T_+ or T_- sites) filled. In this case, both the M and the X atoms are tetrahedrally coordinated. The **zincblende** and **wurtzite** structures are 1:1 tetrahedral structures based on fcc and hcp lattices, respectively. Both structures are favored by p-block compounds that follow the octet rule, and these compounds are usually semiconductors or insulators. The zincblende structure, shown below, can be thought of as two interpenetrating fcc lattices, one of anions and one of cations, offset from each other by a translation of 1/4 along the body diagonal of the unit cell. Examples of compounds with the zincblende structure include CuCl, CuI, ZnSe, HgS, BeS, CdTe, AlP, GaP, SnSb, CSi, and diamond. Additionally, the compound $CuInSe_2$ is zincblende in an ordered, doubled unit cell (the chalcopyrite structure). The solid solution compounds $CuIn_{1-x}Ga_xSe_2$ with this structure are among the most widely studied materials for use in efficient thin film photovoltaic cells. Using ZnS as a representative of zincblende, the coordination of both Zn and S atoms is tetrahedral. The layer sequence, which is AbBcCaAbBcC..., results in six-membered ZnS rings that have the same geometry as the "chair" version of cyclohexane. The chair conformation allows for a relatively long distance between opposite atoms in the ring and, as a result, it is more sterically favorable than the boat form. The sequence of close-packed layers in zincblende, filling only the T_+ sites and leaving the T_- sites empty, is shown below:

- ---------- A
- - - -b- - - T_+
- - - - - - T_-
- ---------- B
- - - -c- - - T_+
- - - - - - T_-
- ---------- C
- - - -a- - - T_+

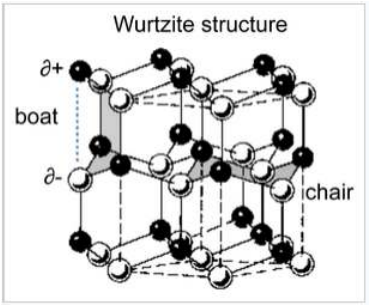
- - - - - - T_-



The zincblende unit cell

The wurtzite structure is a close relative of zinc blende, based on filling half the tetrahedral holes in the hcp lattice. Like zincblende, wurtzite contains planes of fused six-membered rings in the chair conformation. Unlike zincblende, however, the rings joining these planes contain six-membered "boat" rings. The boat aligns the anions so that they are directly above the cations in the structure, a less favorable situation sterically but a more favorable one in terms of electrostatics. As a result, the wurtzite structure tends to favor more polar or ionic compounds (e.g., ZnO, $NH_4^+F^-$) than the zincblende structure. As with zincblende, both ions are in tetrahedral (4:4) coordination and there are typically eight valence electrons in the MX compound. Examples of compounds with this structure include: BeO, ZnO, MnS, CdSe, MgTe, AlN, and NH_4F. The layered structure of wurtzite is AbBaAbB and the layer sequence with T_+ sites filled is illustrated below:

- ---------- A
- - - -b- - - T_+
- - - - - - T_-
- ---------- B
- - - -a- - - T_+
- - - - - - T_-
- ---------- A
- - - -b- - - T_+
- - - - - - T_-
- ---------- B

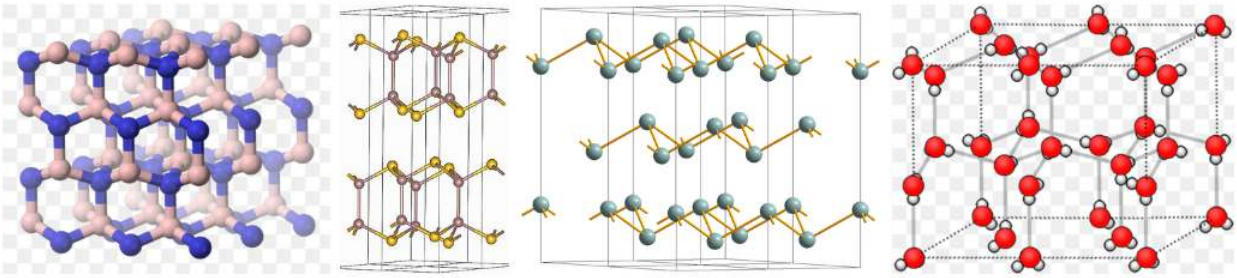


The chair and boat conformations of six-membered ZnS rings in the wurtzite structure.

An interesting consequence of the layer stacking in the wurtzite structure is that the crystals are polar. When cleaved along the c-axis (the stacking axis), crystals of ZnO, ZnS, and GaN have one negatively charged face and an opposite positively charged face. An applied electric field interacts with the crystal dipole, resulting in compression or elongation of the lattice along this direction. For this reason crystals of compounds in the wurtzite structure are typically piezoelectric.

Some compounds are diamorphic and can have either the zincblende or wurtzite structure. Examples of these compounds that have intermediate polarities include CdS and ZnS. SiO_2 exists in polymorphs (crystobalite and tridymite) that resemble zincblende and

wurtzite with O atoms midway between each of the Si atoms. The zincblende and wurtzite structures have efficient packing arrangements for tetrahedrally bonded networks and are commonly found in compounds that have tetrahedral bonding. Water, for example, has a tetrahedral hydrogen bonding network and is wurtzite-type. The undistorted wurtzite and zinc blende structures are typically found for AX compounds with eight valence electrons, which follow the octet rule. AX compounds with nine or ten electrons such as GaSe and GaAs crystallize in distorted variants of the wurtzite structure. In GaSe, the extra electrons form lone pairs and this creates layers in the structure, as can be seen in the figure below. To the right of GaSe, the structures of As, Sb, and SbAs show an ever further breakdown of the structure into layers as more valence electrons are added.



Wurtzite crystal structure | GaSe crystal structure | Crystal structure of Sb, SbAs, and gray As | Crystal structure of hexagonal ice

Hexagonal ice is the most stable polymorph of ice, which is obtained upon freezing at 1 atmosphere pressure. This polymorph (ice-I) has a hcp wurtzite-type structure. Looking at the structure shown at the right, we see that there are irregular arrangements of the O-H---O bonds. In the structure, hydrogen bonding enforces the tetrahedral coordination of each water molecule, resulting in a relatively open structure that is less dense than liquid water. For this reason, ice floats in water.

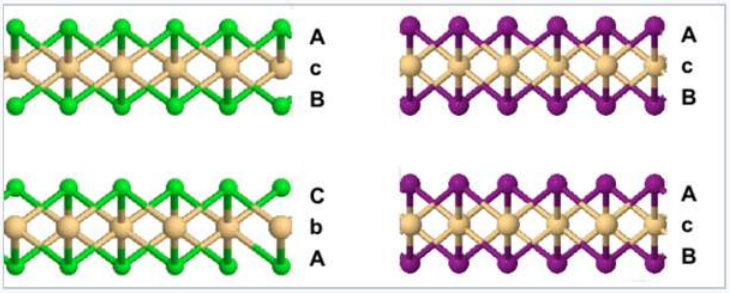
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8.1.2.5: Layered Structures and Intercalation Reactions

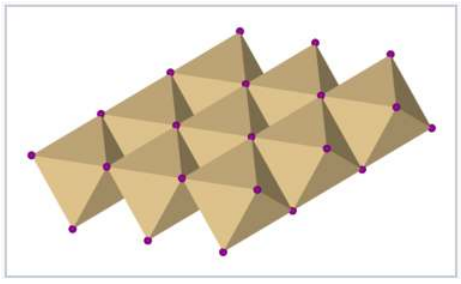
Layered structures are characterized by strong (and typically covalent) bonding between atoms in two dimensions and weaker bonding in the third. A broad range of compounds including metal halides, oxides, sulfides, selenides, borides, nitrides, carbides, and allotropes of some pure elements (B, C, P, As) exist in layered forms. Structurally, the simplest of these structures (for example binary metal halides and sulfides) can be described as having some fraction of the octahedral and/or tetrahedral sites are filled in the fcc and hcp lattices. For example, the $CdCl_2$ structure is formed by filling all the octahedral sites in alternate layers of the fcc lattice, and the CdI_2 structure is the relative of this structure in the hcp lattice.

In the **$CdCl_2$ structure**, the stacking sequence of anion layers is ABCABC...
In the **CdI_2 structure**, the anion stacking sequence is ABAB..., and all the cations are eclipsed along the stacking axis.



Comparison of the $CdCl_2$ (left) and CdI_2 (right) crystal structures

These are examples of **6-3 structures**, because the cations are coordinated by an octahedron of six anions, and the anions are coordinated by three cations to make a trigonal pyramid (like NH_3). Another way to describe these structures is to say that the MX_6 octahedra each share six edges in the MX_2 sheets.



Polyhedral drawing of one layer of the $CdCl_2$ or CdI_2 structure showing edge-sharing MX_6 octahedra

Because these structures place the packing atoms (the anions) in direct van der Waals contact, they are most stable for relatively **covalent** compounds. Otherwise, the electrostatic repulsion between contacting anions would destabilize the structure energetically. More ionic MX_2 compounds tend to adopt the fluorite (CaF_2) or rutile (TiO_2) structures, which are not layered.

Despite the fact that these two structure types are the same at the level of nearest and next-nearest neighbor ions, the CdI_2 structure is much more common than the $CdCl_2$ structure.

$CdCl_2$ structure:

MCl_2 (M = Mg, Mn, Fe, Co, Ni, Zn, Cd)

$NiBr_2$, NiI_2, $ZnBr_2$, ZnI_2

CdI_2 structure:

MCl_2 (M = Ti, V)

MBr_2 (M = Mg, Fe, Co, Cd)

MI_2 (M = Mg, Ca, Ti, V, Mn, Fe, Co, Cd, Ge, Pb, Th)

$M(OH)_2$ (M = Mg, Ca, Mn, Fe, Co, Ni, Cd)

MS_2 (M = Ti, Zr, Sn, Ta, Pt)

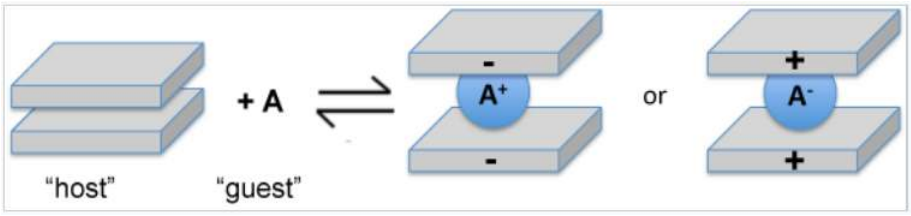
MSe_2 (M = Ti, Zr, Sn, V, Pt)

MTe_2 (M = Ti, Co, Ni, Rh, Pd, Pt)

Physically, layered compounds are **soft** and **slippery**, because the layer planes slide past each other easily. For example, graphite, MoS_2, and talc (a silicate) are layered compounds that are used widely as **lubricants** and lubricant additives.

An important reaction of layered compounds is **intercalation**. In intercalation reactions, guest molecules and ions enter the galleries that separate the sheets, usually with expansion of the lattice along the stacking axis. This reaction is typically reversible if it does not perturb the bonding within the sheets. Often the **driving force for intercalation is a redox reaction**, i.e., electron transfer between the host and guest. For example, lithium metal reacts with TiS_2, MoS_2, and graphite to produce $LiTiS_2$, Li_xMoS_2 ($x < 1$), and LiC_6. In these compounds, lithium is ionized to Li^+ and the sheets are negatively charged. Oxidizing agents such as Br_2, $FeCl_3$, and AsF_5 also react with graphite. In the resulting intercalation compounds, the sheets are positively charged and the intercalated species are anionic.

Intercalation reactions are especially important for electrochemical energy storage in **secondary batteries**, such as **lithium ion** batteries, **nickel-metal hydride** batteries, and **nickel-cadmium** batteries. The reversible nature of the intercalation reaction allows the electrodes to be charged and discharged up to several thousand times without losing their mechanical integrity. In lithium ion batteries, the negative electrode material is typically graphite, which is intercalated by lithium to make LiC_6. Several different oxides and phosphates containing redox active transition metal ions (Mn, Fe, Co, Ni) are used as the positive electrode materials.



Oxidative or reductive intercalation involves the placement of anions or cations between sheets.

Lithium ion batteries based on CoO_2 were first described in 1980[1] by John B. Goodenough's research group at Oxford. In batteries based on CoO_2, which has the CdI_2 structure, the positive electrode half-reaction is:

$$\mathrm{LiCoO_2 \leftrightharpoons Li_{1-x}CoO_2 + x\,Li^+ + xe^-} \tag{8.1.2.5.1}$$

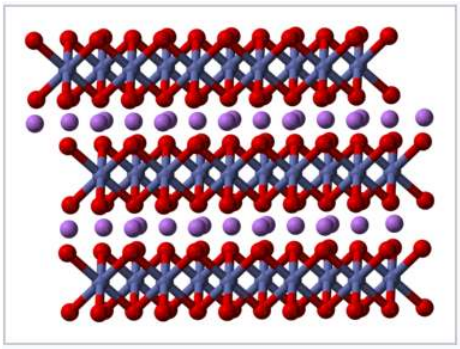
The negative electrode half reaction is:

$$\mathrm{x\,Li^+ + xe^- + x\,C_6 \leftrightharpoons x\,LiC_6} \tag{8.1.2.5.2}$$

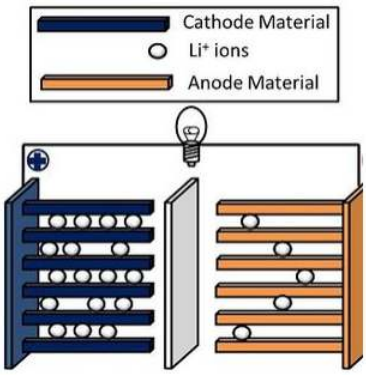
The battery is fully charged when the positive electrode is in the CoO_2 form and the negative electrode is in the LiC_6 form. Discharge involves the motion of Li^+ ions through the electrolyte, forming Li_xCoO_2 and graphite at the two electrodes.



Blue plaque erected by the Royal Society of Chemistry commemorating the development of cathode materials for the lithium-ion battery



Crystal structure of $LiCoO_2$[2]



The lithium ion battery is a "rocking chair" battery, so named because charging and discharging involve moving Li^+ ions from one side to the other. CoO_2 is one example of a positive electrode material that has been used in lithium ion batteries. It has a high energy density, but batteries based on CoO_2 have poor thermal stability. Safer materials include lithium iron phosphate ($LiFePO_4$), and $LiMO_2$ (M = a mixture of Co, Mn, and Ni). These batteries are used widely in laptop computers, portable electronics, cellular telephones, cordless tools, and electric and hybrid vehicles.

A similar intercalation reaction occurs in nickel-cadmium batteries and nickel-metal hydride batteries, except in this case the reaction involves the movement of protons in and out of the $Ni(OH)_2$ lattice, which has the CdI_2 structure:

$$NiO(OH) + H_2O + e^- \longrightarrow Ni(OH)_2 + OH^- \qquad (8.1.2.5.3)$$

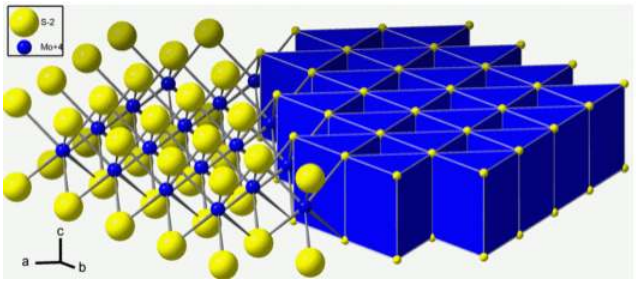
There are many layered compounds that cannot be intercalated by redox reactions, typically because some other stable product is formed. For example, the reaction of layered CdI_2 with Li produces LiI (NaCl structure) and Cd metal.

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8.1.2.6: Bonding in TiS_2, MoS_2, and Pyrite Structures

Many layered dichalcogenides, such as TiS_2 and ZrS_2, have the CdI_2 structure. In these compounds, as we have noted above, the metal ions are octahedrally coordinated by S. Interestingly, the structures of MoS_2 and WS_2, while they are also layered, are different. In these cases, the metal is surrounded by a **trigonal prism** of sulfur atoms. NbS_2, TaS_2, $MoSe_2$, $MoTe_2$, and WSe_2 also have the trigonal prismatic molybdenite structure, which is shown below alongside a platy crystal of MoS_2.

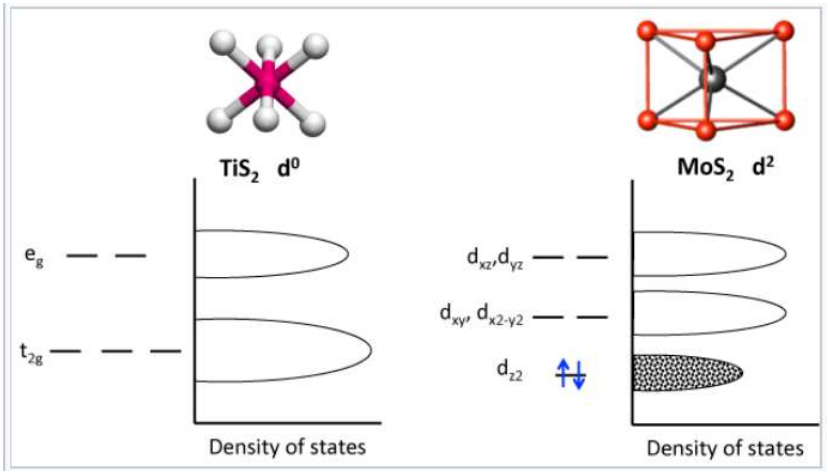




The coordination of the metal ions by a trigonal prism of chalcogenide ions is **sterically unfavorable** relative to octahedral coordination. There are close contacts between the chalcogenide ions, which are eclipsed in the stacking sequence **AbA/BaB/AbA/BaB**... (where "/" indicates the van der Waals gap between layers). What stabilizes this structure?

The molybdenite structure occurs most commonly in MX_2 compounds with a **d^1 or d^2 electron count**. The figure below compares the splitting of d-orbital energies in the octahedral and trigonal prismatic coordination environments:

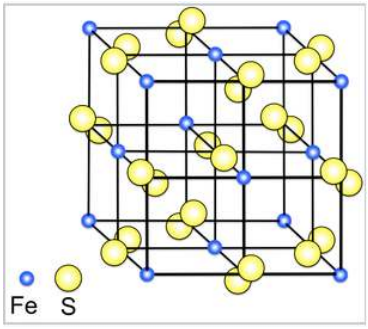
The trigonal prismatic structure is stabilized in MoS_2 by filling the lowest energy band, the d_{z2}. The d_{z2} orbital which points vertically through the triangular top and bottom faces of the trigonal prism, has the least interaction with the sulfide ligands and therefore the lowest energy. The d_{xz} and d_{yz} orbitals, which point at the ligands, have the highest energy. The d_{z2} orbital is lower in energy in this structure than the t_{2g} orbitals are in the octahedral structure of TiS_2.



d-orbital splittings and energy bands in TiS_2 and MoS_2. MoS_2 is a semiconductor with a 1.3 eV gap between its filled and empty bands.

Because it has an unfilled t_{2g} band, TiS_2 is relatively easy to reduce by intercalation with Li. For this reason, $LiTiS_2$ was one of the first intercalation compounds studied by Stanley Whittingham, who developed the concept of the non-aqueous lithium ion battery in the early 1970's.[3] Because it has a filled d_{z2} band, MoS_2 is harder to reduce, but it can be intercalated by reaction with the powerful reducing agent n-butyllithium to make Li_xMoS_2 ($x < 1$). Atoms in the van der Waals planes of these compounds are relatively unreactive, which gives MoS_2 its good oxidative stability and enables its application as a high temperature lubricant. Atoms at the edges of the crystals are however more reactive and in fact are catalytic. High surface area MoS_2, which has a high density of exposed edge planes, is used as a hydrodesulfurization catalyst and is also of increasing interest as an electrocatalyst for the reduction of water to hydrogen.

Layered metal dichalcogenides, including MoS_2, WS_2, and SnS_2, can form closed nanostructures that take the shape of multiwalled onions and multiwalled tubes. These materials were discovered by the group of Reshef Tenne in 1992, shortly after the discovery of carbon nanotubes. Since then nanotubes have been synthesized from many other materials, including vanadium and manganese oxides.



The pyrite (FeS_2) crystal structure. The structure is related to NaCl, with Fe^{2+} and S_2^{2-} ions occupying the cation and anion sites.

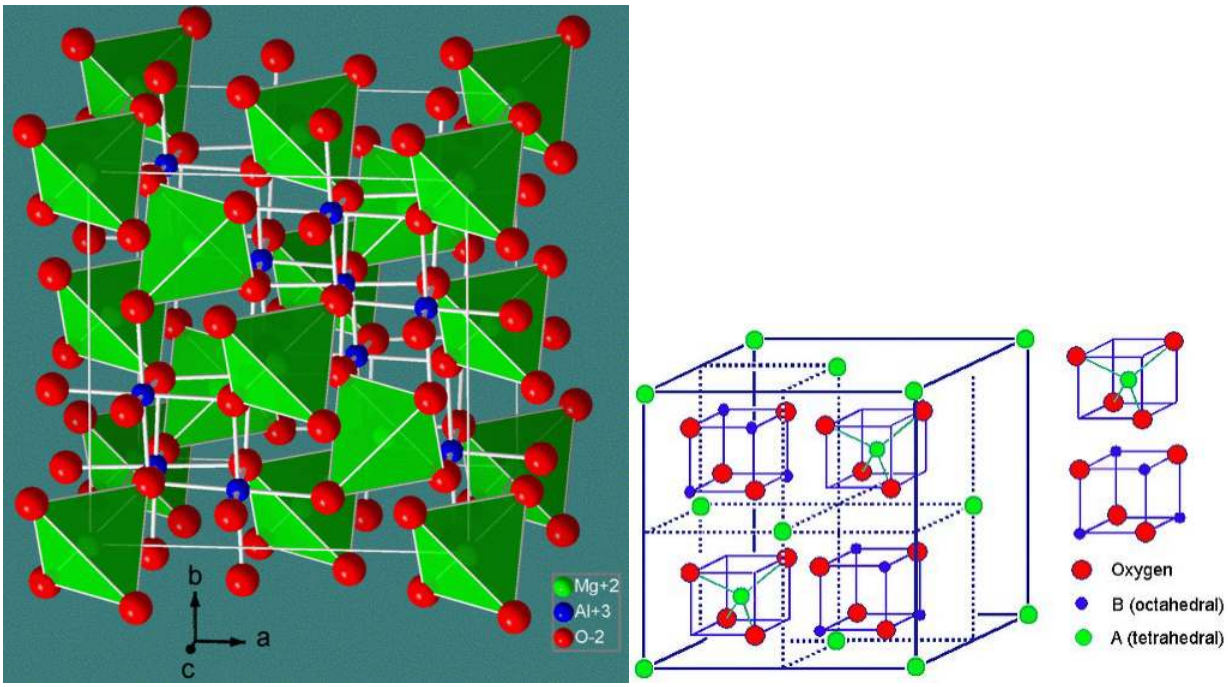
Although early (TiS_2) and late (PtS_2) transition metal disulfides have layered structures, a number of MS_2 compounds in the middle of the transition series, such as MnS_2, FeS_2 and RuS_2, have three-dimensionally bonded structures. For example, FeS_2 has the **pyrite structure**, which is related to the NaCl structure. The reason is that FeS_2 is not $Fe^{4+}(S^{2-})_2$, but is actually $Fe^{2+}(S_2^{2-})$, where S_2^{2-} is the disulfide anion (which contains a single bond like the peroxide anion O_2^{2-}). S^{2-} is too strong a reducing agent to exist in the same compound with Fe^{4+}, which is a strong oxidizing agent. Because FeS_2 is actually $Fe^{2+}(S_2^{2-})$, it is a 1:1 compound and adopts a 1:1 structure.

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8.1.2.7: Spinel, Perovskite, and Rutile Structures

There are three more structures, which are derived from close-packed lattices, that are particularly important because of the material properties of their compounds. These are the **spinel** structure, on which ferrites and other magnetic oxides are based, the **perovskite** structure, which is adopted by ferroelectric and superconducting oxides, and the **rutile** structure, which is a common binary 6:3 structure adopted by oxides and fluorides.



The **spinel structure** is formulated MM'_2X_4, where M and M' are tetrahedrally and octahedrally coordinated cations, respectively, and X is an anion (typically O or F). The structure is named after the mineral $MgAl_2O_4$, and oxide spinels have the general formula AB_2O_4.

In the **normal spinel** structure, there is a close-packed array of anions. The A-site cations fill 1/8 of the tetrahedral holes and the B-site cations fill 1/2 of the octahedral holes. A polyhedral view of the normal spinel unit cell is shown at the left, and a simplified view (with the contents of the back half of the cell removed for clarity) is shown above. Each unit cell contains eight formula units and has a composition $A_8B_{16}O_{32}$.

Inverse spinels have a closely related structure (with the same large unit cell) in which the A-site ions and half of the B-site ions switch places. Inverse spinels are thus formulated $B(AB)O_4$, where the AB ions in parentheses occupy octahedral sites, and the other B ions are on tetrahedral sites. There are also mixed spinels, which are intermediate between the **normal** and **inverse** spinel structure.

Some spinel and inverse spinel AB combinations are:

$A^{2+}B^{3+}$, e.g., $MgAl_2O_4$ (normal spinel)

$A^{4+}B^{2+}$, e.g., $Pb_3O_4 = Pb^{II}(Pb^{II}Pb^{IV})O_4$ (inverse spinel)

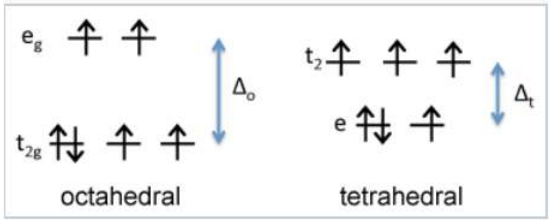
$A^{6+}B^{+}$, e.g., Na_2WO_4 (normal spinel)

Many magnetic oxides, such as Fe_3O_4 and $CoFe_2O_4$, are spinels.

Normal vs. inverse spinel structure

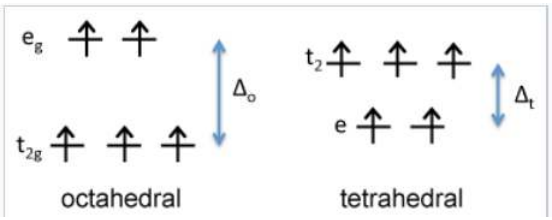
For transition metal oxide spinels, the choice of the normal vs. inverse spinel structure is driven primarily by the **crystal field stabilization energy** (CFSE) of ions in the tetrahedral and octahedral sites. For spinels that contain 3d elements such as Cr, Mn, Fe, Co, and Ni, the electron configuration is typically **high spin** because O^{2-} is a **weak field ligand**.

As an example, we can consider magnetite, Fe_3O_4. This compound contains one Fe^{2+} and two Fe^{3+} ions per formula unit, so we could formulate it as a normal spinel, $Fe^{2+}(Fe^{3+})_2O_4$, or as an inverse spinel, $Fe^{3+}(Fe^{2+}Fe^{3+})O_4$. Which one would have the lowest energy?



d-orbital energy diagram for Fe^{2+}

First we consider the crystal field energy of the **Fe^{2+}** ion, which is d^6. Comparing the tetrahedral and high spin octahedral diagrams, we find that the CFSE in an **octahedral** field of O^{2-} ions is $[(4)(\frac{2}{5}) - (2)(\frac{3}{5})]\Delta_o - P = \mathbf{0.4\Delta_o - P}$. In the **tetrahedral** field, the CFSE is $[(3)(\frac{3}{5}) - (3)(\frac{2}{5})]\Delta_t - P = \mathbf{0.6\Delta_t - P}$. Since Δ_o is about 2.25 times larger than Δ_t, the octahedral arrangement has a larger CFSE and is preferred for Fe^{2+}.



d-orbital energy diagram for Fe^{3+}

In contrast, it is easy to show that **Fe^{3+}**, which is d^5, would have a CFSE of zero in either the octahedral or tetrahedral geometry. This means that Fe^{2+} has a preference for the octahedral site, but Fe^{3+} has no preference. Consequently, we place Fe^{2+} on octahedral sites and **Fe_3O_4 is an inverse spinel**, $Fe^{3+}(Fe^{2+}Fe^{3+})O_4$.

Ferrites are compounds of general formula **$M^{II}Fe_2O_4$**. We can see that magnetite is one example of a ferrite (with M = Fe). Other divalent metals (M = Mg, Mn, Co, Ni, Zn) also form ferrites. Ferrites can be normal or inverse spinels, or mixed spinels, depending on the CFSE of the M^{II} ion. Based on their CFSE, Fe^{2+}, Co^{2+}, and Ni^{2+} all have a strong preference for the octahedral site, so those compounds are all inverse spinels. $ZnFe_2O_4$ is a normal spinel because the small Zn^{2+} ion (d^{10}) fits more easily into the tetrahedral site than Fe^{3+} (d^5), and both ions have zero CFSE. $MgFe_2O_4$ and $MnFe_2O_4$, in which all ions have zero CFSE and no site preference, are mixed spinels. **Chromite** spinels, **$M^{II}Cr_2O_4$**, are always **normal spinels** because the d^3 Cr^{3+} ion has a strong preference for the octahedral site.

Examples of normal and inverse spinel structures:

> **$MgAl_2O_4$** is a **normal spinel** since both Mg^{2+} and Al^{3+} are non-transition metal ions and thus CFSE = 0. The more highly charged Al^{3+} ion prefers the octahedral site, where it is surrounded by six negatively charged oxygen atoms.
>
> **Mn_3O_4** is a **normal spinel** since the Mn^{2+} ion is a high spin d^5 system with zero CFSE. The two Mn^{3+} ions are high spin d^4 with higher CFSE on the octahedral sites (3/5 Δ_O) than on the tetrahedral site (2/5 Δ_t ~ 1/5 Δ_O).
>
> **Fe_3O_4** is an **inverse spinel** since the Fe^{3+} ion is a high spin d^5 system with zero CFSE. Fe^{2+} is a high spin d^6 system with more CFSE on an octahedral site than on a tetrahedral one.
>
> **$NiFe_2O_4$** is again an **inverse spinel** since Ni^{2+} (a d^8 ion) prefers the octahedral site and the CFSE of Fe^{3+} (a d^5 ion) is zero.
>
> **$FeCr_2O_4$** is a **normal spinel** since Fe^{2+} is high spin d^6 ion with $CFSE = [4(\frac{2}{5}) - 2(\frac{3}{5})]\Delta_o = \frac{2}{5}\Delta_o$ on an octahedral site, and Cr^{3+} is a d^3 ion with CFSE = 3(2/5) Δ_O = 6/5 Δ_O. Hence it is more energetically favorable for Cr^{3+} to occupy both of the octahedral sites.

Co_3O_4 is a **normal spinel**. Even in the presence of weak field oxo ligands, Co^{3+} is a low spin d^6 ion with very high CFSE on the octahedral sites, because of the high charge and small size of the Co^{3+} ion. Hence the Co^{3+} ions occupy both octahedral sites, and Co^{2+} occupies the tetrahedral site.

Magnetism of ferrite spinels

Ferrite spinels are of technological interest because of their magnetic ordering, which can be ferrimagnetic or antiferromagnetic depending on the structure (normal or inverse) and the nature of the metal ions. Fe_3O_4, $CoFe_2O_4$, and $NiFe_2O_4$ are all inverse spinels and are ferrimagnets. The latter two compounds are used in magnetic recording media and as deflection magnets, respectively.

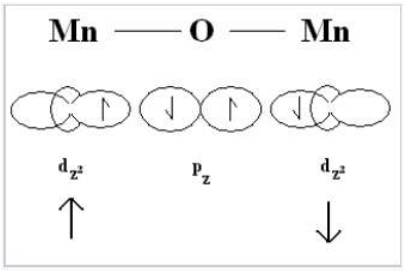
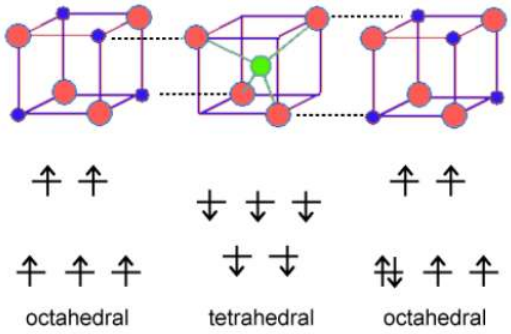


Illustration of antiferromagnetic superexchange between two transition metal cations through a shared oxygen atom.

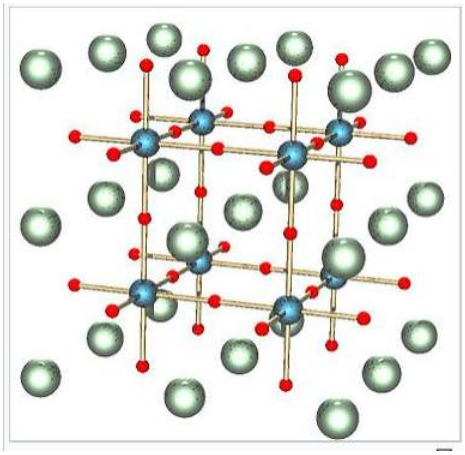
In order to understand the magnetism of ferrites, we need to think about how the unpaired spins of metal ions are coupled in oxides. If an oxide ion is shared by two metal ions, it can mediate the coupling of spins by superexchange as shown at the right. The coupling can be antiferromagnetic, as shown, or ferromagnetic, depending on the orbital filling and the symmetry of the orbitals involved. The **Goodenough-Kanamori rules** predict the local magnetic ordering (ferromagnetic vs. antiferromagnetic) that results from superexchange coupling of the electron spins of transition metal ions. For ferrites, the strongest coupling is between ions on neighboring **tetrahedral and octahedral sites**, and the ordering of spins between these two sites is reliably **antiferromagnetic**.



Because all the tetrahedral and octahedral sites in a spinel or inverse spinel crystal are coupled together identically, it works out that ions on the tetrahedral sites will all have one orientation (e.g., spin down) and ions on all the octahedral sites will have the opposite orientation (e.g., spin up). If the number of spins on the two sites is the same, then the solid will be antiferromagnetic. However, if the **number of spins is unequal** (as in the case of Fe_3O_4, $CoFe_2O_4$, and $NiFe_2O_4$) then the solid will be **ferrimagnetic**. This is illustrated above for Fe_3O_4. The spins on the Fe^{3+} sites cancel, because half of them are up and half are down. However, the four unpaired electrons on the Fe^{2+} ions are all aligned the same way in the crystal, so the compound is ferrimagnetic.

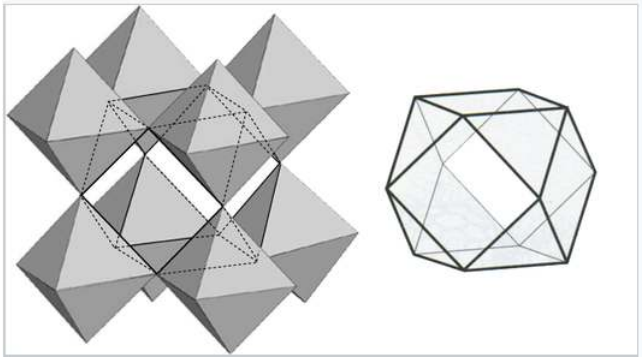
Perovskites are **ternary oxides** of general formula **ABO_3**. More generally, the perovskite formula is ABX_3, where the anion X can be **O, N, or halogen**. The A ions are typically large ions such as Sr^{2+}, Ba^{2+}, Rb^{+}, or a lanthanide 3+ ion, and the B ions are smaller transition metal ions such as Ti^{4+}, Nb^{5+}, Ru^{4+}, etc. The mineral after which the structure is named has the formula $CaTiO_3$.

The perovskite structure has simple cubic symmetry, but is related to the fcc lattice in the sense that the A site cations and the three O atoms comprise a fcc lattice. The B-site cations fill 1/4 of the octahedral holes and are surrounded by six oxide anions.



ABX_3 perovskite structure. A, B, and X are white, blue, and red, respectively.

The coordination of the A ions in perovsite and the arrangement of BO_6 octahedra is best understood by looking at the ReO_3 structure, which is the same structure but with the A-site cations removed. In the polyhedral representation of the structure shown at the right, it can be seen that the octahedra share all their vertices but do not share any octahedral edges. This makes the ReO_3 and perovskite structures flexible, like three-dimensional wine racks, in that the octahedra can **rotate and tilt cooperatively**. Eight such octahedra surround a large **cuboctahedral cavity**, which is the site of the A ions in the perovskite structure. Cations in these sites are coordinated by 12 oxide ions, as expected from the relationship between the perovskite and fcc lattices.



Polyhedral representation of the ReO_3 structure showing the large cuboctahedral cavity that is surrounded by 12 oxygen atoms

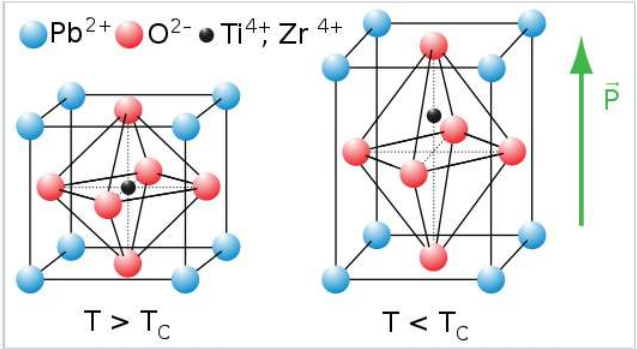
Because the A-site is empty in the ReO_3 structure, compounds with that structure can be reversibly **intercalated** by small ions such as **Li^+ or H^+**, which then occupy sites in the cuboctahedral cavity. For example, smart windows that darken in bright sunlight contain the **electrochromic** material WO_3, which has the ReO_3 structure. In the sunlight, a photovoltaic cell drives the reductive intercalation of WO_3 according to the reaction:

$$x\,H^+ + xe^- + WO_3 \leftrightharpoons H_xWO_3 \qquad (8.1.2.7.1)$$

WO_3 is a light yellow compound containing d^0 W(VI). In contrast, H_xWO_3, which is mixed-valent W(V)-W(VI) = d^1-d^0, has a deep blue color. Such coloration is typical of mixed-valence transition metal complexes because their d-electrons can be excited to delocalized conduction band levels by red light. Because the electrochemical intercalation-deintercalation process is powered by a solar cell, the tint of the windows can adjust automatically to the level of sunlight.

Ferroelectric perovskites

The flexibility of the network of corner-sharing BO_6 octahedra is also very important in ferroelectric oxides that have the perovskite structure. In some perovsites with small B-site cations, such as Ti^{4+} and Nb^{5+}, the cation is too small to fit symmetrically in the BO_6 octahedron. The octahedron distorts, allowing the cation to move off-center. These distortions can be **tetragonal** (as in the example shown at the right), **rhombohedral**, or **orthorhombic**, depending on whether the cation moves towards a vertex, face, or edge of the BO_6 octahedron. Moving the cation off-center in the octahedron creates an **electric dipole**. In ferroelectrics, these dipoles align in neighboring unit cells through cooperative rotation and tilting of octahedra. The crystal thus acquires a net electrical polarization.



Tetragonal distortion of the perovskite unit cell in the ferroelectric oxide PZT, $PbTi_xZr_{1-x}$

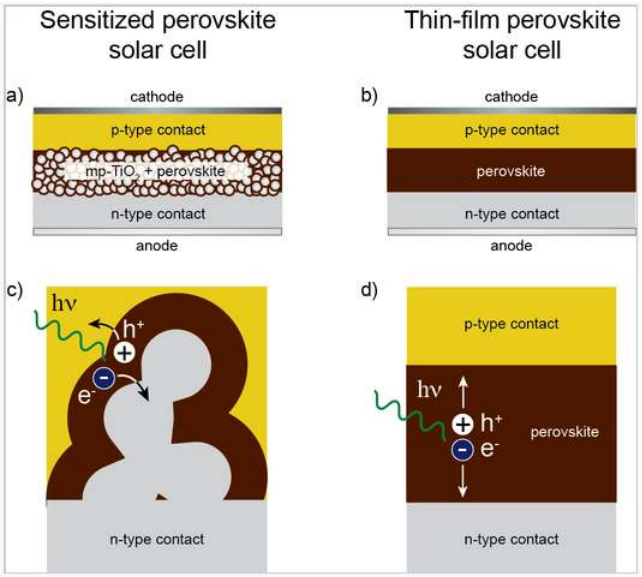
Ferroelectricity behaves analogously to **ferromagnetism**, except that the polarization is electrical rather than magnetic. In both cases, there is a **critical temperature (T_c)** above which the **spontaneous polarization** of the crystal disappears. Below T_c, the electric polarization of a ferroelectric can be switched with a coercive field, and hysteresis loop of polarization vs. field resembles that of a ferromagnet. Above T_c, the crystal is **paraelectric** and has a high dielectric permittivity.

Ferroelectric and paraelectric oxides (along with piezoelectrics and pyroelectrics) have a wide variety of applications as switches, actuators, transducers, and dielectrics for capacitors. **Ferroelectric capacitors** are important in memory devices (FRAM) and in the tuning circuits of cellular telephones. **Multiferroics**, which are materials that are simultaneously ferroelectric and ferromagnetic, are rare and are being now intensively researched because of their potential applications in electrically adressable magnetic memory.

Halide perovskites (ABX_3, X = Cl, Br, I) can be made by combining salts of monovalent A ions ($A^+ = Cs^+$, NH_4^+, RNH_3^+) and divalent metal salts such as $PbCl_2$ or PbI_2. These compounds have sparked recent interest as light absorbers for **thin film solar cells** that produce electricity from sunlight. Lead and tin halide perovskites can be grown as thin films from solution precursors or by thermal evaporation at relatively low temperatures. In some lead halide perovskites, the mobility of electrons and holes is very high, comparable to that of more expensive III-V semiconductors such as GaAs, which must be grown as very pure single crystals at high temperatures for use in solar cells. Because of their high carrier mobility, some lead halide perovskites are also electroluminescent and are of interest as inexpensive materials for light-emitting diodes (LEDs).

Tin and lead halide perovskites were first studied in the 1990s as materials for thin film electronics,[4] and more recently as light absorbers in dye-sensitized solar cells. Soon after the results on dye-sensitized perovskite cells were reported, it was discovered that halide perovskites could also be used in thin film solid state solar cells. The structures of these solar cells are shown schematically at the right. The highest reported solar power conversion efficiencies of perovskite solar cells have jumped from 3.8% in 2009 [5] to

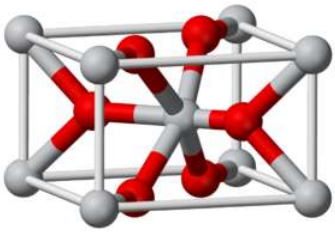
10.2% in 2012[6] and a certified 20.1% in 2014.[7]. The highest performing cells to date contain divalent lead in the perovskite B cation site and a mixture of methylammonium and formamidinium ions in the perovskite A cation site.



a) Solar cell architecture in which a lead halide perovskite absorber coats a layer of nanocrystalline anatase TiO_2. b) Thin-film solar cell, with a layer of lead halide perovskite sandwiched between two selective contacts. c) Charge generation and extraction in the sensitized architecture and d) in the thin-film architecture.

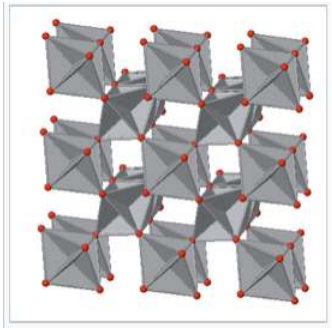
Despite their very impressive efficiency, perovskite solar cells are stable for relatively short periods of time and are sensitive to air and moisture. Current research is focused on understanding the degradation mechanisms of these solar cells and improving their stability under operating conditions.

The **rutile structure** is an important MX_2 (X = O, F) structure. It is a 6:3 structure, in which the cations are octahedrally coordinated by anions, and as such is intermediate in polarity between the CaF_2 (8:4) and SiO_2 (4:2) structures. The mineral rutile is one of the polymorphs of TiO_2, the others (anatase and brookite) also being 6:3 structures.



The rutile structure can be described as a distorted version of the NiAs structure with half the cations removed. Recall that compounds with the NiAs structure were typically metallic because the metal ions are eclipsed along the stacking axis and thus are in relatively close contact. In rutile, the MO_6 **octahedra share edges** along the tetragonal c-axis, and so some rutile oxides, such as

NbO_2, RuO_2 and IrO_2, are also **metallic** because of **d-orbital overlap** along that axis. These compounds are important as electrolyzer catalysts and catalyst supports because they combine high catalytic activity with good electronic conductivity.



View down the tetragonal c-axis of the rutile lattice, showing edge-sharing MO_6 octahedra.

Rutile TiO_2, because of its high refractive index, is the base pigment for white paint. It is a wide bandgap semiconductor that has also been extensively researched as an electrode for water splitting solar cells and as a photocatalyst (primarily as the anatase polymorph) for degradation of pollutants in air and water. Self-cleaning glass exploits the photocatalytic properties of a thin film of TiO_2 to remove oily substances from the glass surface and improve the wetting properties of the glass.

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8.1.2.8: Discussion Questions

- Using the Liverpool 3D visualization website (http://www.chemtube3d.com/solidstate/_table.htm) determine the anion and cation coordination geometries in cadmium chloride and anatase. Describe the arrangement of octahedra (in terms of whether they share edges, faces, etc.) in these structures.
- Count the number of atoms in the Li_3Bi and ReO_3 unit cells, and determine the coordination environments of each of the ions.
- Silicon, germanium, and many other semiconductors adopt the diamond (or zincblende) structure. Assuming that all the atoms are the same size, calculate the volume fraction of the unit cell that is occupied by the atoms. How does the filling fraction of diamond compare to simple cubic and close-packed structures, and what does this tell us about the relationship between coordination number and density?
- Describe the structural basis of ferroelectricity in barium titanate.

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8.2: Bonding in Metals, Semiconductors and Insulators – Band Structure

INTRODUCTION

Characteristic properties of metals include: (1) electrical conductivity, (2) opaqueness and (3) malleability. A very simple model in which the metallic crystal is viewed as a lattice of positive ions surrounded by a “gas” of free electrons provides a crude understanding of the first and third properties. If the crystal has a gas of free electrons, it is easy to see why the application of an electric field will result in the motion of these electrons and thus for the high electrical conductivity. This model also allows one to explain the malleability of metals, as shown in fig. 1b. When a metallic crystal is subject to forces that displace one plane of atoms with respect to another, the environment of the charged species is left unchanged. In contrast, the displacement of neighboring planes in an ionic crystal as a result of a distorting force will lead to cleavage, largely because of changes in the interaction of the charged species (Figure 8.2.1,).

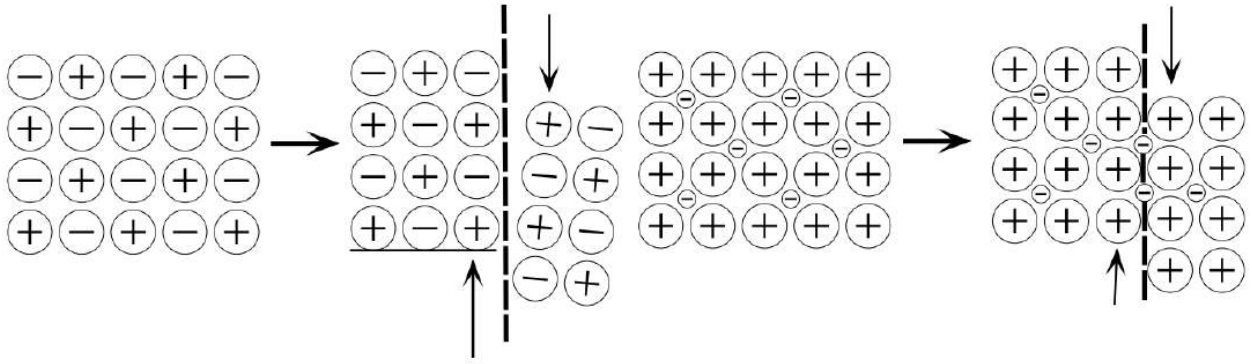


Figure 8.2.1: Mechanical properties of ionic and metallic crystals. (left) In ionic crystals the displacement of neighboring planes by shear forces frequently results in cleavage largely because of the establishment of repulsive forces in the cleavage plane. (right) In metallic crystals the displacement of neighboring planes does not lead to charge effects; slip is a common phenomenon; metals are malleable.

The **free electron gas theory or Drude–Lorentz (D-L) theory** also explains in principle the nature of the attractive bonding forces which hold the metallic ions (the metal) together: the crystal is held together by electrostatic forces of attraction between the positively charged metal ions and the non-localized, negatively charged electrons - the electron gas. The theory in its original form assumes that the classical kinetic theory of gases is applicable to the *electron gas* ; mutual repulsion between electrons was ignored and the electrons were expected to have velocities which are temperature dependent according to a Maxwell-Boltzmann distribution law.

While the Drude-Lorentz theory of metallic bonding was considered a useful model, several shortcomings soon became apparent. The most notable failure consisted of the unexplainable discrepancy between the observed and predicted specific heats of metals (energy in the form of heat, required to increase the temperature of $1\ g$ of a given metal by $1°C$). The D-L theory predicted much larger specific heats than are observed (because the Maxwell-Boltzmann energy distribution has no restrictions as to the number of species allowed to have exactly the same energy). [If there are restrictions as to the number of electrons with identical energy (Pauli exclusion principle!), we have to apply a different form of statistics (Fermi-Dirac statistics).]

ENERGY BAND THEORY BASED ON FORMATION OF MOLECULAR ORBITALS

A different model, and one that is more closely related to the models of the chemical bond discussed earlier, is the *band model*. This model, proposed by Bloch before the development of the molecular-orbital approach to chemical bonding, is actually a molecular-orbital model of metallic crystals. The orbitals characteristic of the whole crystal are obtained as linear combinations of the atomic orbitals of the individual atoms.

From the large electrical conductivity of metals, it appears that at least some of the electrons can move freely through the bulk of the metal. Since even lithium with only one valence electron has eight nearest neighbors (crystallizes in a body-centered cubic lattice), it is clear that the atoms can not be bonded to each other by localized electron-pair bonds (for in that case the lithium atom, which altogether has only three electrons, would have to supply eight or even fourteen valence electrons to establish bonding with

the nearest and next-to-nearest neighbor atoms). The fact that in a metal lattice one atom can simultaneously interact with a large number of others can be explained by considering that metals constitute an extreme example of *delocalized bonding*.

Conditions in metals are not as easily assessed as in organic hydrocarbon chains because metal lattices are three-dimensional structures. However, several important results from the theory of metallic bonding can be understood on a highly simplified model in which the three-dimensional lattice is replaced by a one-dimensional system. Consider the formation of a linear array of lithium atoms from individual lithium atoms:

$$\mathbf{Li} \rightarrow \mathbf{Li-Li} \rightarrow \mathbf{Li-Li-Li} \rightarrow \mathbf{Li-Li-Li-Li} \rightarrow \ldots \tag{8.2.1}$$

The first stage is the formation of a lithium molecule, $\mathbf{Li_2}$, which is comparable to the hydrogen molecule, $\mathbf{H_2}$. The two lithium atoms are bound together by a pair of valence electrons; each lithium atom supplies its 2s-electron which, through orbital overlap, forms a covalent molecular bond (fig. 2). The molecule formed occurs in lithium vapor and differs from the $\mathbf{H_2}$ molecule only by its greater interatomic distance ($\mathbf{Li-Li} = 2.67 \times 10^{-10}\ \mathbf{m}, \mathbf{H-H} = 0.75 \times 10^{-10}\ \mathbf{m}$) and smaller energy of formation. The larger separation and the consequent reduction in bond energy can be attributed to the size of the $\mathbf{Li^+}$ atomic core.

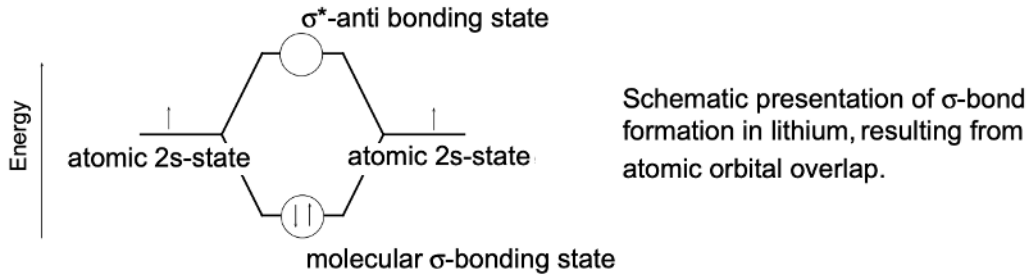


Figure 2 Formation of $\mathbf{Li_2}$ molecule

In the determination of molecular orbital states by **linear combination of atomic orbitals** (LCAO) we obtain more than one solution from the Schrödinger equation. We have so far concentrated mostly on the low energy states, leading to σ or π bonds. We have largely ignored the so-called *antibonding states* which in covalent molecules have energies higher than the original energy states of the isolated reaction partners (presently Li) and, therefore, remain unoccupied (or empty) in two-atomic molecules. In any multi-atom system (such as a piece of metal), the total number of molecular orbital states (electronic states) is always the same as the total number of original atomic states (conservation of electronic states). However, not all of these states are necessarily occupied by electrons.

Consider the hypothetical linear molecule $\mathbf{Li_3}$. Since the valence electron cloud is spherical, the central lithium atom can not give preference to either of its neighbors. The three atomic valence electron clouds overlap to form one continuous distribution and two others with nodes (antibonding states), i.e., three molecular orbitals in all (Fig. 3).

As the length of the chain is increased, the number of electronic states into which the atomic $\mathbf{2}s$ state splits also increases, *the number of states always equaling the number of atoms*. The same occurs when lithium chains are placed side-by-side or stacked on top of each other, so that finally the space lattice of the lithium crystal is obtained. It is of great significance that these electronic states have energies which are bounded by an upper and lower limiting value (see fig. 4). Within these limits the states form an *energy band* of closely spaced values (one gram of lithium contains nearly $\mathbf{10^{23}}$ atoms). Similarly, energy bands can also result from overlapping p and d orbitals. The electronic states (orbitals) within an energy band are filled progressively by pairs of electrons in the same way that the orbitals of an atom were filled in accordance with the Pauli principle. This means that for lithium the electronic states of the 2s band will be exactly half-filled.

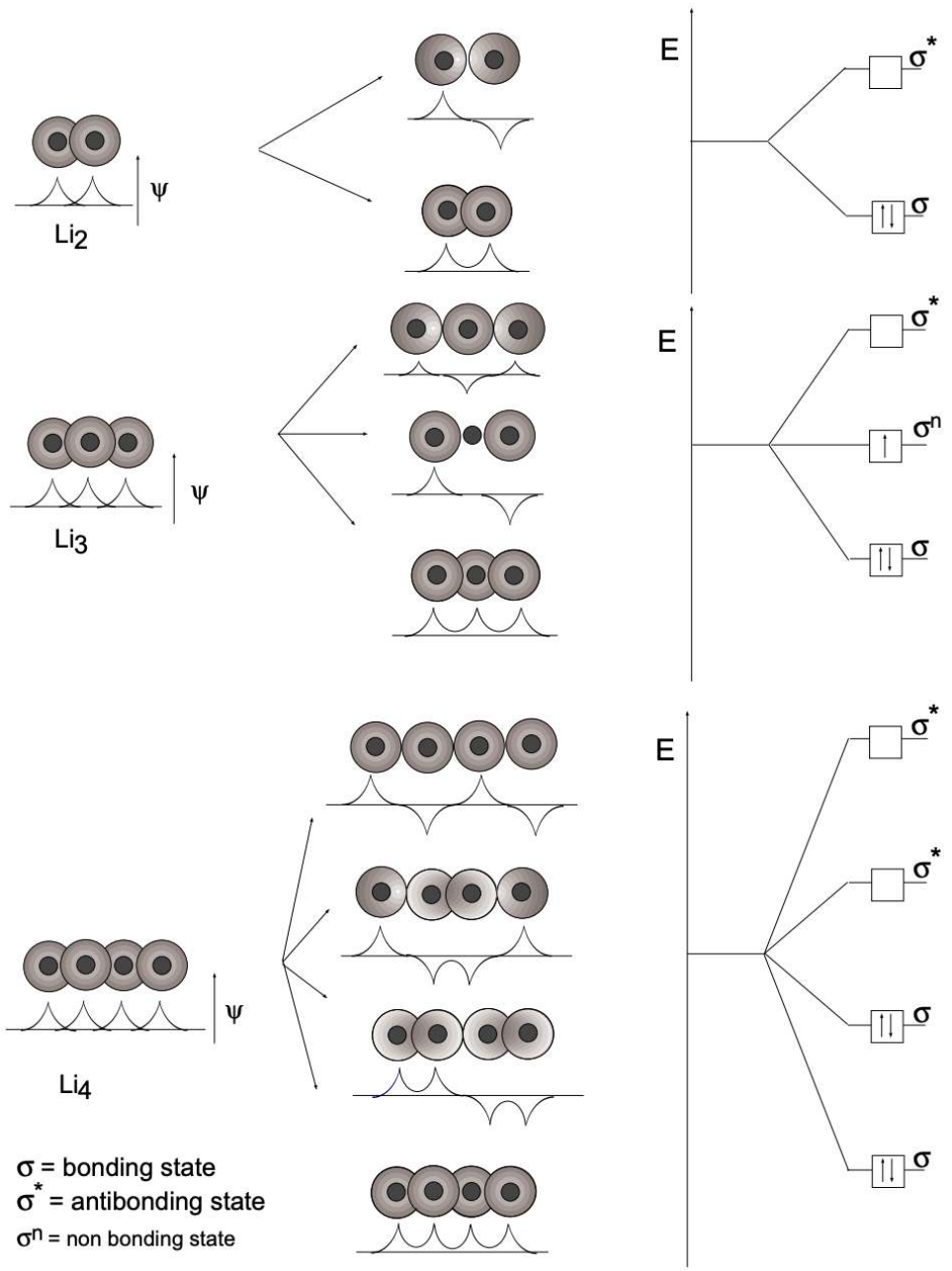


Figure 3 Formation of molecular chains of lithium atoms.

It is of interest to consider why lithium atoms or $\mathbf{Li_2}$ molecules combine to form a metal lattice. In the lithium lattice the smallest distance between neighboring atoms is $\mathbf{3.03 \times 10^{-10}\ m}$, which is larger than in the $\mathbf{Li_2}$ molecule. This reflects the fact that bonds between pairs of atoms in the metal are weaker than they are in the molecule. Nevertheless, the metallic form of lithium is more stable than the molecular form because in the metal one atom has many more neighbors than in the $\mathbf{Li_2}$ molecule. As a result, the binding energy per gram atom of lithium (i.e., per $\mathbf{6.92\ g}$ of lithium) is $\mathbf{163\ kJ}$ for the metal lattice, but only $\mathbf{56\ kJ}$ for one mole of molecule.

> The possibility of hybridization (first advanced by L. Pauling to explain metallic bonding) is also a likely factor for the formation of metallic bonds. Thus strong bonds can be formed when the valence electron clouds become concentrated along the direction in which the bonding partners are situated. According to Pauling the situation can be described by *mesomeric* limiting formulae, just as in the theory of unsaturated carbon compounds. One reason given for hydrogen not forming a metal is its inability to hybridize.

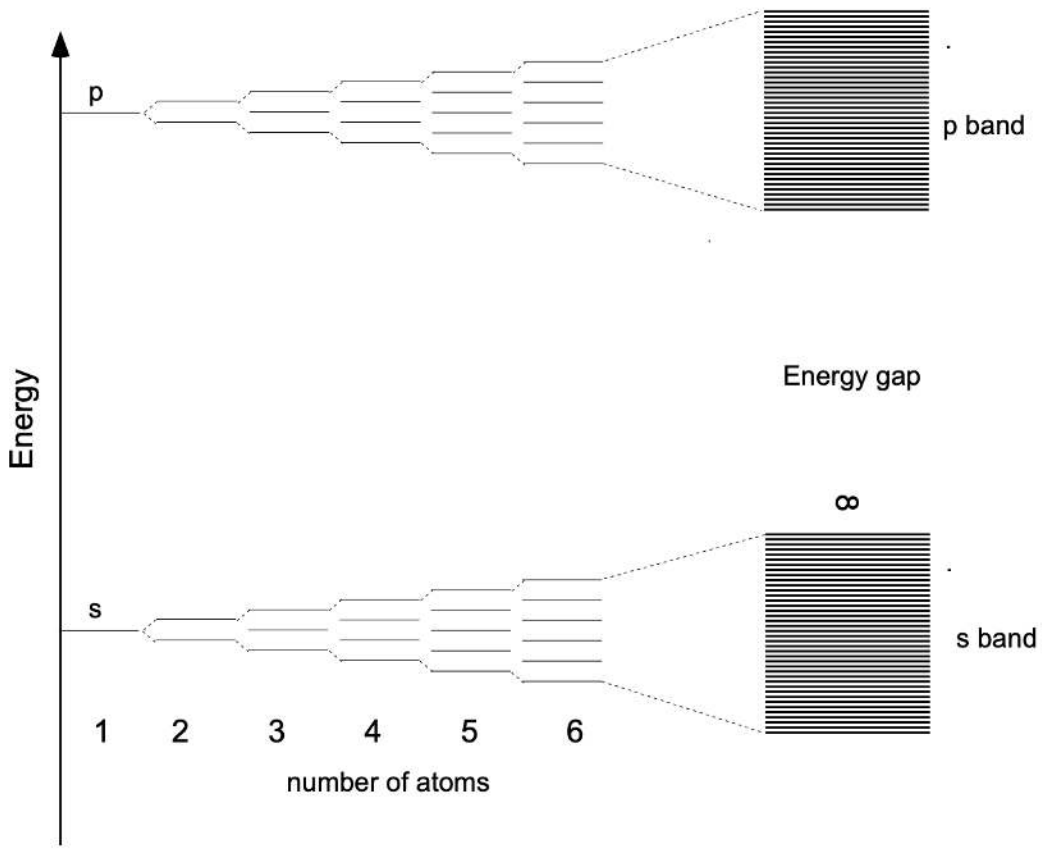


Figure 4 Formation of energy bands from energy levels of constituent atoms

The appearance of bands of allowed electron energies relates to the overlap of electron ψ functions. The width of each energy band is a function of the crystal structure because it determines the number of nearest neighbors in the crystal. Different metal atoms with the same valence, particularly elements in the same group of the periodic table, can often replace each other in arbitrary proportions without altering either the lattice type or the structure of the energy bands. This explains why such metals tend to form a complete series of *solid solutions.* Metallic alloys consist of such solid solutions or of heterogeneous mixtures of such solutions. Within certain limits, even metal atoms of different valence can be interchanged in a lattice.

Structure of Metals

According to the above considerations the band structure of Li metal can be represented as shown in fig. 5. According to previous reasoning, the $2\,s$ band has N states ($N =$ number of atoms) and accommodates $n2s$ electrons (where n is the number of electrons per atom in the $2\,s$ state times N). Thus, this band has only half of the states filled since each state can accommodate two electrons of opposite spin (Pauli exclusion principle). In accordance with the Aufbau principle, the lowest energy states of the band are filled first and the upper states remain empty - but can readily be occupied by electrons upon thermal excitation or the application of an electric field. Since the width of the energy band is of the order of a few volts, spacings of states within the band are of the order of $\sim 10^{-20}\text{eV}\,(1\text{eV} = 1.6 \times 10^{-19}\ \text{J})$, electrons can readily acquire the energy necessary to move into excited states, be accelerated, and move through the metal as *conducting electrons*. Partly filled bands thus constitute *conduction bands*.

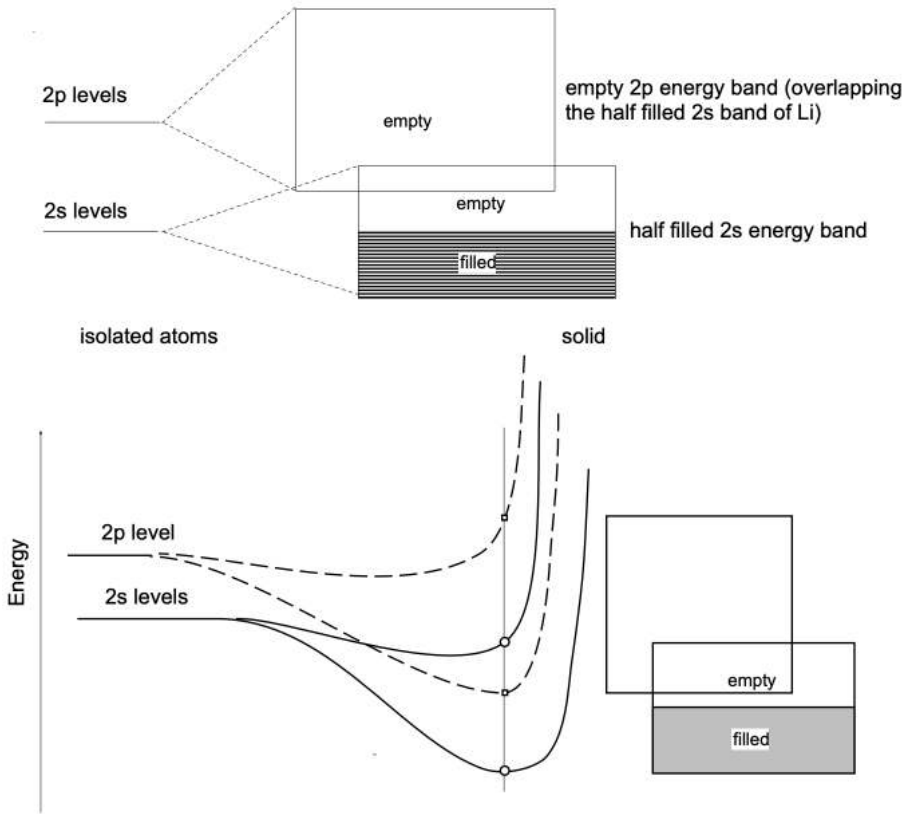


Fig. 5 Schematic energy band configuration for Li .

The conduction mechanism in Mg, for example, appears complicated by the fact that each $3s$ state of the valence shell in the atoms is doubly occupied ($3s^2$). Thus the $3s$ band must be filled completely and no electronic conduction would in principle be expected. Electronic conduction, however, is observed because of a partial overlap of the $3s$ and the empty $3p$ bands. With this overlap, electrons can be activated into empty $3p$ states and exhibit conduction, as in the partly filled s band in Li.

Structure of Insulators and Semiconductors (Molecular Crystals)

The same band model can also account for the lack of conductivity in covalent crystals, such as diamond. In the diamond crystal, with a two-electron bond between every atom and each of its neighbors, the bonding molecular orbitals form a band at much lower energies than the energy of the atomic sp^3 hybrid orbitals, and the antibonding orbitals form a band at energies much higher than the energy of the atomic orbitals. Also, since each atom contributes four orbitals and four electrons, there are just enough electrons to fill the bonding orbitals (corresponding to an electron pair bond joining every atom to each of its neighbors) and the only vacant orbitals are those in the high energy band of antibonding orbitals (see fig. 6).

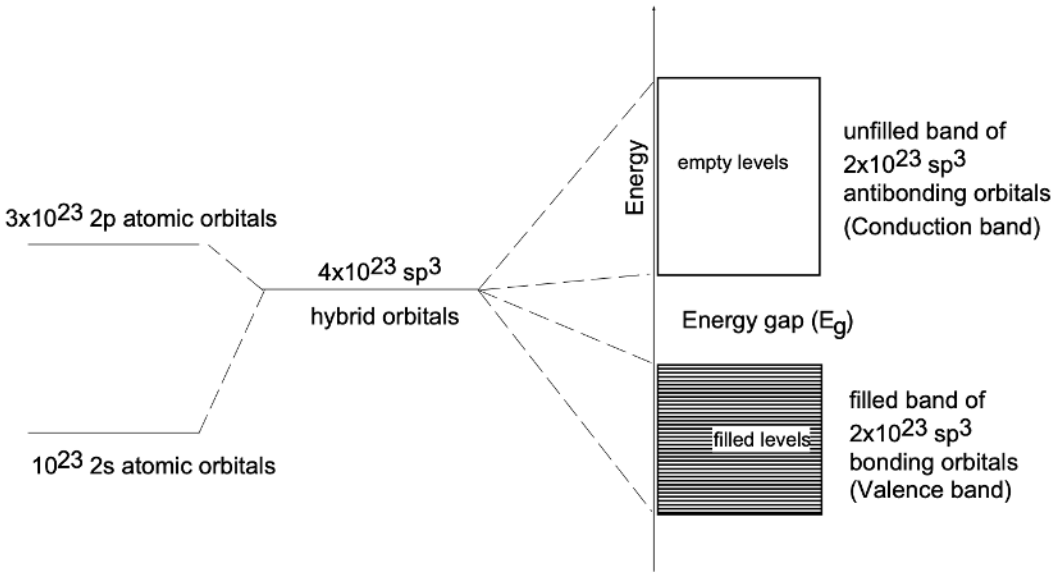


Fig. 6 Band structure of insulators and semiconductors (molecular crystals); the conditions depicted reflect a molar crystal of carbon (diamond).

Both insulators and semiconductors have the same basic band structure – the primary difference is the *width* of the forbidden energy gap ($\mathbf{E_g}$) between the valence and the conduction band.

Insulators, generically, are materials with very high resistivity (see Table I), comprising glasses, polymers, refractories, composites, liquids and gases. In the present context, an insulator is a molecular crystal, such as diamond (C) or sapphire, with a band gap ($\boldsymbol{E_g}$) in excess of $\mathbf{4eV}$ (arbitrary value). Generally such materials will not conduct electricity since their valence band is filled and the energy required to transfer electrons from the valence band to the empty conduction band is far in excess of both the thermal energies at room temperature and the energy provided by radiation of the visible spectrum ($\mathbf{2eV}$). Therefore, insulators (in single crystal form) are normally transparent (colorless); however, if light is excessively or totally scattered at internal heterogeneities (such as grain boundaries), they may be translucent and even opaque. It should also be recognized that impurities ($\mathbf{Cr^{3+}}$ in $\mathbf{Al_2O_3}$) or particular point defects (color centers) may impart a color to the transparent insulator crystals. The color arises because of partial absorption of white light and selective transmission of the other portions of the visible spectrum.

Semiconductors: The conventional semiconductors, silicon (Si) and germanium (Ge), have a band gap ($\mathbf{E_g}$) of $\mathbf{1.1}$ and $\mathbf{0.7eV}$ respectively and therefore absorb visible radiation; they are opaque (fig. 7). Considering the statistical nature of the thermal energy distribution in the solid matrix (Maxwell-Boltzmann), a significant number of electrons in the valence band will, at room temperature, acquire sufficient energy to cross the existing energy gap and thus provide for *semiconductivity*. The conductivity will therefore increase with temperature, contrary to metallic systems, until electron scattering effects, due to increased lattice vibrations (which decrease the mobility of electrons), begin to dominate.

The value of semiconductors for solid state device fabrication lies in the fact that the number and type of conducting electric charge carriers [electrons are $\boldsymbol{n}$-type (negative), holes are p-type (positive)] can be controlled through incorporation of appropriate *dopant elements*. Thus the substitutional incorporation of Group V elements (Sb, As, P) provides for shallow donor levels in the band gap at about $\mathbf{0.01eV}$ from the conduction band. The substitutional incorporation of Group III elements (B, Al) generates *acceptor levels* in the band gap at about $\mathbf{0.01eV}$ from the valence band. The two types of impurities are almost completely ionized at room temperature and give rise to *extrinsic* n-type and p-type conductivity – the basis for the formation of *junction devices* such as diodes and transistors (fig. 8).

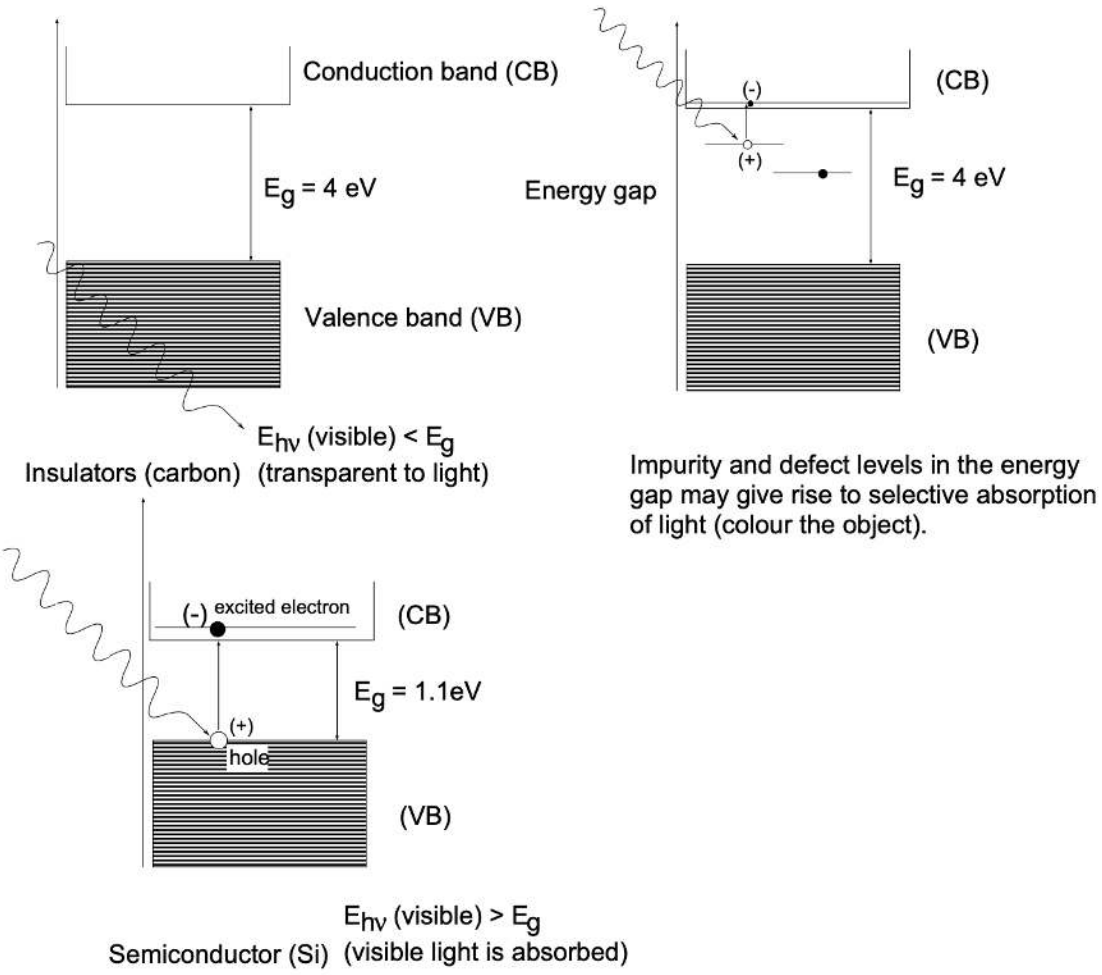


Fig. 7 Optical behavior of insulators and semiconductors

Of increasing importance are compound *III-V (adamantine) semiconductors*, such as GaAs, InSb, InP and GaP (compounds of Group III and Group V elements). Together these compounds provide eight valence electrons and, by sp^3 hybridization, are able to form a diamond-like, covalent crystal structure with semiconductor properties. These

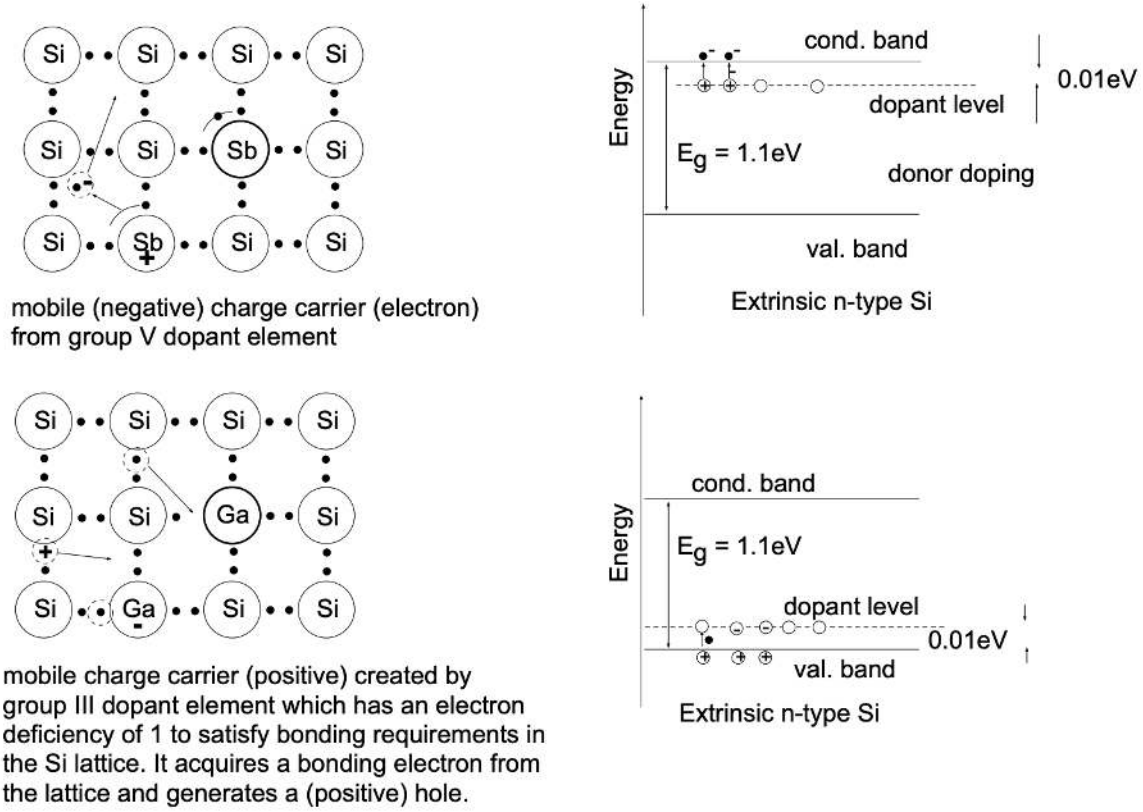


Fig. 8 Extrinsic p- and n-type semiconductors.

compounds (GaAs, for example) exhibit electron mobilities which are higher than those of silicon and, therefore, are of considerable interest for advanced device technology.

Table I. ELECTRICAL RESISTIVITIES OF METALS AND NONMETALS AT 20°C*

Metals	Resistivity, 10^{-8} ohm–m**	Nonmetals	Resistivity, ohm–m**
Silver	1.6	Semiconductors	
Copper	1.67	Silicon	1000.0
Gold	2.3	Germanium	0.09
Aluminum	2.69	Insulators	
Magnesium	4.4	Diamond	10^{10}–10^{11}
Sodium	4.61	Quartz	1.2×10^{12}
Tungsten	5.5	Ebonite	2×10^{13}
Zinc	5.92	Sulfur	4×10^{13}
Cobalt	6.24	Mica	9×10^{13}
Nickel	6.84	Selenium	2×10^{14}
Cadmium	7.4	Paraffin wax	3×10^{16}
Iron	9.71		
Tin	12.8		
Lead	20.6		
Uranium	29		
Zirconium	41		
Manganin	44		
Titanium	55		
Lanthanum	59		
96%Iron–4%Si	62		
Cerium	78		
Nichrome	100		

*From *American Institute of Physics Handbook*, Dwight E. Gray, ed. McGraw-Hill, New York (1963), pp. 4–90; 9–38.

**Note the different units in the two columns

APPENDIX

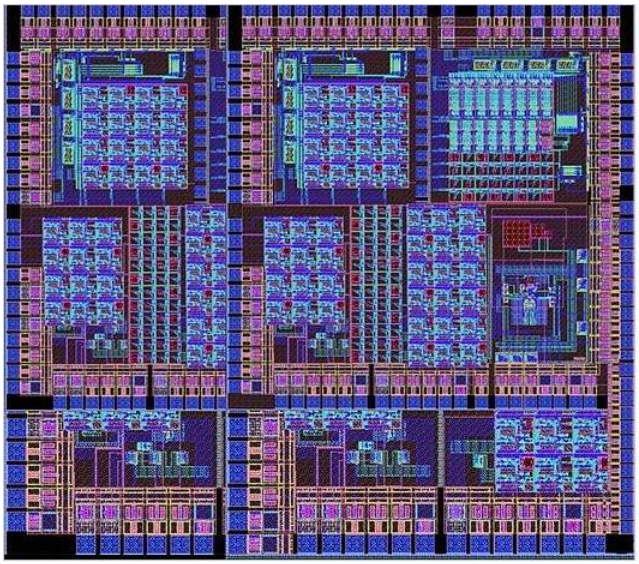
Approximate Energy Values for Some Events and Reactions

Solar Energy Emission	$\sim 10^{30}$ kJ/ day
Convertible Solar Energy on Earth	$\sim 10^{18}$ kJ/ year
Energy Consumption on Earth	$\sim 8 \times 10^{17}$ kJ/ year
Super-Nova Explosion	$\sim 10^{39}$ kJ
100 Mega-Ton H-Bomb Explosion	$\sim 10^{15}$ kJ
Atlas Blast-Off	$\sim 10^{8}$ kJ
Lethal X-Ray Dose	~ 1 kJ
25¢ Piece Falling from Pocket	$\sim 10^{-4}$ kJ
Bee's Wing Beat	$\sim 10^{-6}$ kJ
Moonlight/Face/Second	$\sim 10^{-8}$ kJ

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8.2.1: Prelude to Electronic Properties of Materials - Superconductors and Semiconductors

In Chapter 6 we developed an energy band picture for metals, starting from atomic orbitals and building up the molecular orbitals of the solid metallic crystal. This treatment gave us a useful picture of how electrons behave in metals, moving at very fast speed between scattering events, and migrating in an electric field at a slow drift velocity. It also taught us that a metal is something with a partially filled band, meaning that the Fermi level cuts through one of its bands of orbitals. An insulator or a semiconductor has a similar band picture, except that the bands are either completely full or completely empty. In this case the Fermi level lies in the gap between fully occupied and unoccupied bands. We will see in this chapter that the properties of semiconductors (along with their useful electronic applications) depend on the addition of small amounts of impurities ("dopants") that change the position of the Fermi level, resulting in conduction by electrons or "holes."



Modern integrated circuits contain billions of nanoscale transistors and diodes that are essential for logic and memory functions. Both kinds of devices rely on junctions between crystalline silicon regions that contain a few parts per million of boron or phosphorus impurities.

While the band picture works well for most crystalline materials, it does not tell us the whole story of conduction in solids. That is because the band model (like MO theory) is based on a *one-electron* model. This was an approximation we made at the very beginning of our discussion of MO theory: we used hydrogen-like (one-electron) solutions to the Schrödinger equation to give us the shapes of s, p, d, and f atomic orbitals. In a one-electron atom, these orbitals are degenerate within a given shell, and the energy differences between, e.g., 2s and 2p orbitals arise only when we consider the energy of an electron in the field of other electrons in the atom. Moving from atoms to molecules, we made linear combinations to generate one-electron molecular orbitals (and, in solids, one-electron energy bands). But as in multi-electron atoms, life is not so simple for real molecules and solids that contain many electrons. Electrons repel each other and so their movement in molecules and in solids is ***correlated***. While this effect is weak in a "good" metal such as sodium - where the wavefunctions are highly delocalized - it can be quite important in other materials such as transition metal oxides. Correlated electron effects give rise to **metal-insulator transitions** that are driven by small changes in temperature, pressure, or composition, as well as to **superconductivity** - the passage of current with zero resistance at low temperatures. In this chapter we will develop some simple models to understand these interesting and important electronic properties of solids.

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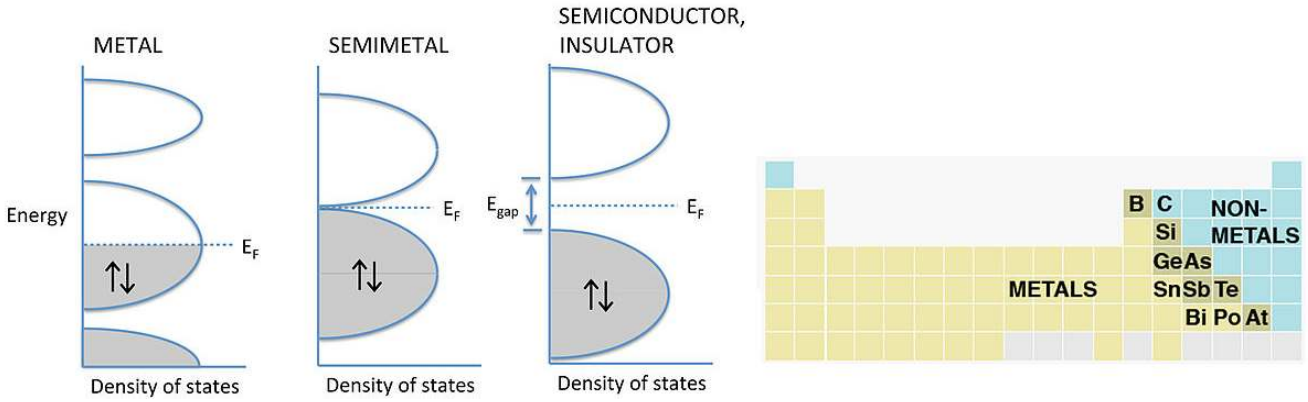
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8.2.2: Periodic Trends- Metals, Semiconductors, and Insulators

As we consider periodic trends in the electronic properties of materials, it is important to review some of the key bonding trends we have learned in earlier chapters:

- Going down the periodic table, atoms in solids tend to adopt structures with higher coordination numbers.
- The second row of the periodic table is special, with strong s-p hybridization and π-bonding between atoms.
- Electrons in higher quantum shells are less strongly bound, so the energy difference between bonding and antibonding orbitals becomes smaller for heavier atoms.

We also know that most of the elements in the periodic table are metals, but the elements in the top right corner are insulating under ordinary conditions (1 atm. pressure) and tend to obey the octet rule in their compounds.



At the transition between metals and non-metals in the periodic table we encounter a crossover in electronic properties, as well as in other properties such as the acidity of the oxides (see Ch. 3). The group of elements at the border is loosely referred to as the metalloids. Several of these elements (such as C, Sn, and As) can exist as different allotropes that can be metals, insulators, or something in between.

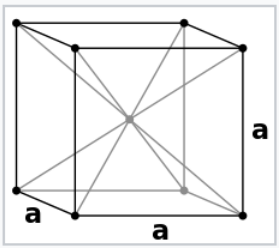
A more rigorous delineation of the electronic properties of these elements (and of many compounds) can be made by considering their band structures and the **temperature dependence of the electronic conductivity**. As we have previously discussed, metals have partially filled energy bands, meaning that the Fermi level intersects a partially filled band. With increasing temperature, metals become poorer conductors because lattice vibrations (which are called phonons in the physics literature) scatter the mobile valence electrons. In contrast, semiconductors and insulators, which have filled and empty bands, become better conductors at higher temperature, since some electrons are thermally excited to the lowest empty band. The distinction between insulators and semiconductors is arbitrary, and from the point of view of metal-insulator transitions, all semiconductors are insulators. We typically call an insulator a semiconductor if its band gap (E_{gap}) is less than about 3 eV. A semimetal is a material that has a band gap near zero, examples being single sheets of sp^2-bonded carbon (graphene) and elemental Bi. Like a narrow gap semiconductor, a semimetal has higher conductivity at higher temperature.

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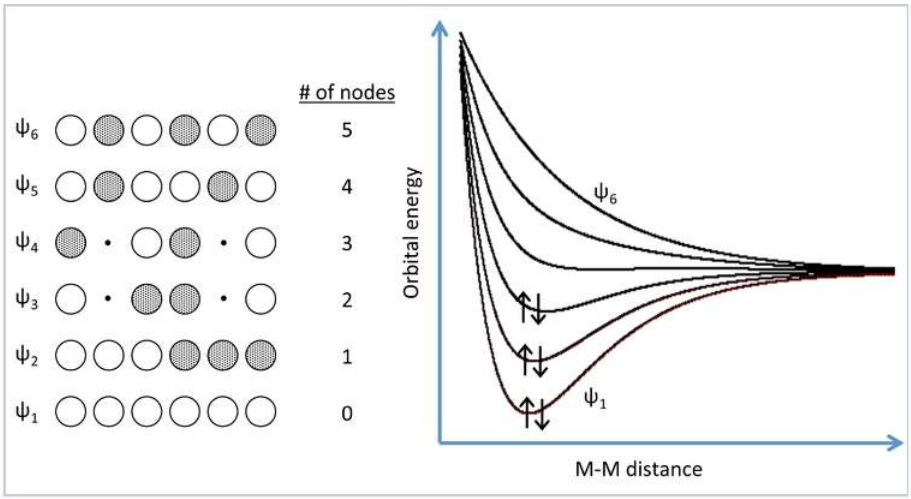
8.2.3: Bonding in Metals

The electron pair description of chemical bonds, which was the basis of the octet rule for p-block compounds, breaks down for metals. This is illustrated well by Na metal, the structure of which is shown at the left. Na has too few valence electrons to make electron pair bonds between each pair of atoms. We could think of the Na unit cell as having eight no-bond resonance structures in which only one Na-Na bond per cell contains a pair of electrons.



Sodium metal crystallizes in the body-centered cubic structure, in which each atom has eight nearest neighbors. Since the electronic configuration of Na is $[Ar]3s^1$, there are only two valence electrons per unit cell that are shared among eight Na-Na bonds. This means that the Na-Na bond order is 1/8 in Na metal.

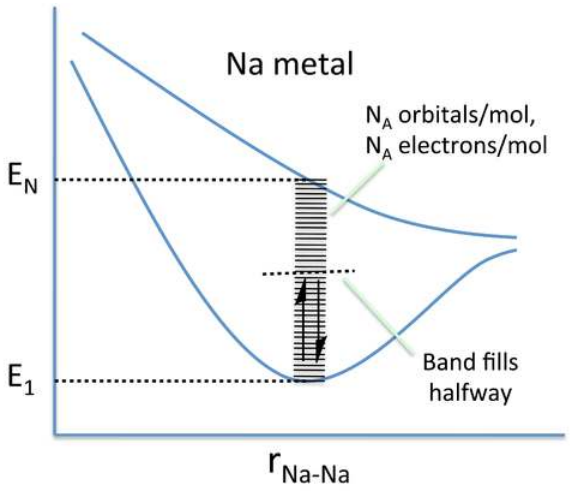
A more realistic way to describe the bonding in metals is through **band theory**. The evolution of energy bands in solids from simple MO theory (Chapter 2) is illustrated at the right for a chain of six Na atoms, each of which has one 3s valence orbital and contributes one valence electron. In general, **n** atomic orbitals (in this case the six Na 3s orbitals) will generate **n** molecular orbitals with **n-1** possible nodes. In Chapter 2, we showed that the energy versus internuclear distance graph for a two hydrogen atom system has a low energy level and a high energy level corresponding to the bonding and antibonding molecular orbitals, respectively. These two energy levels were well separated from each other, and the two electrons in H_2 energetically prefer the lower energy level. If more atoms are introduced to the system, there will be a number of additional levels between the lowest and highest energy levels.



MO picture for a linear chain of six Na atoms. Three of the six MOs can accommodate all six valence electrons. Adding more atoms to the chain makes more molecular orbitals of intermediate energy, which eventually merge into a continuous band of orbitals. For Na, the 3s band is always half-filled because each MO can accommodate two electrons.

In band theory, the atom chain is extrapolated to a very large number - on the order of 10^{22} atoms in a crystal - so that the different combinations of bonding and anti-bonding orbitals create "bands" of possible energy states for the metal. In the language of physics, this approach of building the bands from discrete atomic orbitals is called the "tight-binding" approximation. The number of atoms is so large that the energies can be thought of as a continuum rather than a series of distinct levels. A metal will only

partially fill this band, as there are fewer valence electrons than there are energy states to fill. In the case of Na metal, this results in a half-filled 3s band.



Nearly free electron model

In metals, the valence electrons are delocalized over many atoms. The total energy of each electron is given by the sum of its kinetic and potential energy:

$$E = KE + PE$$
$$E \approx p^2/2m + V$$

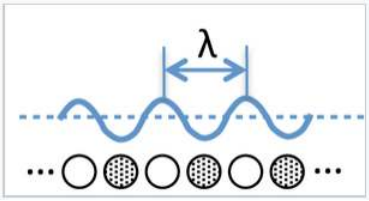
where **p** is the momentum of the electron (a vector quantity), m is its mass, and V is an average potential that the electron feels from the positive cores of the atoms. This potential holds the valence electrons in the crystal but, in the free electron model, is essentially uniform across the crystal.

Electron wavelength and wavenumber

What are the consequences of this model for band theory? For a hypothetical infinite chain (i.e., a 1D crystal) of Na atoms, the molecular orbitals at the bottom of the 3s band are fully bonding and the *wavelength* of electrons (2x the distance between nodes) in these orbitals is very long. At the top of the band, the highest orbital is fully antibonding and the wavelength is 2 times the distance between atoms (2a), since there is one node per atom. Remember that the **wavelength of an electron (λ)** is inversely proportional to its momentum p, according to the de Broglie relation **λ = h/p**.

For a (nearly) free electron, the kinetic energy can be expressed in terms of its wavelength, using $KE = p^2/2m$ and the de Broglie relation:

$$KE = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2} \tag{8.2.3.1}$$



We can think of the wavelength of an electron in a molecular orbital as twice the distance between nodes. If there are N atoms in a linear chain, the wavelength of the nth orbital is given by λ = 2Na/n, where a is the distance between atoms.

At this point, it is convenient to define the **wavenumber** of the electron as **k**, which has units of inverse length and is inversely proportional to λ. **k** is also directly proportional to the momentum **p**. Like **p**, **k** is a vector quantity. In a 1D crystal, **k** can be either

positive or negative, corresponding to an electron moving to the left or right along the chain.

$$k = \frac{2\pi}{\lambda} = \frac{2\pi p}{h} \text{ where h is Planck's constant} \tag{8.2.3.2}$$

The most important property of **k** is that it is *directly proportional to the number of nodes* **n** in a molecular orbital within the band. For a 1D crystal of sodium atoms that contains **N** unit cells, each separated by a distance a, a molecular orbital with n nodes has a wavelength λ = 2Na/n and the wavenumber k = πn/Na. We can see from this definition that k = 0 at the bottom of the band (where λ is infinite) and k = π/a at the top of the band where the MO contains **N** nodes and λ = 2a.

Energies of orbitals in a metallic crystal

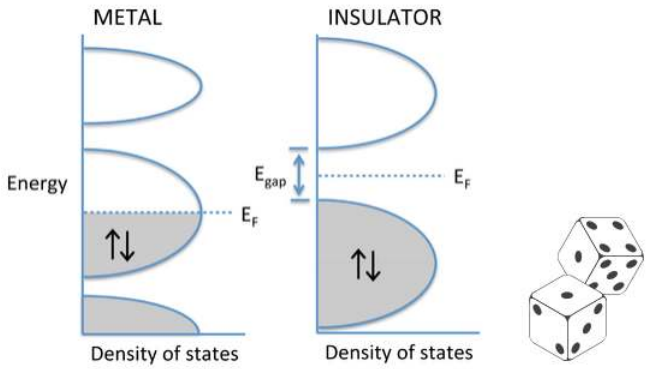
Electrons with long wavelengths do not "feel" the individual atoms in the lattice and so they behave as if they are *nearly free* (but confined to the crystal). Near the bottom of the band, the electron energy increases *parabolically* with the number of nodes (KE $\propto$ $\mathbf{n}^2$), since the momentum **p** is directly proportional to **n**. Because **p** is also directly proportional to **k**, we can write:

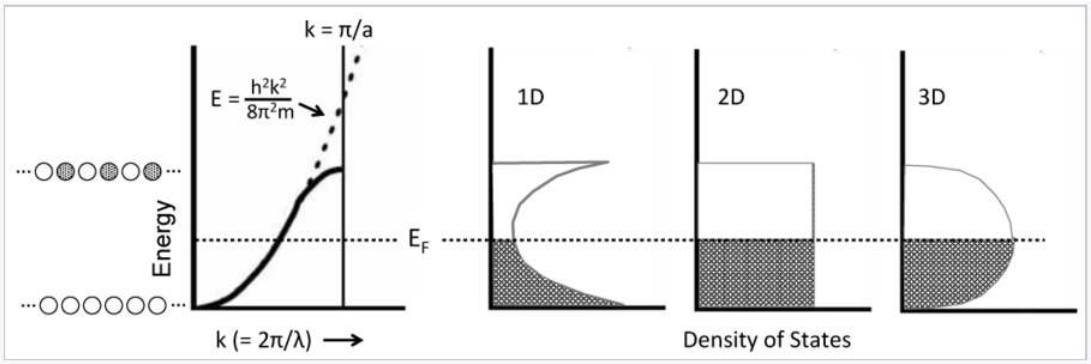
$$KE = \frac{p^2}{2m} = \frac{h^2k^2}{8\pi^2 m} \tag{8.2.3.3}$$

This parabolic relationship is followed as long as the electron wavelength is long compared to the distance between atoms. Near the top of the band, the wavelength becomes shorter and the electrons start to feel the positively charged atomic cores. In particular, the electrons prefer to have the maxima in their wavefunctions line up with the atomic cores, which is the most electrostatically favorable situation. The electron-atom attraction lowers the energy and causes the E vs. k curve to deviate from the parabolic behavior of a "free" electron as shown in the figure below.

Density of States (DOS)

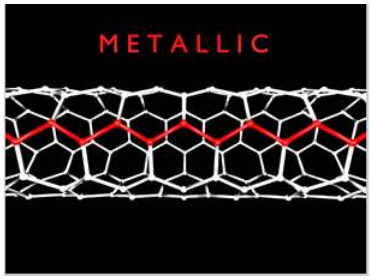
The density of states is defined as the number of orbitals per unit of energy within a band. Because of the parabolic relation between E and k, the density of states for a 1D metallic crystal is highest near the bottom and top of the energy band where the slope of the E vs. k curve is closest to zero. The shape of the DOS curve is different in crystals of higher dimensionality as shown in the figure in the left, because statistically there are more ways to make an orbital with N/2 nodes than there are with zero or N nodes. The situtation is analogous to the numbers you can make by rolling dice. With one die, the numbers 1-6 have equal probability. However, with two dice there is only one way to make a two (snake eyes) or a twelve (boxcars), but many ways to make a seven (a winner!).





Electrons in metals follow a parabolic dispersion curve, where the energy increases with the square of the wavenumber, k. Near the top of the band, the dispersion curve deviates from the parabolic dotted line. Because there is one MO for each value of k, the number of orbitals per unit energy (the density of states, DOS) is highest at the bottom and top of the band for a 1D chain of atoms. The density of states is constant with energy for a 2D crystal, and has a maximum in the middle of the band for a 3D crystal. At low temperature, all the MOs below the Fermi level E_F are occupied, and all the MOs above it are empty.

While most of the time we will talk about 3D crystals that have their maximum DOS near the middle of the energy band, there are examples of quasi-1D systems, such as carbon nanotubes. Metallic carbon nanotubes have strong optical absorption bands that correspond to transitions between the two regions of high DOS (the van Hove singularities) near the bottom and top of the bands.



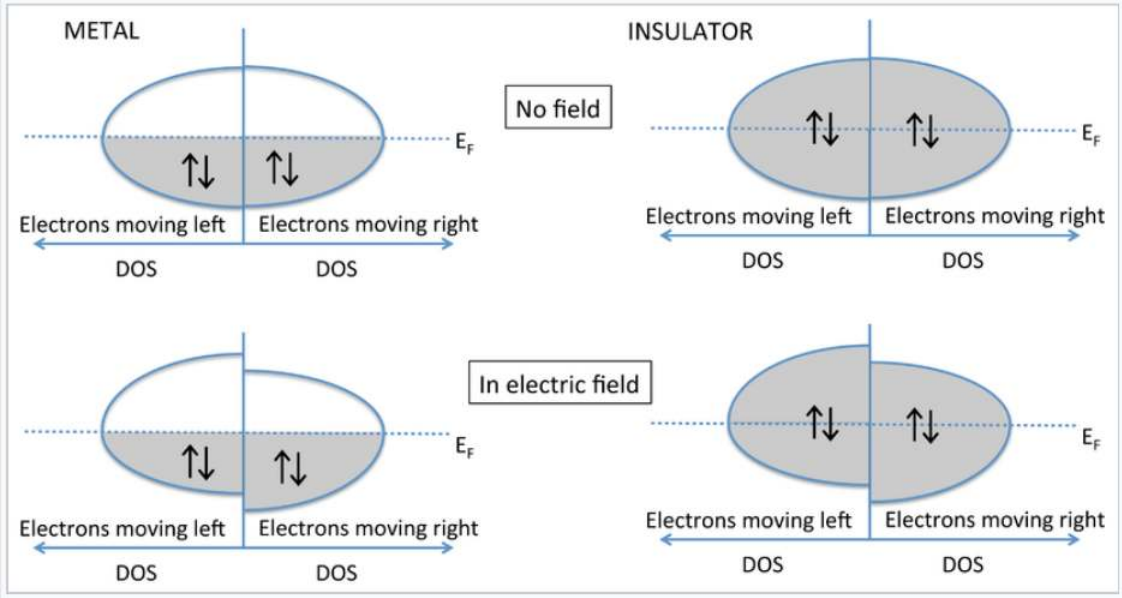
Single-walled carbon nanotubes with "armchair" chirality are metallic and have characteristic sharp absorption bands in the infrared. Prof. Millie Dresselhaus (below) did foundational research on the electronic properties of carbon nanotubes and other low-dimensional conductors.



Metals, semiconductors, and insulators

The degree to which bands fill determines whether a crystalline solid is a metal, semiconductor, or insulator. If the highest occupied molecular orbitals lie within a band - i.e., if the Fermi level E_F cuts through a band of orbitals - then the electrons are free to change their speed and direction in an electric field and the solid is metallic. However, if the solid contains just enough electrons to completely fill a band, and the next highest set of molecular orbitals is empty, then it is a semiconductor or insulator. In this case, there is an energy gap between the filled and empty bands, which are called the valence and conduction bands, respectively. Although the distinction is somewhat arbitrary, materials with a large gap (> 3 eV) are called insulators, and those with smaller gaps are called semiconductors. We will learn more about the properties of semiconductors in Chapter 10.

Why don't insulators conduct electricity? The energy vs. DOS diagram below shows what happens when an electric field is applied to a metal or an insulator. In this case we have changed the diagram to show explicitly the energies of electrons moving left and right. These energies are the same in the absence of an electric field. Once we apply a field (e.g., by putting a voltage across a metal wire), the electrons moving in the direction of the field have lower energy than those moving in the opposite direction. In the case of the metal, the populations of electrons moving with and against the electric field are different, and there is a net flow of current. Note that this can happen only when the Fermi level cuts through a partially filled band. With a semiconductor or insulator, the valence band is filled and the conduction band is empty. Applying an electric field changes the energies of electrons traveling with and against the field, but because the band is filled, the same number are going in both directions and there is no net current flow.



E vs. DOS diagrams comparing the behavior of metals and insulators in an applied electric field.

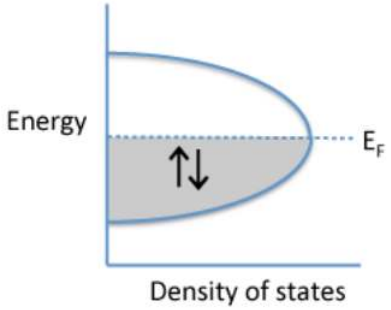
Note that in this picture, all the molecular orbitals extend over the entire crystal. The valence electrons are *delocalized,* even in the case of a semiconductor or insulator. However, there can be no net movement of electrons unless the band is partially filled.

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8.2.4: Conduction in Metals

In metals, the valence electrons are in molecular orbitals that extend over the entire crystal lattice. As we will learn in Chapter 7, metals are almost always crystalline and the individual crystal grains are typically micron size. This means that the spatial extent of the orbitals is *very large* compared to the size of the atoms or the unit cell. The diagram at the left shows a generic plot of electron energy vs. density of states for a metal such as Na, Cu, or Ag. In these cases, there are N orbitals for N electrons, and each orbital can accommodate two electrons. Therefore the Fermi level, which corresponds to the energy of the highest occupied MO at zero temperature, is somewhere in the middle of the band of orbitals. The energy level spacing between orbitals is very small compared to the thermal energy kT, so we can think of the orbitals as forming a continuous band.



Classically, if the electrons in this band were free to be thermally excited, we would expect them to have a specific heat of 3R per mole of electrons. However, experimentally we observe that C_p is only about 0.02 R per mole. This suggests that *only about 1%* of the electrons in the metal can be thermally excited at room temperature. However, essentially *all* of the valence electrons are free to move in the crystal and contribute to electrical conduction. To understand this apparent paradox, we need to recall that the electrons exist in *quantized energy levels.*

Because of quantization, electrons in metals have a Fermi-Dirac distribution of energies. In this distribution, most of the electrons are spin-paired, although the individual electrons in these pairs can be quite far apart since the orbitals extend over the entire crystal. A relatively small number of electrons at the top of the Fermi sea are unpaired by thermal excitation. This is the origin of the Pauli paramagnetism of metals.

How fast are electrons traveling in a typical metal? Because of the bell shape of the E vs. DOS curve, most of the electrons have $E \approx E_F$. At the midpoint energy (E_F) of the band, the MO's have one node for every two atoms. We can calculate the de Broglie wavelength as twice the distance between nodes and thus:

$\lambda = \mathbf{4a}$ at the midpoint of the band.

where **a** is the interatomic spacing. Since a typical value of **a** is about 2 Å, we obtain the **de Broglie wavelength λ ≈ 8 Å**.

Using the de Broglie relation p = h/λ, we can write:

$$\mathbf{p = \frac{h}{\lambda} = m_e v_F} \tag{8.2.4.1}$$

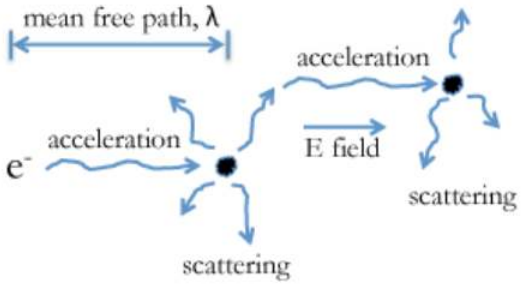
where $\mathbf{m_e}$ is the mass of the electron and $\mathbf{v_F}$ is the velocity of electrons with energy E_F.

Solving for $V_F = \frac{h}{m_e \lambda}$ we obtain $\mathbf{v_F = \frac{(6.62\times10^{-34} Js)}{(9.1\times10^{-31} kg)(8\times10^{-10} m)} = 1.0 \times 10^6 m/s}$

Experimental values of v_F are 1.07 x 10^6 and 1.39 x 10^6 m/s for Na and Ag, respectively, so our approximations are pretty good.

How fast are electrons moving in metals? Really, really fast!! **1,000,000 meters per second!** This is about 1/300 the speed of light, and about 3000 times the speed of sound in air (3 x 10^2 m/s).

However, the **drift velocity** of electrons in metals - the speed at which electrons move in applied electric field - is quite slow, on the order of 0.0001 m/s, or .01 cm/s. You can easily outrun an electron drifting in a metal, even if you have been drinking all night and have been personally reduced to a very slow crawl.



In order to understand the great disparity between the Fermi velocity and the drift velocity of electrons in metals, we need to consider a picture for the scattering of electrons, and their acceleration in an electric field, as shown at the left. If we apply a voltage across a metal (e.g., a metal wire), the electrons are subjected to an electric field **E**, which is the voltage divided by the length of the wire. This electric field exerts a force on the electron, causing it to accelerate. However, the electron is frequently scattered, mostly by phonons (lattice vibrations). Each time the electron is scattered its acceleration starts all over again. The time between scattering events is **τ** and the distance the electrons travel between scattering events is the **mean free path**, **λ**. (Note that this is NOT the same λ as the de Broglie wavelength, they just unfortunately have the same symbol!)

We can write the force on the electron as:

$$\mathbf{F = eE = m_e a = \frac{m_e v_{drift}}{\tau}} \tag{8.2.4.2}$$

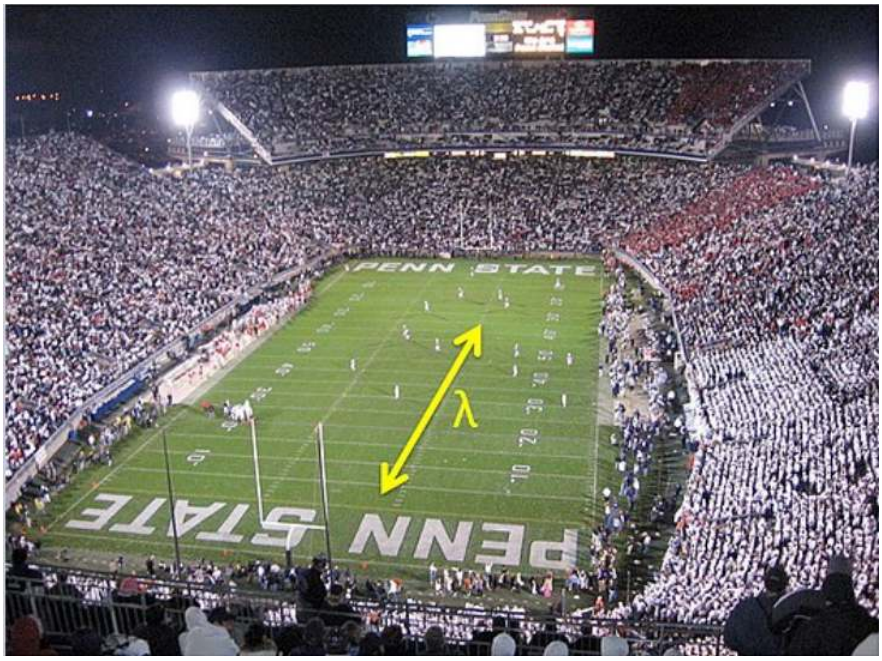
In this equation, **a** is the acceleration in the electric field, $\mathbf{m_e}$ is the mass, and v_{drift} is the **drift velocity** of the electron.

Experimentally, the mean free path is typically obtained by measuring the scattering time. For an electron in Cu metal at 300 K, the scattering time τ is about 2 x 10^{-14} s. From this we can calculate the mean free path as:

$$\lambda = \mathbf{v_{avg}}\tau \approx \mathbf{v_F}\tau = (1 \times 10^6 m/s)(2 \times 10^{-14}) = \mathbf{40nm} \tag{8.2.4.3}$$

The mean free path (40 nm = 400 Å) is quite long compared to the interatomic spacing (2 Å). To put it in perspective, if the interatomic spacing were scaled to the length of a football (0.3 m), the mean free path would be over half the length of the football field (60 m). Thus an electron travels a fairly long way between scattering events and scarcely notices the atomic structure of the metal in which it is traveling.

To summarize, electrons are traveling in metals at the Fermi velocity v_F, which is very, very fast (10^6 m/s), but the flux of electrons is the same in all directions. That is, they are *going nowhere fast*. In an electric field, a very small but directional *drift velocity* is superimposed on this fast random motion of valence electrons.



For ordinary metals, the mean free path of a valence electron (λ) is quite long relative to the interatomic spacing, represented in this analogy as the length of a football.

We can calculate the drift velocity of electrons as the acceleration in the electric field times the scattering time:

From F = ma, we obtain the acceleration (a) as:

$$\mathbf{a = \frac{F}{m_e} = \frac{eE}{m_e}} \tag{8.2.4.4}$$

And thus,

$$\mathbf{v_{drift} = a\tau = \frac{eE\tau}{m_e}} \tag{8.2.4.5}$$

If we divide both sides of this equation by the magnitude of the electric field (**E**), we obtain the **mobility (μ)**:

$$\mu = \frac{\mathbf{v_{drift}}}{\mathbf{E}} = \frac{e\tau}{\mathbf{m_e}} \tag{8.2.4.6}$$

μ has units of velocity/field = cm/s / V/cm = cm^2/Vs

An important consequence of the calculation of v_{drift} is **Ohm's Law**, V = iR. From the equations above, we can see that the drift velocity increases linearly with the applied electric field. The drift velocity (cm/s) is proportional to the current (i, coul/s), and the electric field (E, V/cm) is proportional to the voltage (V):

$$\mathbf{Current\ (i) = nev_{drift} \times area} \tag{8.2.4.7}$$

$$\mathbf{Voltage\ (V) = E \times length} \tag{8.2.4.8}$$

Here **n** is the density of valence electrons (#/cm^3) and **e** is the charge of the electron (coul). Combining these equations with our equation for v_{drift} we obtain:

$$V = i(\frac{m_e}{ne^2\tau})\frac{(}{length}area) = iR \tag{8.2.4.9}$$

Thus, V = iR, where R is the combination of the two terms in parentheses. The first of these is the **resistivity**, ρ, and the second is a geometrical factor.

The **conductivity (σ)** of a metal, which is the inverse of ρ, is proportional to μ, which in turn is proportional to τ (and λ):

$$\sigma = ne\mu = \frac{ne^2\tau}{m_e} \tag{8.2.4.10}$$

We can use this equation to work out the conductivity of a specific metal (Cu), for which n = 8.5 x 10^{22} cm^{-3} and τ = 2 x 10^{-14} s. Putting in the numbers for m_e and e, we obtain σ = 7 x 10^5 Ω^{-1} cm^{-1} for Cu, in good agreement with the measured value (6 x 10^5 $\Omega^{-1}cm^{-1}$).

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8.2.5: Superconductors

Superconductivity refers to the flow of electrical current in a material with zero resistance. Such materials are very important for use in electromagnets, e.g., in magnetic resonance imaging (MRI) and nuclear magnetic resonance (NMR) machines, because once the current starts flowing in the coils of these magnets it doesn't stop. Magnetic levitation using superconductors - which, below a critical field strength, are perfect diamagnets that are not penetrated by magnetic flux lines - is also potentially relevant to future technologies such as magnetically levitated trains.

The phenomenon of superconductivity, first discovered in Hg metal in 1911 by Onnes, continues to be only partially understood. It is of great interest to physicists as a macroscopic quantum phenomenon, and to chemists and materials scientists who try to make better superconductors (especially those that superconduct at higher temperatures) and devices derived from them, such as superconducting quantum interference devices (SQUIDs), which are extremely sensitive magnetometers.

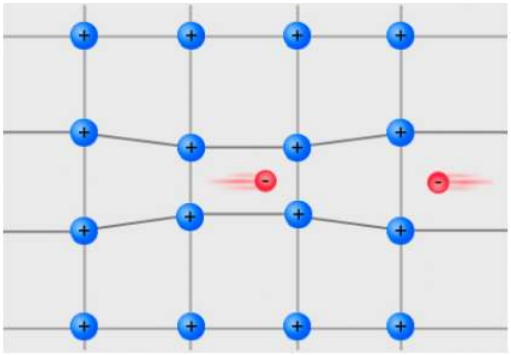


A magnet levitating above a high-temperature superconductor, cooled with liquid nitrogen. Persistent electric current flows on the surface of the superconductor, excluding the magnetic field of the magnet. This current effectively forms an electromagnet that repels the magnet.

Spin pairing and zero resistance

The transition from the metallic to the superconducting state is related to the quantum phenomena of Bose-Einstein condensation and superfluidity. Individual electrons have spin = 1/2, and as such are fermions (particles with half-integer spin). Because of the Pauli exclusion principle, no more than two fermions can occupy the same quantum state (such as an orbital in a molecule or a solid). The familiar consequence of this rule is the aufbau filling of orbitals with spin-paired electrons in each energy level. In contrast, particles with integer spins - which are called bosons - do not have this restriction, and any number of bosons can occupy the same quantized energy level.

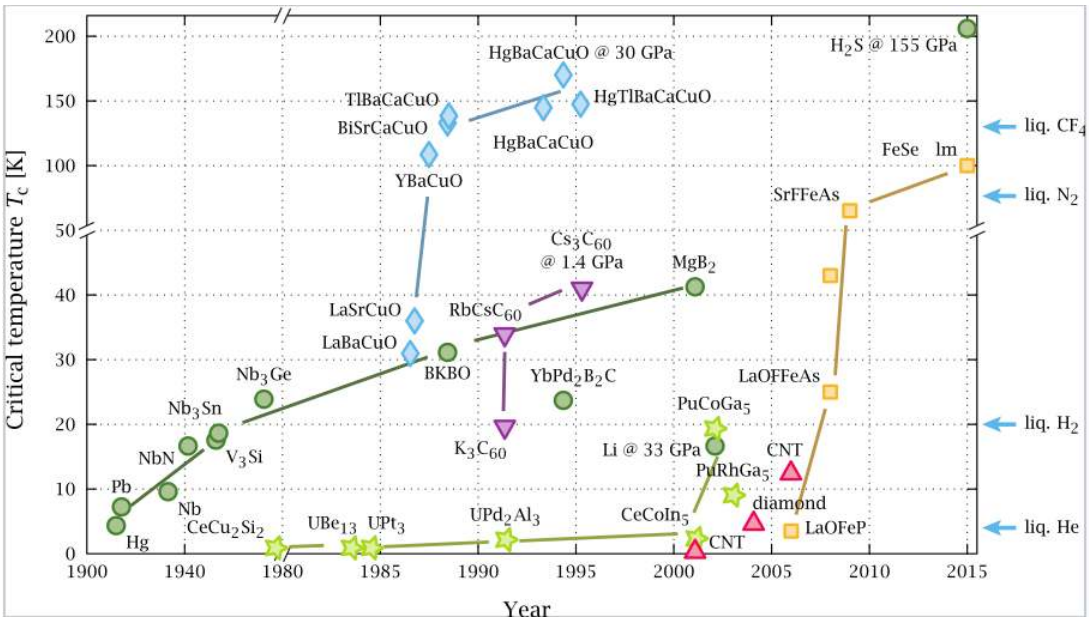
Superconductivity occurs when electrons spin pair into so-called Cooper pairs, which can travel through the lattice together. The electrons in a Cooper pair, although spin-paired, have a long-distance relationship: the spatial extent of a Cooper pair is a few nanometers in cuprate superconductors, and up to one micron in low T_c superconductors such as aluminum. Because its overall spin angular momentum is zero, a Cooper pair is a boson. When the temperature is low enough, the Cooper pairs "condense" into the lowest energy level. The second lowest energy level - which is typically a few meV above the ground state - is not accessible to them as long as the energy gap is larger than the thermal energy, kT. The scattering of electrons by the lattice then becomes forbidden by energy conservation because scattering dissipates energy, and the Cooper pairs cannot change their energy state. Thus the resistance (which arises from scattering, as we learned in Ch. 6) drops abruptly to zero below T_c. However, the Cooper pairs can be broken apart when they move fast, and thus superconductors turn back into normal metals (even below T_c) above some critical current density j_c. This phenomenon is also related to the critical magnetic field, H_c, that quenches superconductivity.



A trampoline for electrons

What causes electrons, which repel each other because of their negative charge, to pair up and travel together in superconductors? The mechanism - which must involve some kind of attractive interaction between electrons - is well understood for "conventional" superconductors which have relatively low transition temperatures, but is not yet known with certainty for high temperature oxide superconductors. In conventional, or BCS superconductors, the spin pairing is mediated by the lattice as shown in the figure at the left. A strong electron-lattice interaction causes a distortion in the lattice as an electron moves through. This elastic deformation is felt as an attractive force by a second electron moving in the opposite direction. This can be thought of as analogous to the interaction of two people jumping on a trampoline. The weight of the first person on the trampoline creates a "well" that attracts the second one, and they tend to move together (even if they don't like each other). Strange as this interaction seems, it is supported experimentally by isotope effects on T_c and by quantitative predictions of T_c values in conventional superconductors.

Bad metals make good superconductors. All superconductors are "normal" metals - with finite electrical resistance - above their critical transition temperature, T_c. If you ask where in the periodic table one might look for superconductors, the answer is surprising. The most conductive metals (Ag, Au, Cu, Cs, etc.) make the worst superconductors, i.e., they have the lowest superconducting transition temperatures, in many cases below 0.01 K. Conversely "bad" metals, such as niobium alloys, certain copper oxides, $K_xBa_{1-x}BiO_3$, MgB_2, FeSe, and alkali salts of C_{60}^{n-} anions, can have relatively high transition temperatures.

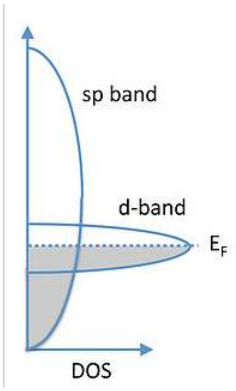


Timeline of superconducting materials, showing T_c vs. year of discovery.

We observe that most good superconductors appear in composition space very **near a metal-insulator transition**. In terms of our microscopic picture, orbital overlap in superconductors is poor, just barely enough to make them act as metals ($\Delta \approx U$) above T_c. In the normal state, superconductors with high T_c - which can be as high as 150 K - are typically "bad" metals. An important

characteristic of such metals is that the **mean free path** of electrons (in the normal state, above T_c) is on the order of the lattice spacing, i.e., **only a few Å**. In contrast, we learned in Ch. 6 that good metals such as Au, Ag, and Cu have electron mean free paths that are two orders of magnitude longer (ca. 40 nm). In a bad metal, the electron "feels" the lattice rather strongly, whereas in a good metal, the electrons are insensitive to small changes in the distance between metals atoms.

What does the band picture look like for a bad metal? The key point is that because orbital overlap is poor, the metal has a **high density of states** at the Fermi level. This is a universal property of high temperature superconductors and provides a clue of where to look for new and improved superconducting materials. Recall that transition elements in the middle of the 3d series (Cr, Fe, Co, Ni) were magnetic because of poor orbital overlap and weak d-d bonding. The elements below these - especially Nb, Ta, and W - have just barely enough d-d orbital overlap to be on the metallic side of the metal-insulator transition and to be "bad" metals. Carbides and nitrides of these elements are typically superconducting, with the carbon and nitrogen atoms serving to adjust the valence electron density, as illustrated in the table below.



Generic E vs. DOS for a bad metal.

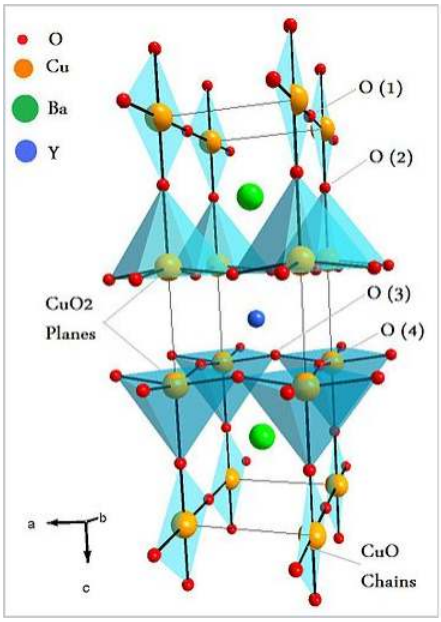
Compound	NbC	Mo_2N	TaC	VN	NbN	TaN	Nb_3Ge
T_c (K)	11.1	5.0	9.7	7.5	15.2	17.8	22.3

High T_c superconductors

In addition to having weak orbital overlap in the metallic state - which results in a high DOS at E_F - high temperature superconductors also typically contain elements in mixed oxidation states (for example, $Cu^{2+/3+}$ or $Bi^{3+/5+}$) that are close in energy to the O^{2-}/O^- couple in the lattice. At ambient pressure, cuprate superconductors have the highest known T_c values, ranging between about 35 and 150 K. The crystal structures of these materials are almost all variants of the perovskite lattice, as shown at the right for the 1-2-3 superconductor $YBa_2Cu_3O_{7-\delta}$. An ideal perovskite lattice would have formula $ABO_3 = A_3B_3O_9$. In $YBa_2Cu_3O_{7-\delta}$, Y and Ba occupy the A cation sites, Cu occupies the B sites, and two of the nine O atoms are missing.

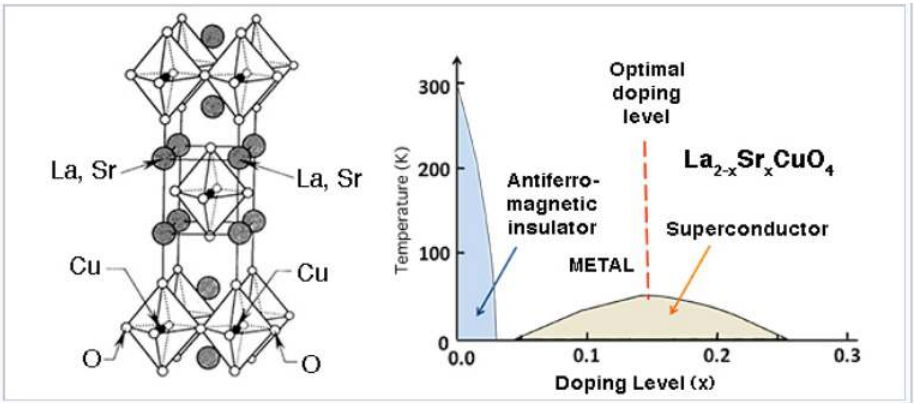
The $YBa_2Cu_3O_{7-\delta}$ lattice consists of mixed-valent copper(II/III) oxide sheets capped by oxygen atoms to form CuO_5 square pyramids. These sheets encapsulate the Y^{3+} cations. Copper(II) oxide ribbons that share the apical oxygen atoms of the square pyramids run in one direction through the structure. In $YBa_2Cu_3O_{7-\delta}$ and related materials, one component of the structure (here the Cu-O ribbons) acts as a **charge reservoir** to control the doping of the planar CuO_2 sheets, which are the elements of the structure

that carry the supercurrent. Cuprate superconductors with Bi, Tl, or Hg-containing charge reservoir layers and multiple, eclipsed CuO_2 sheets in the unit cell tend to have the highest T_c values.



Crystal structure of $YBa_2Cu_3O_{7-\delta}$ (YBCO), the first superconductor with T_c above the boiling point of liquid nitrogen.

The connection between the metal-insulator transtion and superconductivity is nicely illustrated in the phase diagram of $La_{2-x}Sr_xCuO_4$, the first cuprate superconductor, which was discovered in 1986 by Georg Bednorz and K. Alex Müller. This compound has a rather simple structure in which rocksalt La(Sr)O layers are intergrown with perovskite La(Sr)CuO_3 layers. Undoped La_2CuO_4 contains only Cu^{2+} ions and is an antiferromagnetic insulator. As a small amount of Sr^{2+} is substituted for La^{3+}, some of the Cu^{2+} is oxidized to Cu^{3+}, and the lattice is doped with holes. As the doping level increases, the antiferromagnetic phase undergoes a first-order phase transition to a "bad" metal, and at slightly higher doping density the superconducting phase appears. The proximity of the superconducting phase to the metal-insulator transition is a hallmark of cuprate superconductors. A maximum T_c of 35K is observed at x = 0.15. Doping at higher levels moves the Fermi level beyond the point of highest DOS in the d-band of Cu and the superconducting phase then gradually disappears. It is interesting to compare this phase diagram with that of V_2O_3 (above), which also undergoes an antiferromagnetic insulator to "bad" metal transition as it is doped.



Crystal structure and phase diagram of the cuprate superconductor $La_{2-x}Sr_xCuO_4$. (LSCO)

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8.2.6: Semiconductors- Band Gaps, Colors, Conductivity and Doping

Semiconductors, as we noted above, are somewhat arbitrarily defined as insulators with **band gap energy ≤ 3.0 eV** (~290 kJ/mol). This cutoff is chosen because, as we will see, the conductivity of undoped semiconductors drops off exponentially with the band gap energy and at 3.0 eV it is very low. Also, materials with wider band gaps (e.g. $SrTiO_3$, E_{gap} = 3.2 eV) do not absorb light in the visible part of the spectrum

There are a number of places where we find semiconductors in the periodic table:

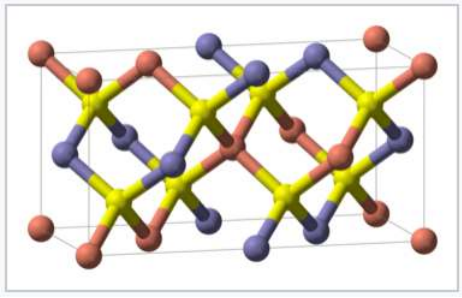
- Early transition metal oxides and nitrides, especially those with d^0 electron counts such as TiO_2, TaON, and WO_3
- Oxides of later 3d elements such as Fe_2O_3, NiO, and Cu_2O
- Layered transition metal chalcogenides with d^0, d^2 and d^6 electron counts including TiS_2, ZrS_2, MoS_2, WSe_2, and PtS_2
- d^{10} copper and sliver halides, e.g., CuI, AgBr, and AgI
- Zincblende- and wurtzite-structure compounds of the p-block elements, especially those that are isoelectronic with Si or Ge, such as GaAs and CdTe. While these are most common, there are other p-block semiconductors that are not isoelectronic and have different structures, including GaS, PbS, and Se.



A 2" wafer cut from a GaAs single crystal. GaAs, like many p-block semiconductors, has the zincblende structure.

The **p-block octet semiconductors** are by far the most studied and important for technological applications, and are the ones that we will discuss in detail.

Zincblende- and wurtzite-structure semiconductors have 8 valence electrons per 2 atoms. These combinations include 4-4 (Si, Ge, SiC,…), 3-5 (GaAs, AlSb, InP,…), 2-6 (CdSe, HgTe, ZnO,…), and 1-7 (AgCl, CuBr,…) semiconductors. Other variations that add up to an octet configuration are also possible, such as $Cu^{I}In^{III}Se_2$, which has the **chalcopyrite** structure, shown at the right.



The **chalcopyrite structure** is adopted by ABX_2 octet semiconductors such as $Cu^{I}In^{III}Se_2$ and $Cd^{II}Sn^{IV}P_2$. The unit cell is doubled relative to the parent **zincblende structure** because of the ordered arrangement of cations. Each anion (yellow) is coordinated by two cations of each type (blue and red).

How does the **band gap energy** vary with **composition**? There are two important trends

(1) Going **down a group** in the periodic table, the gap **decreases**:

C (diamond) > Si > Ge > α-Sn

E_{gap} (eV): 5.4 1.1 0.7 0.0

This trend can be understood by recalling that E_{gap} is related to the **energy splitting between bonding and antibonding orbitals**. This difference decreases (and bonds become weaker) as the principal quantum number increases.

(2) For isoelectronic compounds, **increasing ionicity** results in a **larger band gap**.

Ge < GaAs < ZnSe

0.7 1.4 2.8 eV

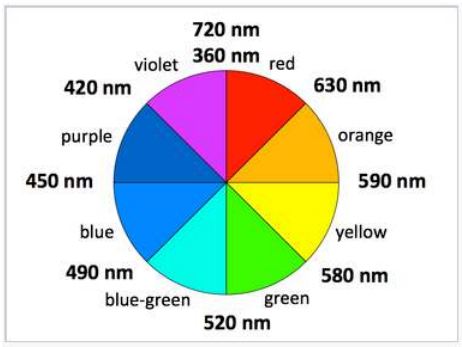
Sn < InSb < CdTe < AgI

0.0 0.2 1.6 2.8 eV

This trend can also be understood from a simple MO picture, as we discussed in Ch. 2. As the electronegativity difference Δχ increases, so does the energy difference between bonding and antibonding orbitals.

The band gap is a very important property of a semiconductor because it determines its color and conductivity. Many of the applications of semiconductors are related to band gaps:

- Narrow gap materials ($Hg_xCd_{1-x}Te$, VO_2, InSb, Bi_2Te_3) are used as infrared photodetectors and thermoelectrics (which convert heat to electricity).
- Wider gap materials (Si, GaAs, GaP, GaN, CdTe, $CuIn_xGa_{1-x}Se_2$) are used in electronics, light-emitting diodes, and solar cells.



Color wheel showing the colors and wavelengths of emitted light.

Semiconductor solid solutions such as $GaAs_{1-x}P_x$ have band gaps that are intermediate between the end member compounds, in this case GaAs and GaP (both zincblende structure). Often, there is a linear relation between composition and band gap, which is referred to as **Vegard's Law**. This "law" is often violated in real materials, but nevertheless offers useful guidance for designing materials with specific band gaps. For example, red and orange light-emitting diodes (LED's) are made from solid solutions with compositions of $GaP_{0.40}As_{0.60}$ and $GaP_{0.65}As_{0.35}$, respectively. Increasing the mole fraction of the lighter element (P) results in a larger band gap, and thus a higher energy of emitted photons.

Colors of semiconductors

The color of absorbed and emitted light both depend on the band gap of the semiconductor. Visible light covers the range of approximately 390-700 nm, or 1.8-3.1 eV. The **color of emitted light** from an LED or semiconductor laser corresponds to the band gap energy and can be read off the color wheel shown at the right.



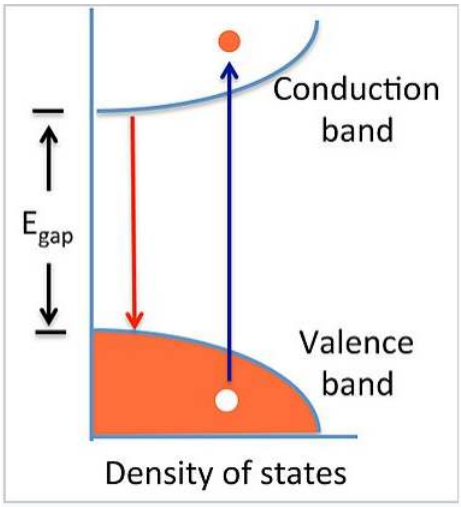
Fe_2O_3 powder is reddish orange because of its 2.2 eV band gap

The color of **absorbed light** includes the band gap energy, but also all colors of higher energy (shorter wavelength), because electrons can be excited from the valence band to a range of energies in the conduction band. Thus semiconductors with band gaps in the infrared (e.g., Si, 1.1 eV and GaAs, 1.4 eV) appear black because they absorb all colors of visible light. Wide band gap semiconductors such as TiO_2 (3.0 eV) are white because they absorb only in the UV. Fe_2O_3 has a band gap of 2.2 eV and thus absorbs light with $\lambda < 560$ nm. It thus appears reddish-orange (the colors of light reflected from Fe_2O_3) because it absorbs green, blue, and violet light. Similarly, CdS (E_{gap} = 2.6 eV) is yellow because it absorbs blue and violet light.

Electrons and holes in semiconductors

Pure (undoped) semiconductors can conduct electricity when electrons are promoted, either by heat or light, from the valence band to the conduction band. The promotion of an **electron** (e^-) leaves behind a **hole** (h^+) in the valence band. The hole, which is the absence of an electron in a bonding orbital, is also a mobile charge carrier, but with a positive charge. The motion of holes in the lattice can be pictured as analogous to the movement of an empty seat in a crowded theater. An empty seat in the middle of a row can move to the end of the row (to accommodate a person arriving late to the movie) if everyone moves over by one seat. Because the movement of the hole is in the opposite direction of electron movement, it acts as a positive charge carrier in an electric field.

The opposite process of excitation, which creates an electron-hole pair, is their recombination. When a conduction band electron drops down to recombine with a valence band hole, both are annihilated and energy is released. This release of energy is responsible for the emission of light in LEDs.



An electron-hole pair is created by adding heat or light energy E ≥ E_{gap} to a semiconductor (blue arrow). The electron-hole pair recombines to release energy equal to E_{gap} (red arrow).

At equilibrium, the creation and annihilation of electron-hole pairs proceed at equal rates. This dynamic equilibrium is analogous to the dissociation-association equilibrium of H^+ and OH^- ions in water. We can write a mass action expression:

$$n \times p = K_{eq} = n_i^2$$

where n and p represent the number density of electrons and holes, respectively, in units of cm^{-3}. The intrinsic carrier concentration, n_i, is equal to the number density of electrons or holes in an undoped semiconductor, where $n = p = n_i$.

Note the similarity to the equation for water autodissociation:

$$[H^+][OH^-] = K_w$$

By analogy, we will see that when we increase n (e.g., by doping), p will decrease, and vice-versa, but their product will remain constant at a given temperature.

Temperature dependence of the carrier concentration. Using the equations $K_{eq} = e^{(\frac{-\Delta G^o}{RT})}$ and $\Delta G^o = \Delta H^o - T\Delta S^o$, we can write:

$$n \times p = n_i^2 = e^{(\frac{\Delta S^o}{R})} e^{(\frac{-\Delta H^o}{RT})} \tag{8.2.6.1}$$

The entropy change for creating electron hole pairs is given by:

$$\Delta S^o = Rln(N_V) + Rln(N_V) = Rln(N_C N_V) \tag{8.2.6.2}$$

where N_V and N_C are the effective density of states in the valence and conduction bands, respectively.

and thus we obtain

$$n_i^2 = N_C N_V e^{(-\Delta H^o RT)} \tag{8.2.6.3}$$

Since the volume change is negligible, $\Delta H^o \approx \Delta E^o$, and therefore $\frac{\Delta H^o}{R} \approx \frac{E_{gap}}{k}$, from which we obtain

$$n_i^2 = N_C N_V e^{(\frac{-E_{gap}}{kT})} \tag{8.2.6.4}$$

and finally

$$\mathbf{n = p = n_i = (N_C N_V)^{\frac{1}{2}} e^{(\frac{-E_{gap}}{2kT})}} \tag{8.2.6.5}$$

For pure Si (E_{gap} = 1.1 eV) with N ≈ 10^{22}/cm^3, we can calculate from this equation a carrier density n_i of approximately 10^{10}/cm^3 at 300 K. This is about 12 orders of magnitude lower than the valence electron density of Al, the element just to the left of Si in the periodic table. Thus we expect the conductivity of pure semiconductors to be many orders of magnitude lower than those of metals.

Conductivity of intrinsic semiconductors

The conductivity (σ) is the product of the number density of carriers (n or p), their charge (e), and their mobility (μ). Recall from Chapter 6 that μ is the ratio of the carrier drift velocity to the electric field and has units of cm^2/Volt-second. Typically electrons and holes have somewhat different mobilities (μ_e and μ_h, respectively) so the conductivity is given by:

$$\sigma = ne\mu_e + pe\mu_h \tag{8.2.6.6}$$

For either type of charge carrier, we recall from Ch. 6 that the mobility μ is given by:

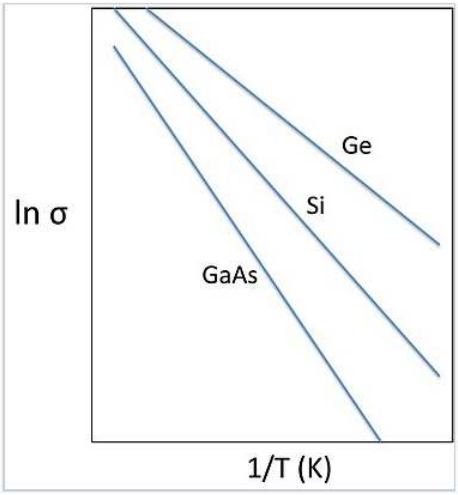
$$\mu = \frac{v_{drift}}{E} = \frac{e\tau}{m} \tag{8.2.6.7}$$

where e is the fundamental unit of charge, τ is the scattering time, and m is the effective mass of the charge carrier.

Taking an average of the electron and hole mobilities, and using n = p, we obtain

$$\sigma = \sigma_o e^{\left(\frac{-E_{gap}}{2kT}\right)},\ where\ \sigma_o = 2(N_C N_V)^{\frac{1}{2}} e\mu \tag{8.2.6.8}$$

By measuring the conductivity as a function of temperature, it is possible to obtain the activation energy for conduction, which is $E_{gap}/2$. This kind of plot, which resembles an Arrhenius plot, is shown at the right for three different undoped semiconductors. The slope of the line in each case is $-E_{gap}/2k$.



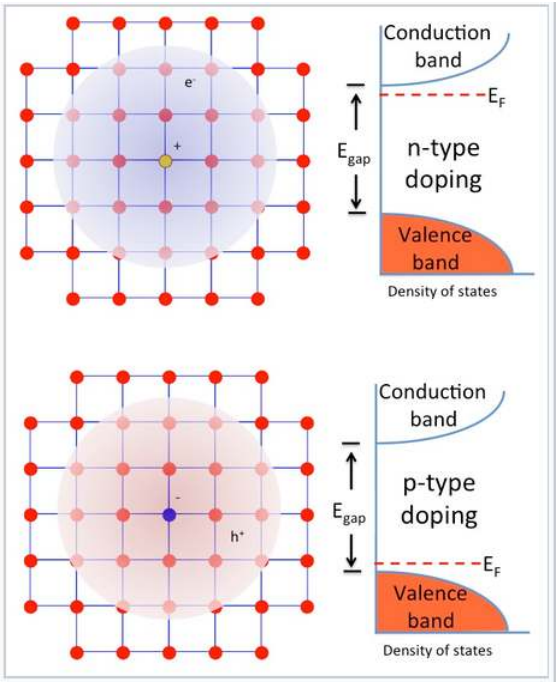
Plots of ln(σ) vs. inverse temperature for intrinsic semiconductors Ge (E_{gap} = 0.7 eV), Si (1.1 eV) and GaAs (1.4 eV). The slope of the line is $-E_{gap}/2k$.

Doping of semiconductors. Almost all applications of semiconductors involve controlled **doping**, which is the substitution of impurity atoms, into the lattice. Very small amounts of dopants (in the parts-per-million range) dramatically affect the conductivity of semiconductors. For this reason, very pure semiconductor materials that are carefully doped - both in terms of the concentration and spatial distribution of impurity atoms - are needed.

n- and p-type doping. In crystalline Si, each atom has four valence electrons and makes four bonds to its neighbors. This is exactly the right number of electrons to completely fill the valence band of the semiconductor. Introducing a phosphorus atom into the lattice (the positively charged atom in the figure at the right) adds an extra electron, because P has five valence electrons and only needs four to make bonds to its neighbors. The extra electron, at low temperature, is bound to the phosphorus atom in a hydrogen-like molecular orbital that is much larger than the 3s orbital of an isolated P atom because of the high dielectric constant of the semiconductor. In silicon, this "expanded" Bohr radius is about 42 Å, i.e., 80 times larger than in the hydrogen atom. The energy needed to ionize this electron – to allow it to move freely in the lattice - is only about 40–50 meV, which is not much larger

the thermal energy (26 meV) at room temperature. Therefore the Fermi level lies just below the conduction band edge, and a large fraction of these extra electrons are promoted to the conduction band at room temperature, leaving behind fixed positive charges on the P atom sites. The crystal is **n-doped**, meaning that the majority carrier (electron) is negatively charged.

Alternatively, boron can be substituted for silicon in the lattice, resulting in **p-type** doping, in which the majority carrier (hole) is positively charged. Boron has only three valence electrons, and "borrows" one from the Si lattice, creating a positively charged hole that exists in a large hydrogen-like orbital around the B atom. This hole can become delocalized by promoting an electron from the valence band to fill the localized hole state. Again, this process requires only 40–50 meV, and so at room temperature a large fraction of the holes introduced by boron doping exist in delocalized valence band states. The Fermi level (the electron energy level that has a 50% probability of occupancy at zero temperature) lies just above the valence band edge in a p-type semiconductor.



n- and p-type doping of semiconductors involves substitution of electron donor atoms (light orange) or acceptor atoms (blue) into the lattice. These substitutions introduce extra electrons or holes, respectively, which are easily ionized by thermal energy to become free carriers. The Fermi level of a doped semiconductor is a few tens of mV below the conduction band (n-type) or above the valence band (p-type).

As noted above, the doping of semiconductors dramatically changes their conductivity. For example, the intrinsic carrier concentration in Si at 300 K is about 10^{10} cm^{-3}. The mass action equilibrium for electrons and holes also applies to doped semiconductors, so we can write:

$$n \times p = n_i^2 = 10^{20} cm^{-6} \; at \; 300K \tag{8.2.6.9}$$

If we substitute P for Si at the level of one part-per-million, the concentration of electrons is about 10^{16} cm^{-3}, since there are approximately 10^{22} Si atoms/cm^3 in the crystal. According to the mass action equation, if n = 10^{16}, then p = 10^4 cm^{-3}. There are three consequences of this calculation:

- The density of carriers in the doped semiconductor (10^{16} cm^{-3}) is much higher than in the undoped material (~10^{10} cm^{-3}), so the conductivity is also many orders of magnitude higher.
- The activation energy for conduction is only 40–50 meV, so the conductivity does not change much with temperature (unlike in the intrinsic semiconductor)
- The minority carriers (in this case holes) do not contribute to the conductivity, because their concentration is so much lower than that of the majority carrier (electrons).

Similarly, for p-type materials, the conductivity is dominated by holes, and is also much higher than that of the intrinsic semiconductor.

Chemistry of semiconductor doping. Sometimes it is not immediately obvious what kind of doping (n- or p-type) is induced by "messing up" a semiconductor crystal lattice. In addition to substitution of impurity atoms on normal lattice sites (the examples given above for Si), it is also possible to dope with vacancies - missing atoms - and with interstitials - extra atoms on sites that are not ordinarily occupied. Some simple rules are as follows:

- For substitutions, adding an **atom to the right** in the periodic table results in **n-type** doping, and an atom to the **left** in **p-type** doping.

  For example, when TiO_2 is doped with Nb on some of the Ti sites, or with F on O sites, the result is n-type doping. In both cases, the impurity atom has one more valence electron than the atom for which it was substituted. Similarly, substituting a small amount of Zn for Ga in GaAs, or a small amount of Li for Ni in NiO, results in p-type doping.

- **Anion vacancies** result in **n-type** doping, and **cation vacancies** in **p-type** doping.

  Examples are anion vacancies in CdS_{1-x} and WO_{3-x}, both of which give n-type semiconductors, and copper vacancies in $Cu_{1-x}O$, which gives a p-type semiconductor.

- **Interstitial cations** (e.g. Li) donate electrons to the lattice resulting in **n-type** doping. Interstitial anions are rather rare but would result in p-type doping.

Sometimes, there can be both p- and n-type dopants in the same crystal, for example B and P impurities in a Si lattice, or cation and anion vacancies in a metal oxide lattice. In this case, the two kinds of doping **compensate** each other, and the doping type is determined by the one that is in higher concentration. A dopant can also be present on more than one site. For example, Si can occupy both the Ga and As sites in GaAs, and the two substitutions compensate each other. Si has a slight preference for the Ga site, however, resulting in n-type doping.

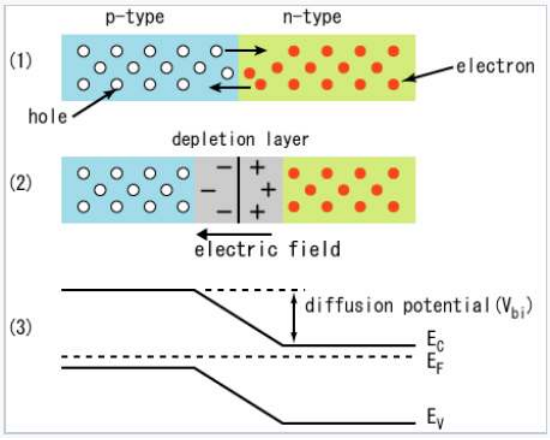
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8.2.7: Semiconductor p-n Junctions

Semiconductor p-n junctions are important in many kinds of electronic devices, including diodes, transistors, light-emitting diodes, and photovoltaic cells. To understand the operation of these devices, we first need to look at what happens to electrons and holes when we bring p-type and n-type semiconductors together. At the junction between the two materials, mobile electrons and holes annihilate each other, leaving behind the fixed + and - charges of the electron donor and electron acceptor dopants, respectively. For example, on the n-side of a silicon p-n junction, the positively charged dopants are P^+ ions and on the p-side the negatively charged dopants are B^-. The presence of these uncompensated electrical charges creates an electric field, the **built-in field** of the p-n junction. The region that contains these charges (and a very low density of mobile electrons or holes) is called the **depletion region**.

The electric field, which is created in the depletion region by electron-hole recombination, repels both the electrons (on the n-side) and holes (on the p-side) away from the junction. The concentration gradient of electrons and holes, however, tends to move them in the opposite direction by diffusion. At equilibrium, the flux of mobile carriers is zero because the field-driven migration flux is equal and opposite to the concentration-driven diffusion flux.



When p-type and n-type semiconductors are joined, electrons and holes are annihilated at the interface, leaving a depletion region that contains positively and negatively charged donor and acceptor atoms, respectively. At equilibrium, the Fermi level (E_F) is uniform throughout the junction. E_F lies just above the valence band on the p-type side of the junction and just below the conduction band on the n-type side.

The width of the depletion layer depends on the screening length in the semiconductor, which in turn depends on the dopant density. At high doping levels, the depletion layer is narrow (tens of nanometers across), whereas at low doping density it can be as thick as 1 μm. The depletion region is the only place where the electric field is nonzero, and the only place where the bands bend. Elsewhere in the semiconductor the field is zero and the bands are flat.

In the middle of p-n junction, the Fermi level energy, E_F, is halfway between the valence band, VB, and the conduction band, CB, and the semiconductor is intrinsic ($n = p = n_i$)

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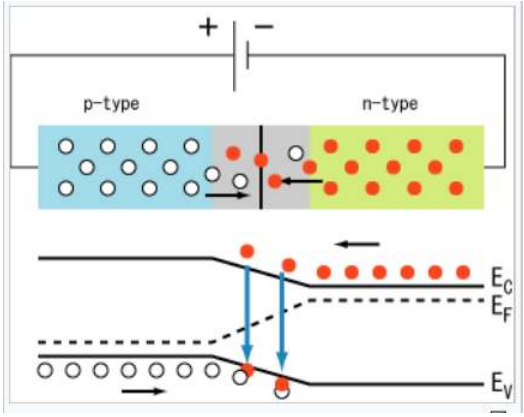
8.2.8: Diodes, LEDs and Solar Cells

Diodes are semiconductor devices that allow current to flow in only one direction. Diodes act as rectifiers in electronic circuits, and also as efficient light emitters (in LEDs) and solar cells (in photovoltaics). The basic structure of a diode is a junction between a p-type and an n-type semiconductor, called a p-n junction. Typically, diodes are made from a single semiconductor crystal into which p- and n- dopants are introduced.



Closeup of a diode, showing the square-shaped semiconductor crystal *(black object on left)* (John Maushammer, Wikipedia, CC-BY-SA)

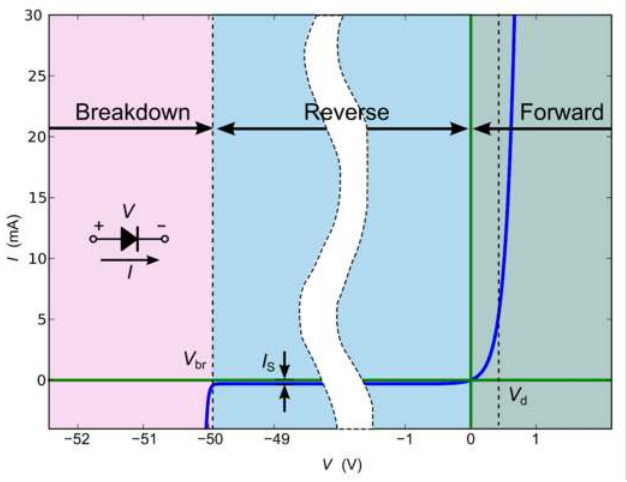
If the n-side of a diode is biased at positive potential and the p-side is biased negative, electrons are drawn to the n-side and holes to the p-side. This reinforces the built in potential of the p-n junction, the width of the depletion layer increases, and very little current flows. This polarization direction is referred to as "back bias." If the diode is biased the other way, carriers are driven into the junction where they recombine. The electric field is diminished, the bands are flattened, and current flows easily since the applied bias lowers the built-in potential. This is called "forward bias."



Electrons (red) and holes (white) in a forward-biased diode. (S-kei. Wikipedia, CC-BY-SA)

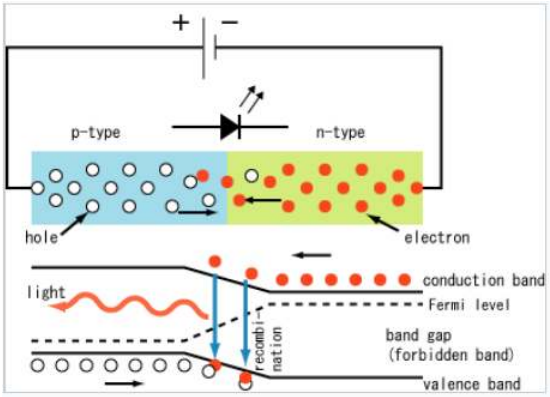
The figure on the left illustrates a forward-biased diode, through which current flows easily. As electrons and holes are driven into the junction (black arrows in lower left figure), they recombine (downward blue arrows), producing light and/or heat. The Fermi level in the diode is indicated as the dotted line. There is a drop in the Fermi level (equal to the applied bias) across the depletion layer. The corresponding diode i-V curve is shown on the right. The current rises exponentially with applied voltage in the forward

bias direction, and there is very little leakage current under reverse bias. At very high reverse bias (typically tens of volts) diodes undergo avalanche breakdown and a large reverse current flows.



Diode i-V curve

A **light-emitting diode** or **LED** is a kind of diode that converts some of the energy of electron-hole recombination into light. This radiative recombination process always occurs in competition with non-radiative recombination, in which the energy is simply converted to heat. When light is emitted from an LED, the photon energy is equal to the bandgap energy. Because of this, LED lights have pure colors and narrow emission spectra relative to other light sources, such as incandescent and fluorescent lights. LED lights are energy-efficient and thus are typically cool to the touch.



Light-emitting diode (LED). (S-kei. Wikipedia, CC-BY-SA)

Direct-gap semiconductors such as GaAs and GaP have efficient luminescence and are also good light absorbers. In direct gap semiconductors, there is no momentum change involved in electron-hole creation or recombination. That is, the electrons and holes originate at the same value of the momentum wavevector **k**, which we encountered in Ch. 6. **k** is related to the momentum (also a vector quantity) by **p** = h**k**/2π. In a direct-gap semiconductor, the top of the valence band and the bottom of the conduction band most typically both occur at **k** = 0. Since the momentum of the photon is close to zero, photon absorption and emission are strongly allowed (and thus kinetically fast). Polar semiconductors such as GaAs, GaN, and CdSe are typically direct-gap materials. **Indirect-gap** semiconductors such as Si and Ge absorb and emit light very weakly because the valence band maximum and conduction band minimum do not occur at the same point in k-space. This means that a lattice vibration (a phonon) must also be created or annihilated in order to conserve momentum. Since this "three body" (electron, hole, phonon) process has low probability, the radiative recombination of electrons and holes is slow relative to non-radiative decay - the thermalization of electron-hole

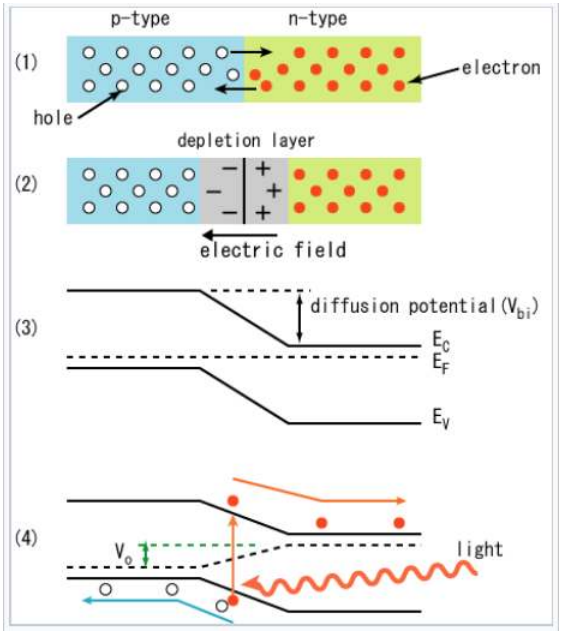
energy as lattice vibrations - in indirect-gap semiconductors. The momentum selection rule thus prevents light absorption/emission and there are no pure Si LEDs or Si-based lasers.



Prof. Shuji Nakamura holding a blue LED.

While red, orange, yellow, and green LEDs can be fabricated relatively easily from AlP-GaAs solid solutions, it was initially very difficult to fabricate blue LEDs because the best direct gap semiconductor with a bandgap in the right energy range is a nitride, GaN, which is difficult to make and to dope p-type. Working at Nichia Corporation in Japan, Shuji Nakamura succeeded in developing a manufacturable process for p-GaN, which is the basis of the blue LED. Because of the importance of this work in the development of information storage (Blu-Ray technology) and full-spectrum, energy-efficient LED lighting, Nakamura shared the 2014 Nobel Prize in Physics with Isamu Asaki and Hiroshi Amano, both of whom had made earlier contributions to the development of GaN diodes.

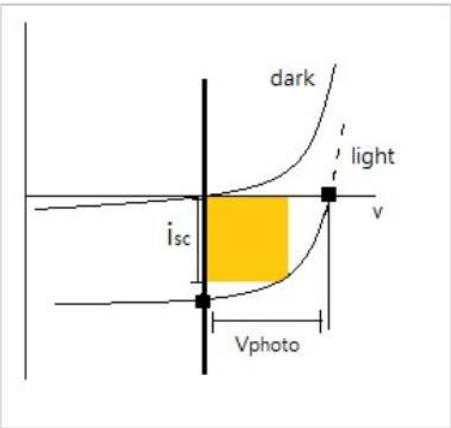
A **Solar cell**, or photovoltaic cell, converts light absorbed in a p-n junction directly to electricity by the photovoltaic effect. Photovoltaics is the field of technology and research related to the development of solar cells for conversion of solar energy to electricity. Sometimes the term solar cell is reserved for devices intended specifically to capture energy from sunlight, whereas the term photovoltaic cell is used when the light source is unspecified.



Photovoltaic effect in a semiconductor p-n junction. (S-kei. Wikipedia, CC-BY-SA)

Photocurrent in p-n junction solar cells flows in the diode reverse bias direction. In the dark, the solar cell simply acts as a diode. In the light, the photocurrent can be thought of as a constant current source, which is added to the i-V characteristic of the diode. The

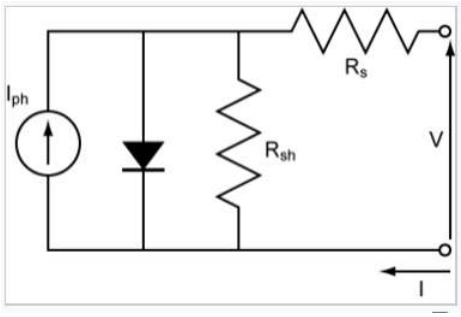
relationship between the dark and light current in a photovoltaic cell is shown in the diagram at the left.



Current-voltage characteristic of a solar cell in the dark and under illumination with band gap light. The short-circuit photocurrent is indicated as i_{sc}, and the open-circuit photovoltage is V_{photo}. The maximum power generated by the solar cell is determined by the area of the orange box.

The built-in electric field of the p-n junction separates e^- h^+ pairs that are formed by absorption of bandgap light in the depletion region. The electrons flow downhill, towards the n-type side of the junction, the holes flow uphill towards the p-side. If $h\nu \geq E_{gap}$, light can be absorbed by promoting an electron from the valence band to the conduction band. Any excess energy is rapidly thermalized. Light with $h\nu > E_g$ thus can store only E_g worth of energy in an e^- h^+ pair. If light is absorbed outside of depletion region, i.e., on the n- or p-side of the junction where there is no electric field, minority carriers must diffuse into the junction in order to be collected. This process occurs in competition with electron-hole recombination. Because impurity atoms and lattice defects make efficient recombination centers, semiconductors used in solar cells (especially indirect-gap materials such as Si, which must be relatively thick in order to absorb most of the solar spectrum) must be very pure. Most of the cost of silicon solar cells is associated with the process of purifying elemental silicon and growing large single crystals from the melt.

In the photodiode i-V curve above, V_{photo} is typically only about 70% of the bandgap energy E_{gap}. The photocurrent is limited by the photon flux, the recombination rate, and the re-emission of absorbed light.[6] The area of the orange rectangle indicates the power generated by the solar cell, which can be calculated as P = i x V. In good single crystal or polycrystalline solar cells made of Si, GaAs, CdTe, $CuIn_xGa_{1-x}Se_2$, or $(CH_3NH_3)PbI_3$ the quantum yield (the ratio of short circuit photocurrent to photon flux) is close to unity.

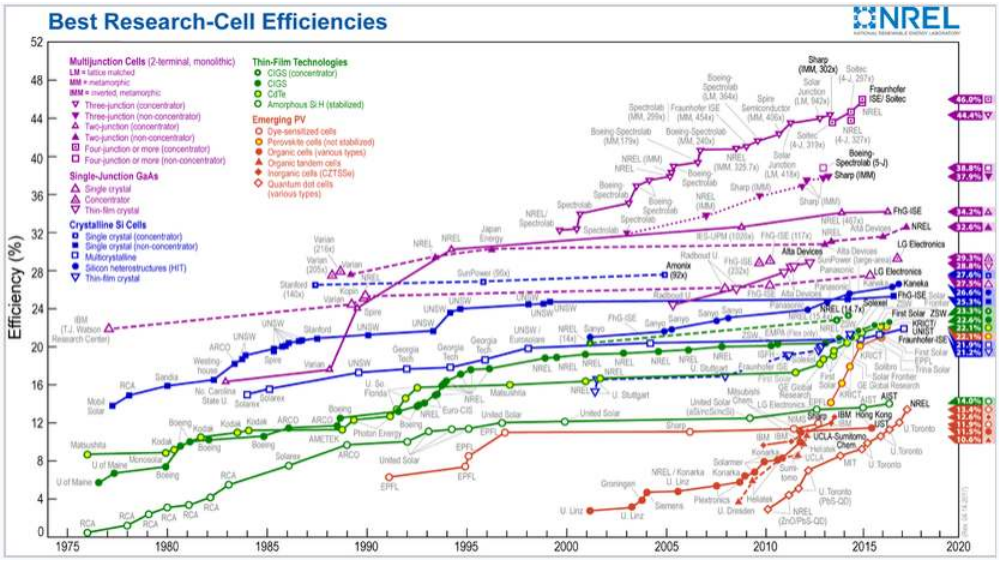


The equivalent circuit of a p-n junction solar cell, which results in the "light" i-V curve shown in the figure above. The solar cell is effectively a diode with a reverse-bias current source provided by light-generated electrons and holes. The shunt resistance (R_{sh}) in the equivalent circuit represents parasitic electron-hole recombination. A high shunt resistance (low recombination rate) and low series resistance (R_s) are needed for high solar cell efficiency.

Solar cells have many current applications. Individual cells are used for powering small devices such as electronic calculators. Photovoltaic arrays generate a form of renewable electricity, particularly useful in situations where electrical power from the grid is

unavailable such as in remote area power systems, Earth-orbiting satellites and space probes, remote radio-telephones and water pumping applications. Photovoltaic electricity is also increasingly deployed in grid-tied electrical systems.

The cost of installed photovoltaics (calculated on a per-watt basis) has dropped over the past decade at a rate of about 13% per year, and has already reached grid parity in Germany and a number of other countries.[7] Photovoltaic grid parity is anticipated in U.S. power markets in the 2020 timeframe.[8] A major driver in the progressively lower cost of photovoltaic power is the steadily increasing efficiency of solar cells, which is shown in the graphic at the right. Higher efficiency solar cells require less area to deliver the same amount of power, and this lowers the "balance of system" costs such as wiring, roof mounting, etc., which scale as the area of the solar panels. Progress towards higher efficiency reflects improved processes for making photovoltaic materials such as silicon and gallium arsenide, as well as the discovery of new materials. Silicon solar cells are a mature technology, so they are now in the flat part of the learning curve and are approaching their maximum theoretical efficiencies. Newer technologies such as organic photovoltaics, quantum dot solar cells, and lead halide perovskite cells are still in the rising part of the learning curve.

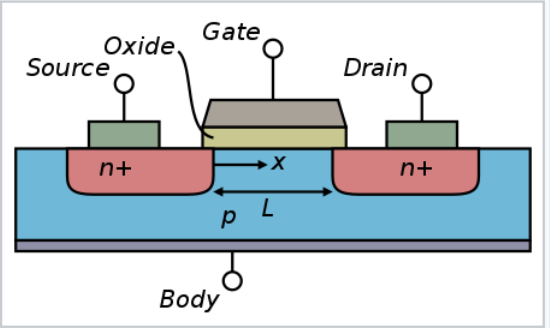


Reported timeline of solar cell energy conversion efficiencies since 1976 (National Renewable Energy Laboratory)

A **field effect transistor (FET)** is a transistor that uses an electric field to control the width of a conducting channel and thus the current in a semiconductor material. It is classified as unipolar transistor, in contrast to bipolar transistors.

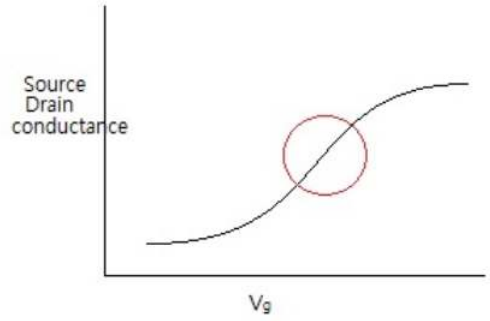
Field effect transistors function as current amplifiers. The typical structure of Si-based FETs is one in which two n-type regions (the source and the drain) are separated by a p-type region. An oxide insulator over the p-type region separates a metal gate lead from the semiconductor. This structure is called a metal-oxide-semiconductor FET (or MOSFET). When voltage is applied between source and drain, current cannot flow because either the n-p or the p-n junction is back-biased. When a positive potential is applied to the gate, however, electrons are driven towards the gate, and locally the semiconductor is "inverted" to n-type. Then the current flows easily between the n-type source and drain through the n-channel. The current flow between the source and drain is many

times larger than the current through the gate, and thus the FET can act as an amplifier. Current flow can also represent a logical "1," so FETs are also used in digital logic.



Cross section of an n-type MOSFET

In electronic devices such as microprocessors, field-effect transistors are kept in the off-state most of the time in order to minimize background current and power consumption. The FET shown above, which has n-type source and drain regions, is called an NMOS transistor. In a PMOS transistor, the source and drain regions are p-type and the gate is n-type. In **CMOS** (complementary metal-oxide semiconductor) integrated circuits, both NMOS and PMOS transistors are used. CMOS circuits are constructed in such a way that all PMOS transistors must have either an input from the voltage source or from another PMOS transistor. Similarly, all NMOS transistors must have either an input from ground or from another NMOS transistor. This arrangement results in low static power consumption.



Transistors are most useful in the range of gate voltage (indicated by the red circle in the figure at the left) where the source-drain current changes rapidly. In this region it is possible to effect a large change in current between source and drain when a small signal is applied to the gate. An important figure of merit for FETs is the **subthreshold slope**, which is the slope a plot of log(current) vs. V_{gate}. An ideal subthreshold slope is one decade of current per 60 mV of gate bias. Typically, a decade change in source-drain current can be achieved with a change in gate voltage of ~70 mV. The performance of FETs as switches and amplifiers is limited by the subthreshold slope, which in turn is limited by the capacitance of the gate. It is desirable to have a very high gate capacitance, which requires a thin insulating oxide, but also to have a small leakage current, which requires a thick oxide. A current challenge in the semiconductor industry is to continue to scale FETs to even smaller nanoscale dimensions while maintaining acceptable values of these parameters. This is being done by developing new gate insulator materials that have higher dielectric constants than silicon oxide and do not undergo redox reactions with silicon or with metal gate leads. Only a few known materials (such as hafnium oxynitride and hafnium silicates) currently meet these stringent requirements.

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8.3: X-rays and X-ray Diffraction

HISTORICAL INTRODUCTION

X-rays were discovered during the summer of 1895 by Wilhelm Röntgen at the University of Würtzburg (Germany). Röntgen was interested in the *cathode rays* (beams of electrons) developed in discharge tubes, but it is not clear exactly which aspects of cathode rays he intended to study. By chance he noticed that a fluorescent screen ($\mathbf{ZnS + Mn^{++}}$) lying on a table some distance from the discharge tube emitted a flash of light each time an electrical discharge was passed through the tube. Realizing that he had come upon something completely new, he devoted his energies to investigating the properties of the unknown ray " $\boldsymbol{X}$ " which produced this effect. The announcement of this discovery appeared in December 1895 as a concise ten page publication.

The announcement of the discovery of X-rays was received with great interest by the public. Röntgen himself prepared the first photographs of the bones in a living hand, and use of the radiation was quickly adopted in medicine. In the succeeding fifteen years, however, very few fundamental insights were gained into the nature of X-radiation. There was some indication that the rays were waves, but the evidence was not clear-cut and could be interpreted in several ways. Then, at the University of Munich in 1912, Max von Laue performed one of the most significant experiments of modern physics. At his suggestion, Paul Knipping (who had just completed a doctoral thesis with Röntgen) and Walter Friedrich (a newly appointed assistant to Sommerfeld) directed a beam of X-rays at a crystal of copper sulfate and attempted to record the scattered beams on a photographic plate. The first experiment was unsuccessful. The result of a second experiment was successful. They observed the presence of spots produced by diffracted X-ray beams grouped around a larger central spot where the incident X-ray beam struck the film. This experiment demonstrated conclusively that X-radiation consisted of waves and, further, that the crystals were composed of atoms arranged on a *space lattice*.

ORIGIN OF X-RAY SPECTRA

The interpretation of X–ray spectra according to the Bohr theory (LN-1) of electronic levels was first (and correctly) proposed by W. Kossel in 1920: the electrons in an atom are arranged in shells (K, L, M, N, corresponding to n = 1, 2, 3, 4, ..., etc.). Theory predicts that the energy differences between successive shells increase with decreasing n and that the electron transition from n = 2 to n = 1 results in the emission of very energetic (short wavelength) radiation (fig. 1), while outer shell transitions (say, from $\boldsymbol{n = 5}$ to $\boldsymbol{n = 4}$) yield low energy radiation (long wavelength). For hydrogen, you recall, the wave number of the emitted radiation associated with a particular electron transition is given by the Rydberg equation:

$$\bar{\nu} = \left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) R$$

For "hydrogen-like" atoms with the atomic number $\boldsymbol{Z}$ (containing one electron only) the corresponding Rydberg equation becomes:

$$\bar{\nu} = \left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) RZ^2$$

From this relationship it is apparent that the energy difference associated with electron transitions increases strongly with the atomic number and that the wavelength of radiation emitted during such transitions moves with increasing $\boldsymbol{Z}$ from the $\mathbf{10^{-7}\ m}$ range to the $\mathbf{10^{-10}\ m}$ range (radiation now defined as **X**-rays).

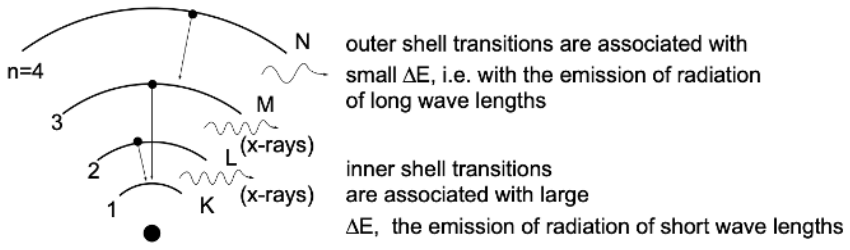


Figure 1 X-rays are generated by inner shell electron transitions

To bring about such inner shell transitions requires the generation of an *electron vacancy*: an electron must be removed, for example from the **K** shell ($\mathbf{n = 1}$), of an atom. Such a vacancy is conveniently produced in an X-ray tube by an electron beam (generated by a heated filament which is made a cathode) impinging, after being subjected to an accelerating potential of several

kV, into a target material made anode (fig. 2). The impinging electrons will transfer part of their energy to electrons of the target material and result in electronic excitation. If the energy of the arriving electrons is high enough, some may knock out a **K** shell electron in the target and thus generate a vacancy. [It should be clear that a $\mathbf{K} \rightarrow \mathbf{L}$ excitation cannot take place since the **L** shell is filled: excitation must involve $(n = 1) \rightarrow (n = \infty)$.] When such a vacancy is generated, it can readily be filled by an electron from the L shell or the M shell of the same atom. These internal electron transitions give rise to the emission of "characteristic" X-radiation which, because of its short wavelength, has extremely high "penetrating" power.

> Since an electron beam is used to generate X-rays, the X-ray tube has to be evacuated: to dissipate the energy flux arriving at the target, the anode support (onto which the target is mounted) is water-cooled.

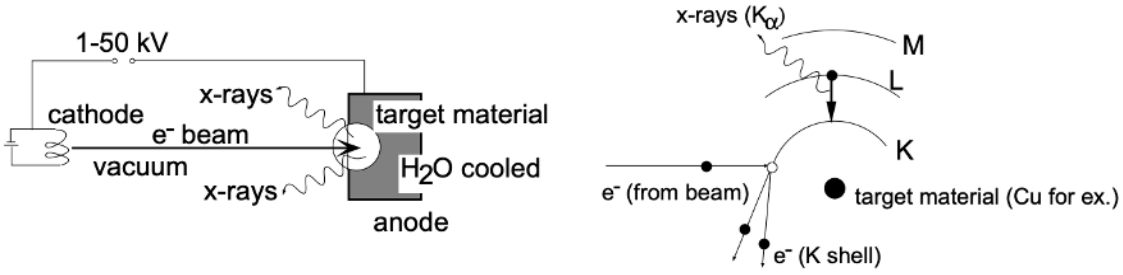


Figure 2 Generation of x-rays

Under standard operating conditions, the characteristic radiation emitted by the target comprises two sharp lines, referred to as $\mathbf{K}_\alpha$ and $\mathbf{K}_\beta$ lines (fig. 3). They are associated, respectively, with electron transitions from $n = 2$ to $n = 1$ and from $n = 3$ to $n = 1$.

Emitted X-ray spectra were extensively studied by H.G.J. Moseley who established the relationship between the wavelength of characteristic radiation and the atomic number **Z** of the radiation emitting target material (fig. 4). Experimentally he found that the $\mathbf{K}_\alpha$ lines for various target materials (elements) exhibit the relationship:

$$\lambda K_\alpha \propto \frac{1}{Z^2} \quad (\bar{\nu} K_\alpha \propto Z^2)$$

Moseley's empirical relationship (which reflects a behavior in agreement with the Rydberg equation) can be quantified. While the energy levels associated with outer electron transitions are significantly affected by the "screening" effect of inner electrons (which is variable and cannot as yet be determined from first principles), the conditions associated with X-ray generation are simple. Very generally, the screening effect of the innermost electrons on the nuclear charge is accounted for in an effective nuclear charge $(Z - \sigma)$ and the Rydberg equation assumes the form:

$$\bar{\nu} = \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) R(Z - \sigma)^2$$

where $\sigma =$ screening effect

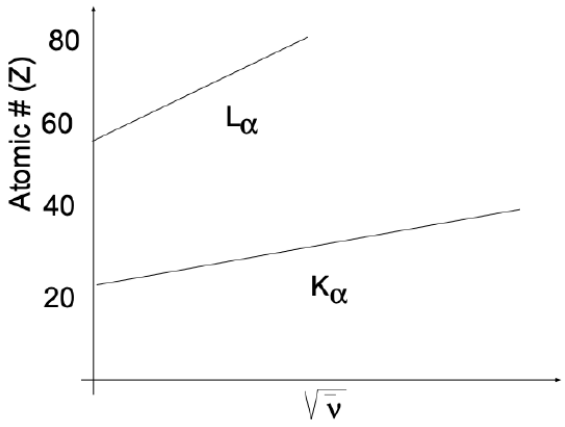


Figure 4 Moseley relationship for $\mathbf{K}_\alpha$ and $\mathbf{L}_\alpha$ radiation

Considering the transition $n_2 \rightarrow n_1$, screening of the full nuclear charge is only provided by the one electron remaining in the K shell. Thus it is possible to use the ν modified Rydberg equation, taking $\sigma = 1$. Accordingly, we have:

$$\bar{\nu}K_\alpha = \left(\frac{1}{2^2} - \frac{1}{1^2}\right) R(Z-1)^2 = -\frac{3}{4}R(Z-1)^2$$

where: $\mathbf{R} =$ Rydberg constant and $\mathbf{Z} =$ atomic number of the target material. [The minus sign (-) only reflects radiative energy given off by the system.]

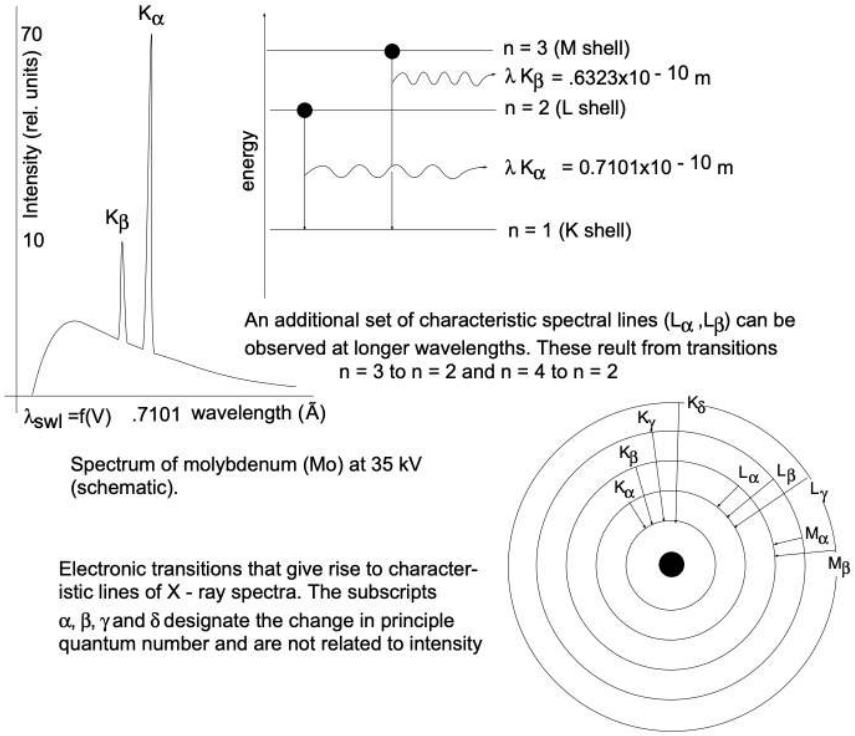


Figure 3 Electronic transitions giving rise to characteristic X- ray spectra.

Similarly, for the characteristic L_α series of spectral lines ($n = 3$ to $n = 2$) we find, after removal of one $\mathbf{L}$ electron, that the screening of the electrons in the $\mathbf{K}$ shell and the remaining electrons in the L shell reduces the nuclear charge by 7.4 (empirical value).

$$\bar{\nu}L_\alpha = \left(\frac{1}{3^2} - \frac{1}{2^2}\right) R(Z-7.4)^2 = -\frac{5}{36}R(Z-7.4)^2$$

A second look at the X-ray spectrum of a Mo target, obtained with an electron accelerating potential of **35kV** (fig. 5), shows that the characteristic radiation (K_α, K_β) appears superimposed on a continuous spectrum (continuously varying λ) of lower and varying intensity. This continuous spectrum is referred to as **bremsstrahlung** (*braking radiation*) and has the following origin. Electrons, impinging on the target material, may lose their energy by transferring it to orbiting electrons, as discussed above; in many instances, however, the electrons may come into the proximity of the force fields of *target nuclei* and, in doing so, will be "slowed down" or decelerated to a varying degree,

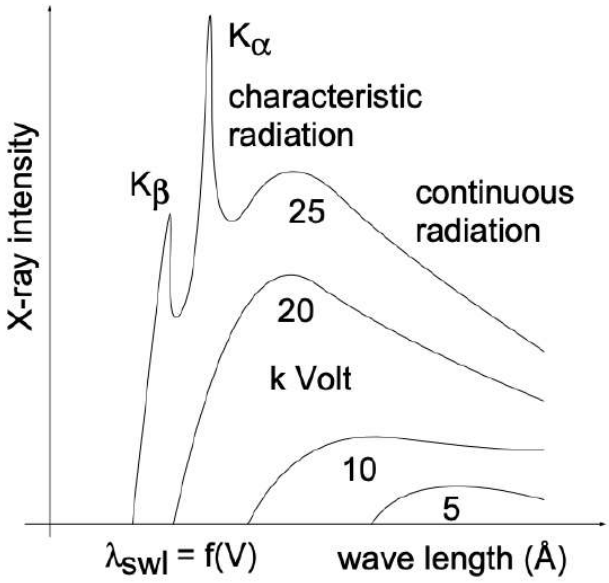


Figure 5 X-ray spectrum of Mo target as a function of applied Voltage.

ranging from imperceptible deceleration to total arrest. The energy lost in this slowing down process is emitted in the form of radiation (braking radiation, or bremsstrahlung). This energy conversion, as indicated, can range from partial to complete (fig. 6). The

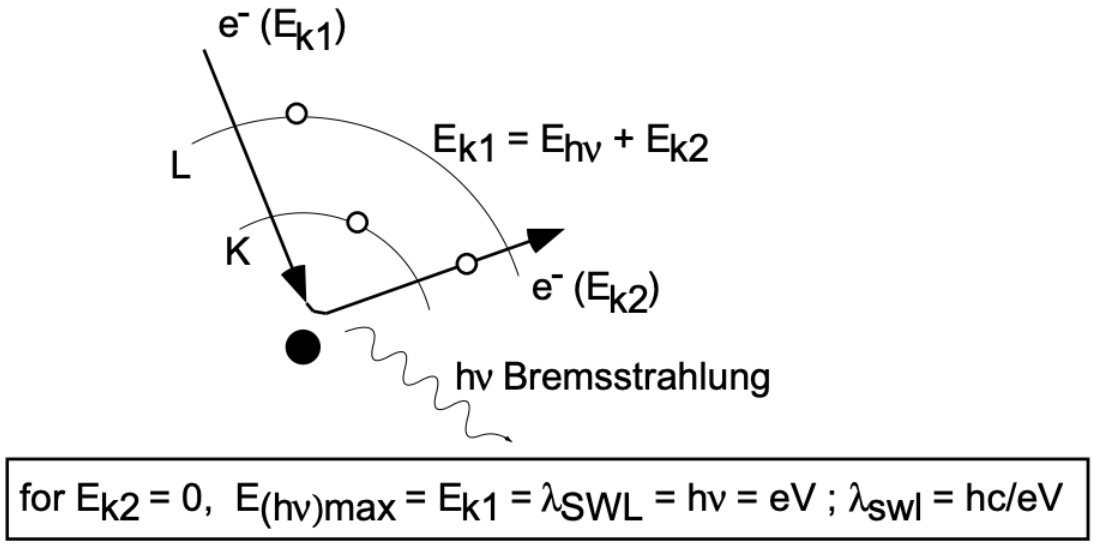


Figure 6 Origin of Bremsstrahlung; the continuous part of the X-ray spectrum

incident electrons have an energy of $\mathbf{e \cdot V}$ (electronic charge times accelerating Voltage) in the form of kinetic energy $(\mathbf{mv^2/2})$, and their total energy conversion gives rise to a *Shortest Wavelength* $(\boldsymbol{SWL})$ - the cut-off of the continuous spectrum for decreasing values of $\boldsymbol{\lambda}$ (fig. 5). Analytically, we have:

$$\mathbf{eV = h\upsilon_{max} = h\frac{c}{\lambda_{SWL}} \quad ; \quad \lambda_{SWL} = \frac{hc}{eV}}$$

From this relationship it is evident that the cut-off of the continuous spectrum toward decreasing $\boldsymbol{\lambda}$'s $(\boldsymbol{\lambda_{SWL}})$ is controlled by the accelerating potential (fig. 5).

"FINE STRUCTURE" OF CHARACTERISTIC X-RAYS

It is customary to consider the characteristic $\mathbf{X}$-ray spectral lines as discrete lines $(\mathbf{K_\alpha}, \boldsymbol{K_\beta, L_\alpha, L_\beta}$, etc.). In reality, they are not discrete since the electron shells involved in the associated electron transitions have energy *sublevels* (s, p, d orbitals). These

sublevels give rise to a "fine structure" insofar as the K_α lines are doublets composed of $K_{\alpha 1}$ and $K_{\alpha 2}$ lines. Similarly, L_α, L_β, etc., exhibit a fine structure.

These considerations suggest that X-ray spectra contain information concerning the energetics of electronic states. Obviously, analysis of X-rays emitted from a target of unknown composition can be used for a quantitative chemical analysis. [This approach is taken routinely in advanced scanning electron microscopy (SEM) where X-rays, generated by the focused electron-beam, are analyzed in an appropriate spectrometer.]

In fundamental studies it is also of interest to analyze soft (long λ) X-ray spectra. For example, take the generation of X-rays in sodium (Na). By generating an electron vacancy in the K shell, a series of K_α and K_β lines will result. The cascading electron generates vacancies in the $2p$ level, which in turn can be filled by electrons entering from the 3s level (generation of "soft" X-rays). If the X-rays are generated in a Na vapor, the $3s \rightarrow 2p$ transition will yield a sharp line; on the other hand, if X-rays are analyzed in sodium metal, the same transition results in the emission of a continuous broad band, about 30Å in width. This finding confirms the existence of an *energy band* (discussed earlier).

An analysis of the width and intensity distribution of the X-ray band provides experimental data concerning the energy band width and the energy state density distribution within the energy band (fig. 7).

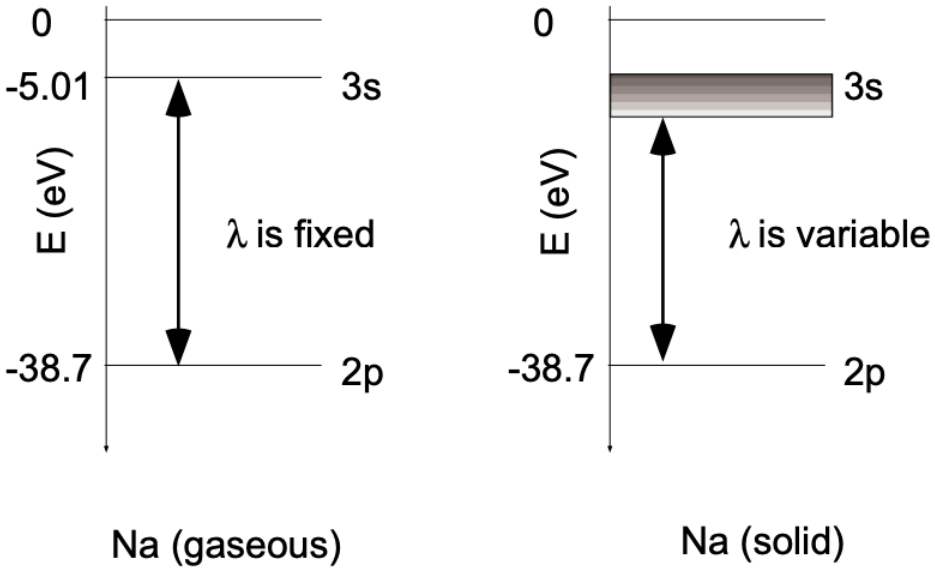


Figure 7 Soft X-rays from 3s - 2p transitions in solid Na and Na vapor

X-RAYS FOR STRUCTURAL ANALYSIS

The extensive use of X-rays for the analysis of atomic structural arrangements is based on the fact that waves undergo a phenomenon called *diffraction* when interacting with systems (diffracting centers) which are spaced at distances of the same order of magnitude as the wavelength of the particular radiation considered. X-ray diffraction in crystalline solids takes place because the atomic spacings are in the 10^{-10} m range, as are the wavelengths of X-rays.

DIFFRACTION AND BRAGG'S LAW

The atomic structure of crystalline solids is commonly determined using one of several different X-ray diffraction techniques. Complementary structure information can also be obtained through electron and neutron diffraction. In all instances, the radiation used must have wavelengths in the range of 0.1 to 10Å because the resolution (or smallest object separation distance) to which any radiation can yield useful information is about equal to the wavelength of the radiation, and the average distance between adjacent atoms in solids is about 10^{-10} m(1Å). Since there is no convenient way to focus X-rays with lenses and to magnify images, we do not attempt to look directly at atoms. Rather, we consider the interference effects of X-rays when scattered by the atoms, comprising a crystal lattice. This is analogous to studying the structure of an optical diffraction grating by examining the interference pattern produced when we shine visible light on the grating. (The spacing of lines on a grating is about 0.5 to 1 µm and

the wavelength of visible radiation ranges from 0.4 to 0.8 μm.) In the optical grating the ruled lines act as scattering centers, whereas in a crystal it is the atoms (more correctly, the electrons about the atom) which scatter the incident radiation.

The geometrical conditions which must be satisfied for diffraction to occur in a crystal were first established by Bragg. He considered a monochromatic (single wavelength) beam of X-rays with coherent radiation (X-rays of common wave front) to be incident on a crystal, as shown in fig. 8. Moreover, he established that the atoms which

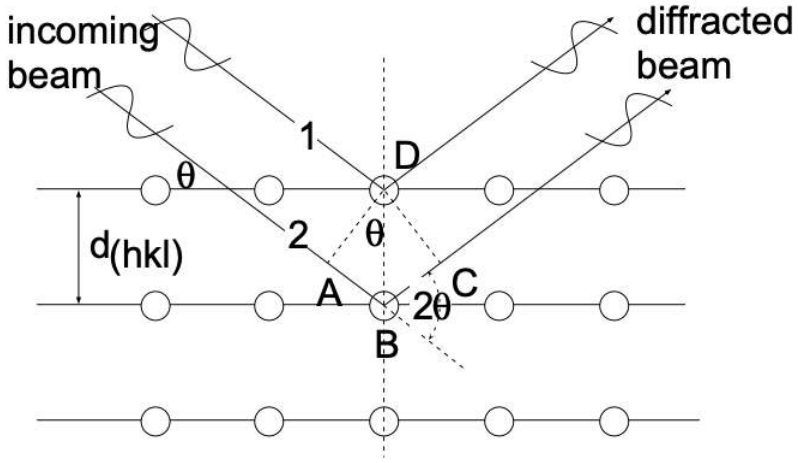


Figure 8 Bragg's law, assuming the planes of atoms behave as reflecting planes.

constitute the actual scattering centers can be represented by sets of parallel planes (in which the atoms are located) which act as mirrors and "reflect" the X-rays. In cubic systems the spacing of these planes, $\mathbf{d_{(hkl)}}$ (see $\mathbf{LN-4}$), is related to the lattice constant (a):

$$\mathbf{d_{(hkl)} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}} \tag{1}$$

For constructive interference of the scattered X-rays (the appearance of a diffraction peak) it is required that the beams, scattered on successive planes, be "in phase" (have again a common wave front) after they leave the surface of the crystal. In terms of the beams labeled 1 and 2 in fig. 8 this requires that the distance $\mathbf{\overline{AB} + \overline{BC}}$ be equal to an integral number of wavelengths (λ) of the indicent radiation. Accordingly:

$$\mathbf{\overline{AB} + \overline{BC} = n\lambda \quad (n = 1, 2, 3, ...)}$$

Since $\mathbf{\overline{AB} = \overline{BC}}$ and $\sin\theta = \frac{\overline{AB}}{d_{(hkl)}}$ $\left[\overline{AB} = d_{(hkl)} \sin\theta\right]$:

$$\mathbf{n\lambda = 2\, d_{(hkl)} \sin\theta} \tag{2}$$

This relation is referred to as *Bragg's Law* and describes the angular position of the diffracted beam in terms of λ and $d_{(hkl)}$. In most instances of interest we deal with first order diffraction ($n = 1$) and, accordingly, Bragg's law is:

$$\lambda = 2d_{(hkl)} \sin\theta$$

[We are able to make $n = 1$ because we can always interpret a diffraction peak for $n = 2, 3, ...$ as diffraction from (nh $nknl$) planes - i.e., from planes with one-nth the interplanar spacing of $d_{(hkl)}$.].

If we consider fig. 8 as representative for a "diffractometer" set-up (fig. 11), we have a collimated beam of X-rays impinging on a (100) set of planes and at 2θ to the incident beam a detector which registers the intensity of radiation. For a glancing incident beam (small θ) the detector will register only background radiation. As θ increases to a value for which $2d\sin\theta = \lambda$, the detector will register high intensity radiation - we have a diffraction peak. From the above it is evident that the diffraction angle (θ) increases as the interplanar spacing, $\mathbf{d_{(hkl)}}$, decreases.

The diffraction experiment as presently considered is intended to provide quantitative information on the volume (the lattice constant a) and shape characteristics (SC, BCC, FCC) of the unit cell. The intensity of diffraction peaks depends on the phase relationships between the radiation scattered by all the atoms in the unit cell. As a result, it happens quite often that the intensity of

a particular peak, whose presence is predicted by Bragg's law, is zero. (This is because Bragg's law deals not with atom positions, but only with the size and shape of the unit cell.) For example, consider the intensity of the (100) diffraction peak of a crystal which has a BCC unit cell. The phase relationships show that the X-rays scattered at the top and bottom faces of the unit cell, (100) planes, interfere constructively, but are 180° out of phase with the X-rays scattered by the atom at the center of the unit cell. The resultant intensity is therefore zero. The rules which govern the presence of particular diffraction peaks in the different cubic Bravais lattices (SC, BCC and FCC) are given in Table I.

TABLE I. *Selection Rules for Diffraction Peaks in Cubic Systems*

Bravais Lattice	Reflections Present	Reflections Absent
Simple Cubic	All	None
Body-Centered Cubic	$(h+k+l) =$ even	$(h+k+l) =$ odd
Face-Centered Cubic	h, k, l unmixed (either all odd or all even)	h, k, l mixed

The rules given are strictly true only for unit cells where a single atom is associated with each lattice point. (Unit cells with more than one atom per lattice point may have their atoms arranged in positions such that reflections cancel. For example, diamond has an FCC Bravais lattice with two atoms per lattice point. All reflections present in diamond have unmixed indices, but reflections such as {200}, {222} and {420} are missing. The fact that all reflections present have unmixed indices indicates that the Bravais lattice is FCC – the extra missing reflections give additional information as to the exact atom arrangement.)

A hypothetical diffraction experiment: A material is known to be of simple cubic structure; determine a, the lattice constant, by X-ray diffraction. In theory, the question may be answered by placing the crystal into a diffractometer, rotating it into all possible positions relative to the incident X-ray beam and recording all diffracting 2θ values. From the above we know that the smallest observed θ value must correspond to diffraction on {100} planes and also that $d_{(100)} = a$. We may now use Bragg's equation to determine a, the lattice constant:

$$\lambda = 2d\sin\theta = 2a\sin\theta$$
$$a = \frac{\lambda}{2\sin\theta} \tag{8.3.1}$$

There are two simplifying assumptions in this problem: (1) we know the system is SC and (2) we are able, through rotation, to bring all planes present into diffraction conditions.

EXPERIMENTAL APPROACHES TO X-RAY DIFFRACTION

In the context of this course we are interested in making use of X-ray diffraction for the purpose of (a) identifying (cubic) crystal systems, (b) determining the lattice constant, a, and (c) identifying particular planes or meaningful orientations. The possible approaches can, in principle, be identified through an examination of Bragg's law. The Bragg condition for particular $d_{(hkl)}$ values can be satisfied by adjusting either one of two experimental variables: (a) λ, the wavelength of the X-ray beam used, or (b) θ, the orientation of the crystal planes relative to the incident X-rays.

(a) Fixed θ. Variable λ: One means of satisfying Bragg's law is to irradiate a stationary single crystal (θ fixed for all planes within the crystal) with an X-ray beam of "white" radiation, which contains the characteristic and continuous spectrum produced by an X-ray tube. (For λ variable we have the simultaneous exposure of a crystal to a range of λ values). Each set of planes will reflect (diffract) the particular λ which satisfies the Bragg condition for the fixed θ. The diffracted beams may conveniently be recorded with a Polaroid camera or, alternately, with an electronic imaging device. It is possible to analyze either the transmitted or the back-reflected X-rays. This experimental procedure is referred to as the **Laue technique** (fig. 9); it is mostly conducted in the back-reflection mode. Note that the approach taken makes it possible to determine the values of θ for each reflection, but not the corresponding λ. Therefore, the technique cannot be used, for example, to determine lattice constants. However, it is very valuable if particular planes or crystal orientations are to be identified.

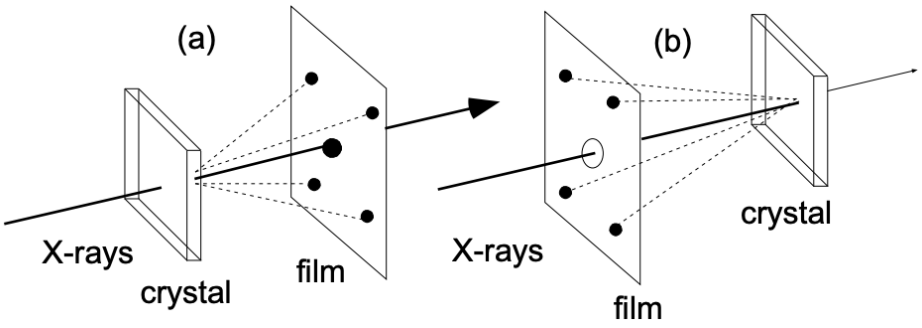


Figure 9: Laue diffraction in (a) transmission and (b) back-reflection mode.

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(b)Fixed λ (Monochromatic X-Rays), Variable θ: The basic prerequisite for this approach is the availability of a monochromatic X-radiation of known wavelength (λ). Such radiation can be conveniently obtained by using a crystal (i.e., its diffracting property) as a filter or monochromator (fig. 10). Filter action is achieved by positioning the crystal in such a way that the unfiltered radiation emitted by the X-ray tube becomes incident at an angle, θ, on a set of low index planes which satisfy Bragg's law for the highest intensity radiation (K_α) emitted. The condition of a fixed λ and variable θ is experimentally used in two techniques. Using a **diffractometer** (fig. 11), we place a sample (ground to a powder) into the center of a rotating stage and expose it to a monochromatic X-ray beam. The sample is rotated into diffraction condition and the diffraction angle determined.

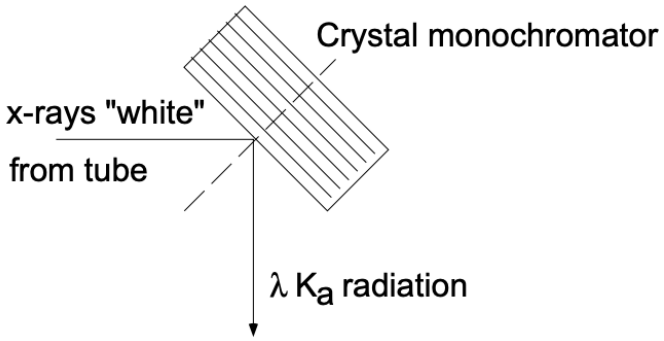


Figure 10 Isolation of monochromatic radiation from target radiation

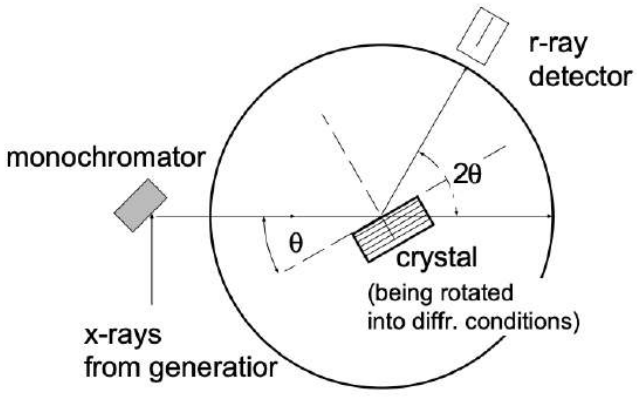


Figure 11 X-ray Diffractometer setup.

In the **Debye-Scherrer method** (fig.12) the sample is ground to a powder and placed (in an ampoule) into the center of a Debye-Scherrer camera. Exposed to monochromatic X-rays, in this way a large number of diffracted cone-shaped beams are generated

such that the semiangles of the cones measure 2θ, or twice the Bragg angle for the particular diffracting crystallographic planes. The reason diffracted beams are cone-shaped is that the planes in question (within the multitude of randomly oriented grains) give rise to diffraction for any orientation around the incident beam as long as the incident beam forms the appropriate Bragg angle with these planes – thus there is a rotational symmetry of the diffracted beams about the direction of the incident beam. Those planes with the largest interplanar spacing have the smallest Bragg angle, θ.

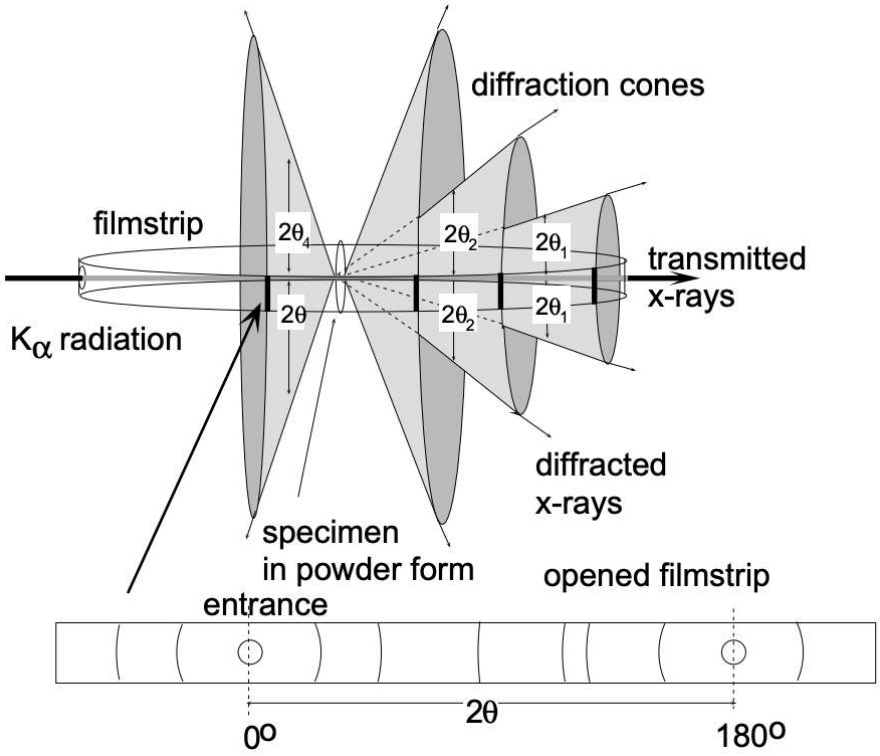


Figure 12 Debye-Scherrer powder diffraction setup and analysis

In a Debye-Scherrer arrangement, after exposing a powder of a crystalline material to monochromatic X-rays, the developed film strip will exhibit diffraction patterns such as indicated in fig. 12. Each diffraction peak (dark line) on the film strip corresponds to constructive interference at planes of a particular interplanar spacing $[d_{(hkl)}]$. The problem now consists of "indexing" the individual lines - i.e., determining the Miller indices (hkl) for the diffraction lines:

$$\begin{aligned} \text{Bragg:} \quad \lambda &= 2\, d_{(hkl)} \sin\theta \quad ; d_{(hkl)} = \frac{a}{\sqrt{h^2+k^2+l^2}} \\ \lambda^2 &= 4\, d^2_{(hkl)} \sin^2\theta \quad ; d^2_{(hkl)} = \frac{a^2}{(h^2+k^2+l^2)} \end{aligned} \tag{8.3.2}$$

Substitution and rearrangement of above yields:

$$\frac{\sin^2\theta}{(h^2+k^2+|^2)} = \frac{\lambda^2}{4a^2} = \text{const.}$$

Accordingly, we find that for all lines (θ values) of a given pattern, the relationship

$$\frac{\sin^2\theta_1}{(h^2+k^2+|^2)_1} = \frac{\sin^2\theta_2}{(h^2+k^2+l^2)_2} = \frac{\sin^2\theta_3}{(h^2+k^2+l^2)_3} = \text{const.}$$

holds. Since the sum $(h^2+k^2+l^2)$ is always integral and $\lambda^2/4a^2$ is a constant, the problem of indexing the pattern of a cubic system is one of finding a set of integers $(h^2+k^2+l^2)$ which will yield a constant quotient when divided one by one into the observed $\sin^2\theta$ values. (Certain integers such as $7, 15, 23$, etc. are impossible because they cannot be formed by the sum of three squared integers.)

Indexing in step-by-step sequence is thus performed as follows: θ values of the lines are obtained from the geometric relationship of the unrolled film strip. Between the exit hole of the X-ray beam $(2\theta = 0°)$ and the entrance hole $(2\theta = 180°)$ the angular

relationship is linear (fig. 12). The increasing θ values for successive lines are indexed $\theta_1, \theta_2, \theta_3$, etc., and $\sin^2\theta$ is determined for each. If the system is simple cubic we know that all planes present will lead to diffraction and the successive lines (increasing θ) result from diffraction on planes with decreasing interplanar spacing: (100), (110), (111), (200), (210), (211), (220), etc. From equation (3) above we recognize:

$$\frac{\sin^2\theta_1}{1} = \frac{\sin^2\theta_2}{2} = \frac{\sin^2\theta_3}{3} = \frac{\sin^2\theta_4}{4} = \frac{\sin^2\theta_5}{5} = \text{const.}$$

If the system is **BCC**, however, we know from the selection rules that only planes for which $(h+k+l) =$ even will reflect. Thus:

$$\frac{\sin^2\theta_1}{2} = \frac{\sin^2\theta_2}{4} = \frac{\sin^2\theta_3}{6} = \frac{\sin^2\theta_4}{8} \text{ etc. } = \text{const.}$$

[SC can be differentiated from BCC through the fact that no sum of three squared integers can yield 7, but 14 can be obtained from planes (321)].

For FCC systems, the selection rules indicate reflections on planes with unmixed h,k,l indices:

$$\frac{\sin^2\theta_1}{3} = \frac{\sin^2\theta_2}{4} = \frac{\sin^2\theta_3}{8} == \text{const.}$$

After proper indexing, the constant is obtained:

$$\frac{\sin^2\theta}{(h^2+k^2+L^2)} = \text{const.}$$

and the particular Bravais lattice is identified. The lattice constant of the unit cell is subsequently obtained, knowing the wavelength of the incident radiation:

$$\frac{\sin^2\theta}{(\mathrm{h}^2+\mathrm{k}^2+\mathrm{l}^2)} = \text{const.} = \frac{\lambda^2}{4a^2}$$
$$a^2 = \frac{\lambda^2}{4\sin^2\theta}\left(h^2+k^2+1^2\right) \tag{8.3.3}$$
$$a = \frac{\lambda}{2\sin\theta}\sqrt{\left(h^2+k^2+1^2\right)}$$

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8.4: The Imperfect Solid State

INTRODUCTION

Real crystals are never perfect: they always contain a considerable density of defects and imperfections that affect their physical, chemical, mechanical and electronic properties. The existence of defects also plays an important role in various technological processes and phenomena such as annealing, precipitation, diffusion, sintering, oxidation and others. It should be noted that defects do not necessarily have adverse effects on the properties of materials. There are many situations in which a judicious control of the types and amounts of imperfections can bring about specific characteristics desired in a system. This can be achieved by proper processing techniques. In fact, “defect engineering” is emerging as an important activity.

All defects and imperfections can be conveniently considered under four main divisions: *point defects*, *line defects* or dislocations, *planar defects* or interfacial or grain boundary defects, and *volume defects*. We can also add here *macroscopic* or *bulk defects* such as pores, cracks and foreign inclusions that are introduced during production and processing of the solid state. Point defects are inherent to the equilibrium state and thus determined by temperature, pressure and composition of a given system. The presence and concentration of other defects, however, depend on the way the solid was originally formed and subsequently processed.

Briefly consider the effects of *imperfections* or crystal defects on a few important properties of solids. The electrical behavior of semiconductors, for example, is largely controlled by crystal imperfections. The conductivity of silicon can thus be altered in type (n or p) and by over eight orders of magnitude through the addition of minute amounts of electrically active dopant elements. In this case, each atom of dopant, substitutionally incorporated, represents a point defect in the silicon lattice. The fact that such small amounts of impurity atoms can significantly alter the electrical properties of semiconductors is responsible for the development of the transistor and has opened up the entire field of solid state device technology. Practically none of the semiconducting properties that led to these engineering accomplishments are found in a “perfect” crystal. They are properties peculiar to the defective solid state.

The existence of dislocations (line defects) in crystals provides a mechanism by which permanent change of shape or mechanical deformation can occur. A crystalline solid free of dislocations is brittle and practically useless as an engineering material. While the existence of dislocations in crystals insures ductility (ability to deform), the theoretical strength of crystalline solids is drastically reduced by their presence.

We should recognize that dislocations play a central role in the determination of such important properties as strength and ductility. In fact, virtually all mechanical properties of crystalline solids are to a significant extent controlled by the behavior of line imperfections.

The ability of a ferromagnetic material (such as iron, nickel or iron oxide) to be magnetized and demagnetized depends in large part on the presence of two-dimensional imperfections known as *Bloch walls*. These interfaces are boundaries between two regions of the crystal which have a different magnetic state. As magnetization occurs, these defects migrate and by their motion provide the material with a net magnetic moment. Without the existence of Bloch walls all ferromagnetic materials would be permanent magnets. In fact, electromagnets would not exist if it were not for this type of defect.

The presence of surface defects such as cracks causes brittle materials like glass to break at small applied stresses. This fact is familiar to anyone who has broken a glass tube by first filing a small notch (or crack) into the surface. Removal of cracks from the surface of glass either by etching in hydrofluoric acid or by flame polishing almost always raises the fracture strength. For example, glass in the absence of any surface cracks has a fracture strength of $\sim 10^{10} \text{Newton/m}^2$ (as opposed to real glass which has a fracture strength of $\sim 0^7$ Newton $/\text{m}^2$).

POINT DEFECTS

Formation of Point Defects

An incontrovertible law of nature states: “Nothing is perfect”. This law applies to humans as well as to the inorganic world of crystalline solids and can be formulated as the 2nd law of thermodynamics:

$$\mathbf{F = H - TS} \tag{1}$$

where $\mathbf{F}$ is the free energy of a given system, $\mathbf{H}$ is the heat content or enthalpy and TS is the entropy, or disorder, term. If a reaction takes place at a temperature T, we find the change in $\mathbf{F}(\Delta\mathbf{F})$ related to a change in $\mathbf{H}(\Delta\mathbf{H})$, the heat content, and possibly also a change in TS ($T\Delta S$). Such is the case when defects are formed in a perfect solid: The energy distribution in a solid (Maxwell-Boltzmann) suggests that a number of individual atoms may acquire enough thermal energy to be displaced from the equilibrium lattice site into an interstitial position. This process of point defect formation requires energy and leads to lattice strain which constitutes, as discussed earlier, an increase in the heat content of the system (ΔH is positive and increases linearly with the number of defects formed). The departure from perfection by the generation of defects leads to disorder (ΔS is positive). The magnitude of disorder generated (ΔS) is very large during the initial step from perfection to slight disarray, but the increase in disorder (with a given number of defects generated) decreases as the overall disorder increases.

Correspondingly the term $T\Delta S$ drops rapidly at the beginning and then flattens out. The net result (fig. 1), free energy, exhibits a minimum for a certain number of defects in the

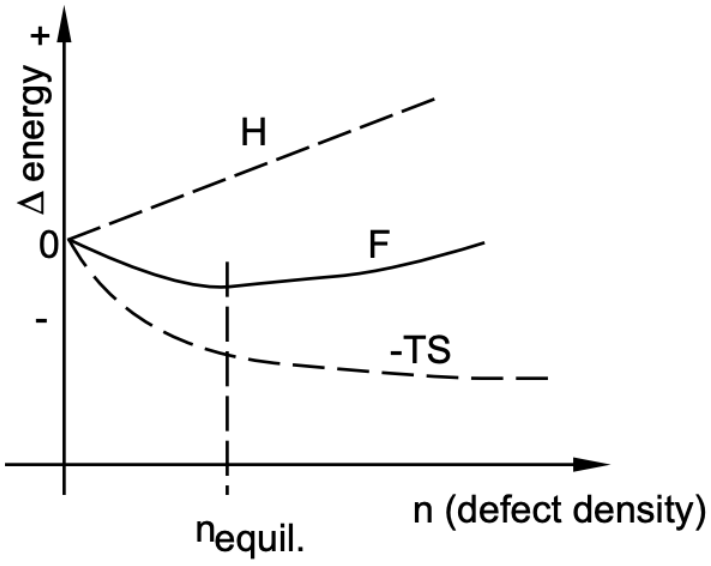


Figure 1 Thermodynamics of point defect formation

solid [equilibrium defect density = f (temperature)]; the F_{minimum} suggests also that the transition from perfection to equilibrium defect structure is spontaneous: it occurs naturally!

While the detailed mechanisms for the formation of atomic vacancies in solids are still the subject of extensive research, the associated equilibrium energetics are clear: calculations of the thermal energy of atoms in a lattice show that the average vibrational energy of lattice atoms is much less than $\mathbf{1eV}$ (the approximate energy change associated with vacancy formation, i.e., the least amount of energy required to form a vacancy) at room temperature. Therefore a lattice atom will only acquire the energy $\mathbf{\Delta H_d}$, the energy required to form the defect, upon the occurrence of a large energy fluctuation. Since the relative probability of an atom having an energy $\mathbf{\Delta H_d}$ or more in excess of the ground state energy is $e^{-\Delta H_d/kT}$, the probability that an atomic site is vacant varies in the same way. In a (molar) crystal containing $\mathbf{N}$ atomic sites, the number $\mathbf{n_d}$ of vacant sites is, therefore,

$$\mathbf{n_d = ANe^{-\Delta H_d/kT}} \tag{2}$$

where

- $\mathbf{n_d}$ is the number of defects (in equilibrium at $\mathbf{T}$)
- $\mathbf{N}$ is the total number of atomic sites per mole
- $\mathbf{\Delta H_d}$ is the energy necessary to form the defect
- $\mathbf{T}$ is the absolute temperature ($\mathbf{K}$)
- $\mathbf{k}$ is the Boltzmann constant
- $\mathbf{A}$ is a proportionality constant

Point Defects in “Pure” Metallic Systems

Point defects in “pure” crystalline metals are defects of atomic dimensions, such as impurity atoms, the absence of a matrix atom and/or the presence of a matrix atom in the wrong place. Some of these point defects are shown in fig. 2. An impurity atom that occupies a normal lattice site is called a *substitutional impurity atom* and an impurity atom found in the interstice between matrix atoms is called an *interstitial impurity atom*. Whether a foreign atom will occupy a substitutional

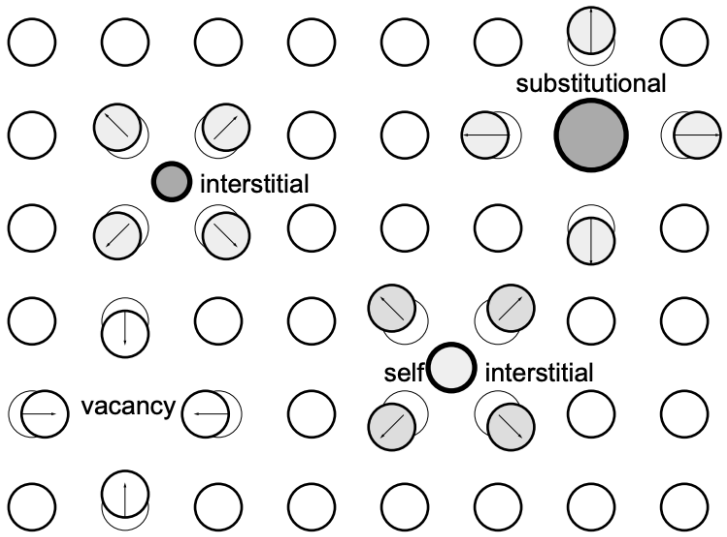


Figure 2 Point defects in crystalline solids

or interstitial site depends largely on the size of the atom relative to the size of the site. Small atoms are usually interstitial impurities, while larger atoms are usually substitutional impurities.

A *vacancy* is an atom site, normally occupied in the perfect crystal, from which an atom is missing. Often the term “vacancy” is used to denote a so-called *Schottky defect*, which is formed when an atom or an ion leaves a normal lattice site and repositions itself in a lattice site on the surface of the crystal. This may be the result of atomic rearrangement in an existing crystal at a high temperature when atomic mobility is high because of increased thermal vibrations. A vacancy may also originate in the process of crystallization as a result of local disturbances during the growth of new atomic planes on the crystal surface. Vacancies are point defects of a size nearly equal to the size of the original (occupied) site; the energy of the formation of a vacancy is relatively low - usually less than 1 eV.

The number of vacancies at equilibrium at each temperature in a crystal can be determined from eq. (2), in which ΔH_d is the energy necessary to take an atom from a regular site of the crystal and place it on the surface for a Schottky-type defect. When a solid is heated a new higher equilibrium concentration of vacancies is established, usually first at crystal surfaces and then in the vicinity of dislocations and grain boundaries which provide sites for the atoms which have left their normal lattice site. Vacancies gradually spread throughout the crystal (from the surfaces into the bulk). On cooling the vacancy concentration is lowered by "diffusion of vacancies" to grain boundaries or dislocations, which act as sinks. In both cases, the new equilibrium vacancy concentration is established only after a finite amount of time. The rate at which vacancies move from point to point in the lattice decreases exponentially with decreasing temperature. Thus, on very rapid cooling (quenching) from a high temperature near the melting point most of the vacancies do not have time to diffuse to sinks and are said to be "frozen in". This gives a considerably greater ("non-equilibrium") concentration of vacancies in quenched specimens than that indicated by the thermal equilibrium value.

The concentration of vacant lattice sites in pure materials is very small at low temperatures - about one vacancy every 10^8 atom sites - and increases with increasing temperature to about one vacancy every 10^3 sites at the melting temperature. Vacancies are important because they control the rate of matrix (or substitutional) atom diffusion - i.e., atoms are able to move around in a crystalline solid primarily because of the presence of vacancies. (The mechanism by which they move is the same as that associated with moving a car in a filled parking lot to the exit). This is shown schematically in fig. 3. *Self-interstitials* are generally not encountered in close-packed

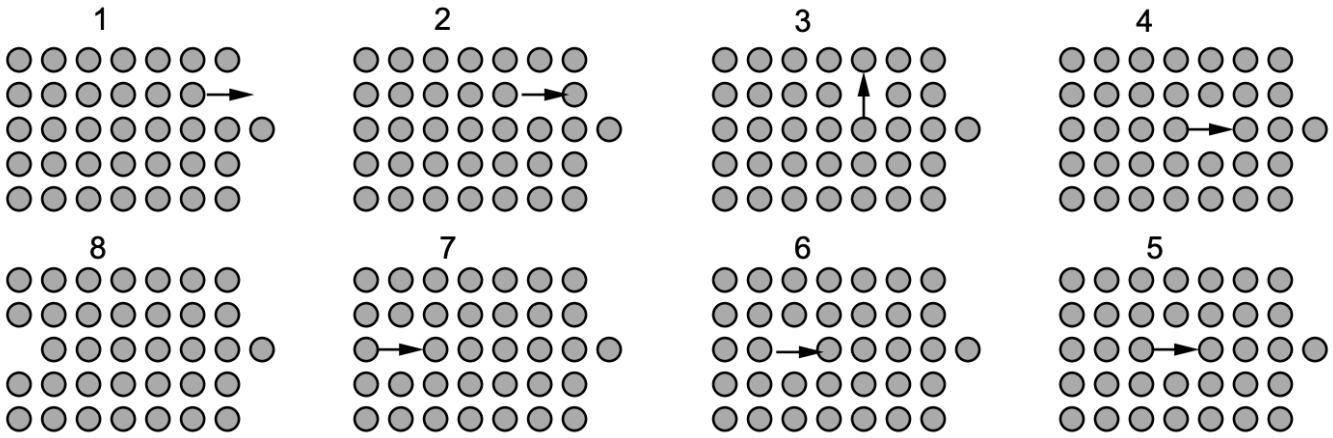


Figure 3 Dynamics of vacancy movements in a close packed solid

metallic systems, but may be introduced by irradiation. For example, high-energy neutrons from atomic fission can knock metal atoms from their regular sites into interstitial sites, creating vacancy-interstitial pairs.

Point Defects in Ionic Solids

Point defects in ionic structures differ from those found in pure elements because of the charge neutrality requirement. For example, in a pure monovalent ionic material a cation vacancy must have associated with it either a cation interstitial or an anion vacancy to maintain charge neutrality. Similar requirements hold for anion vacancies. A vacancy pair defect (migration of a cation and an anion to the surface) is usually called a *Schottky imperfection*, and a vacancy-interstitial pair defect is referred to as a *Frenkel imperfection* (an anion or cation has left its lattice position, which becomes a vacancy, and has moved to an interstitial position). These two types of imperfections are shown in fig. 4. Self-interstitials are much more common in ionic structures than in pure elements because many ionic compounds have relatively large interstitial sites available. That is, there are often interstitial sites in the unit cell that have nearly the

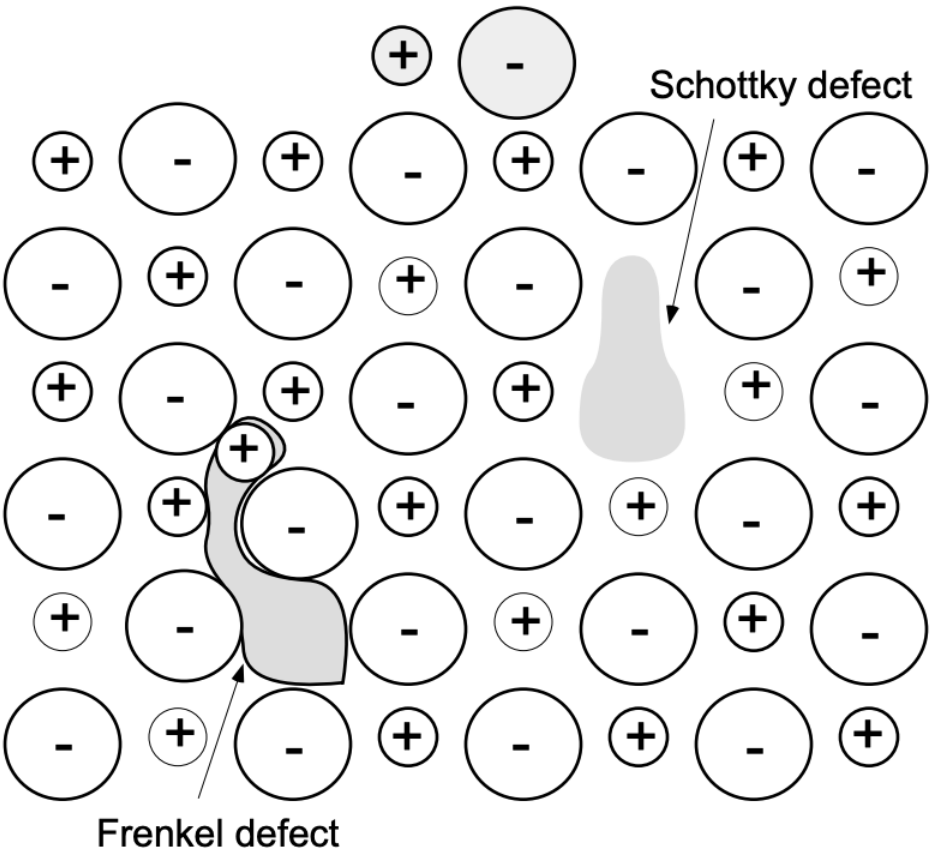


Figure 4 Point defects in ionic solids

same surroundings as normal atom sites. (For example, in BeO the Be atoms fill only one-half the available tetrahedral sites, leaving four possible cation interstitial sites per unit cell. Thus a Be atom could go from a regular lattice site to an almost equivalent interstitial site with little distortion of the lattice.)

Foreign atoms in ionic crystals produce defects that also must maintain charge neutrality. For example, in NaCl a monovalent cation, such as lithium, may simply replace one of the sodium ions as a substitutional impurity. But a divalent cation, such as calcium, replacing a sodium ion must be accompanied by either a cation vacancy or an anion interstitial if charge neutrality is to be maintained. Correspondingly, monovalent impurity cations in a divalent structure (e.g., Na in MgO) must be accompanied by an appropriate number of cation interstitials or anion vacancies.

Point Defects in Covalently Bonded Solids

Substitutional impurities in covalently bonded materials can create a unique imperfection in the electronic structure if the impurity atom is from a group in the periodic table other than the matrix atoms. For example, you already considered Group V and Group III elements in a Group IV matrix, such as As or B in Si.

When foreign atoms are incorporated into a crystal structure, whether in substitutional or interstitial sites, we say that the resulting phase is a *solid solution* of the matrix material (solvent) and the foreign atoms (solute). The term “solid solution”, however, is not restricted to the low solute contents of doped semiconductor systems; there are many solid solutions, such as metallic alloys, that comprise a wide composition range.

LINE DEFECTS

Line imperfections, or *dislocations*, in crystalline solids are defects that produce lattice distortions centered about a line. A dislocation is simply the edge of an extra inserted fractional plane of atoms (fig. 5). Normally the symbol ⊥ is used to represent a *positive*

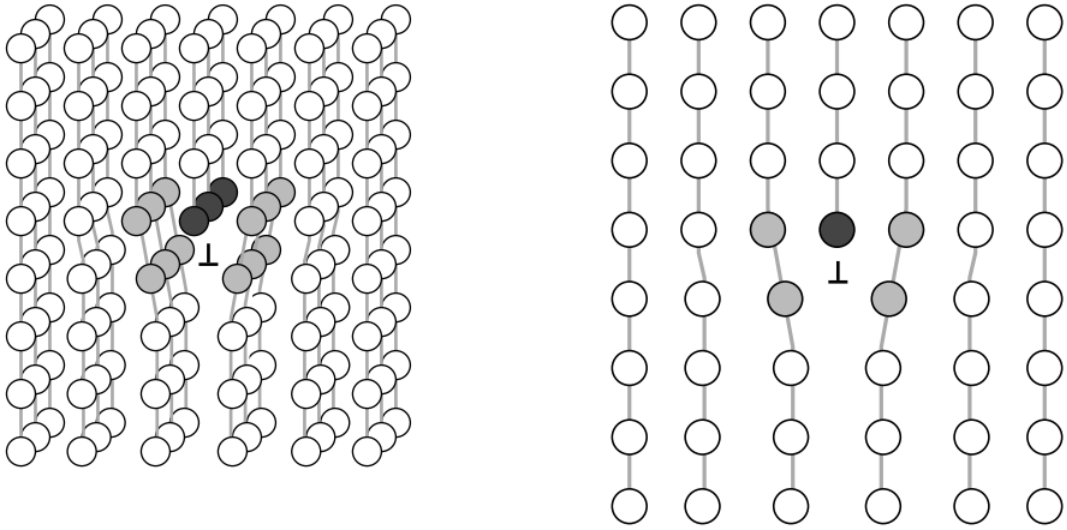


Figure 5 Schematic presentation of a dislocation; the last row of atoms (dark) in the inserted fractional plane

dislocation (extra fractional plane) and ⊤ is used to represent a *negative dislocation* (missing fractional plane).

The importance of dislocations is readily demonstrated in the deformation of crystalline materials. The plane in which a dislocation moves through the lattice is called a *slip plane*. With an applied shear stress the dislocation moves, atomic row by atomic row, and one part of the crystal is displaced relative to the other. When the dislocation has passed through the crystal, the portion of the crystal above the *slip plane* has shifted one atomic distance relative to the portion below the slip plane. In other words, the motion of the dislocation has caused the crystal to change its shape - to be permanently deformed (fig. 6).

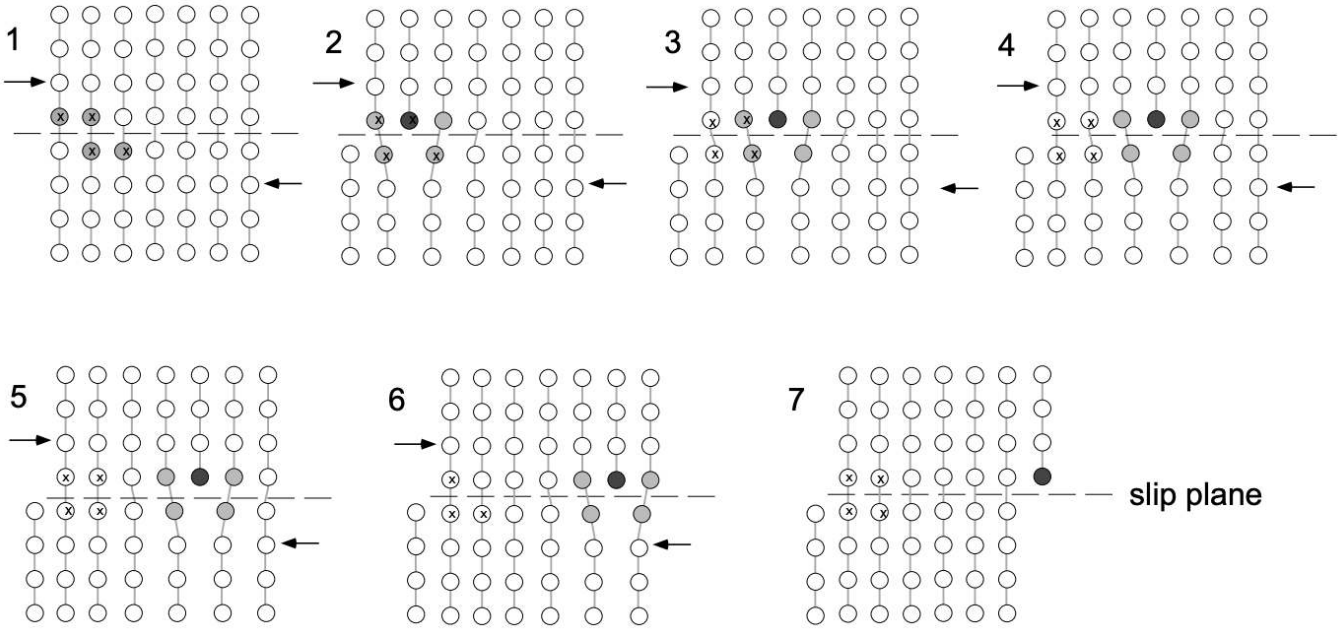


Figure 6 Plastic deformation of crystalline solid by slip associated with stress induced motion of dislocation

Please note: on either side of the dislocation the crystal lattice is essentially perfect, but in the immediate vicinity of the dislocation the lattice is severely distorted. For a positive edge dislocation, the presence of the extra half plane causes the atoms above the slip plane to be put in compression, while those below the slip plane are put in tension. Consequently, the edge dislocation will have a stress field around it that is compressive above the slip plane and tensile below the slip plane.

Plastic Deformation By Slip:

When single crystals of metal (or semiconductor) are pulled in tension, they will begin to deform (elongate) plastically at relatively low stress levels, and “blocks” of the crystals slide over one another because of dislocation motion. Simultaneously, so-called *slip lines* appear on their surface. It is found that deformation by slip occurs most easily on planes with high atomic density and with large interplanar spacing, while the direction of slip is in all instances an atomically “close-packed direction”. For FCC structures we therefore observe as the primary slip system {111} planes in direction, while in BCC structures the primary slip occurs on {110} planes in directions. (It should be noted that an alternate deformation mechanism is “deformation twinning”, presently not to be considered.)

Dislocation Climb:

Climb is the name given to the motion of dislocations when the extra “half” plane is extended farther into a crystal or partially withdrawn from it. Clearly, the climb process is not a motion of the plane, but rather its growth or shrinking as a result of the addition of atoms or “vacancies” respectively from the environment of the dislocation (fig. 7).

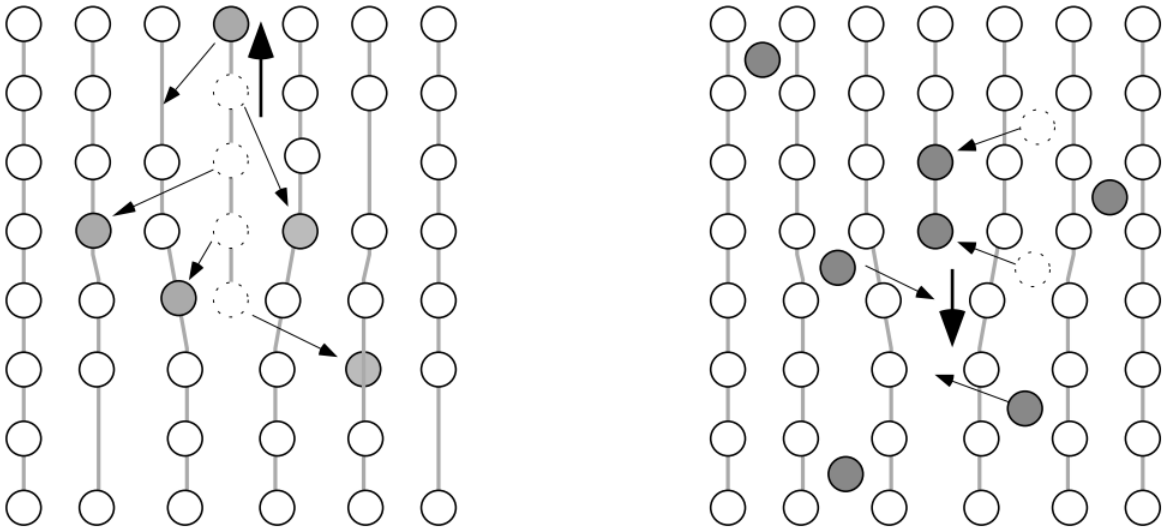


Figure 7 Dislocation climb by (a) loss of atoms to surrounding vacancies and (b) incorporation of interstitial atoms.

Multiplication of Dislocations:

Since during slip each dislocation leaves the matrix, macroscopic deformation could not take place given normal dislocation densities in the range of $10^6 - 10^8/\text{cm}^3$. Examination of the deformed crystals indicates that multiplication of dislocations takes place during deformation. While there are a multitude of multiplication mechanisms, the one most extensively studied is the Frank-Read Source (not to be discussed in detail).

Dislocation Interactions:

The relative ease with which dislocations move across a solid matrix can be attributed to the severe displacements of atoms in the core of dislocations. If these local stresses are reduced, the mobility of dislocations - and thus the ease of slip - is reduced. It is found that impurities in the vicinity of dislocation cores tend to reduce the local distortion energy of the dislocations and thus stabilize the system against slip. In many systems impurities are intentionally added (e.g., solid solution hardening) to increase the strength of materials. Similarly, micro-precipitates tend to impede dislocation motion (e.g., precipitation hardening).

INTERFACIAL IMPERFECTIONS

The several different types of interfacial, or planar imperfections, in solids can be grouped into the following categories:

1. Interfaces between solids and gases, which are called *free surfaces;*
2. Interfaces between regions where there is a change in the electronic structure, but no change in the periodicity of atom arrangement, known as *domain boundaries;*
3. Interfaces between two crystals or grains of the same phase where there is an orientation difference in the atom arrangement across the interface; these interfaces are called *grain boundaries;*

4. Interfaces between different phases, called *phase boundaries*, where there is generally a change of chemical composition and atom arrangement across the interface.

Grain boundaries are peculiar to crystalline solids, while free surfaces, domain boundaries and phase boundaries are found in both crystalline and amorphous solids.

Free Surfaces

Because of their finite size, all solid materials have free surfaces. The arrangement of atoms at a free surface differs slightly from the interior structure because the surface atoms do not have neighboring atoms on one side. Usually the atoms near the surface have the same crystal structure but a slightly larger lattice parameter than the interior atoms.

Perhaps the most important aspect of free surfaces is the *surface energy* (γ) associated with surfaces of any solid. The source of this surface energy may be seen by considering the surroundings of atoms on the surface and in the interior of a solid. To bring an atom from the interior to the surface, we must either break or distort some bonds - thereby increasing the energy. The surface energy is defined as the increase in energy per unit area of new surface formed. In crystalline solids, the surface energy depends on the crystallographic orientation of the surface - those surfaces that are planes of densest atomic packing are also the planes of lowest surface energy. This is because atoms on these surfaces have fewer of their bonds broken or, equivalently, have a larger number of nearest neighbors within the plane of the surface. Typical values of surface energies of solids range from about 10^{-1} to $1\ \mathrm{J/m^2}$. Generally, the stronger the bonding in the crystal, the higher the surface energy.

Surface energies can be reduced by the adsorption of foreign atoms or molecules from the surrounding atmosphere. For example, in mica the surface energy of freshly cleaved material in a vacuum is much higher than the surface energy of the same surface cleaved in air. In this instance, oxygen is adsorbed from the air to partially satisfy the broken bonds at the surface. Impurity atom adsorption makes it almost impossible to maintain atomically clean surfaces. As a result, surface properties such as electron emission, rates of evaporation and rates of chemical reactions are extremely dependent on the presence of any adsorbed impurities. These properties will be different if the measurements are made under conditions giving different surface adsorption.

Grain Boundaries

Grain boundaries separate regions of different crystallographic orientation. The simplest form of a grain boundary is an interface composed of a parallel array of edge dislocations. This particular type of boundary is called a tilt boundary because the misorientation is in the form of a simple tilt about an axis, parallel to the dislocations. Tilt boundaries are referred to as low-angle boundaries because the angle of misorientation is generally less than $10°$.

When a grain boundary has a misorientation greater than $10°$ or $15°$, it is no longer practical to think of the boundary as being made up of dislocations because the spacing of the dislocations would be so small that they would lose their individual identity. The grain boundary represents a region a few atomic diameters wide where there is a transition in atomic periodicity between adjacent crystals or grains.

Grain boundaries have an interfacial energy because of the disruption in atomic periodicity in the vicinity of the boundary and the broken bonds that exist across the interface. The interfacial energy of grain boundaries is generally less than that of a free surface because the atoms in a grain boundary are surrounded on all sides by other atoms and have only a few broken or distorted bonds.

Solids with grain boundaries are referred to as *polycrystalline*, since the structure is composed of many crystals - each with a different crystallographic orientation. In the case of iron the grain boundary structure can be revealed by preferential chemical attack (*etching*) at the grain boundaries, while the grain structure in polyethylene is revealed by the use of polarized light. The grain structure is usually specified by giving average grain diameter or by using a scheme developed by the American Society for Testing and Materials (ASTM). In the ASTM procedure the grain size is specified by a “grain size number” (n) where

$$N = 2^{n-1} \tag{8.4.1}$$

with N equal to the number of grains per square inch when the sample is viewed at 100X magnification. For example, at a magnification of $X = 100$, a material with grain size number 8 will show 128 grains per inch ^{2} - this material in effect has (at $X = 1$) 1.28×10^6 grains per square inch. If the grains are approximately square in cross section, this corresponds to an average grain dimension of $8.8 \times 10^{-4}\mathrm{in}^*$.

In polycrystalline samples the individual grains usually have a random crystallographic orientation with respect to one another, and the grain structure is referred to as *randomly oriented*. In some instances, however, the grains all have the same orientation to within a few degrees. In this instance the material is said to have a *preferred orientation* or *texture*.

Phase Boundaries

A *phase* is defined as a *homogeneous, physically distinct and mechanically separable portion of the material with a given chemical composition and structure*. Phases may be substitutional or interstitial solid solutions, ordered alloys or compounds, amorphous substances or even pure elements; a crystalline phase in the solid state may be either polycrystalline or exist as a single crystal.

Solids composed of more than one element may - and often do - consist of a number of phases. For example, a dentist's drill, something painfully familiar to all of us, consists of a mixture of small single crystals of tungsten carbide surrounded by a matrix of cobalt. Here the cobalt forms a continuous phase. Polyphase materials such as the dentist's drill are generally referred to as *composite materials*. Composite materials have great importance in the engineering world because they have many attractive properties that set them apart from single-phase materials. For example, the dentist's drill has good abrasive characteristics (due to the hard carbide particles) and good toughness and impact resistance (due to the continuous cobalt matrix). Neither the tungsten carbide nor the cobalt has both abrasion resistance and impact resistance, yet the proper combination of the two phases yields a composite structure with the desired properties.

*

ASTM has as yet not issued specifications in SI units!

The nature of the interface separating various phases is very much like a grain boundary. Boundaries between two phases of different chemical composition and different crystal structure are similar to grain boundaries, while boundaries between different phases with similar crystal structures and crystallographic orientations may be analogous to low-angle grain boundaries in both energy and structure.

The concept of a solid consisting of a continuous phase and a discontinuous phase (or phases) leads to a simple classification of the various types of composite materials. Table 1 gives this classification, which is based on the structure (whether amorphous or crystalline) of the continuous and discontinuous phases.

TABLE 1

Classification of Composite or Multiphase Materials

Continuous Phase	Discontinuous Phase (or Phases)	Examples
Crystalline	Crystalline	All metallic systems such as cast iron, steel, soft solder, etc.; most natural rocks such as granite and marble.
Crystalline	Amorphous	None of practical significance.
Amorphous	Crystalline	Most man-made ceramics such as building bricks and electrical insulator porcelain, concrete, partially crystalline polymers, some polymer-crystalline particle composites.
Amorphous	Amorphous	Fiberglass, asphalt, wood, hydrated cement, other gels.

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8.5: Glasses

INTRODUCTION

When a liquid phase is cooled to below its freezing temperature, it usually transforms into a crystalline solid, i.e. it crystallizes. Some liquids, because of complex molecular configuration or slow molecular transport, do not “crystallize” (assume an ordered configuration) upon being cooled to low temperatures, but instead form a rigid disordered network, known as glass, which is very similar in structure to that of the liquid. Most metals and alkali halides crystallize easily upon cooling through the freezing temperature because the structural rearrangement from the liquid to the crystalline state is simple and bonding is nondirectional. At temperatures just above the freezing temperature, most metals and molten salts have fluidities approximately equivalent to that of water at room temperature. Thus, the required structural rearrangements can take place relatively easily.

In contrast, many inorganic silicates form glasses upon cooling because the fluidity at and even above the freezing temperature is very low. This glass formation is related to the high silicon-oxygen single-bond energies and the directional bonding requirements imposed by $\mathbf{sp^3}$ hybridization of silicon. The disordered liquid cannot flow easily and thus cannot undergo the rearrangements required for crystallization. Moreover, the fluidity decreases very rapidly as the temperature is lowered. [For large organic and polymeric liquids, crystallization is difficult because of their chain lengths. In polymer systems the intermolecular bonding (Van der Waals) is weak and expected to permit individual molecules to readily slide past one another. Thus, it is the "difficult" structural rearrangement required for crystallization that induces glass formation in these systems.]

The fluidity of liquids (the reciprocal of the viscosity) is a measure of their ability to flow. In turn, the viscosity (η) (fig. 1) is a measure of their resistance to flow.

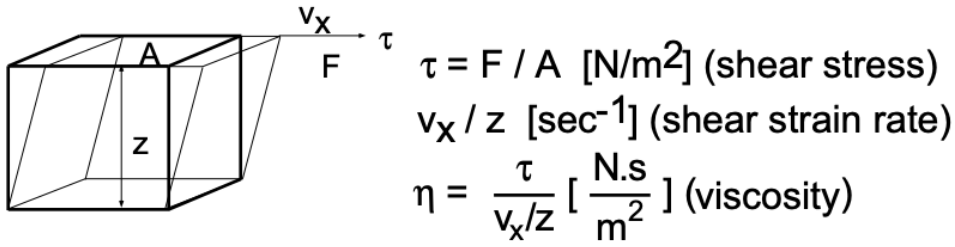


Figure 1 Dimensional analysis of viscosity

Viscosity is formulated as the ratio of an applied shear stress to the resultant shear-strain rate - its dimensions are Newton seconds per $\mathbf{meter^2}$. Liquid flow, involving the motion of molecules past one another, requires the breaking and making of new bonds. Thus the fluidity, like chemical reactions and diffusion in solids (to be discussed later) is expected to exhibit an exponential temperature dependence and may be modelled as:

$$\frac{1}{\eta} \propto e^{-}\left(\frac{\text{Bond Energy}}{kT}\right) \tag{8.5.1}$$

It is noteworthy that inorganic glasses occur in nature as do organic glasses (such as the sap from trees) whereas metallic glasses do not occur naturally and have been manufactured only within the last two decades. The major obstacle to achieving metallic glasses was our inability to cool metallic melts to room temperature at rates high enough so that ordering (and thus crystallization) is prevented.

The *glass transition* point, T_g, (temperature at which a supercooled liquid becomes a glass) is for glasses what the melting point, T_m, is for crystalline solids. Characteristic for almost all glass-forming materials is that at T_g a change in the temperature dependence of the density $(\Delta V/\Delta T)$ takes place [where the viscosity is in the range 10^4 to $10^6 Ns/m^2$ (the viscosity of H_2O is $1.5 \times 10^{-3} Ns/m^2$, or about nine orders of magnitude less)]. At higher temperatures (lower viscosities) the structural units are able to reorganize themselves quickly as a quasi-equilibrium liquid. At temperatures below T_g reorganization among the structural units virtually ceases and the resulting rigid material is referred to as a glass. The experimental value obtained for T_g depends on the time scale of the experiment. On slow cooling, for example, the structural units have more time to reorganize and, thus, T_g is lower (fig. 2).

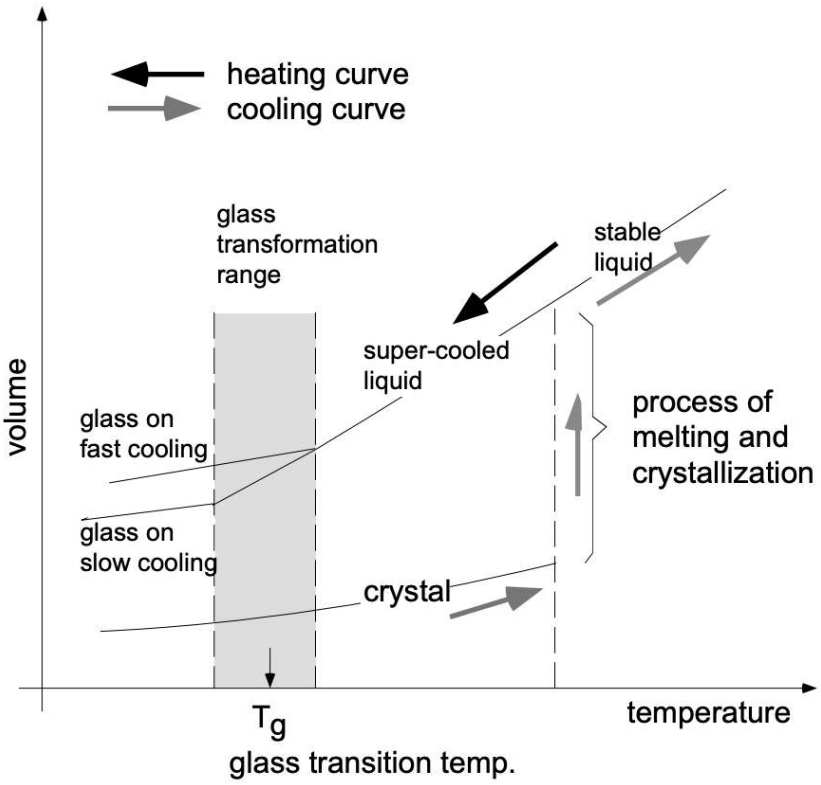


Figure 2 Volume changes associated with heating and cooling in systems susceptible to glass formation.

METALLIC GLASSES

The existence of metallic glasses shows the generality of the glass-forming process. In addition, the physical picture in this case is especially simple. Even with the highest presently attainable cooling rates (up to 10^{7}°C/s), no "pure" metal has yet been obtained in a glassy state. However, if the liquid is an alloy of two (or more) metals whose atoms differ greatly in size, the crystallization process is more difficult and can be prevented in many instances by extremely rapid cooling of the melt (10^{6}°C/sec). The two experimental techniques for rapid cooling are (1) propelling a liquid drop at high velocity and "splatting" it against a cooled copper surface, (2) flattening a liquid drop between a piston and an anvil or between two rolls and (3) "spinning" the melt by transferring it in a continuous mode onto a rapidly rotating, cooled wheel (fig. 3). X-ray patterns of the solidified alloys are similar to those of liquid metals - this and other evidence suggest that they are "amorphous", that their structure is that of a glass.

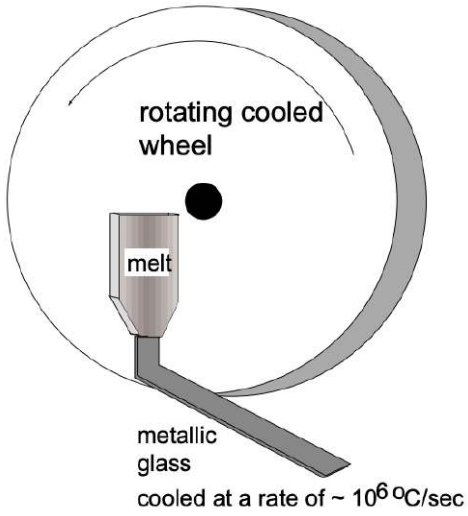


Figure 3 Production of metalic glass by melt spinning

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Another method for preparing metallic glasses is by vacuum deposition onto a substrate cooled to approximately 80K. Again, pure metals crystallize under these conditions, but suitable alloys form glasses, some of which are stable when brought to room temperature. An example is the silver-copper system in which the two solid metals have only about eight percent solubility in each other. If a melt containing 50 wt.% silver and 50 wt.% copper is slowly cooled, two crystalline phases are produced. When this same alloy is obtained by vacuum deposition, a metastable metallic glass is formed. Initially the glass has metallic electrical conductivity comparable to that of the liquid alloy. When the glass is heated for $1/2$ hour at $380\ \mathrm{K}$, it converts to a crystalline, metastable face-centered cubic solid solution. Only on heating at about $500\ \mathrm{K}$ does the equilibrium, two-phase structure form. Many pure nonmetallic elements, however, such as S, Se, Ge and Si, form a stable glass under suitable conditions.

THE GLASSY STATE

The properties and chemical composition of the glass used for optical purposes differ greatly from those of the glass used for baking dishes. Likewise, the glass used for window panes differs from the glass used for artwork or optical purposes. However, (most) inorganic glasses have one thing in common: they are ceramic materials (compounds that contain metallic and non-metallic elements, most often oxygen) with the amorphous structure of a frozen liquid.

Quartz glass is not crystalline at room temperature because the rearrangement of interatomic bonds between Si and O required for the establishment of order is impeded: the viscosity of glass is so high at room temperature that millions of years would be required for it to crystallize (see above). Hence, glass can be viewed as a perfectly rigid "liquid", being exceptional in that its extraordinarily high viscosity slows down its flow properties even on an expanded time scale.

Upon cooling of liquid “glass” we observe that $\Delta V/\Delta T$ (the contraction with lowering of T) changes. This may be seen by following the three basic steps in the production of glass: (1) the melting of quartz sand (minute crystals of silica), (2) the shaping of the glass while in a viscous state and (3) the controlled cooling of the shaped article. The $\mathrm{SiO_4}$ tetrahedra in the sand (crystals) are arranged in an ordered pattern (fig. 4), but in the molten state the crystal matrix breaks up into strings and rings of tetrahedra in irregular patterns (fig. 5). Because the temperature is very high, the groupings continually break up and reform, making the mass fluid.

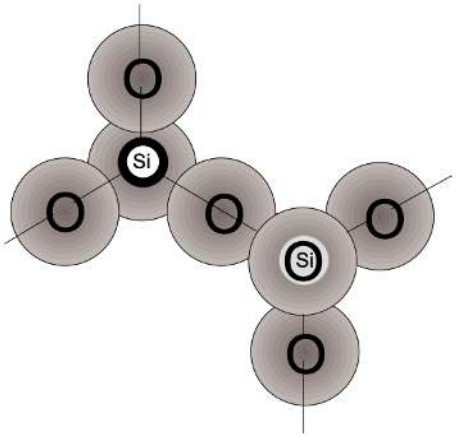


Figure 4 Basic Si - O - Si - units as established with $\mathrm{sp^3}$ hybridization of Si

Upon cooling of molten $\mathrm{SiO_2}$ the tetrahedra form larger groupings and the glass becomes more viscous, permitting it to be shaped by blowing, rolling, pressing, etc. With continuing cooling, larger groupings of tetrahedra form as their kinetic energy decreases. These two phenomena are responsible for the increase in viscosity and the shrinkage that takes place during the cooling period. Beyond the glass transformation temperature changes in configuration of the tetrahedra virtually cease because the glass, to all intents and purposes, has lost its fluidity.

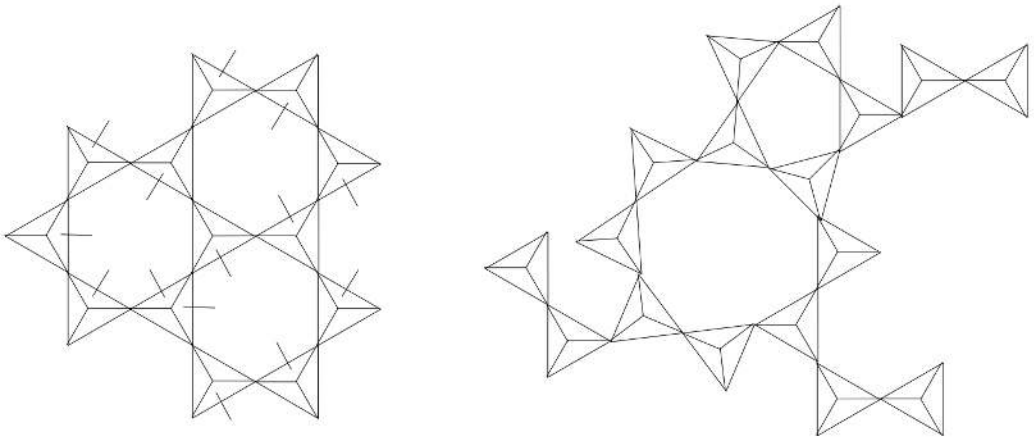


Figure 5 Two-dimensional view of tetrahedra as in silicondioxide structures: (a) in crystalline, ordered structures and (b) in disordered glassy (amorphous) structures.

OXIDE GLASSES

The bonding forces responsible for the formation of network structure in crystalline SiO_2 produce similar networks in glasses of other oxides such as B_2O_3 and P_2O_5 which are thus also considered as primary *network formers* (the present discussion will be limited to silica glasses). If an oxide, such as Na_2O, is added to silica glass, a bond in the network is broken and the relatively mobile sodium ion becomes a part of the structure (fig. 6). Examples of such *network modifiers* are $N_2O, K_2O, Li_2O, CaO, MgO$ and PbO.

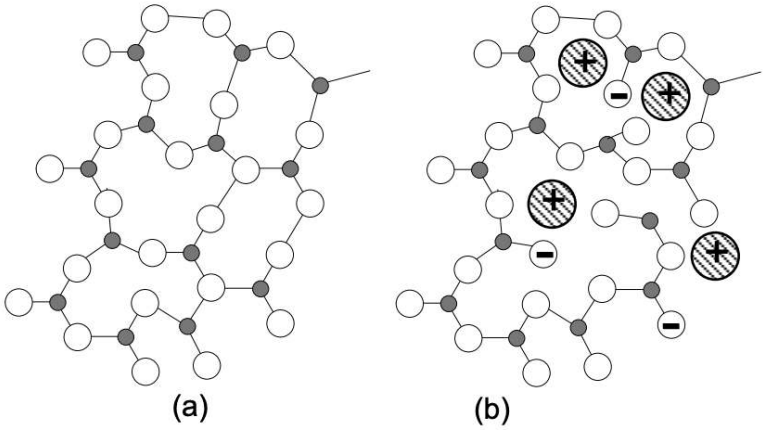


Figure 6 Schematic glass networks; (a) SiO_2 network (b) SiO_2 network modified through addition of Na_2O.

With increase in the amount of modifier, the average number of oxygen-silicon bonds forming bridges between silicon between silicon atoms decreases as follows:

O/Si Ratio in Glass	Bridging-O-Si Bonds/Si atom
2.0	4 (fig. 7)
2.5	3
3.0	2

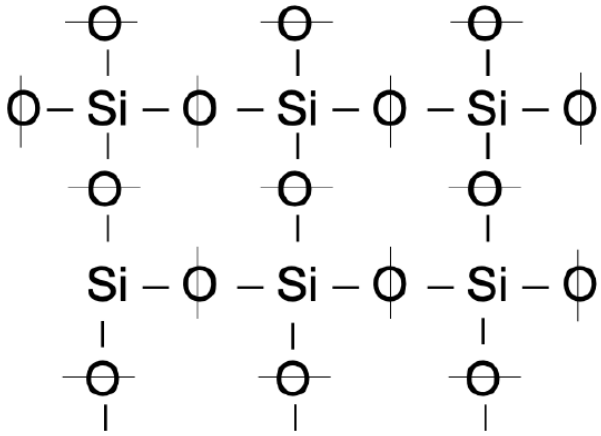


Figure 7 Schematic of SiO_2 network; the O to Si ratio is 2 : 1 as indicated by the chemical formula

Two bridging bonds per silicon atom will correspond, for example, to a linear chain structure, and any further increase in modifier would reduce the length of the chain. The principal effect of a modifier is to lower the melting and working temperature by decreasing the viscosity. An excess of modifier can make the structural units in the melt sufficiently simple and mobile that crystallization occurs in preference to the formation of a glass.

The compositions and properties of typical glasses are listed in Table 1. Soda-lime glass not only has the advantage of being made from inexpensive raw materials, but also the practical convenience of low working temperatures (fig. 8). Most glass-forming operations (pressing, drawing, etc.) begin at the temperature corresponding to the working point, but can continue while the glass cools.

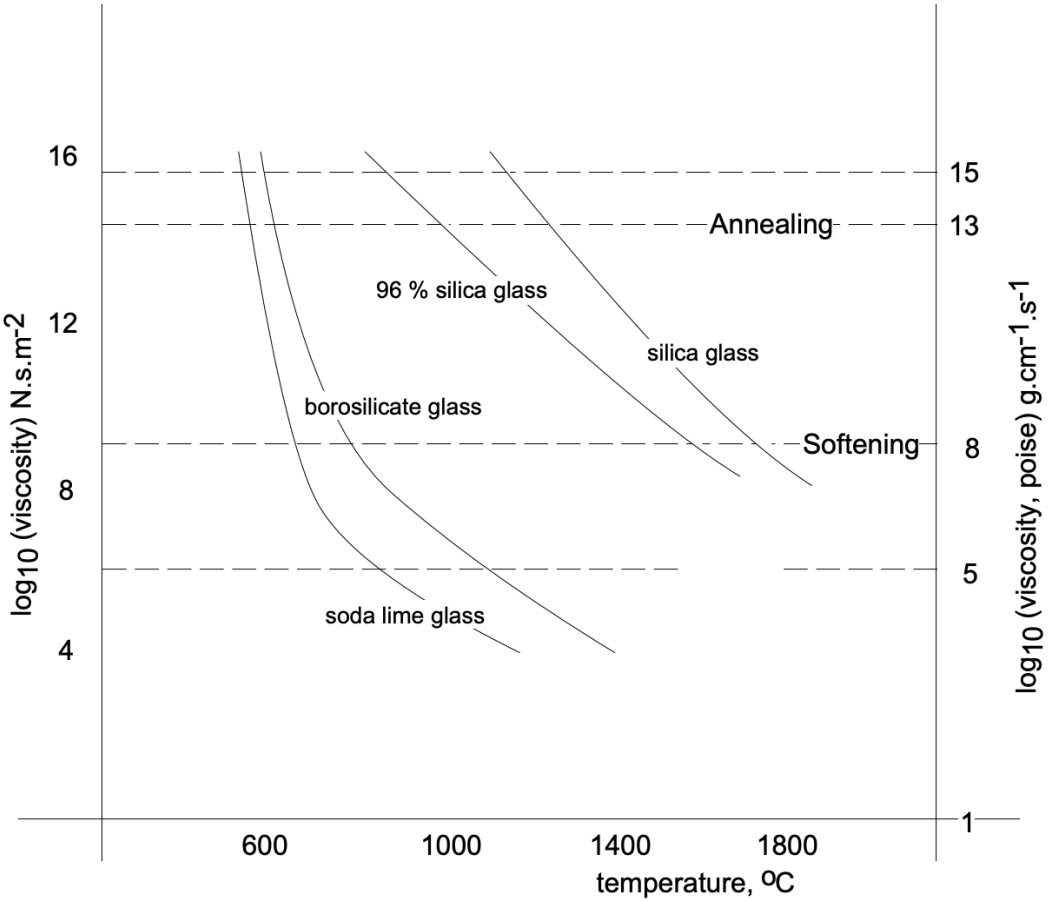


Figure 8 Important temperatures in fabrication of silicate glasses (the temperatures are related to viscosity which in turn controls workability)

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ANNEALING OF GLASS

In order to relieve the internal stresses that may develop during glass formation, all commercial glassware is annealed (slowly cooled) immediately after shaping. This slow cooling operation is carried out in industry by placing the shaped objects on a conveyor belt which transports them first through a reheating zone and then through sections having successively lower temperatures in a furnace called the *lehr*.

TABLE 1. Typical Oxide Glasses

	Composition, w/o								
Type	SiO_2	Na_2O	K_2O	CaO	MgO	B_2O_3	Al_2O_3	Other	Properties or uses
Soda-lime	72	14		9	4		1		Window glass
Silica glass (fused quartz)	99.5+								High-temperature applications; low coefficient of expansion
96% silica glass	96.3	<0.2	<0.2			2.9	0.4		Comparable to fused quartz
Borosilicate	80.5	3.8	0.5			12.9	2.2		Resistant to heat and to chemicals
Light flint optical	54	1	8					37PbO	High index of refraction
Surface-strengthened glass	55	16	2	2		2	19	$4TiO_2$	Cookware
Glass-ceramic	56				15		20	$9TiO_2$	Radomes

The transformation of a liquid to a glass actually takes place over a range of temperatures at which the glass shrinks (thermal contraction). The glass does not undergo a change from disordered liquid structure to crystal structure as iron does at its transformation temperature; in glass, the transformation temperature is the temperature below which viscosity prevents any further configurational changes. Any contraction beyond the transformation temperature range is due only to the lower kinetic energy of the groupings.

The transformation temperature of a given “glass composition” depends on its constituents and upon the rate of cooling. Slow cooling results in a lower transformation range because the tetrahedra will have more time to rearrange (to some degree). This results in tighter packing of tetrahedra as the mass reaches its transformation range. When the glass reaches room temperature, its volume will be smaller when cooled slowly than glass melt which has been cooled rapidly. Hence, slower cooling from the melt results in a denser glass. (See fig. 2.)

Glass is thermodynamically unstable at room temperature because configuration changes (which require eons of years to come about!) would result in a lower free energy configuration. However, the changes are so slow that they may be considered negligible.

PROPERTIES OF GLASSES

The strong covalent bonds that exist between the atoms of inorganic glasses plus the lack of crystal structure give glass unusual characteristics. Thus, quartz glass is:

1. (a) Chemically stable;
2. (b) A poor conductor of heat and electricity;

3. (c) Inherently transparent;
4. (d) Inherently strong.

Chemical Stability

All glasses are immune to oxidation (decay) because their atoms are fully oxidized. Glass composed of 100 percent silica tetrahedra is extraordinarily inert. It resists the action of most acids (the most notable exception is hydrofluoric acid, utilized to etch glass), but it is attacked by strong alkalis. (The bottles containing liquid alkalis on a chemist's shelf have a clouded surface.)

Conductivity

The ability of a material to conduct electricity is dependent upon the presence of electrons in the conduction band, separated in glasses by as much as 10eV from the valence band. Because the electrons in glass are tightly bonded, glass is a very poor conductor of electricity - in fact, the large energy gap makes glass an excellent insulator. Glass is also a poor conductor of heat. Thus, hot common glass may crack when cold water is poured onto it because the surface exposed to the cold water will shrink while the dimensions of the interior remain unaffected.

Strength

Glass is harder than many types of steel and is also very elastic, as evidenced by the speed and accuracy with which glass marbles rebound when they meet.

Glass has "no" crystal structure, and hence the phenomenon of slip cannot take place. This, together with the strong bonding between atoms, gives glass a very high compressive strength and a theoretical tensile strength of about $10^7 kN/m^2$ (significantly higher than that of steel). (Glass fibers with an actual tensile strength of $4 \times 10^7 kN/m^2$ have been produced.) Since glass has a "liquid structure" it may be considered "saturated with dislocations". [If a piece of metal has a very high dislocation density (eg., due to cold working) the dislocations interfere with each other's movements. Therefore, with increasing dislocation density a piece of metal becomes harder and stronger, but also more brittle.] Since the molecular structures in glass are unable to move, the presence of minute cracks or imperfections in glass permits stress concentrations to localize and exceed the bond strength between atoms - common glass will crack. Thus, in actual practice, the strength of glass is, by a factor of 100 to 1000, less than the theoretical strength, and glass is brittle. For example, a freshly made electric light bulb may not crack when initially dropped, but its surface becomes damaged and, after it rebounds and strikes the floor a few more times, it breaks.

The inherent high strength of fibrous glass is utilized in the fiberglass sections employed for boats and automobile bodies. Before being pressed into shape fiberglass is mixed with a synthetic resin which serves to protect the fibers from scratching. Since the fibers thus retain their high strength, fiberglass sections are very strong for their weight.

STRENGTHENED GLASS

The glass scientist has produced objects made of glass which can be struck with a hammer or dropped from a tall building without breaking. Two techniques are employed in strengthening glass - one physical and one chemical. Both techniques are based on the fact that, when there is the slightest imperfection (minute scratch) on the surface, glass remains extraordinarily strong in compression but becomes weak in tension. Thus the strengthening treatment consists of *prestressing* a glass object by inducing compressive strains in its exterior and thereby enabling it to counteract any tensile stresses which develop under tension.

In physical prestressing, the shaped object is heated to just below its softening point (surface flows are annealed out) and its surface is then chilled by means of a blast of air or an oil bath. Under these conditions the exterior of the glass cools and contracts immediately, but since glass is a poor conductor of heat the interior will not contract - the glass will not crack because the interior remains plastic. When the interior starts to cool, it cannot contract because the exterior has already set, but, in attempting to contract, the interior continues to draw the exterior together. A built-in compressive stress then develops in the outer layers of the glass. When a tensile stress is applied to this glass, it is counteracted by these compressive stresses. Thus the prestressed glass will not shatter until the surface compression is exceeded.

As long as its surface remains intact, prestressed glass continues to be strong and shock-resistant. However, if a deep scratch develops on the surface, the tensile stresses set up in the interior by the surface compression are released and the glass will shatter into thousands of tiny particles. Therefore prestressed articles must be cut to exact size and all holes drilled prior to prestressing. Among the many uses for this type of glass are plate-glass doors, side windows of automobiles and portholes of ships.

Ion exchange is a chemical technique for prestressing glass objects. The first step is to place the shaped object into a molten salt bath containing potassium ions, which replace the sodium ions on the surface of the glass. The potassium ions are larger than the sodium ions and, in accommodating them, the surface of the glass becomes more crowded - thus inducing compressive strains on the exterior. Glass of this type, characterized by very high strength, is useful for a great variety of applications. Its flexural strength can be as high as $10^6 kN/m^2$ compared with $10^5 kN/m^2$ for untreated glass.

DEVITRIFICATION OF GLASS

Under certain conditions glass will become “contaminated” with crystalline particles. A glass in this condition is termed *devitrified*, which is simply another way of stating that it has partially or completely crystallized. Devitrified glass, unless of the very special variety that is deliberately produced, is undesirable since the crystalline areas form large crystals and are extremely weak and brittle, as well as being translucent only. Crystalline segregations in glass are known as stones

RECRYSTALLIZED GLASS (GLASS CERAMICS)

Recrystallized glass, also known as polycrystalline glass, is commonly produced by adding nucleating agents to the glass batch. Subsequently the glass can be formed into a desired shape by any of the conventional glass forming processes and then be heat-treated to promote recrystallization. Recrystallized glass possesses increased impact strength, hardness and thermal shock resistance compared with conventional non-crystalline glasses. One commonplace application of a recrystallized glass is in the manufacture of the so-called refrigerator-to-oven cooking dishes.

COLORED GLASSES

We recognize that glass is normally colorless due to the fact that all electrons are “tightly bonded” and no electronic excitations in the energy range of the visible light spectrum are possible. Glass, however, may be made to absorb selectively in the visible spectrum (thus becoming colored) by any one of three processes:

(1) Addition of ions of transition metals. Such ions provide electronic excitation possibilities to visible light. Typical ions added are:

Cr^{++}	blue	
Cr^{+++}	green	
Co^{++}	pink	(8.5.2)
Mn^{++}	orange	
Fe^{++}	blue-green	

(2) Addition of colloidal particles (ϕ 40 to 2000Å). These small particles, while not impeding light transmission (because of their small size) exhibit selective absorption and complementary reflection. Au particles (at 10^{-4} g/cm^3) give colors which vary with particle size:

Au	$\phi 4 - 10$ nm	pink	
Au	$\phi 10 - 75$ nm	ruby	(8.5.3)
Au	$\phi 75 - 110$ nm	green	
Au	$\phi 110 - 170$ nm	brown	

(3) Addition of colored crystals. Some glasses are colored by means of crystals dispersed throughout. An example is the scarlet glass made by the early Egyptians (brought about by the addition of red copper oxide). Another example is red color from the addition of red Pb_2CrO_6 whereas Cr_2O_3 yields green color.

GLASS FIBER

Glass fiber, or fiberglass* as it is commonly known, is glass in fiber form. It is made by one of several processes, each of which involves the drawing out of the filaments from glass in the viscous state. Modern technical developments date from World War I when Germany had to find a substitute for asbestos as insulating material.

The process whereby continuous filament glass fiber is made is particularly interesting. The glass batch is melted in the glass tank furnace and the molten glass is molded into ordinary sized marbles. These marbles are fed into an electric furnace which has a platinum-alloy bushing containing many tiny holes. When the glass marbles reach the holes, the glass flows through them and is

drawn down vertically, forming individual filaments. These filaments can then be twisted into a “yarn” and spun on normal textile spindles as required. About one third of an ounce of glass produces about one hundred miles of filament at a rate of about 6,000 feet per minute.

Glass wool, on the other hand, is produced by a different process. The most common technique, known as the Crown process, produces a thick matte of short glass fibers which are held together by a polymer binder. In the Crown method, a thick stream of molten glass is poured into a rapidly rotating steel dish that has tiny vents around its periphery. The glass is forced through these vents by centrifugal force, forming relatively short fibers with diameters of about 0.0007 cm. The matte is then passed through curing ovens where the binder sets and is then cut into sizes suitable for insulation.

*

Fiberglass is really a registered trade name.

SHEET AND PLATE GLASS PRODUCTION

The main types of flat glass produced are drawn sheet and float glass. The processes involved are highly automated.

Flat drawn glass is used for windows and other applications where accuracy of thickness and a high surface finish are not vital. In this process the molten glass is drawn up vertically from the end of a large rectangular tank furnace, the thickness of the drawn sheet being controlled principally by the size of the slot in the steel form held just above the surface of the molten glass. A steel starting dummy is used to commence the drawing action, but this is cracked off once it passes through. Once started, this process is continuous, the cooled and solidified sheet merely being cracked off in suitable lengths once it leaves the rolls.

The *float process* is the most recent advance in the production of plate glass with a high surface finish. In the float process, flat, fire-finished, stress-free glass is formed by preventing contact between the glass sheet and anything solid. The glass leaves the glass-tank in a continuous molten strip and is floated immediately onto the surface of a bath of molten tin. The tin bath is surrounded by a non-oxidizing atmosphere and, while in this atmosphere, the glass is heated sufficiently to prevent the development of internal stresses. As the glass sheet leaves the float bath chamber it enters an annealing furnace. Glass produced by the float process is free from distortion and has fire-finished surfaces that are smoother and flatter than those of normal polished plate glass.

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8.6: Phase Equilibria and Phase Diagrams

PHASE EQUILIBRIA AND PHASE DIAGRAMS

Phase diagrams are one of the most important sources of information concerning the behavior of elements, compounds and solutions. They provide us with the knowledge of phase composition and phase stability as a function of temperature (T), pressure (P) and composition (C). Furthermore, they permit us to study and control important processes such as phase separation, solidification, sintering, purification, growth and doping of single crystals for technological and other applications. Although phase diagrams provide information about systems *at equilibrium*, they can also assist in predicting phase relations, compositional changes and structures *in systems not at equilibrium*.

GASES, LIQUIDS AND SOLIDS

Any material (elemental or compound) can exist as a gas, a liquid or a solid, depending on the relative magnitude of the attractive interatomic or intermolecular forces vs the disruptive thermal forces. It is thus clear that the stability (existence) of the different states of aggregation, which are referred to as *phases*, is a function of temperature and pressure (since with increased pressure the atoms, for exampled of a gas phase, are closer spaced and thus subject to increased interatomic attraction).

In general terms, a “phase” is a homogeneous, physically distinct, mechanically separable portion of a material with a given chemical composition. To illustrate this definition, let us look at a few examples of common multi-phase systems. Ice cubes in water constitute a two-phase system (ice and liquid water), unless we include the vapor above the glass in our system, which would make it a three-phase system. A mixture of oil and water would also be a two-phase system. Just as oil and water represent two distinct liquid phases, two regions of a solid with distinctly different composition or structure separated by boundaries represent two solid phases.

If we look at a one-component system, such as liquid water, we recognize that because of the energy distribution of the water molecules, some water molecules will always possess sufficient energy to overcome the attractive forces on the surface of $\mathbf{H_2O}$ and enter into the gas phase. If thermal energy is continuously supplied to a liquid in an open container, the supply of high energy molecules (which leave the liquid phase) is replenished and the temperature remains constant - otherwise the loss of high energy molecules will lower the temperature of the system. The total quantity of heat necessary to completely "vaporize" one mole of a liquid at its boiling point is called its *molar heat of vaporization*, designated by $\mathbf{\Delta H_V}$. Similarly, the heat required to completely melt one mole of a solid (the heat required to break the bonds established in the solid phase) is called the *(latent) heat of fusion* ($\mathbf{\Delta H_V}$).

Visualize a liquid in a sealed container with some space above the liquid surface. Again, some of the most energetic liquid molecules will leave the liquid phase and form a "gas phase" above the liquid. Since gas molecules will thus accumulate in the gas phase (at a constant temperature), it is inevitable that as a result of collisions in the gas phase some molecules will re-enter the liquid phase and a situation will be established whereby the rate of evaporation will equal the rate of condensation – i.e., a dynamic equilibrium between the liquid and gas phase will exist. The established pressure in the gas phase is referred to as the *equilibrium vapor pressure*, which is normally significantly less for solids than for liquids.

For obvious reasons it is desirable to know for any given material the conditions (P, T) under which the solid state, the liquid state and the gaseous state are stable, as well as the conditions under which the solid and liquid phases may coexist. These conditions are graphically presented in *equilibrium phase diagrams*, which can be experimentally determined.

ONE-COMPONENT PHASE DIAGRAM

Figure 1 illustrates the temperatures and pressures at which water can exist as a solid, liquid or vapor. The curves represent the points at which two of the phases coexist in equilibrium. At the point $\boldsymbol{T_t}$ vapor, liquid and solid coexist in equilibrium. In the fields of the diagram (phase fields) only one phase exists. Although a diagram of this kind delineates the boundaries of the phase fields, it does not indicate the quantity of any phase present.

It is of interest to consider the slope of the liquid/solid phase line of the $\mathbf{H_2O}$ phase diagram. It can readily be seen that if ice – say at $\mathbf{-2^\circ C}$ – is subjected to high pressures, it will transform to liquid $\mathbf{H_2O}$. (An ice skater will skate not on ice, but on water.) This particular pressure sensitivity (reflected in the slope of the solid/liquid phase line) is characteristic for materials which have a

higher coordination number in the liquid than in the solid phase (H_2O, Bi, Si, Ge). Metals, for example have an opposite slope of the solid/liquid phase line, and the liquid phase will condense under pressure to a solid phase.

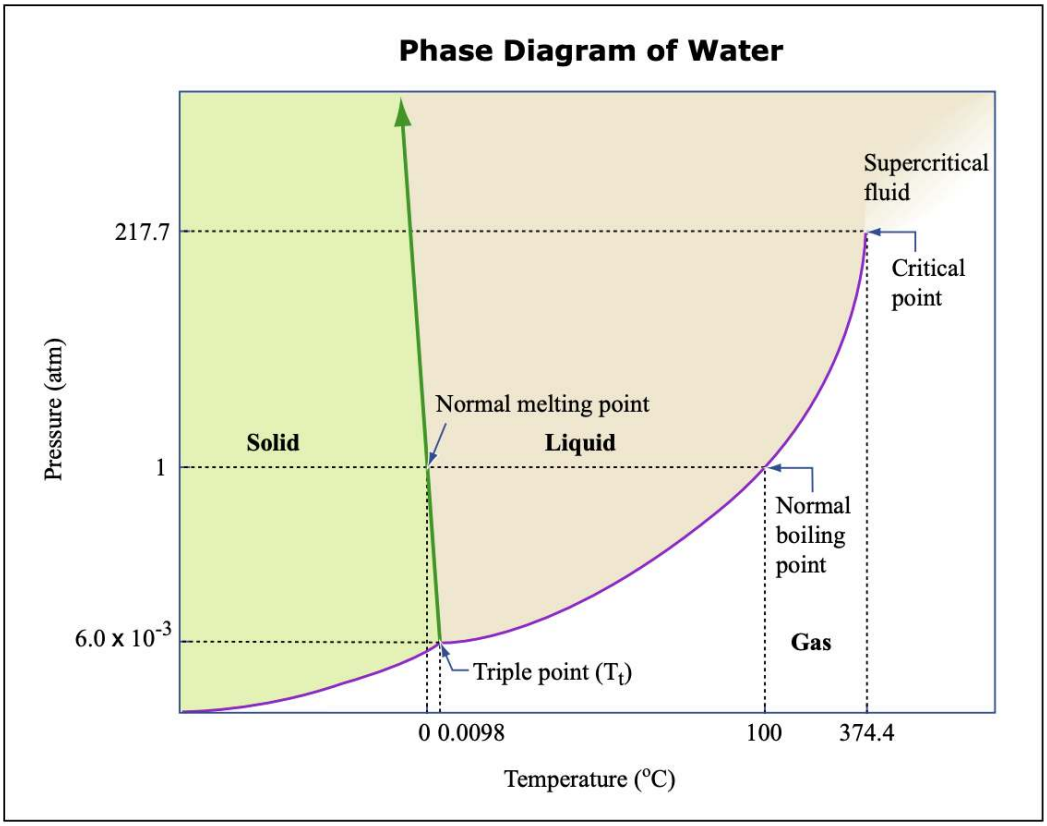


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Fig. 1 Pressure/Temperature Diagram for Water. (Not drawn to scale.)

PHASE RULE AND EQUILIBRIUM

The phase rule, also known as the Gibbs phase rule, relates the number of components and the number of degrees of freedom in a system at equilibrium by the formula

$$F = C - P + 2 \tag{1}$$

where F equals the number of degrees of freedom or the number of independent variables, C equals the number of components in a system in equilibrium and P equals the number of phases. The digit 2 stands for the two variables, temperature and pressure.

$$CaCO_3(s) \leftrightarrows CaO(s) + CO_2(g) \tag{2}$$

There are also three different chemical constituents, but the number of components is only two because any two constituents completely define the system in equilibrium. Any third constituent may be determined if the concentration of the other two is known. Substituting into the phase rule (eq. [1]) we can see that the system is univariant, since $F = C - P + 2 = 2 - 3 + 2 = 1$. Therefore only one variable, either temperature or pressure, can be changed independently. (The number of components is not always easy to determine at first glance, and it may require careful examination of the physical conditions of the system at equilibrium.)

The phase rule applies to dynamic and reversible processes where a system is heterogeneous and in equilibrium and where the only external variables are temperature, pressure and concentration. For one-component systems the maximum number of variables to be considered is two - pressure and temperature. Such systems can easily be represented graphically by ordinary rectangular coordinates. For two-component (or binary) systems the maximum number of variables is three pressure, temperature and concentration. Only one concentration is required to define the composition since the second component is found by subtracting

from unity. A graphical representation of such a system requires a three-dimensional diagram. This, however, is not well suited to illustration and consequently separate two-coordinate diagrams, such as pressure vs temperature, pressure vs composition and temperature vs composition, are mostly used. Solid/liquid systems are usually investigated at constant pressure, and thus only two variables need to be considered – the vapor pressure for such systems can be neglected. This is called a condensed system and finds considerable application in studying phase equilibria in various engineering materials. A condensed system will be represented by the following modified phase rule equation:

$$F = C - P + 1 \tag{3}$$

where all symbols are the same as before, but (because of a constant pressure) the digit 2 is replaced by the digit 1, which stands for temperature as variable. The graphical representation of a solid/liquid binary system can be simplified by representing it on ordinary rectangular coordinates: temperature vs concentration or composition.

PHASE DIAGRAM

With the aid of a suitable calorimeter and energy reservoir, it is possible to measure the heat required to melt and evaporate a pure substance like ice. The experimental data obtainable for a mole of ice is shown schematically in fig. 2. As heat is added to the solid, the temperature rises along line "a" until the temperature of fusion (T_f) is reached. The amount of heat absorbed per mole during melting is represented by the length of line " b ", or ΔH_F. The amount of heat absorbed per mole during evaporation at the boiling point is represented by line " d ". The reciprocal of the slope of line "a", (dH/dT), is the heat required to change the temperature of one mole of substance (at constant pressure) by 1°CF.(dH/dT) is the molar heat capacity of a material, referred to as " C_p ". As the reciprocal of line "a" is C_p (solid), the reciprocals of lines "c" and "e" are C_p (liquid) and C_p (vapor) respectively.

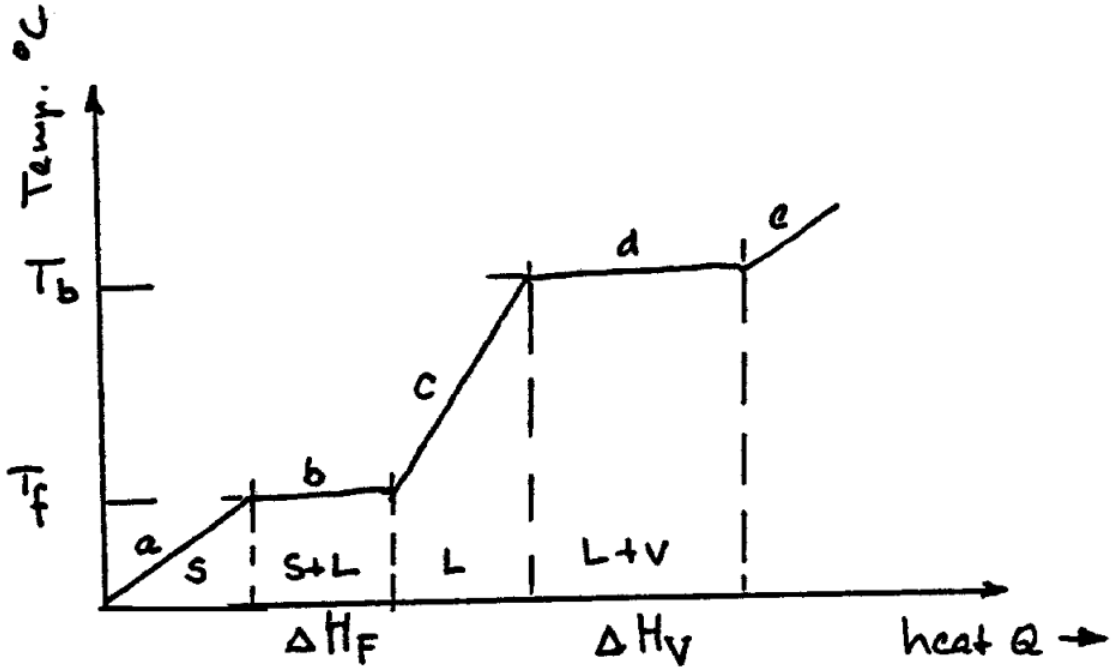


Fig. 2 H vs T Diagram for Pure H_2O. (Not to scale.)

From a thermodynamic standpoint, it is important to realize that fig. 2 illustrates the energy changes that occur in the system during heating. Actual quantitative measurements show that 5.98 kJ of heat are absorbed at the melting point (latent heat of fusion) and 40.5 kJ per mole (latent heat of evaporation) at the boiling point. The latent heats of fusion and evaporation are unique characteristics of all pure substances. Substances like Fe, Co, Ti and others, which are allotropic (exhibit different structures at different temperatures), also exhibit latent heats of transformation as they change from one solid state crystal modification to another.

ENERGY CHANGES

When heat is added from the surroundings to a material system (as described above), the energy of the system changes. Likewise, if work is done on the surroundings by the material system, its energy changes. The difference in energy (ΔE) that the system experiences must be the difference between the heat absorbed (Q) by the system and the work (W) done on the surroundings. The energy change may therefore be written as:

$$\Delta E = Q - W \tag{4}$$

If heat is liberated by the system, the sign of Q is negative and work done is positive. Q and W depend on the direction of change, but ΔE does not. The above relation is one way of representing the **First Law of Thermodynamics** which states that the energy of a system and its surroundings is always conserved while a change in energy of the system takes place. The energy change, ΔE, for a process is independent of the path taken in going from the initial to the final state.

In the laboratory most reactions and phase changes are studied at constant pressure. The work is then done solely by the pressure (P), acting through the volume change, ΔV.

$$W = P\Delta V \quad \$and\$ \quad \Delta P = 0 \tag{5}$$

Hence:

$$Q = \Delta E + P\Delta V \tag{6}$$

Since the heat content of a system, or the *enthalpy* H, is defined by.

$$H = E + PV \tag{7}$$

$$\Delta H = \Delta E + P\Delta V \tag{8}$$

so that:

$$\Delta H = Q - W + P\Delta V \tag{9}$$

or

$$\Delta H = Q \tag{10}$$

Reactions in which ΔH is negative are called *exothermic* since they liberate heat, whereas *endothermic* reactions absorb heat. Fusion is an endothermic process, but the reverse reaction, crystallization, is an exothermic one.

ENTROPY AND FREE ENERGY

When a gas condenses to form a liquid and a liquid freezes to form a crystalline solid, the degree of internal order increases. Likewise, atomic vibrations decrease to zero when a perfect crystal is cooled to $0°K$. Since the term *entropy*, designated by S, is considered a measure of the degree of disorder of a system, a perfect crystal at $0°K$ has zero entropy.

The product of the absolute temperature, T, and the change in entropy, ΔS, is called the entropy factor, $T\,\Delta S$. This product has the same units (Joules/mole) as the change in enthalpy, ΔH, of a system. At constant pressure, P, the two energy changes are related to one another by the Gibbs free energy relation:

$$\Delta F = \Delta H - T\Delta S \tag{11}$$

where

$$F = H - TS \tag{12}$$

The natural tendency exhibited by all materials systems is to change from one of higher to one of lower free energy. Materials systems also tend to assume a state of greater disorder whereby the entropy factor $T\Delta S$ is increased. The free energy change, ΔF, expresses the balance between the two opposing tendencies, the change in heat content (ΔH) and the change in the entropy factor ($T\Delta S$).

If a system at constant pressure is in an equilibrium state, such as ice and water at $0°C$, for example, at atmospheric pressure it cannot reach a lower energy state. At equilibrium in the ice-water system, the opposing tendencies, ΔH and $T\Delta S$, equal one another

so that $\Delta F = 0$. At the fusion temperature, T_F:

$$\Delta S_F = \frac{\Delta H_F}{T_F} \tag{13}$$

Similarly, at the boiling point:

$$\Delta S_v = \frac{\Delta H_v}{T_v} \tag{14}$$

Thus melting or evaporation only proceed if energy is supplied to the system from the surroundings.

The entropy of a pure substance at constant pressure increases with temperature according to the expression:

$$\Delta S = \frac{C_p \Delta T}{T} \quad (\text{since } : \Delta H = C_p \Delta T) \tag{15}$$

where C_p is the heat capacity at constant pressure, $\Delta C_p, \Delta H, T$ and ΔT are all measurable quantities from which ΔS and ΔF can be calculated.

F vs T

Any system can change spontaneously if the accompanying free energy change is negative. This may be shown graphically by making use of F vs T curves such as those shown in fig. 3.

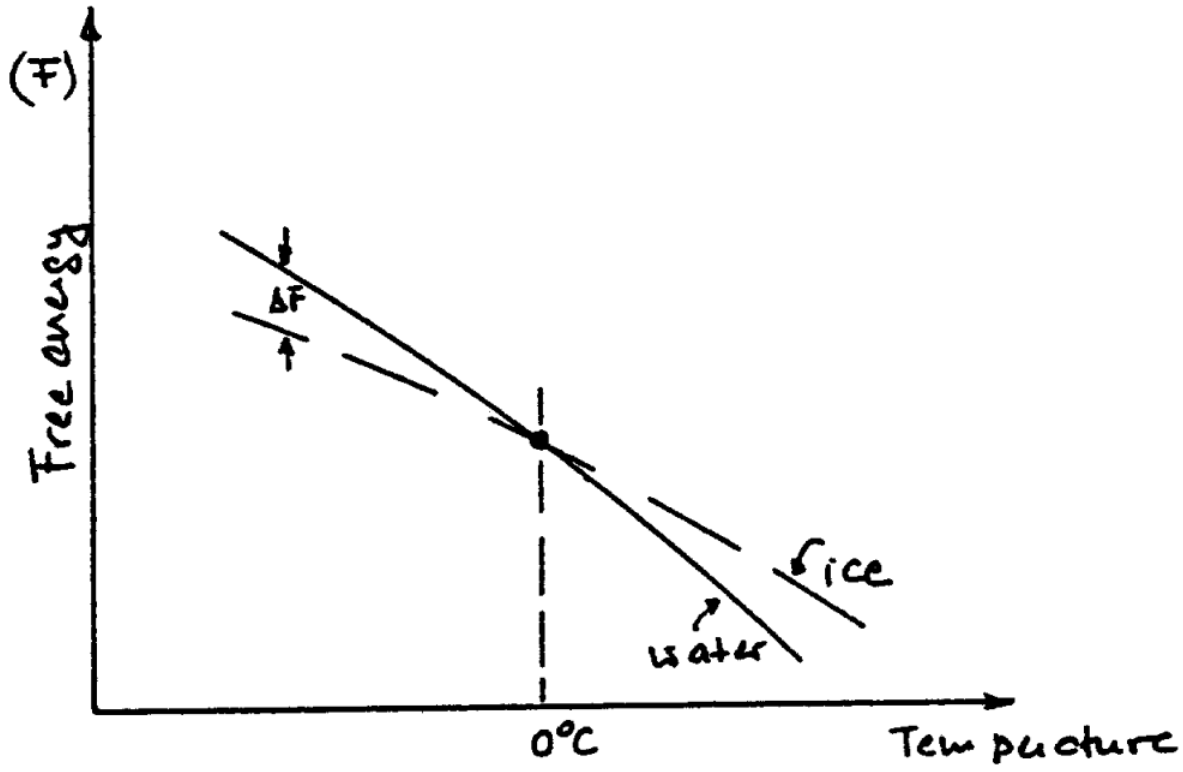


Fig. 3 Free energy is a function of temperature for ice and water.

The general decrease in free energy of all the phases with increasing temperature is the result of the increasing dominance of the temperature-entropy term. The increasingly negative slope for phases which are stable at increasingly higher temperatures is the result of the greater entropy of these phases.

PHASE DIAGRAMS (TWO-COMPONENT SYSTEMS)

SOLID SolutionS

A solution can be defined as a homogeneous mixture in which the atoms or molecules of one substance are dispersed at random into another substance. If this definition is applied to solids, we have a *solid solution*. The term “solid solution” is used just as “liquid solution” is used because the solute and solvent atoms (applying the term solvent to the element in excess) are arranged at random. The properties and composition of a solid solution are, however, uniform as long as it is not examined at the atomic or molecular level.

Solid solutions in alloy systems may be of two kinds: substitutional and interstitial. A substitutional solid solution results when the solute atoms take up the positions of the solvent metal in the crystal lattice. Solid solubility is governed by the comparative size of the atoms of the two elements, their structure and the difference in electronegativity. If the atomic radii of a solvent and solute differ by more than 15% of the radius of the solvent, the range of solubility is very small. When the atomic radii of two elements are equal or differ by less than 15% in size and when they have the same number of valency electrons, substitution of one kind of atom for another may occur with no distortion or negligible distortion of the crystal lattice, resulting in a series of homogeneous solid solutions. For an unlimited solubility in the solid state, the radii of the two elements must not differ by more than 8% and both the solute and the solvent elements must have the same crystal structure.

In addition to the atomic size factor, the solid solution is also greatly affected by the electronegativity of elements and by the relative valency factor. The greater the difference between electronegativities, the greater is the tendency to form compounds and the smaller is the solid solubility. Regarding valency effect, a metal of lower valency is more likely to dissolve a metal of higher valency. Solubility usually increases with increasing temperature and decreases with decreasing temperature. This causes precipitation within a homogeneous solid solution phase, resulting in hardening effect of an alloy. When ionic solids are considered, the valency of ions is a very important factor.

CONSTRUCTION OF EQUILIBRIUM PHASE DIAGRAMS OF TWO-COMPONENT SYSTEMS

To construct an equilibrium phase diagram of a binary system, it is a necessary and sufficient condition that the boundaries of one-phase regions be known. In other words, the equilibrium diagram is a plot of solubility relations between components of the system. It shows the number and composition of phases present in any system under equilibrium conditions at any given temperature. Construction of the diagram is often based on solubility limits determined by thermal analysis – i.e., using cooling curves. Changes in volume, electrical conductivity, crystal structure and dimensions can also be used in constructing phase diagrams.

The solubility of two-component (or binary) systems can range from essential insolubility to complete solubility in both liquid and solid states, as mentioned above. Water and oil, for example, are substantially insoluble in each other while water and alcohol are completely intersoluble. Let us visualize an experiment on the water-ether system in which a series of mixtures of water and ether in various proportions is placed in test tubes. After shaking the test tubes vigorously and allowing the mixtures to settle, we find present in them only one phase of a few percent of ether in water or water in ether, whereas for fairly large percentages of either one in the other there are two phases. These two phases separate into layers, the upper layer being ether saturated with water and the lower layers being water saturated with ether. After sufficiently increasing the temperature, we find, regardless of the proportions of ether and water, that the two phases become one. If we plot solubility limit with temperature as ordinate and composition as abscissa, we have an isobaric [constant pressure (atmospheric in this case)] phase diagram, as shown in fig. 4. This system exhibits a *solubility gap*.

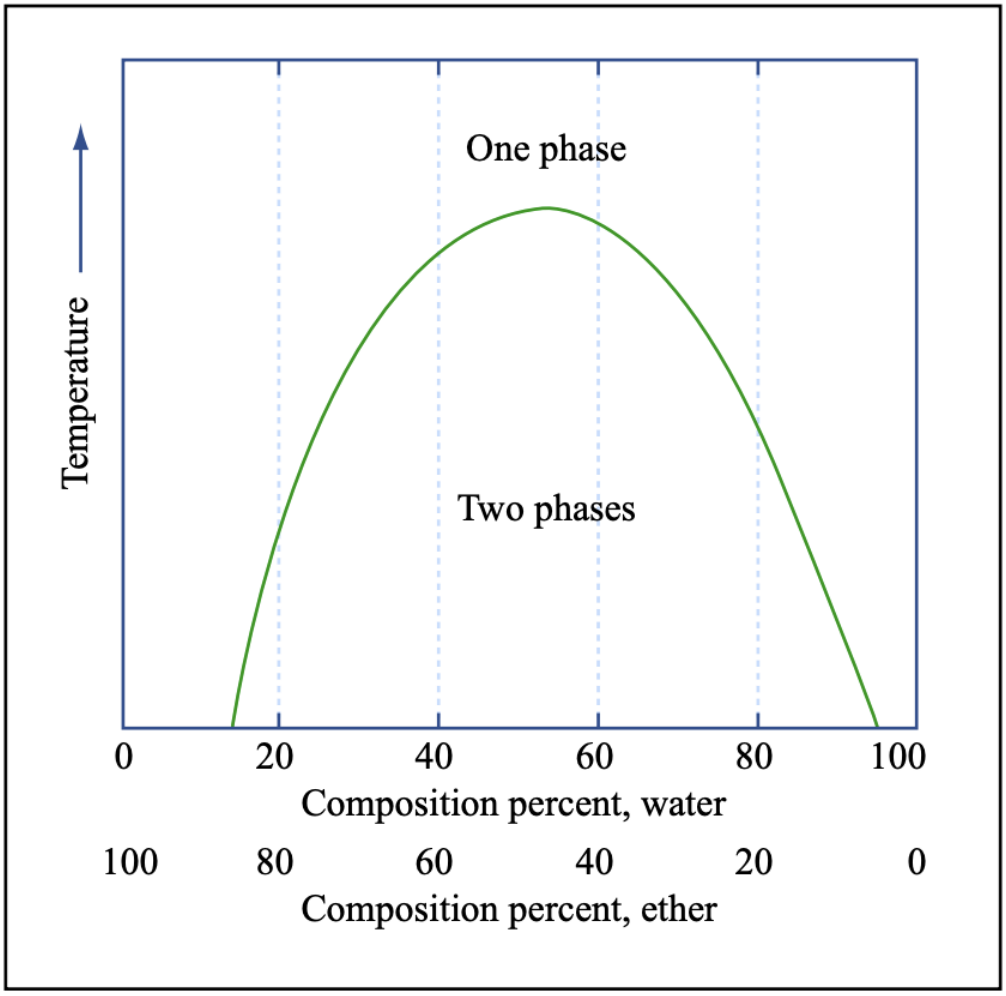


Image by MIT OpenCourseWare.

Fig. 4 Schematic representation of the solubilities of ether and water in each other.

COOLING CURVES

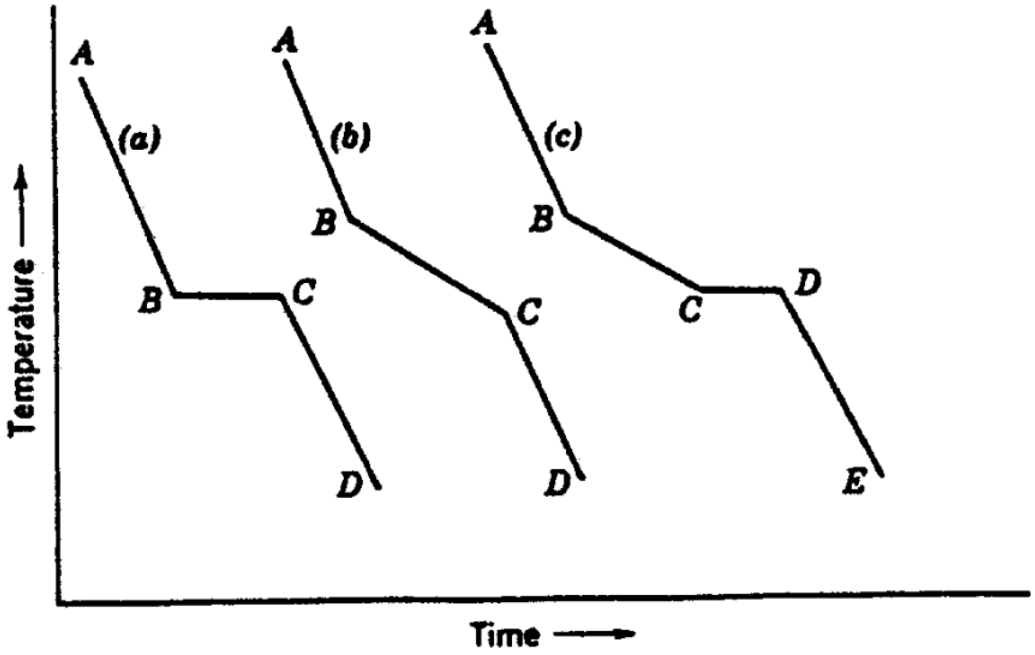


Fig. 5 Cooling curves: (a) pure compound; (b) binary solid solution; (c) binary eutectic system.

SOLID Solution EQUILIBRIUM DIAGRAMS

Read in Jastrzebski: First two paragraphs and Figure 3-4 in Chapter 3-8, "Solid Solutions Equilibrium Diagrams," pp. 91-92.

Read in Smith, C. O. The Science of Engineering Materials. 3rd ed. Englewood Cliffs, NJ: Prentice-Hall, 1986. ISBN: 9780137948840. Last two paragraphs and Figure 7-8 in Chapter 7-3-1, "Construction of a Simple Equilibrium Diagram," pp. 247-248.

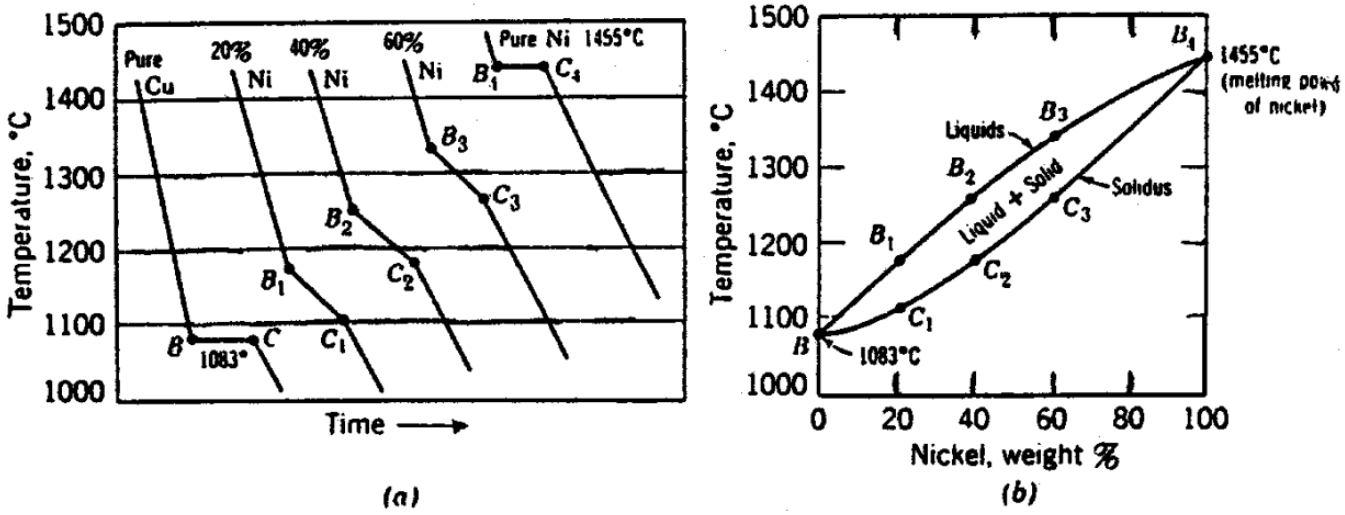


Fig. 6 Plotting equilibrium diagrams from cooling curves for Cu-Ni solid solution alloys. (a) Cooling curves; (b) equilibrium diagram.

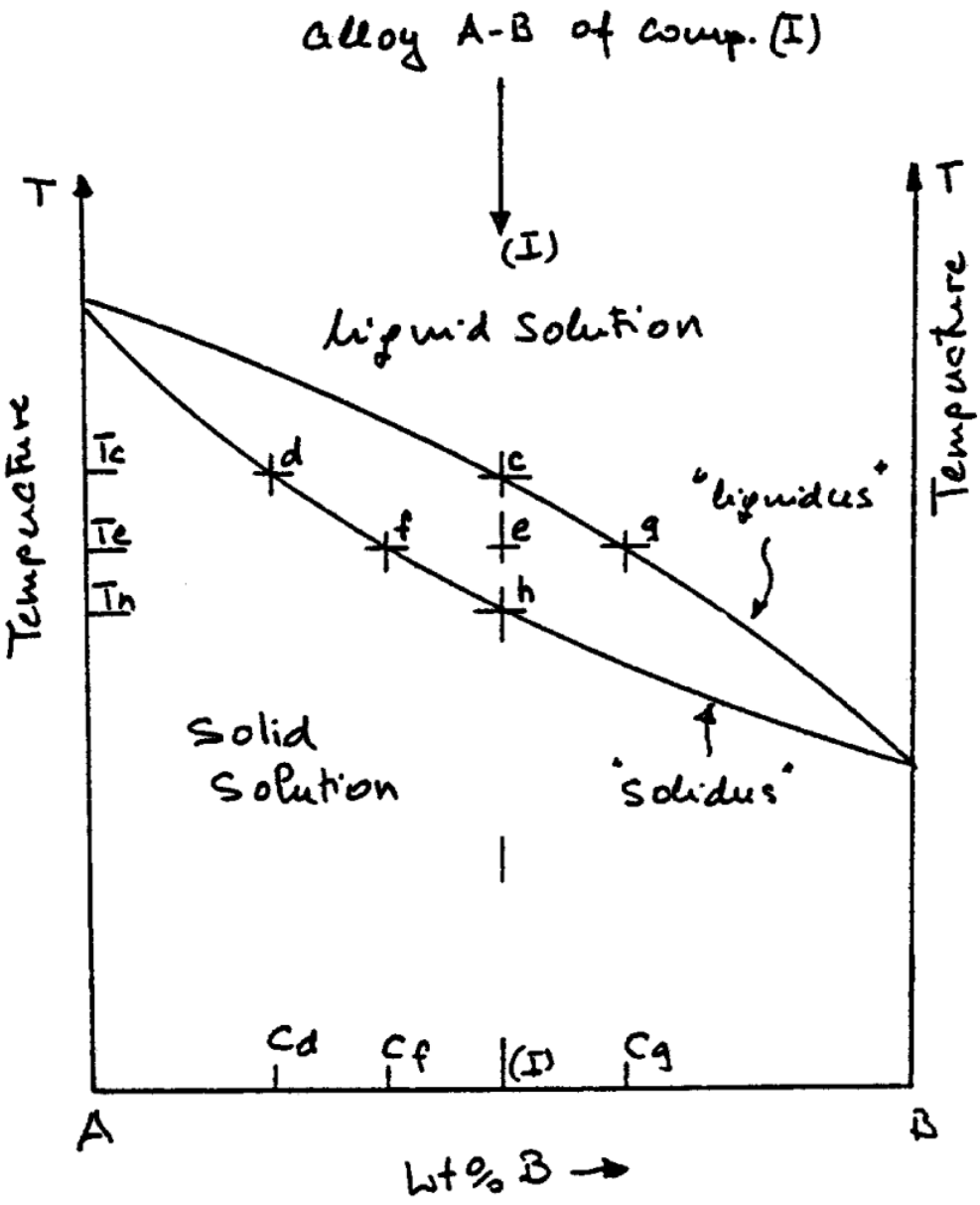


Fig. 7

INTERPRETATION OF PHASE DIAGRAMS

From the above discussion we can draw two useful conclusions which are the only rules necessary for interpreting equilibrium diagrams of binary systems.

Rule 1 - Phase composition: To determine the composition of phases which are stable at a given temperature we draw a horizontal line at the given temperature. The projections (upon the abscissa) of the intersections of the isothermal line with the liquidus and the solidus give the compositions of the liquid and solid, respectively, which coexist in equilibrium at that temperature. For example, draw a horizontal temperature line through temperature T_e in fig. 7. The T_e line intersects the solidus at f and the liquidus at g, indicating solid composition of $f\%$ of B and $(100-f)\%$ of A. The liquid composition at this temperature is $g\%$ of B and $(100-g)\%$ of A. This line in a two-phase region is known as a tie line because it connects or "ties" together lines of one-fold saturation - i.e., the solid is saturated with respect to B and the liquid is saturated with respect to A.

Rule 2 - The Lever Rule: To determine the relative amounts of the two phases, erect an ordinate at a point on the composition scale which gives the total or overall composition of the alloy. The intersection of this composition vertical and a given isothermal line is the fulcrum of a simple lever system. The relative lengths of the lever arms multiplied by the amounts of the phase present

must balance. As an illustration, consider alloy I in fig. 7. The composition vertical is erected at alloy I with a composition of $e\%$ of B and $(100-e)\%$ of A. This composition vertical intersects the temperature horizontal (T_e) at point e. The length of the line " $f-e-g$ " indicates the total amount of the two phases present. The length of line "$e-g$" indicates the amount of solid. In other words:

$$\begin{aligned} \frac{eg}{fg} \times 100 &= \%\text{ of solid present} \\ \frac{fg}{fg} \times 100 &= \%\text{ of liquid present} \end{aligned} \tag{8.6.1}$$

These two rules give both the *composition* and the *relative quantity* of each phase present in a two-phase region in any binary system in equilibrium regardless of physical form of the two phases. The two rules apply only to two-phase regions.

ISOMORPHOUS SYSTEMS

An isomorphous system is one in which there is complete intersolubility between the two components in the vapor, liquid and solid phases, as shown in fig. 9. The $\mathrm{Cu-Ni}$ system is both a classical and a practical example since the monels, which enjoy extensive commercial use, are $\mathrm{Cu-Ni}$ alloys. Many practical materials systems are isomorphous.

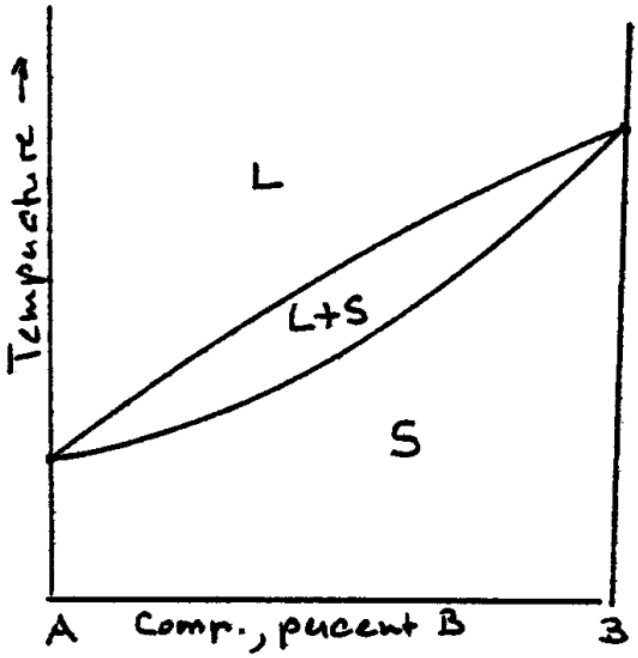


Fig. 9 Schematic phase diagram for a binary system, A-B, showing complete intersolubility (isomorphism) in all phases.

INCOMPLETE SOLUBILITY

Read in Smith, C. O. The Science of Engineering Materials. 3rd ed. Englewood

Cliffs, NJ: Prentice-Hall, 1986. ISBN: 9780137948840.

Chapter 7-3-5, "Incomplete Solubility," pp. 252-253.

EUTECTIC SYSTEMS

Read in Smith: Chapter 7-3-6, "Eutectic," pp. 253-256.

EQUILIBRIUM DIAGRAMS WITH INTERMEDIATE COMPOUNDS

Read in Jastrzebski, Z. D. *The Nature and Properties of Engineering Materials*. 2nd ed.

New York, NY: John Wiley & Sons, 1976. ISBN: 9780471440895.

Chapter 3-11,"Equilibrium Diagrams with Intermediate Compounds," pp. 102-103.

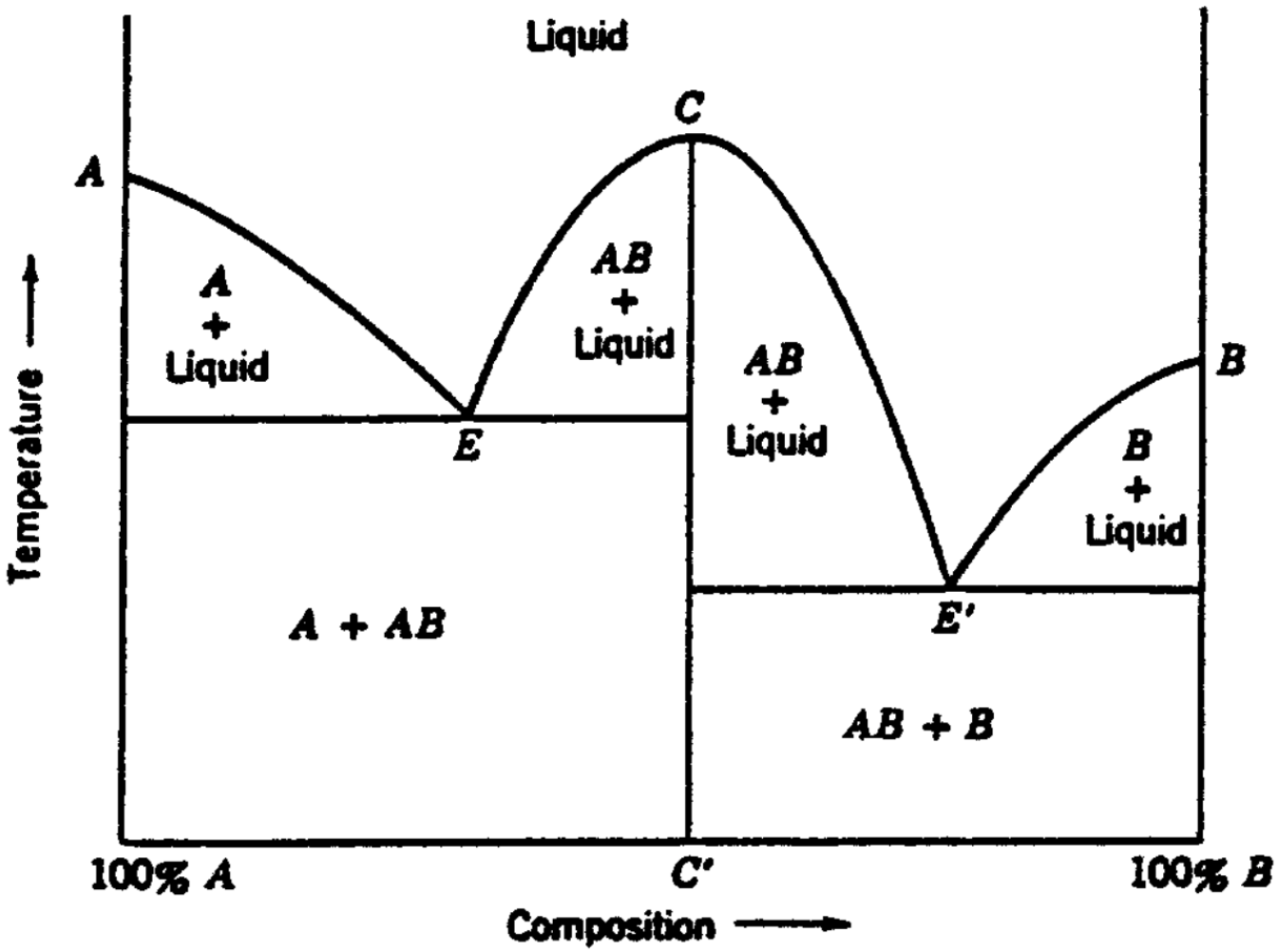


Fig. 15 Binary system showing an intermediate compound. C is the melting point (maximum) of the compound AB having the composition C'. E is the eutectic of solid A and solid AB. E' is the eutectic of solid AB and solid B.

TWO-COMPONENT SYSTEMS

A pressure-temperature diagram is extremely useful when one wishes to discuss a one-component system. A component in this case is an element or compound (for example, Fe, MgO, or H_2O). As long as there is only one component present, the system may be adequately described by the two variables, pressure and temperature. In a two-component system, a third variable is needed; this is composition. The two-component system may be described by a three dimensional pressure - temperature composition diagram. It is however in the framework of this course not appropriate to deal with the complexities of the 3D phase diagram at this point and, since most materials are used under isobaric (constant pressure) conditions, we will first discuss an isobaric two-dimensional diagram of temperature versus composition. At a later point we will explain how the one component pressure-temperature and the isobaric two-component temperature-composition diagrams may be combined to construct the three-dimensional pressure-temperature-composition diagram of a two-component system.

Temperature-composition diagrams

A two-component temperature-composition diagram at constant pressure is called a binary phase diagram or equilibrium diagram. Temperature is plotted as the ordinate and composition as the abscissa. In the system AB, the composition is usually expressed in terms of the mole fraction of B, x_B, or the weight percent of B, w/o B. (The mole fraction of B is equal to the number of moles of B divided by the sum of the number of moles of A plus the number of moles of B. The weight percent of B is equal to the product of

100 and the weight of B divided by the sum of the weights of A and B.) The composition need not be specified in terms of A since the sum of the mole fraction of B and the mole fraction of A is equal to one, and the sum of the weight percent of A and the weight percent of B is equal to 100. For pure A, both x_B and w/o B are zero; and for pure B they are one and 100, respectively.

A typical binary phase diagram (Figure 1) indicates those phases present in equilibrium at any particular temperature and composition at the constant pressure for which the phase diagram was determined. At low temperatures, the only phase present is the solid designated by S in the phase diagram. Pure A melts at the temperature T_{fA} and pure B melts at the temperature T_{fB} Alloys of composition between pure $A\,(x_B = 0)$ and pure $B\,(x_B = 1)$ exist only in the solid state of aggregation until the temperature of the solidus line is reached. The solidus is represented in the phase diagram by the lower curve extending from T_{fA} to T_{fB}. Below the solidus temperature only solid exists; but above the solidus, there is a two-phase region $(L + S)$ in which both liquid and solid phases are in equilibrium. The liquid-plus-solid region extends from the solidus temperature over a finite temperature interval for all alloys of the system AB. The extent of the temperature interval reduces to zero for the pure components A and B. since according to the one-component pressure-temperature diagram, at any particular pressure there is only one temperature at which liquid and solid are in equilibrium.

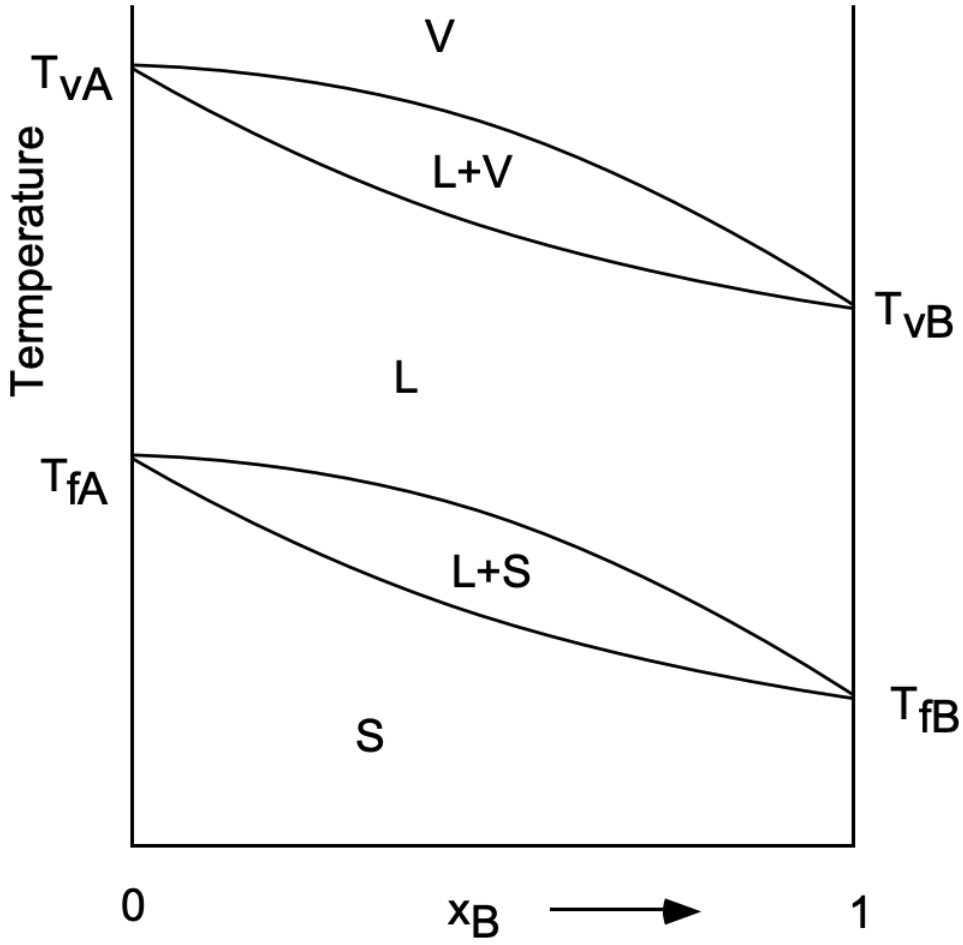


Figure 1 • Binary Phase Diagram. A binary phase diagram is an isobaric temperature composition diagram. In this case there is complete volubility in the solid, liquid, and vapor states of aggregation, and only one phase is found for each state of aggregation. At low temperatures, the material of any composition is solid; at higher temperatures there is a two-phase liquid-plus-solid region, a liquid region, a liquid-plus-vapor region and, at very high temperatures, an all-vapor region.

The upper boundary of the liquid-plus-solid region is the liquidus temperature. Above this temperature, any alloy of the system exists as a liquid phase until the temperature increases to that level at which vaporization begins. The pure compositions A and B vaporize completely at T_{vA} and T_{vB}, because the liquid and vapor phases for a pure component at constant pressure can be in equilibrium at only one temperature. Alloys of intermediate composition do not completely vaporize at any one temperature but

over a finite temperature interval.This is shown in the phase diagram of Figure 1 by the liquid-plus-vapor ($L + V$) region. At temperatures above this region, only the vapor phase exists.

Metallurgists or materials scientists are more often concerned with the liquid and solid phases and less often with the vapor phase. For this reason, and the fact that it is difficult to determine vapor phase diagrams, most binary diagrams extend no higher in temperature than the all-liquid region.

Cooling through a two-phase field

Solidification or melting of an intermediate alloy may be illustrated by the enlarged view of a two-phase field shown in Figure 2.

If an alloy of composition $\mathbf{x_o}$, originally liquid at temperature $\mathbf{T_1}$, is cooled, it remains liquid until the temperature reaches the liquidus temperature at point 2. At this temperature T_2, the first particle of solid appears. This solid does not have the same composition as the parent liquid. The composition of the first solid formed at $\mathbf{T_2}$ is found by constructing an isothermal line from 2 to $2'$. This isotherm is called a tie-line. The composition of the solid and liquid phases in equilibrium at a particular temperature is given by the intersection of the tie-line at that temperature with the solidus and liquidus curves, respectively. Thus at temperature T_2, the solid has the composition $\times 2'$ and the liquid the composition x_2 (where $x_2 = x_0$).

Upon further cooling to T_3, the composition of the liquid has shifted to the left along the liquidus to $\times 3$, and the composition of the solid has shifted to the left along the solidus to $x3'$ because at T_3, the only liquid and solid compositions that can be in equilibrium with one another are $x3$ and $x3'$ respectively.

Despite the fact that both liquid and solid have compositions different from the alloy composition, the overall alloy (liquid and solid together) retains its original composition x_0. As the temperature approaches the solidus temperature $\mathbf{T_5}$, the solid composition approaches x', (where $x_5' = x_0$) and the last quantity of liquid of composition x_5 freezes. At temperatures below the solidus, the solid composition remains unchanged, for example, at $\mathbf{T_6}$ the solid composition is $\mathbf{x_0}$.

The above analysis applies only to solidification at such a slow rate of cooling that equilibrium is achieved at every temperature. This is not always the case, however.

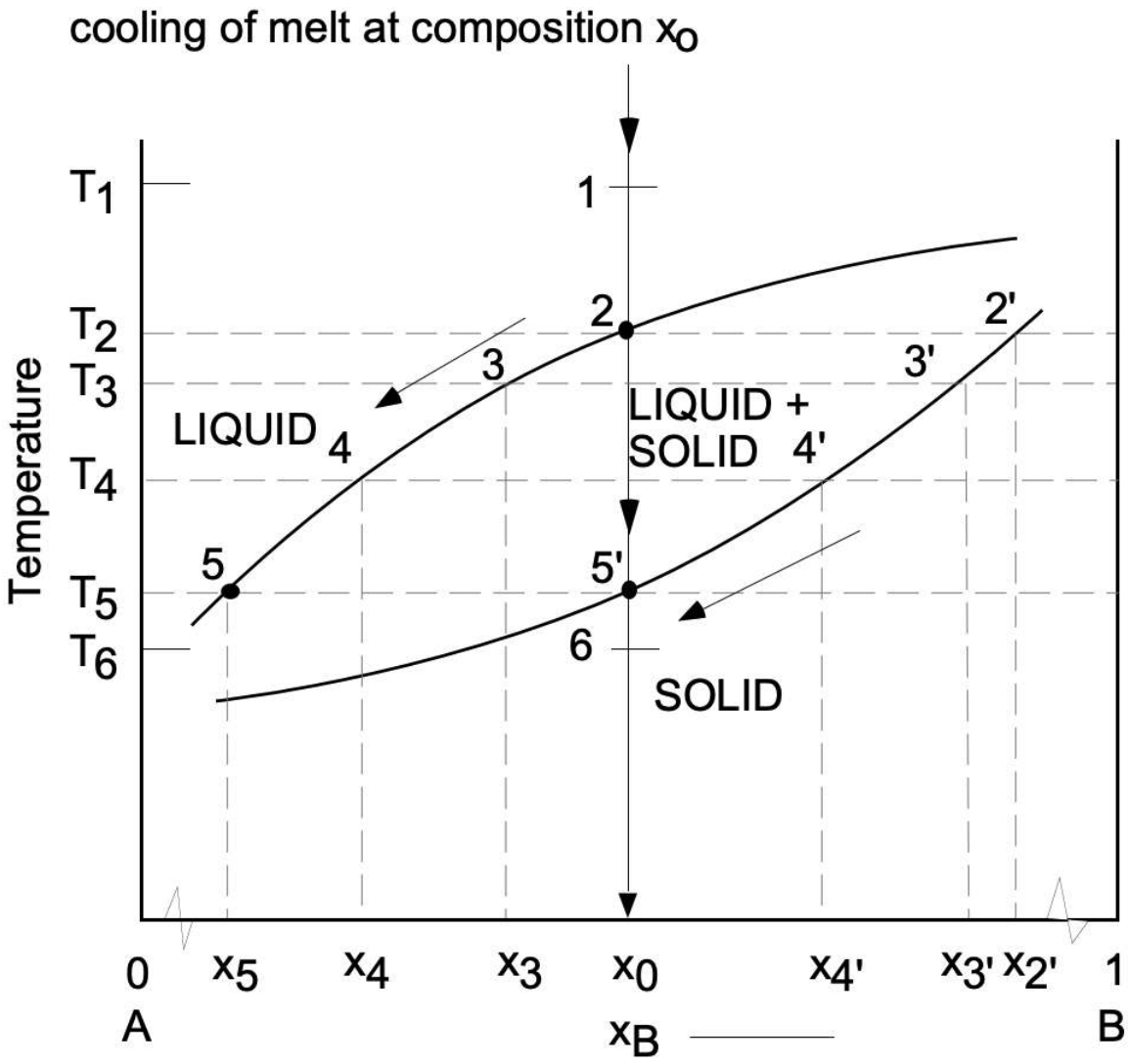


Figure 2 · Cooling Through a Two-Phase Field. As an alloy of composition x_0 is cooled from the liquid region through the two-phase liquid-plus-solid field, the first particle of solid forms at temperature T_2 and is of composition $x_{2,}$. The composition of the solid is given by the intersection of the isothermal tie line with the solidus, and the composition of the liquid by the intersection of the tie-line with the liquidus. As the temperature is decreased, the composition of the solid and of the liquid shifts to the left until at T_5 the solid is of composition x_0 and the last of the liquid freezes.

lever law

To determine exactly how much liquid and solid are present at any given temperature, let us derive a relation known as the "lever law." If one mole of alloy of composition x_0 is chosen as a basis, then, at any temperature T. the fraction of liquid f_L is found as follows: The sum of the fractions of liquid and solid must equal one, that is,

$$f_S + f_L = 1$$

The number of moles of B present in the alloy must be the same as the number of moles of B present in the solid phase plus the number of moles of B present in the liquid phase, that is,

$$x_O = x_S f_S = xL f_L$$

Since

$$f_S = 1 - f_L$$

we may substitute and obtain

$$x_O = x_S - x_S fL + x_L f_L$$

On rearranging and solving for $\mathbf{f_L}$ we find that

$$f_L = (x_S - x_0) / (x_S - xL) .$$

This relation is called the "lever law" because the fraction of one of the two phases present is equal to the opposite side of the tie-line $(\mathbf{x_S - x_O})$ divided by the entire tie-line $(x_S - x_L)$ In this way the tie-line acts as though it were a lever whose fulcrum is at the point x_0. In a similar way it is found that

$$f_s = (x_O - x_L) / (x_S - xL) .$$

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