INORGANIC



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Inorganic

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This text was compiled on 08/24/2026

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Glossary

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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.

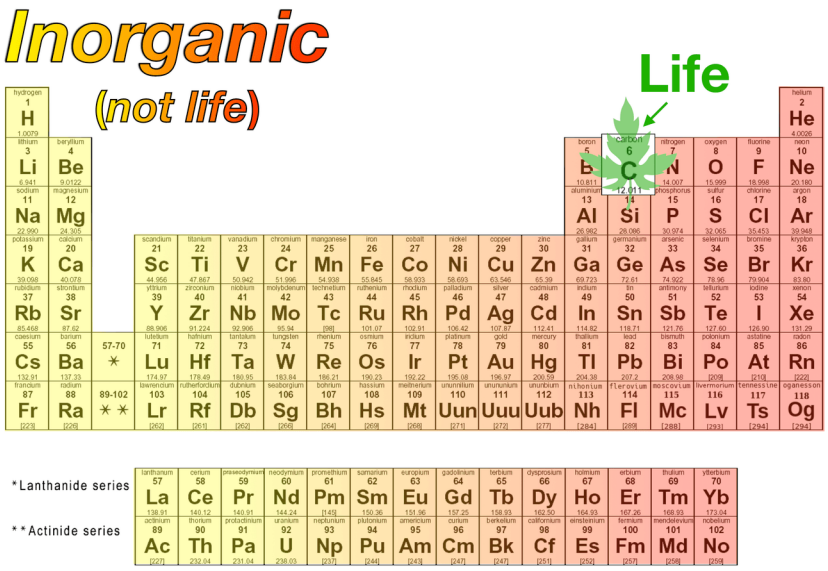


Figure 1.1.1. An illustration of the historic meaning of "organic" and "inorganic". The modern understanding of organic and inorganic chemistry is not consistent with these historical meanings. (Kathryn Haas; CC-NC-BY-SA)

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 available at the end of this section.

Answers

What are the Sub-Fields of Inorganic Chemistry?

There are a lot of correct answers here! The point here is that you notice that Inorganic Chemistry is a very broad field. It has something for almost everyone because many other fields overlap with Inorganic Chemistry. You might notice that some of the sub-fields you identified are also interdisciplinary fields between inorganic chemistry and another discipline. For a list of some of the subfields of Inorganic Chemistry, check this Wikipedia article.

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1.2: Inorganic vs Organic Chemistry

The division between the fields of Inorganic and Organic chemistry has become blurred. For example, let's look at one of the major classes of catalysts used for organic synthesis reactions: organometalic catalysts (Figure 1.2.1). Organometallic catalysts like these, and all organometallic compounds, contain metals that are bonded to carbon or carbon-containing molecules. So, are they "inorganic" because they contain metals, or "organic" because they contain carbon? These illustrate that clear divisions between organic and inorganic chemistry do not exist. Further, metal ions are common in biology and so the idea that metals are "inorganic" and thus classed as "non-living or non-biological" is incorrect. A canonical example is the organometallic catalyst adenosylcobalbumin, which is an important biological cofactor containing a cobalt (Co) ion (Figure 1.2.1, right) and a cobalt-carbon bond.

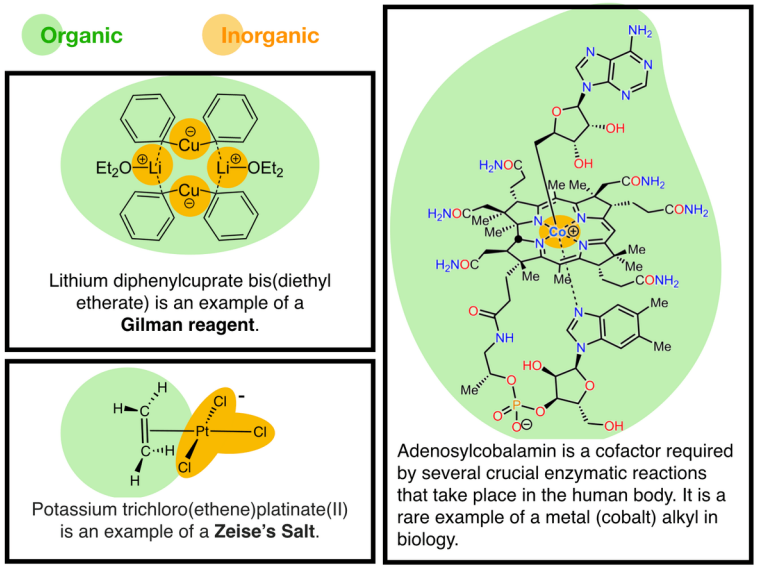
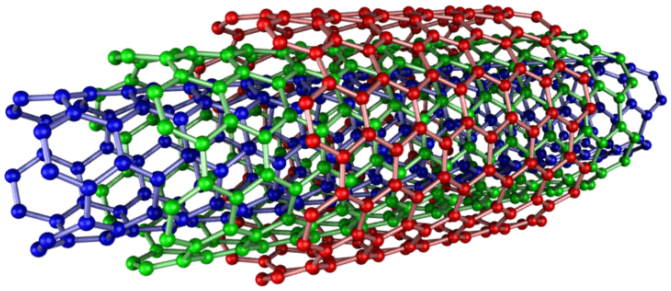


Figure 1.2.1: Some examples of organometallic catalysts. These compounds catalyze organic reactions or biochemical reactions and they are compounds that contain both carbon and metals. These compounds are examples of molecules that cannot be defined only as organic molecules or only as inorganic molecules. Adenosylcobalbumin is an example of an organometallic catalyst that is present in biology, further illustrating that "inorganic" metals are important cofactors in biology. This image is based on information on the Wikipedia article on Organometallic Chemistry and is created from images found there; attribution to images created by Alsosaid1987, AdoCbl-ColorCoded, CC BY-SA 4.0 and Smokefoot, Zeise'sSalt, CC BY-SA 3.0. (Kathryn Haas; CC-BY-SA)

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



Buckminsterfullerene is a type of fullerene with the formula C_{60}



Triple-walled armchair **carbon nanotube**

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

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

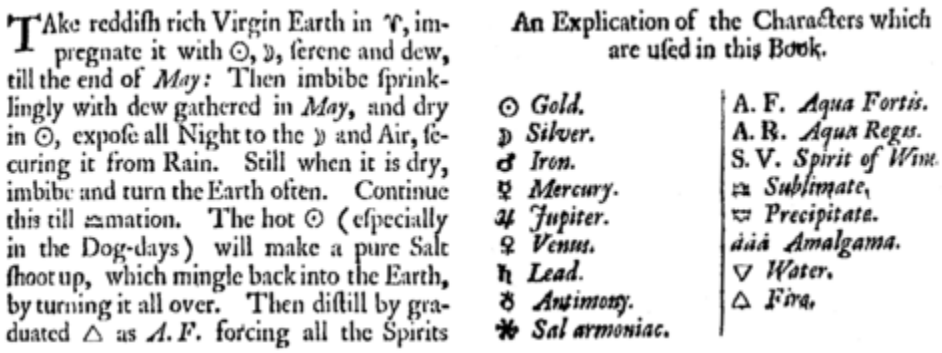
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1.3: History of Inorganic Chemistry

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.*
ȧȧȧ *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 ($ceHNO3$), sulfuric acid ($\mathrm{H_2SO_4}$), 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 ($\mathrm{Fe_4[Fe(CN)_6]_3}$). 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.

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

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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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

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

***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).

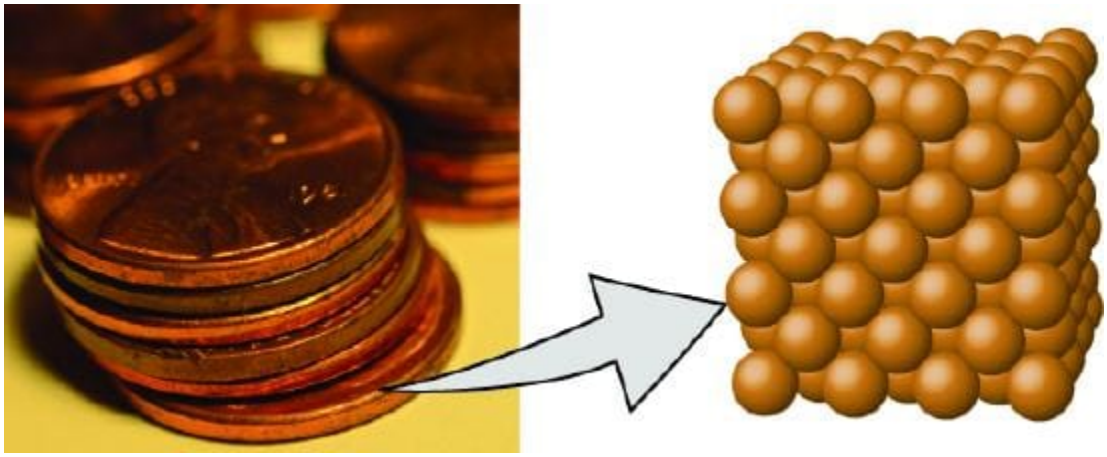


Figure 2.1.1***:*** *A pre-1982 copper penny (left) contains approximately* 3×10^{22} *copper atoms (several dozen are represented as brown spheres at the right), each of which has the same chemical properties. (credit: modification of work by "slgckgc"/Flickr)*

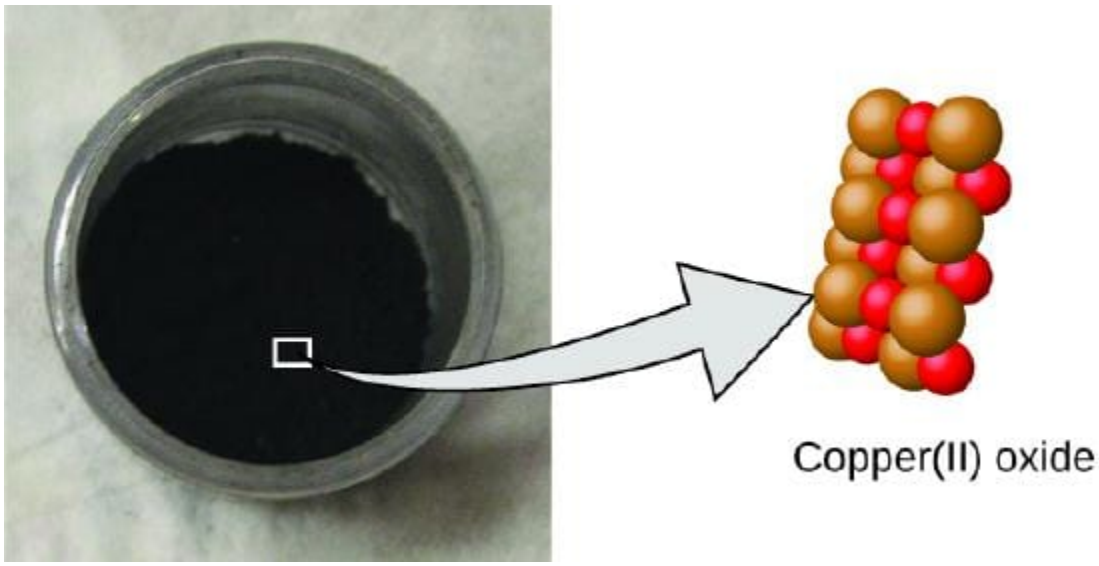


Figure 2.1.2***:*** *Copper(II) oxide, a powdery, black compound, results from the combination of two types of atoms—copper (brown spheres) and oxygen (red spheres)—in a 1:1 ratio. (credit: modification of work by "Chemicalinterest"/Wikimedia Commons)*

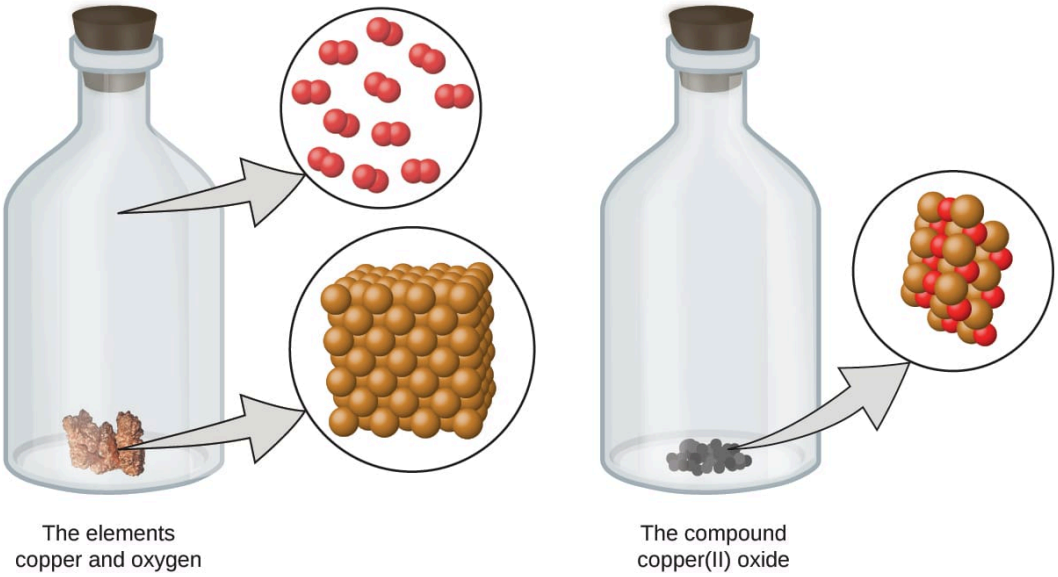


Figure 2.1.3*: When the elements copper (a shiny, red-brown solid, shown here as brown spheres) and oxygen (a clear and colorless gas, shown here as red spheres) react, their atoms rearrange to form a compound containing copper and oxygen (a powdery, black solid). (credit copper: modification of work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

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

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?

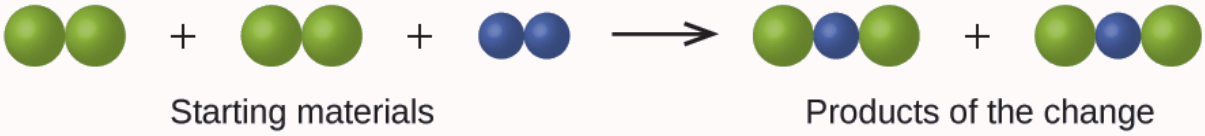


Solution

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).

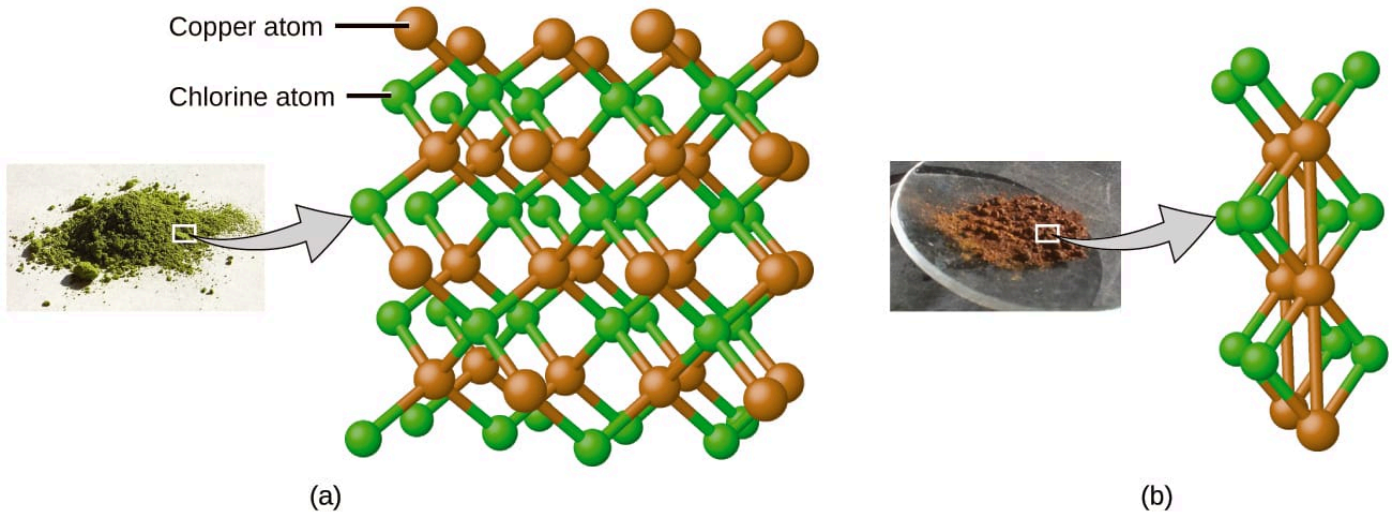


Figure 2.1.4*: Compared to the copper chlorine compound in (a), where copper is represented by brown spheres and chlorine by green spheres, the copper chlorine compound in (b) has twice as many chlorine atoms per copper atom. (credit a: modification of work by "Benjah-bmm27"/Wikimedia Commons; credit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

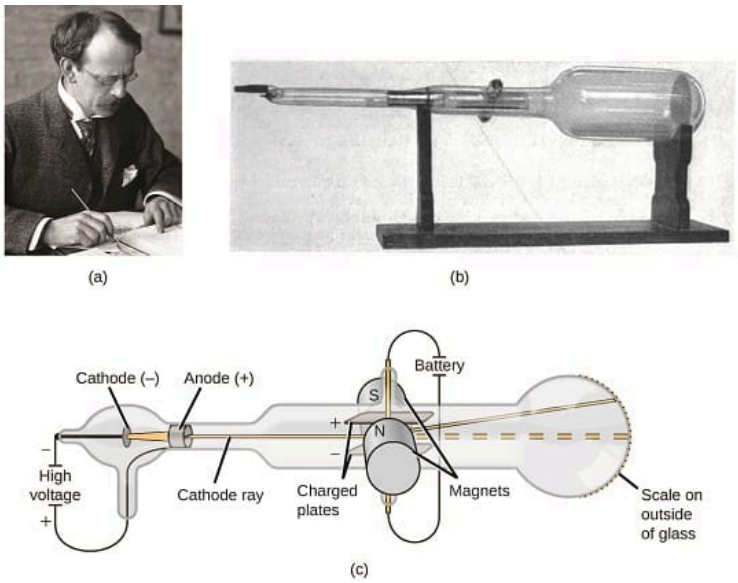
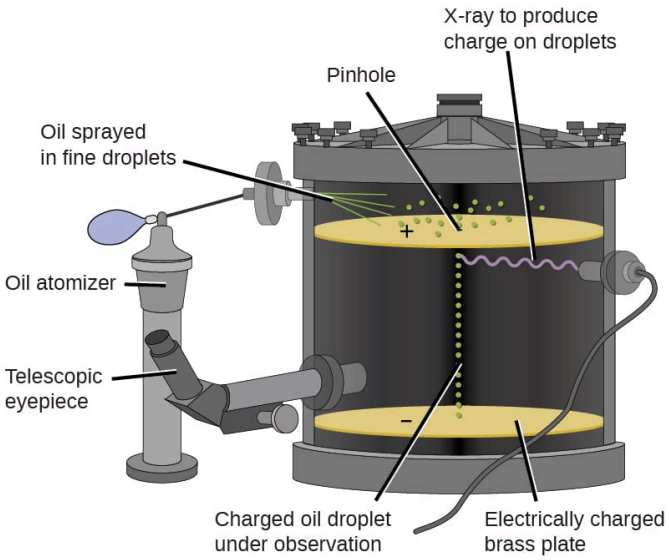


Figure 2.1.5*: (a) J. J. Thomson produced a visible beam in a cathode ray tube. (b) This is an early cathode ray tube, invented in 1897 by Ferdinand Braun. (c) In the cathode ray, the beam (shown in yellow) comes from the cathode and is accelerated past the anode toward a fluorescent scale at the end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

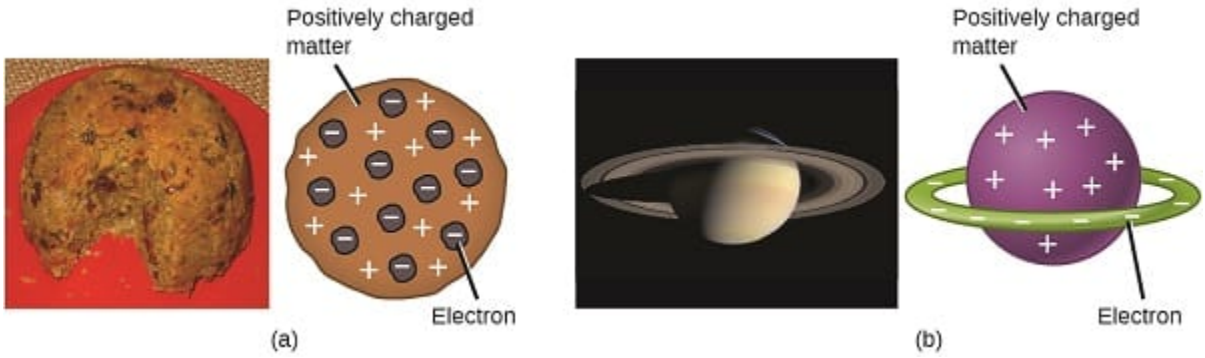


Figure 2.1.7*: (a) Thomson suggested that atoms resembled plum pudding, an English dessert consisting of moist cake with embedded raisins ("plums"). (b) Nagaoka proposed that atoms resembled the planet Saturn, with a ring of electrons surrounding a positive "planet." (credit a: modification of work by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

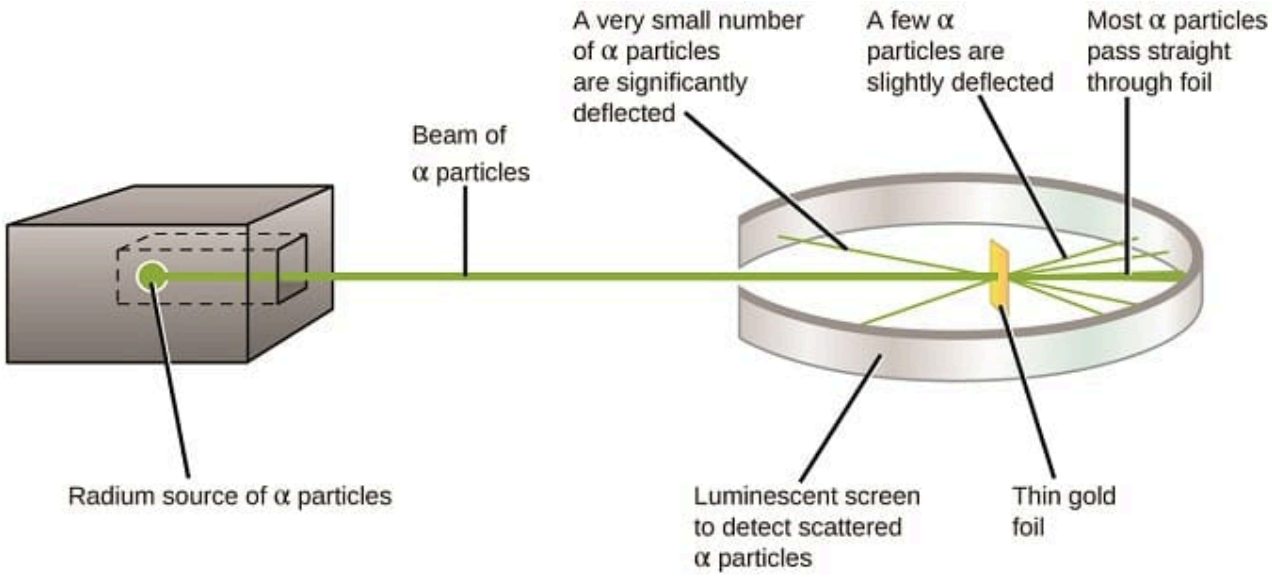


Figure 2.1.8***:*** *Geiger and Rutherford fired α particles at a piece of gold foil and detected where those particles went, as shown in this schematic diagram of their experiment. Most of the particles passed straight through the foil, but a few were deflected slightly and a very small number were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

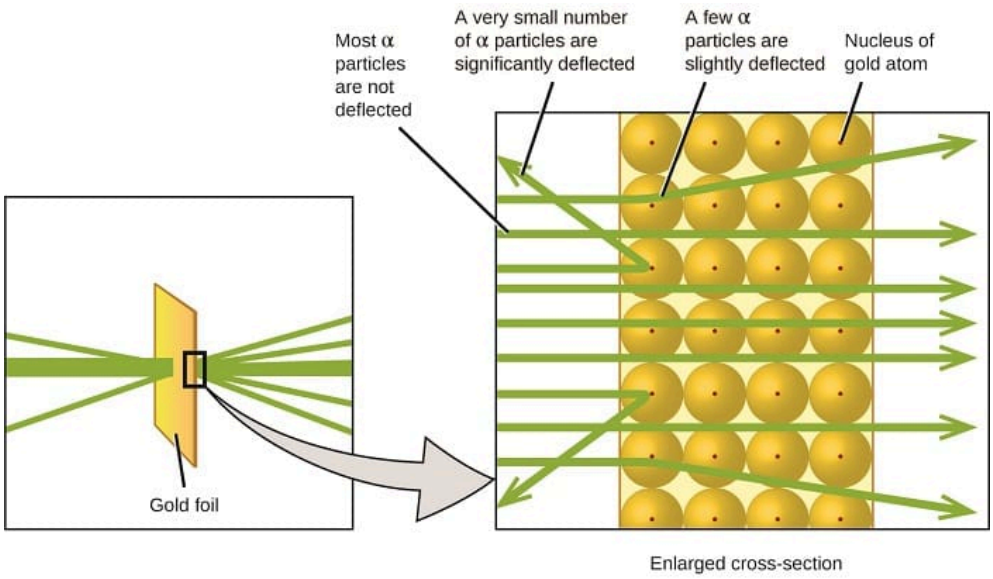


Figure 2.1.9*: The α particles are deflected only when they collide with or pass close to the much heavier, positively charged gold nucleus. Because the nucleus is very small compared to the size of an atom, very few α particles are deflected. Most pass through the relatively large region occupied by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

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Video 2.1.2***: An Introduction to Subatomic Particles***

Summary

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

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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

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- 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.
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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):

$$\frac{molar\ mass\ \left(\not{g}/mol\right)}{density\ \left(\not{g}/cm^3\right)} = molar\ \ volume\ \left(cm^3/mol\right)$$

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.

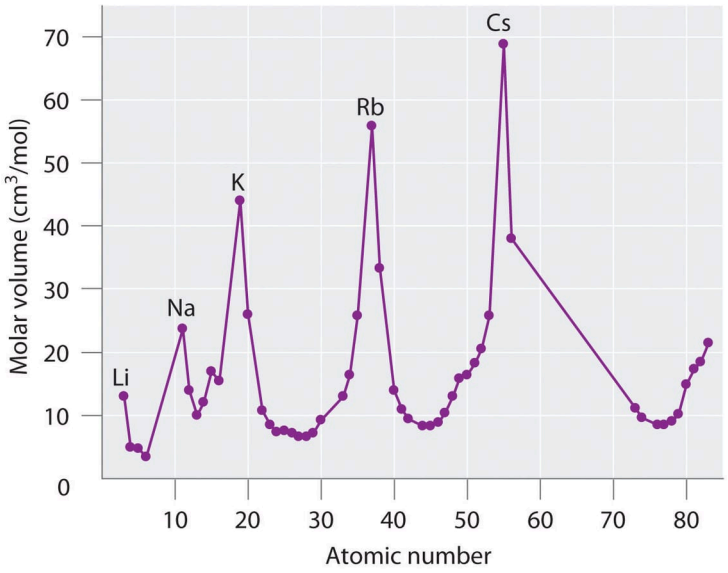


Figure 3.4.2 Variation of atomic volume with atomic number, adapted from Meyer's plot of **1870:** *Note the periodic increase and decrease in atomic volume. Because the noble gases had not yet been discovered at the time this graph was formulated, the peaks correspond to the alkali metals (group 1).*

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. — R^2O	Gruppe II. — RO	Gruppe III. — R^2O^3	Gruppe IV. RH^4 RO^2	Gruppe V. RH^3 R^2O^5	Gruppe VI. RH^2 RO^3	Gruppe VII. RH R^2O^7	Gruppe VIII. — RO^4
1	H=1							
2	Li=7	Be=9,4	B=11	C=12	N=14	O=16	F=19	
3	Na=23	Mg=24	Al=27,3	Si=28	P=31	S=32	Cl=35,5	
4	K=39	Ca=40	— =44	Ti=48	V=51	Cr=52	Mn=55	Fe=56, Co=59, Ni=59, Cu=63.
5	(Cu=63)	Zn=65	— =68	— =72	As=75	Se=78	Br=80	
6	Rb=85	Sr=87	?Yt=88	Zr=90	Nb=94	Mo=96	— =100	Ru=104, Rh=104, Pd=106, Ag=108.
7	(Ag=108)	Cd=112	In=113	Sn=118	Sb=122	Te=125	J=127	
8	Cs=133	Ba=137	?Di=138	?Ce= 40	—	—	—	— — — —
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.

YouTube Video

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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.

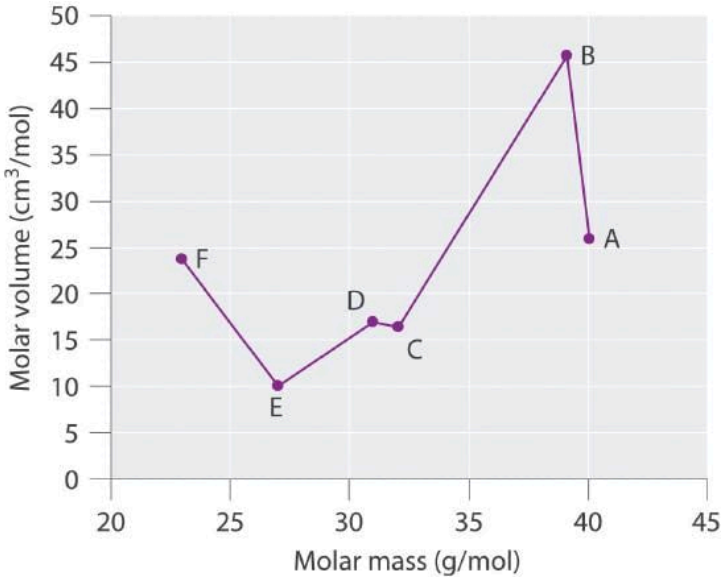
Species	Molar Mass (g/mol)	Density (g/cm^3)	Molar Volume (cm^3/mol)
A	40.078		25.85
B	39.09	0.856	
C	32.065		16.35
D		1.823	16.98
E	26.98		9.992
F	22.98	0.968	

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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Modified by Joshua Halpern

Video from TED-Ed Lou Serocp

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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.

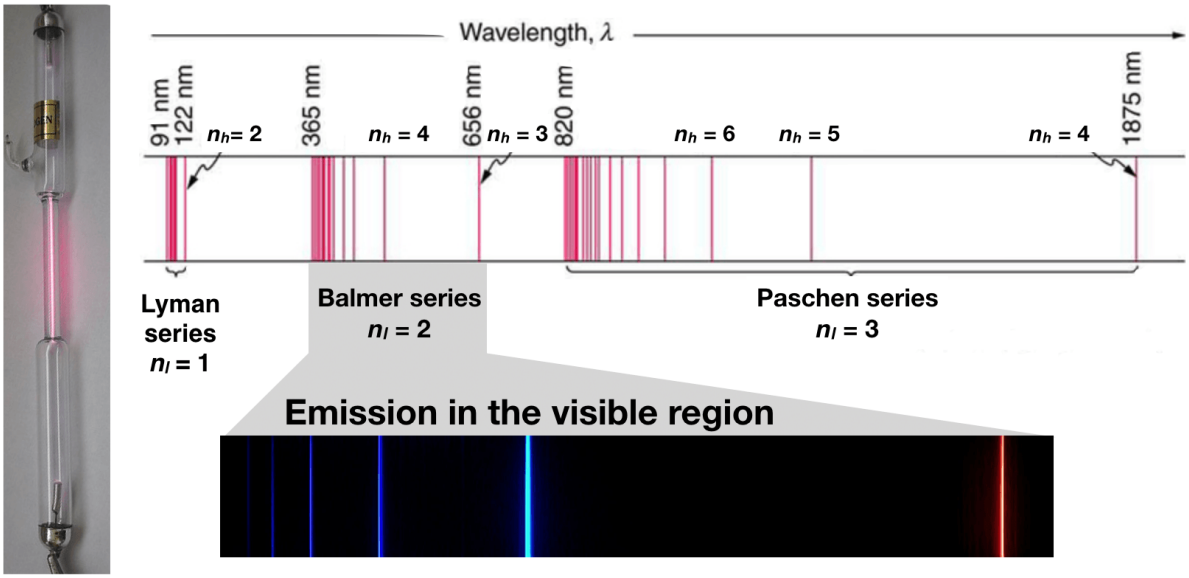


Figure 2.1.2.1: The emission of light by hydrogen atoms. (left) A sample of excited hydrogen atoms emits a characteristic red light. (bottom) When the light emitted by a sample of excited hydrogen atoms is split into its component wavelengths by a prism, four characteristic violet, blue, green, and red 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., $n_l = 1$)?

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

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* ($n_l = 1$)

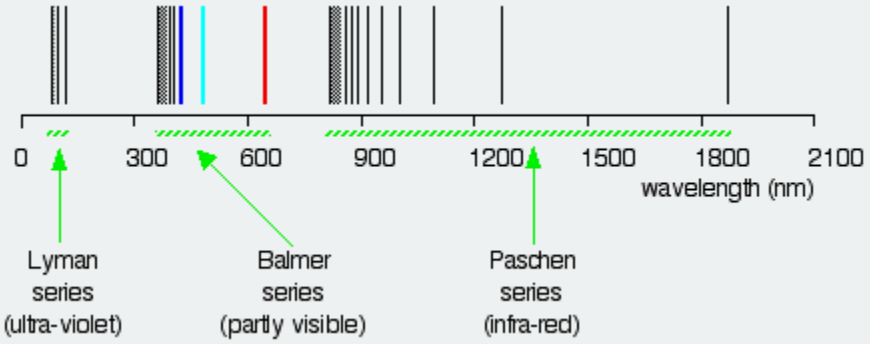
n_h	2	3	4	5
λ **(nm)**	121	102	97	94
$\tilde{u}$ **(cm^{-1})**	82,2291	97,530	102,864	105,332

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 $Ref2.1.2.2$ (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 $Ref2.1.2.2$ 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 available at the end of this section.

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.

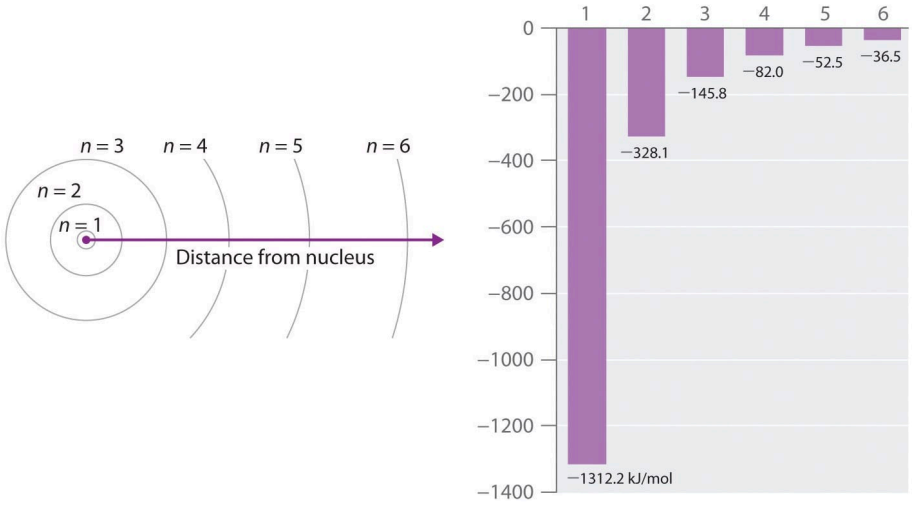
The Bohr Model

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* = ∞ 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.



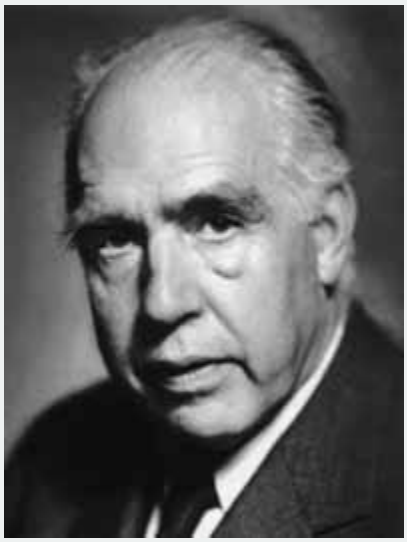
(a) Hydrogen orbits (Bohr model). Orbits are not drawn to scale.

(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 $2.1.2.2a$). 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 $2.1.2.1$).

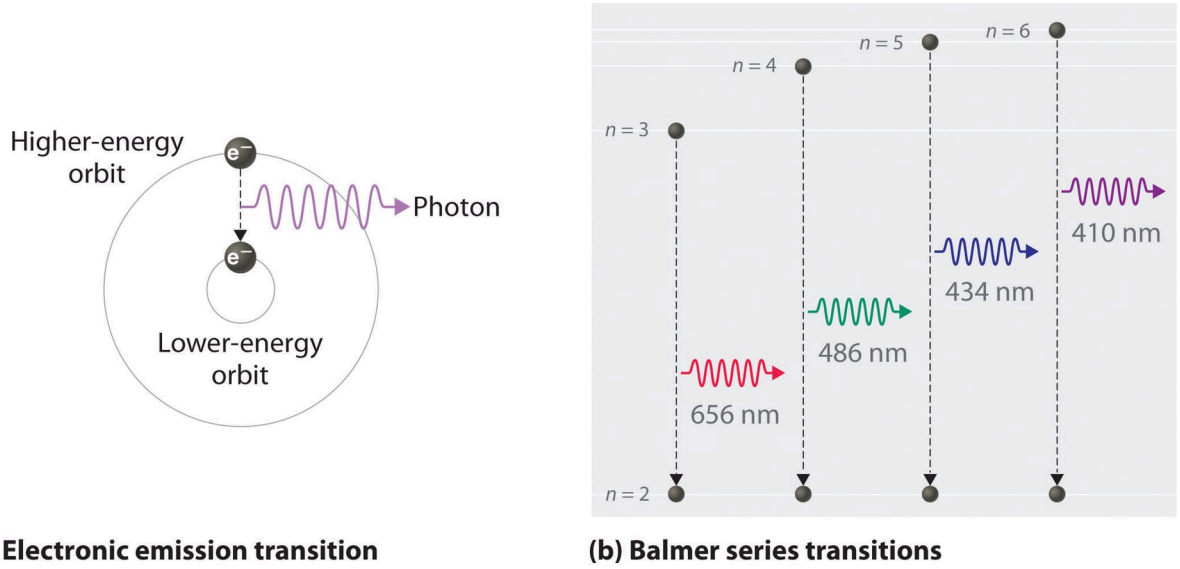


Figure 2.1.2.3: *The emission of light by a hydrogen atom in an excited state. (a) Light is emitted when the electron undergoes a transition from an orbit with a higher value of n (at a higher energy) to an orbit with a lower value of n (at lower energy). (b) The Balmer series of emission lines is due 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 (Δ*E*) 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 Δ*E* 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 × 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 :

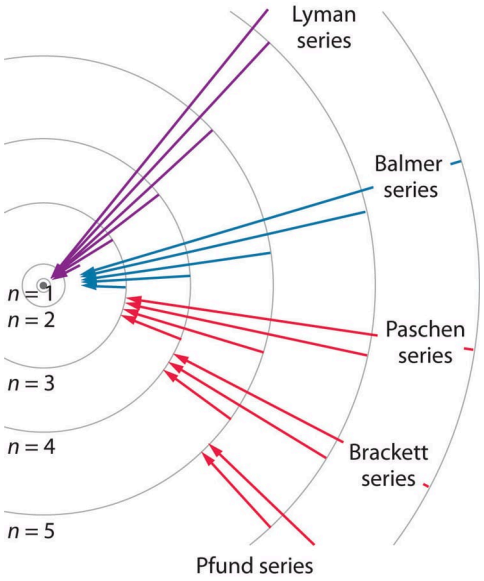


Figure 2.1.2.4: Electron transitions responsible for the various series of lines observed in the emission spectrum of hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (n = 1); these transitions release a great deal of energy, corresponding 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 available at the end of this section.

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.

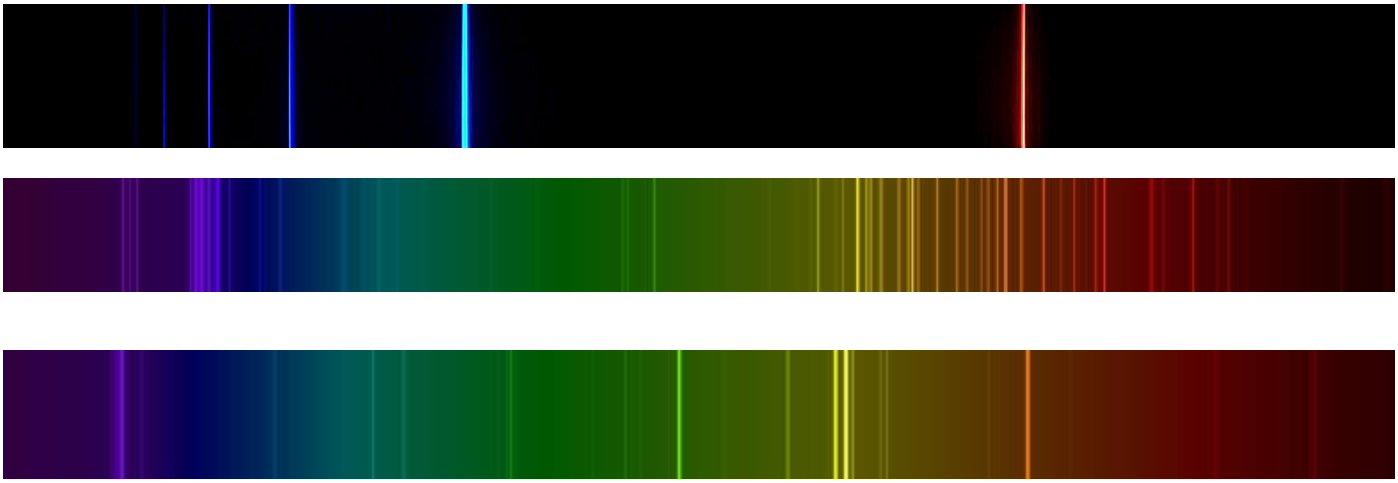


Figure 2.1.2.5: The emission spectra of elements compared to hydrogen. **Top:** hydrogen gas (atomized to hydrogen atoms in the discharge tube). **Middle:** neon. **Bottom:** mercury. The strongest lines in the hydrogen spectrum are in the far UV Lyman series starting at 124 nm and below. The strongest 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.

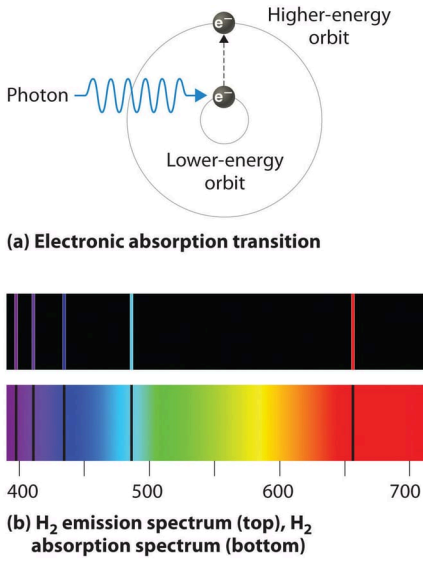


Figure 2.1.2.6: Absorption and emission spectra. Absorption of light by a hydrogen atom. (a) When a hydrogen atom absorbs a photon of light, an electron is excited to an orbit that has a higher energy and larger value of n. (b) Images of the emission and absorption spectra of hydrogen are shown here.

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.

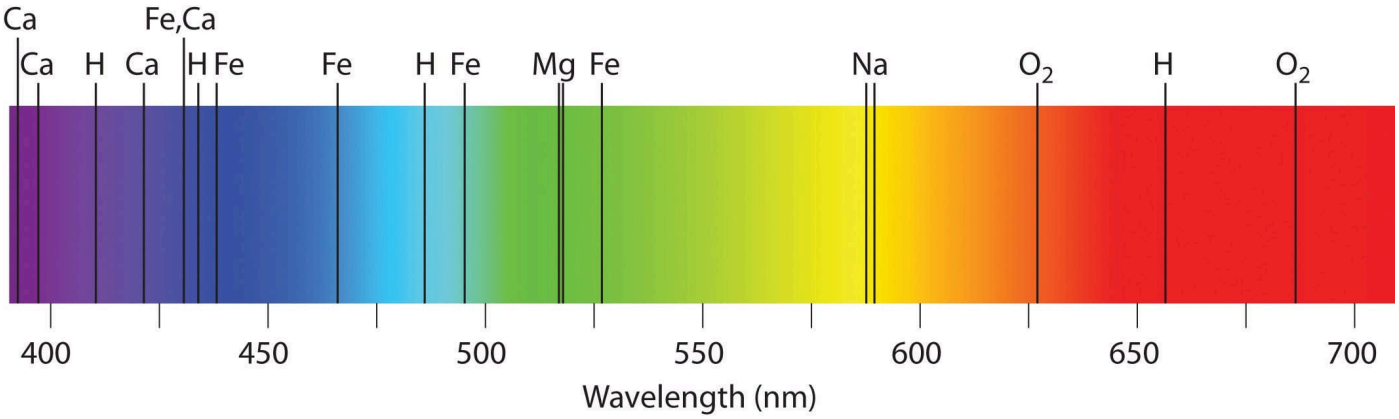


Figure 2.1.2.7: *The visible spectrum of sunlight. The characteristic dark lines are mostly due to the absorption of light by elements that are present in the cooler outer part of the sun's atmosphere; specific elements are indicated by the labels. The lines at 628 and 687 nm, however, are due to the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

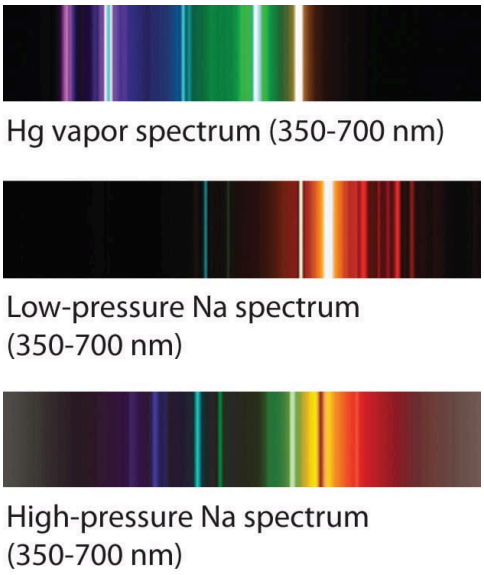


Figure 2.1.2.8: *The emission spectra of sodium and mercury. Many street lights use bulbs that contain sodium or mercury vapor. Due to the very different emission spectra of these elements, they emit light of different colors. The lines in the sodium lamp are broadened by collisions. The dark line in 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)

Answers

Exercise 2.1.2.1: The Pfund Series

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

Exercise 2.1.2.1: The Pfund Series

4.65 × 10^3 nm; infrared

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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.

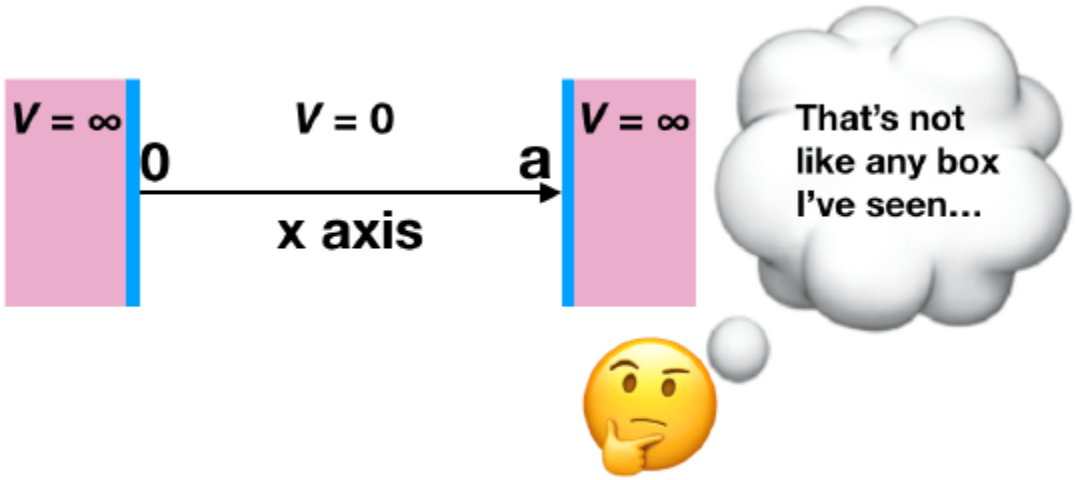


Figure 2.2.1.1. An illustration of the particle in the box model (particle not shown). The box is actually just a one-dimensional space, often assigned to the x-dimension (the x-axis). The particle has wave properties and is trapped in the box. Since no forces act on the particle inside the box, the 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 \(0a\)). 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:

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

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 available at the end of this section.

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 $\pi, h,$ 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:

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

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

Answer available at the end of this section.

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

$r = \frac{2\pi}{h}\sqrt{2m_eE}$

Answer available at the end of this section.

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:

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

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

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.

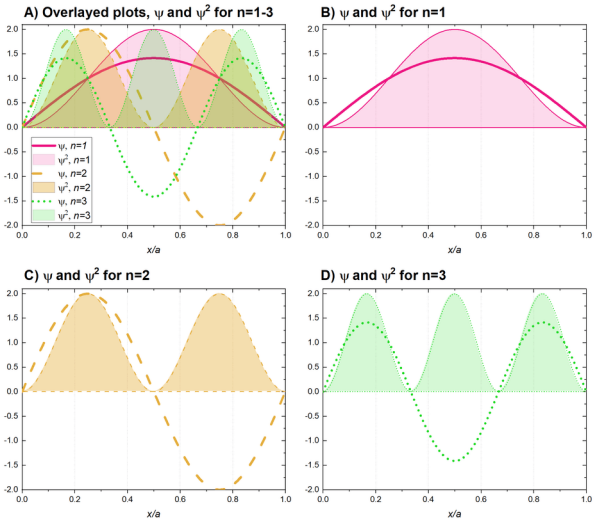


Figure 2.2.1.2. Plots of the 1-D ψ and ψ^2 for $n = 1$, $n = 2$, and $n = 3$ of a box of length a. The wavefunction (ψ) is plotted as a thick solid, dashed, or dotted line. The square of the wavefunction (ψ), which represents the probability of finding the particle at position x, is plotted as the thinner 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 available at the end of this section.

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 available at the end of this section.

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).

Answers

Exercise 2.2.1.1

Here is the Hamiltonian 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.

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

Exercise 2.2.1.2**: Prove that Equation** 2.2.1.3 **is true**

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

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.*

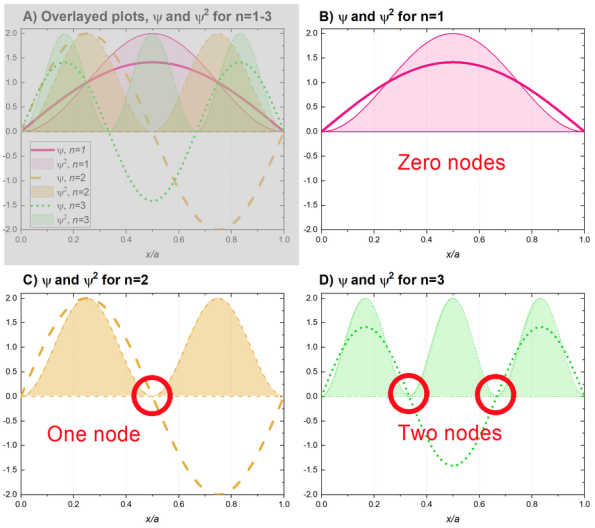
$$-r^2 = \frac{-8\pi^2 m_e E}{h^2}$$

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

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

Exercise 2.2.1.4

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

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

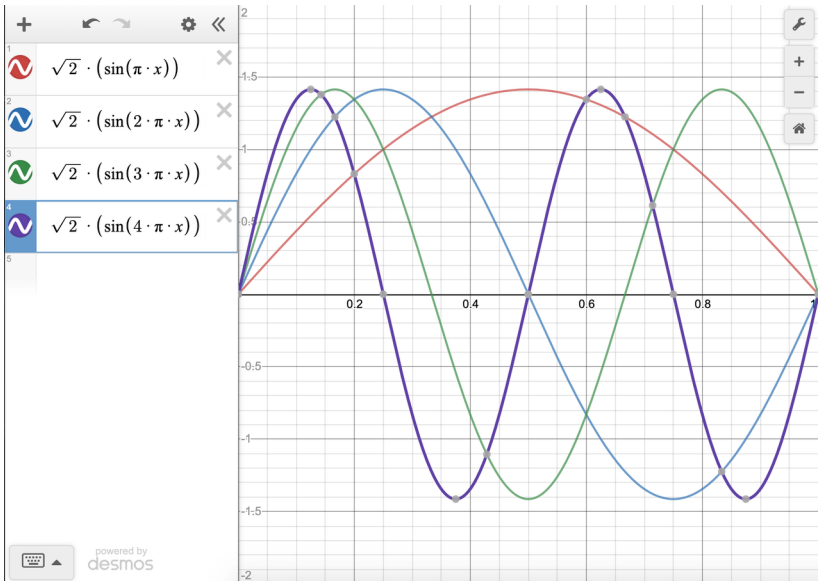
For n=2,3,4 you would repeat the process above. You will get the following functions:

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

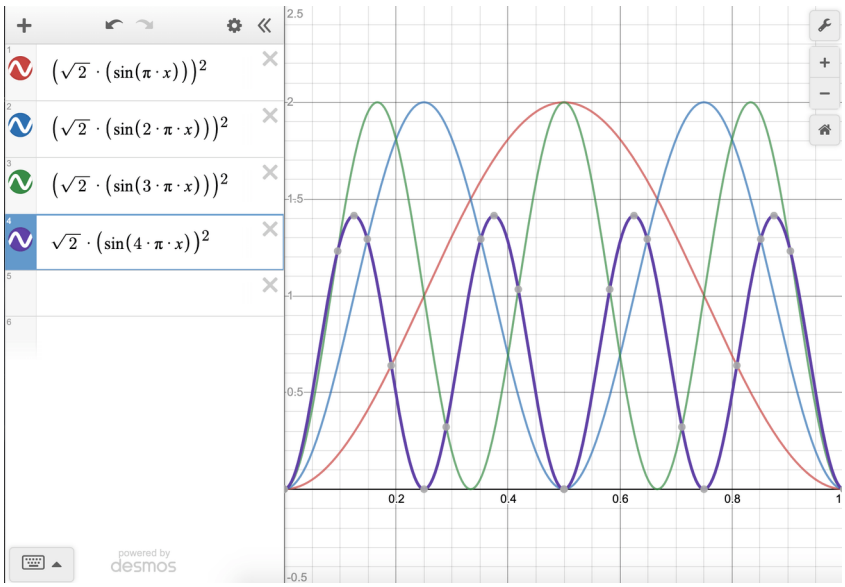
For n=3: $\psi = \sqrt{2}\left(\sin\left(3\pi x\right)\right)$

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 $n = 5$.

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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) available at the end of this section.

Answer (b) available at the end of this section.

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 available at the end of this section.

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.

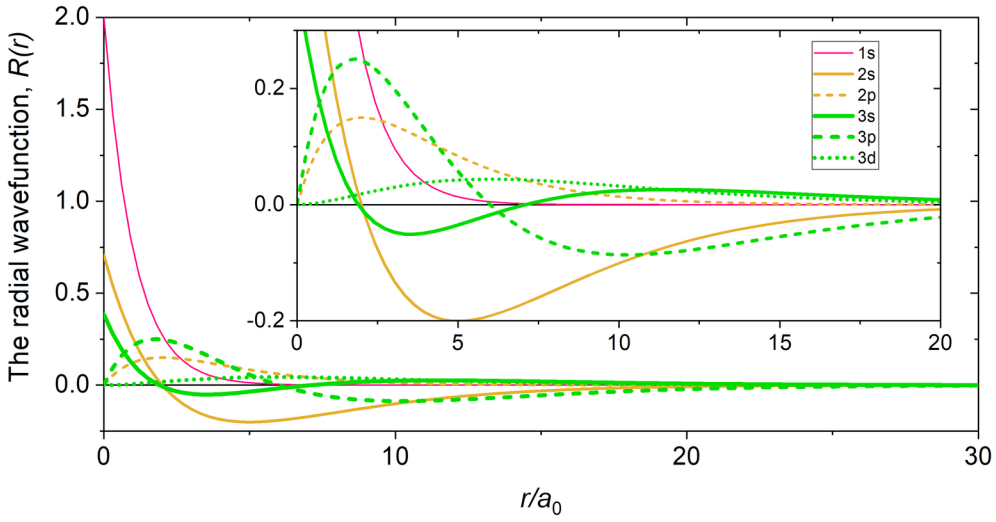


Figure 2.2.2.1. Plots of the radial wavefunction, $R_{n,l}(r)$, for the first three shells. The wavefunctions are plotted relative to $\frac{r}{a_0}$, where $a_0 = 52.9pm = 0.529\mathring{A}$ is the Bohr Radius (the radius of a hydrogen 1s orbital). The expressions for these radial wavefunctions ($R_{n,l}(r)$) 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 $a_0 = 52.9pm = 0.529\mathring{A}$ 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	$\frac{2}{27}\left[\frac{Z}{3a_0}\right]^{3/2}\left(27-18\frac{Zr}{a_0}-2(\frac{Zr}{a_0})^2\right) e^{-Zr/3a_0}$
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 $a_0 = 52.9pm = 0.529\mathring{A}$. 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 $\frac{r}{a_0}$.

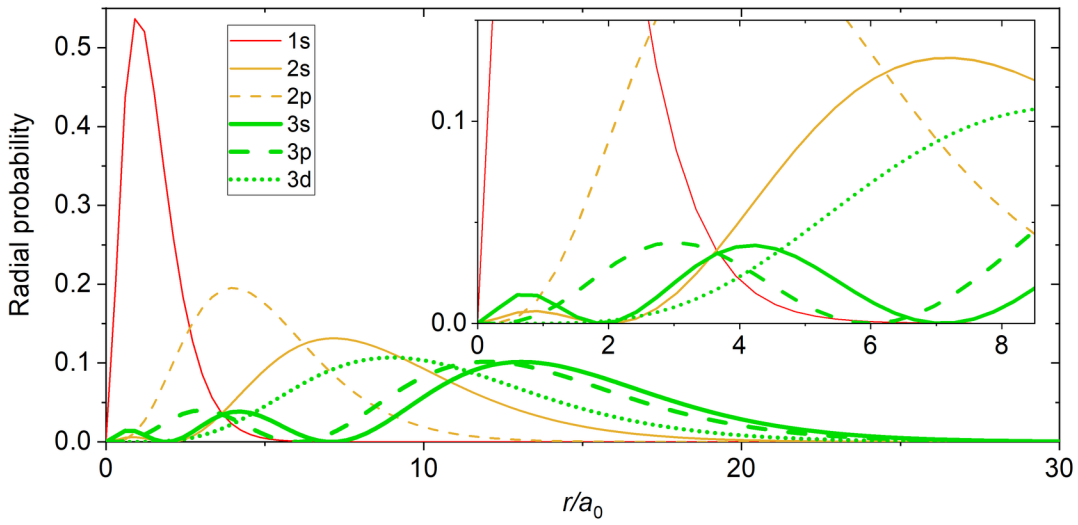


Figure 2.2.2.2: Plots of the normalized radial probability functions for the first three shells. The radial wavefunctions ($R_{n,l}(r)$) are shown in Table 2.2.2.2. (Kathryn Haas; CC-NC-BY-SA)

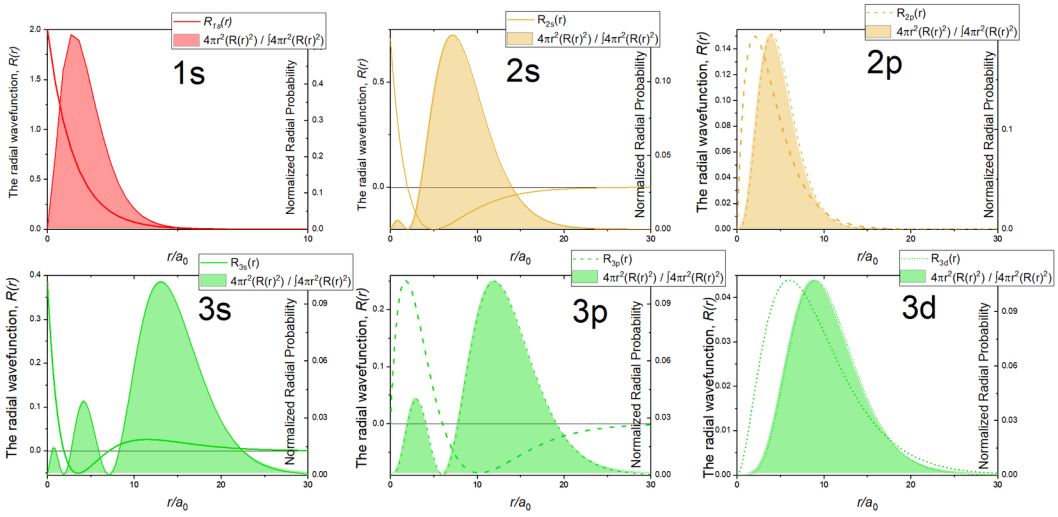


Figure 2.2.2.2. Plots of the normalized radial probability function for each orbital in the first three shells (shaded curves). The radial wavefunctions are also shown (Table 2.2.2.2). The y-axis on the left of each plot corresponds to the radial wavefunction (line); the y-axis on the right of each plot 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 $2s$ 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.

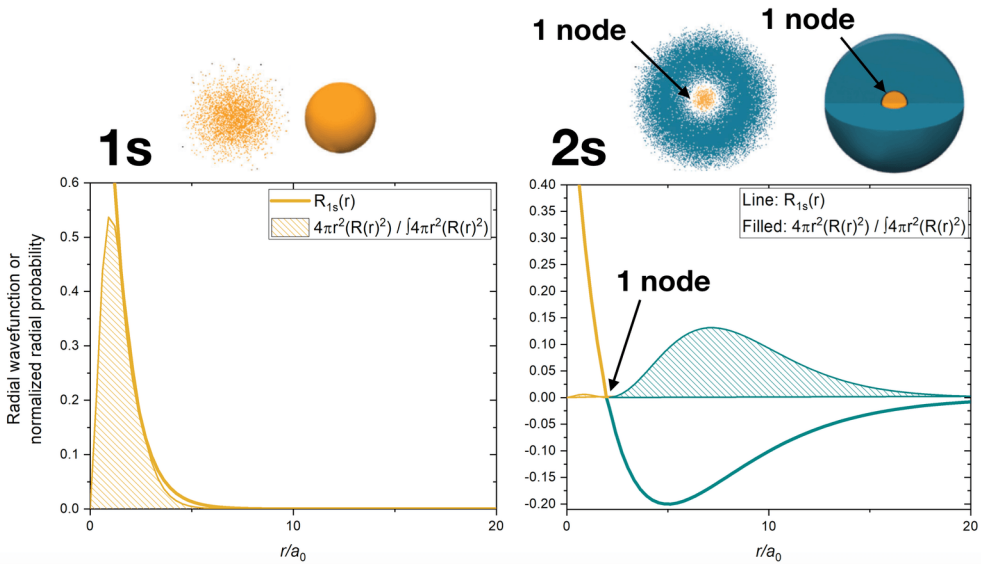


Figure 2.2.2.3: Visualization of the 1s and 2s atomic orbitals. Each orbital is shown as both an electron probability density plot and a contour plot above its wavefunction and probability density function. The 1s orbital has zero radial nodes. The 2s orbital has one radial node where its wavefunction 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 available at the end of this section.

Exercise 2.2.2.1

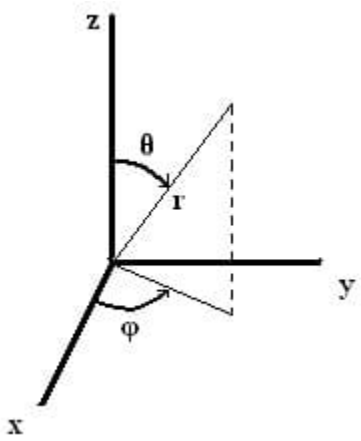
Draw a rough plot of the following:

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 available at the end of this section.

Answer, 4s available at the end of this section.

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



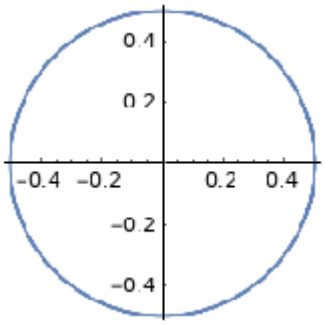
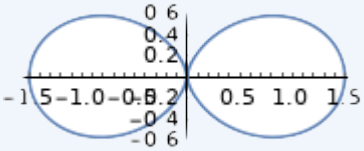
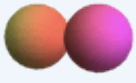
The angular contribution to the wavefunction, $Y_{l,m_l}(\theta,\phi)$, describes the wavefunction's shape, or the angle with respect to a coordinate system. To describe the direction in space, we use spherical coordinates that tell us distance *and* orientation in 3-dimensional space. There are three 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.

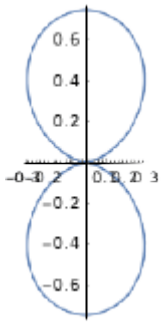
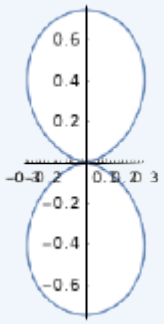
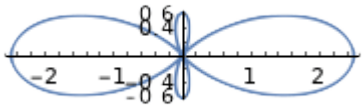
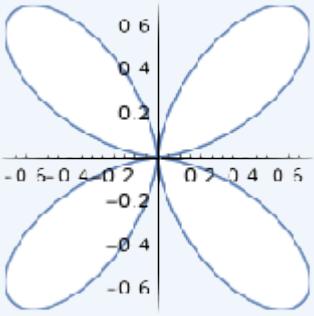
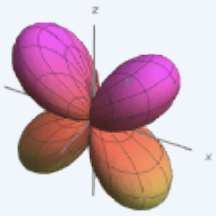
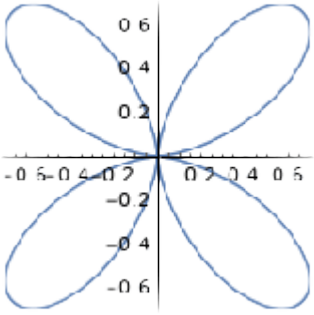
$$Y_{l,m_l}(\theta,\phi) = \left(\frac{1}{4\pi}\right)^{1/2} y(\theta,\phi)$$

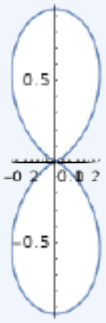
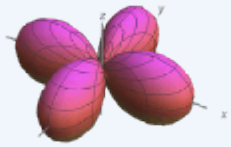
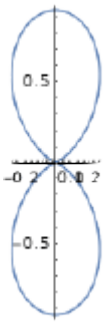
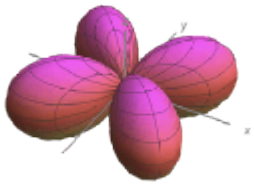
$Y_{l,m_l}(\theta,\phi)$, is slightly more difficult to describe than the radial contribution was. This is partly because $Y_{l,m_l}(\theta,\phi)$ contains imaginary numbers, which have no real, physical meaning. However, the angular part of the wavefunction becomes more "real" when you square it to 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	$m_l=0$	$\frac{\sqrt{6}}{2}\cos\theta$	$\frac{1}{\sqrt{2\pi}}$		

subshell	m_l (orbital)	θ	ϕ	Plots of θ^2	orbital shapes
$l = 1$, 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	$m_l = -1$	$\frac{\sqrt{15}}{2}\sin\theta\cos\theta$	$\frac{1}{\sqrt{2\pi}}e^{-i\phi}$		

subshell	m_l (orbital)	θ	ϕ	Plots of θ^2	orbital shapes
$l = 2$, 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.

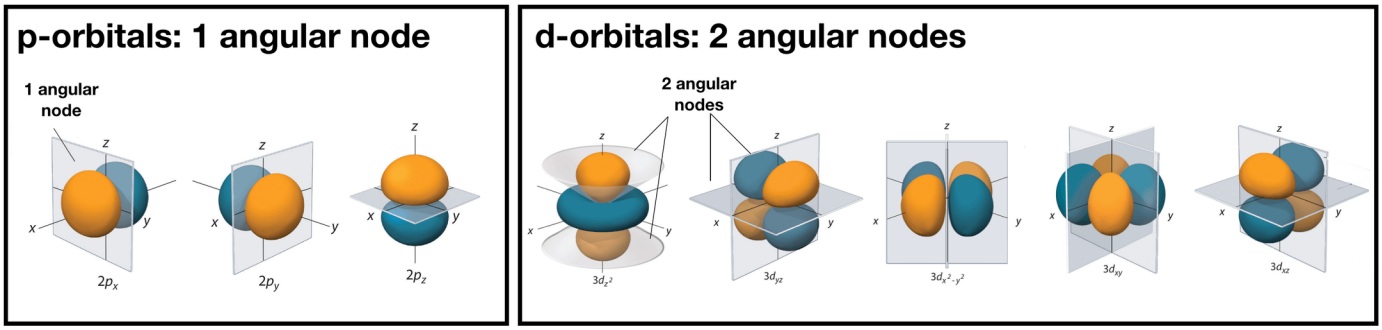
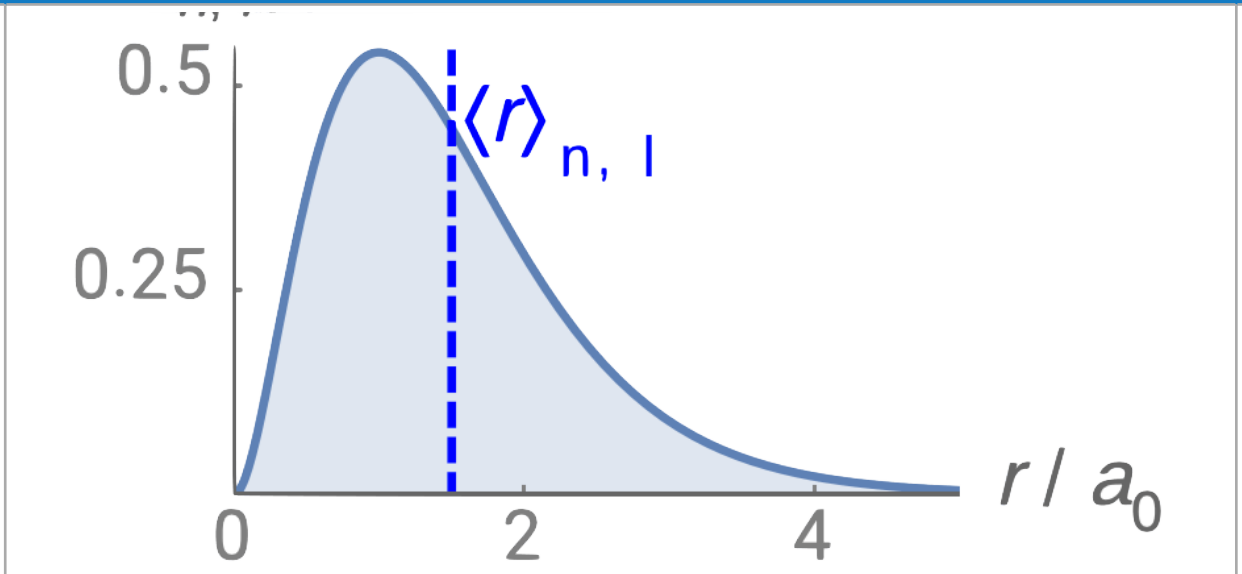
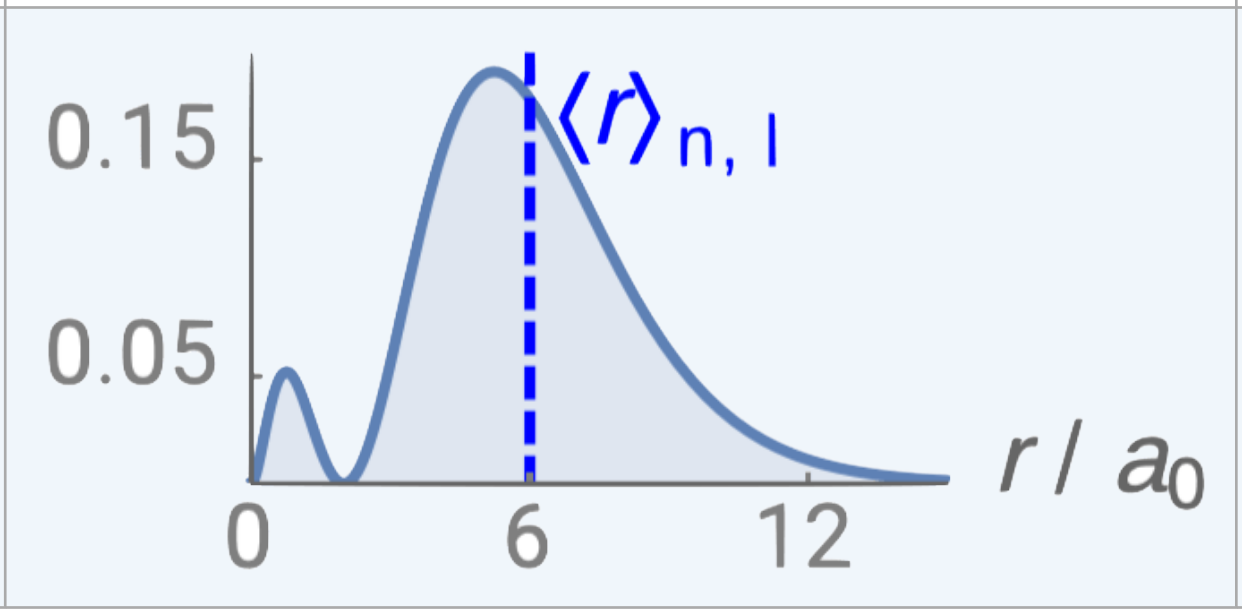


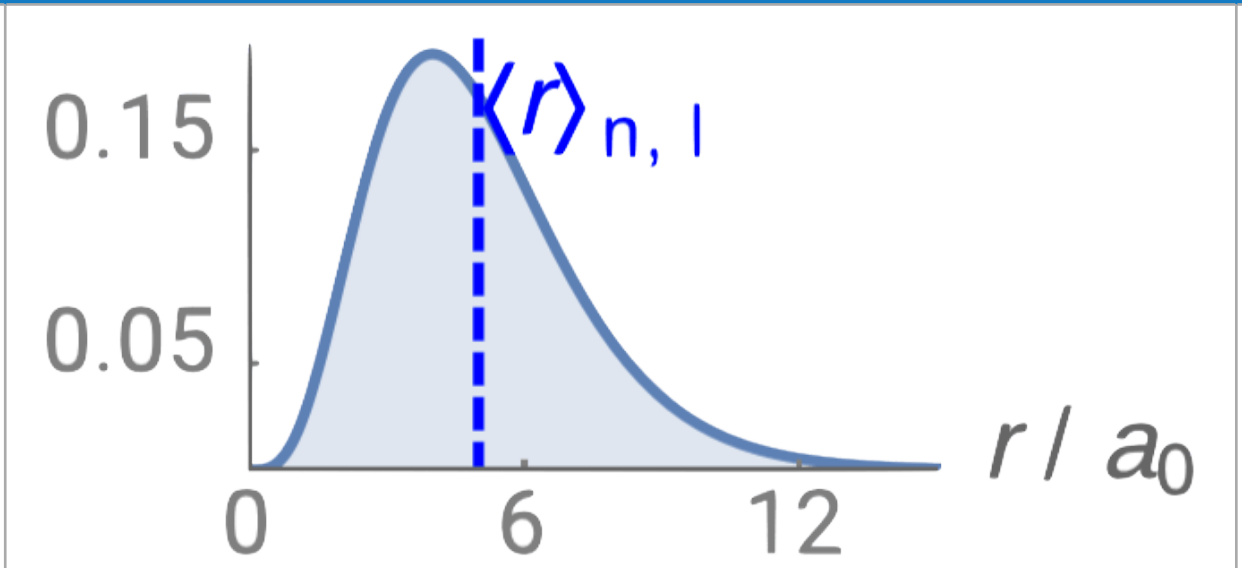
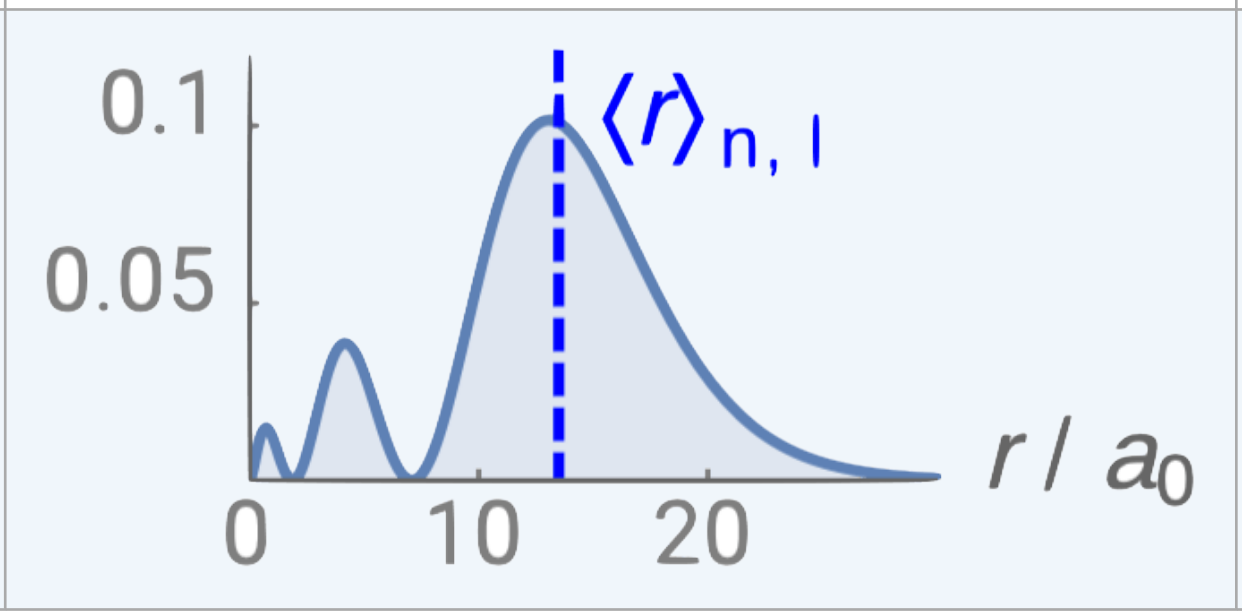
Figure 2.2.2.4: The angular nodes in p-orbitals and d-orbitals are shown. Every p orbital has one angular node, and every d orbital has two angular nodes. The number of angular nodes in any orbital is equal to the value of the quantum number, l. (CC BY-NC-SA; anonymous by request)

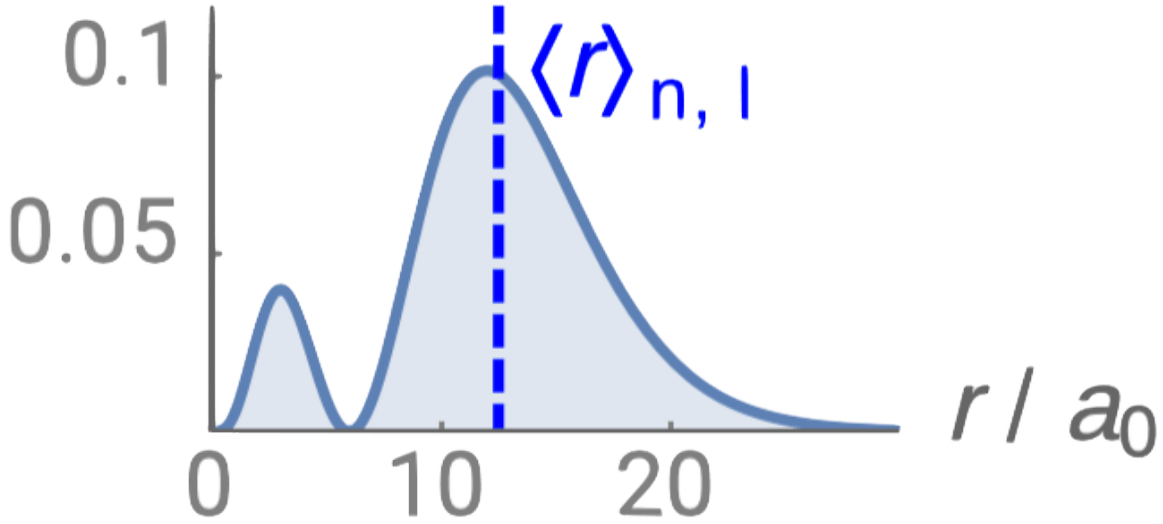
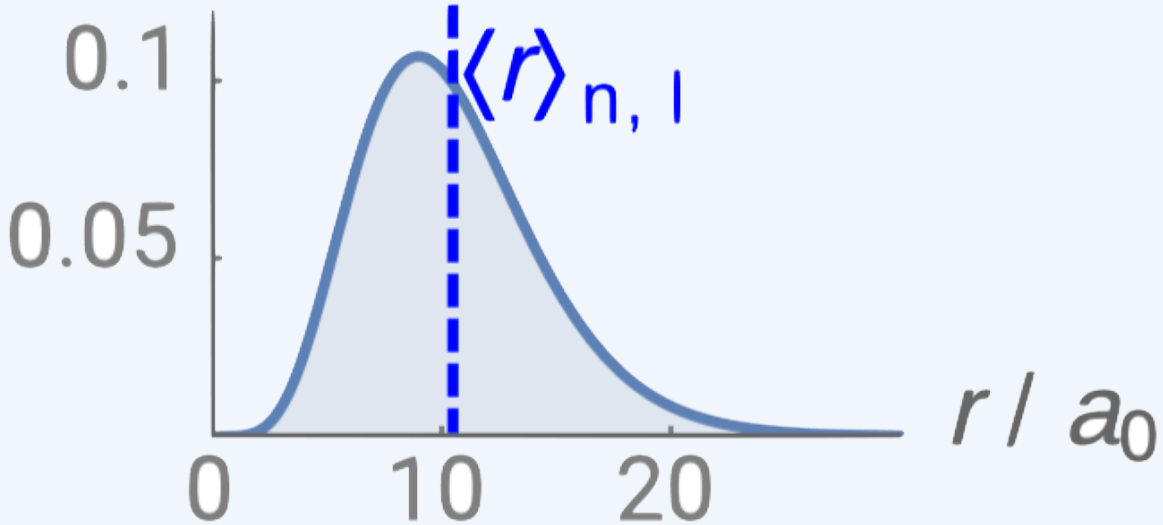
Atomic Orbitals

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	Radi Nod
1s		0
2s		1

Orbital	Radial Probability	Radi Node
2p		0
3s		2

Orbital	Radial Probability	Radi Nod
3p		1
3d		0

Answers

Exercise 2.2.2.1

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.

Exercise 2.2.2.1

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 $1eV = 8065.6cm^{-1}$.

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

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.

Exercise 2.2.2.1

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

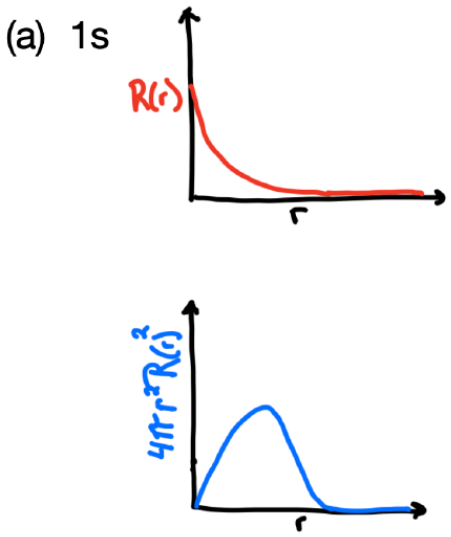
4d: $n - 1 - l = 4 - 1 - 2 = 1$, one radial nodes

f-orbital

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

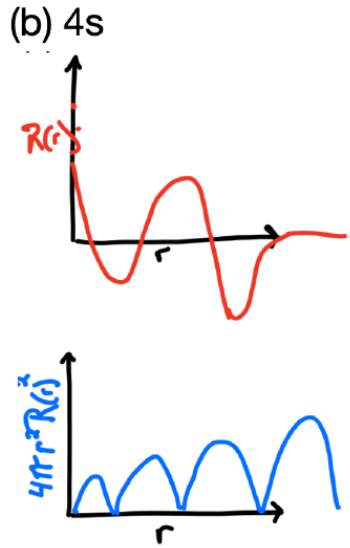
Exercise 2.2.2.1

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).



Exercise 2.2.2.1

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.



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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.

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(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.

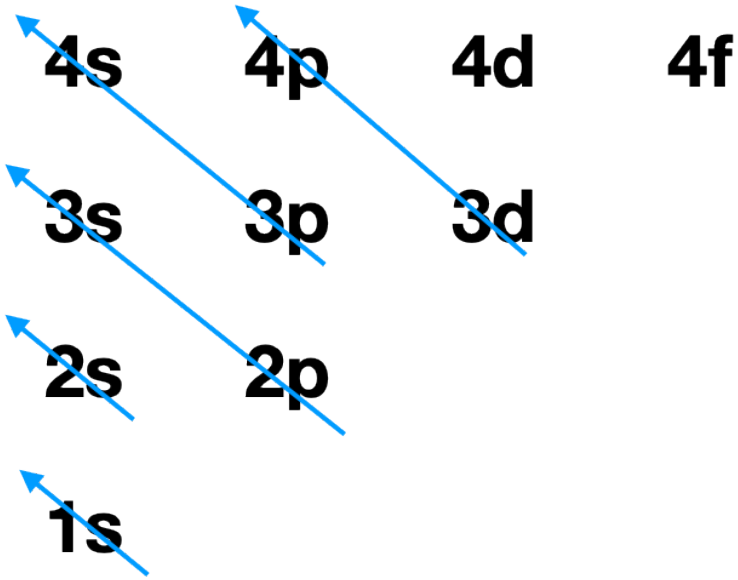
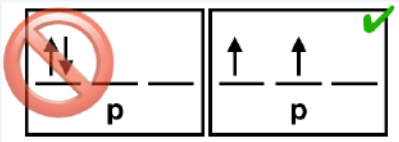


Figure 2.2.3.1. The order of filling of ground state electron orbitals is 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, etc... (CC-BY-NC-SA; Kathryn Haas)

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



# of electrons in a p-subshell	Arrangement (unpaired electrons, n)	Spin Multiplicity (n + 1)
1	(n = 1)	2
2	(n = 2)	3
3	(n = 3)	4
4	(n = 2)	3
5	(n = 1)	2
6	(n = 0)	1

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)

(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 $-\frac{1}{2}$.

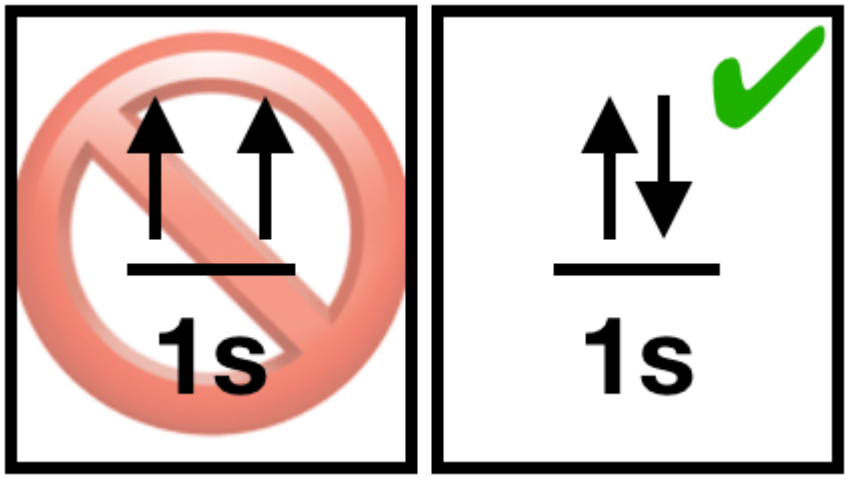


Figure 2.2.3.3**.** Pauli's principle tells us that paired electrons must have opposite spin. (Kathryn Haas; CC-NC-BY-SA)

(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.

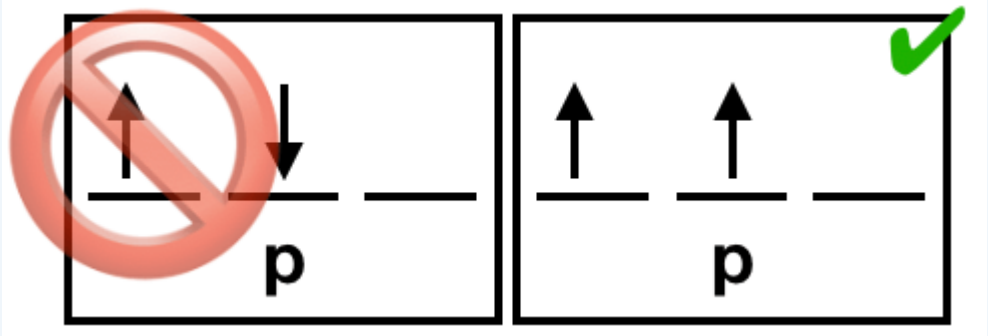


Figure 2.2.3.4**.** Unpaired electrons should have identical spins due to the exchange interaction. (Kathryn Haas; CC-NC-BY-SA)

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

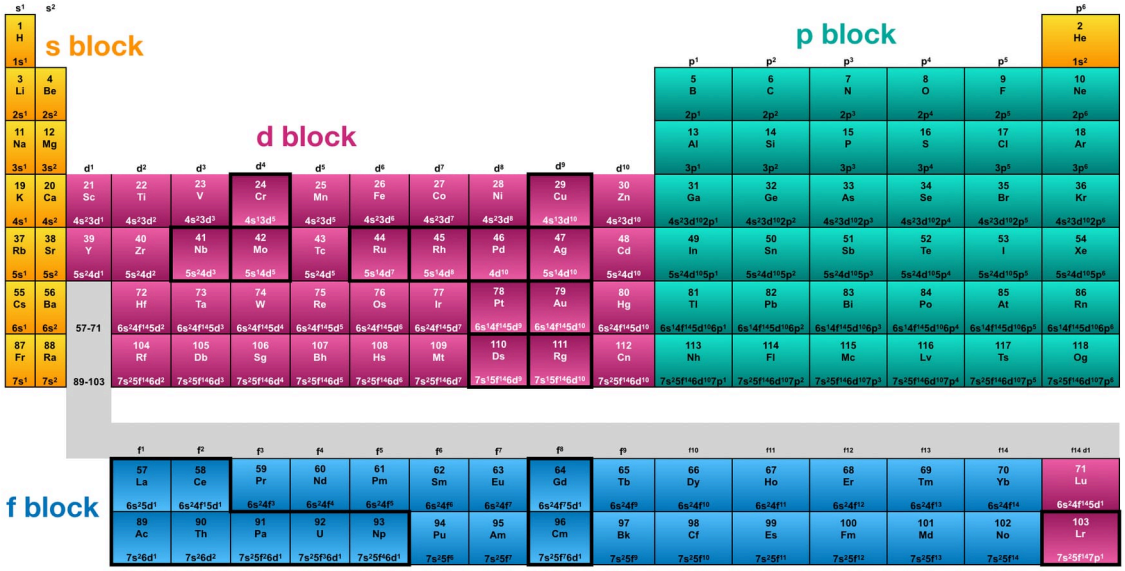


Figure 2.2.3.5. This is a depiction of the periodic table that highlights the s-, p-, d-, and f- blocks in different colors. Violations of the expected trend in electron configurations are outlined in a heavy black line. Several elements of the d block and f block violate the general trends in electron 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

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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*)

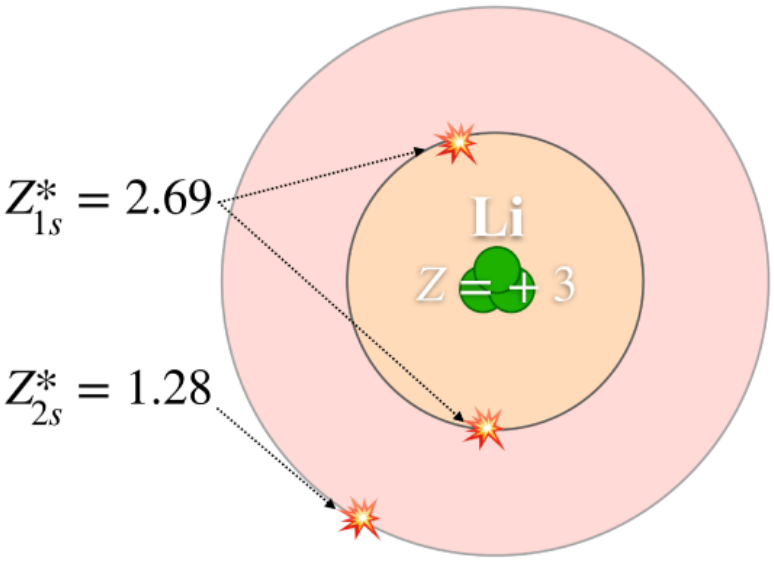


Figure 2.2.4.1. In a lithium atom, the nuclear charge (Z) is +3. 1s electrons experience an effective nuclear charge (Z*) of +2.69, and 2s electrons experience an Z* of +1.28. (CC-BY-NC-SA; Kathryn Haas)

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).

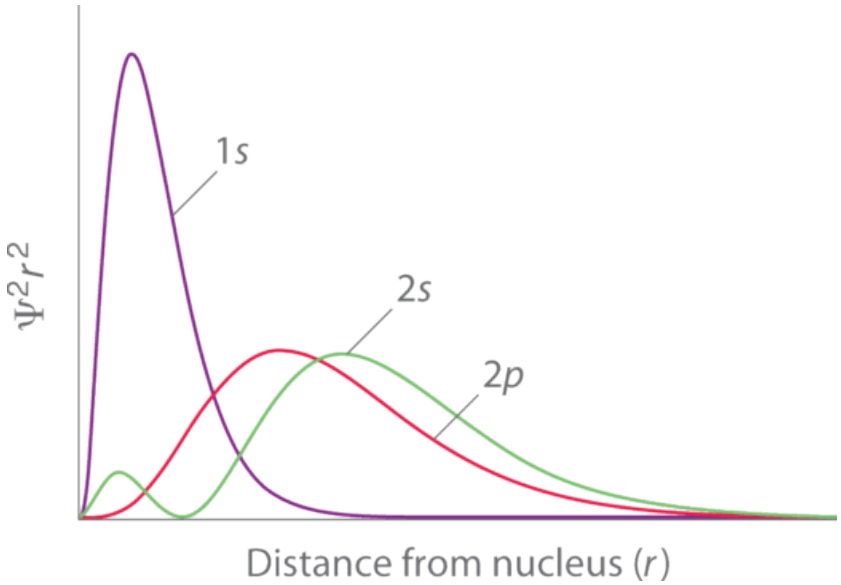


Figure 2.2.4.2. Orbital Penetration. A comparison of the radial probability distribution of the 2s and 2p orbitals for various states of the hydrogen atom shows that the 2s orbital penetrates inside the 1s orbital more than the 2p orbital does. Consequently, when an electron is in the small inner lobe 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.

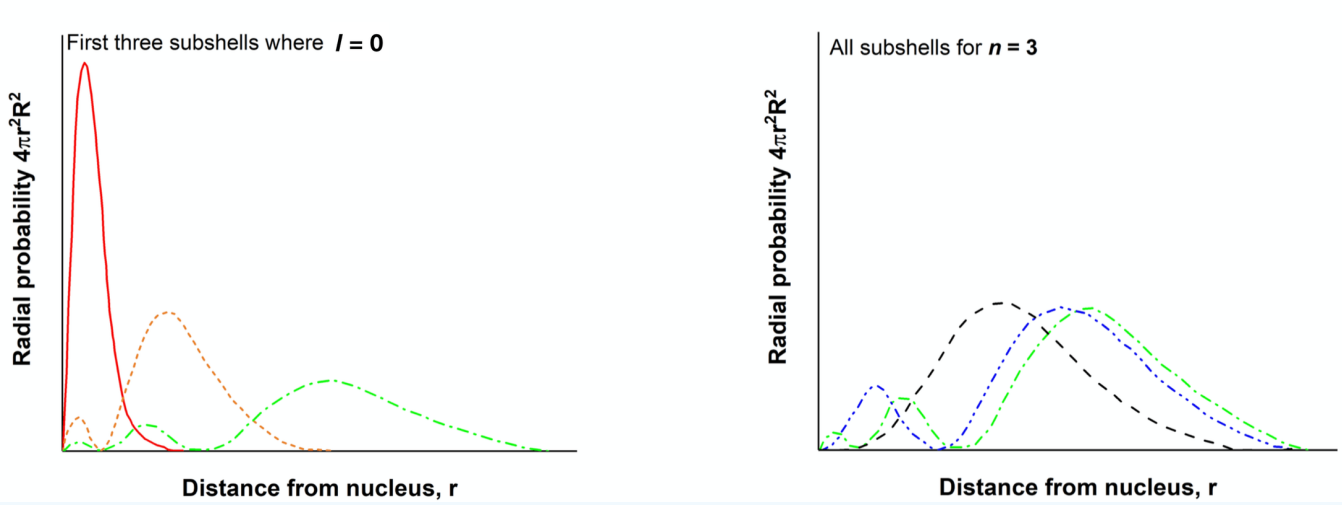
Within the same shell value (n), the penetrating power of an electron follows this trend in subshells (m_l):

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 available at the end of this section.

Slater's rules for estimating Z*

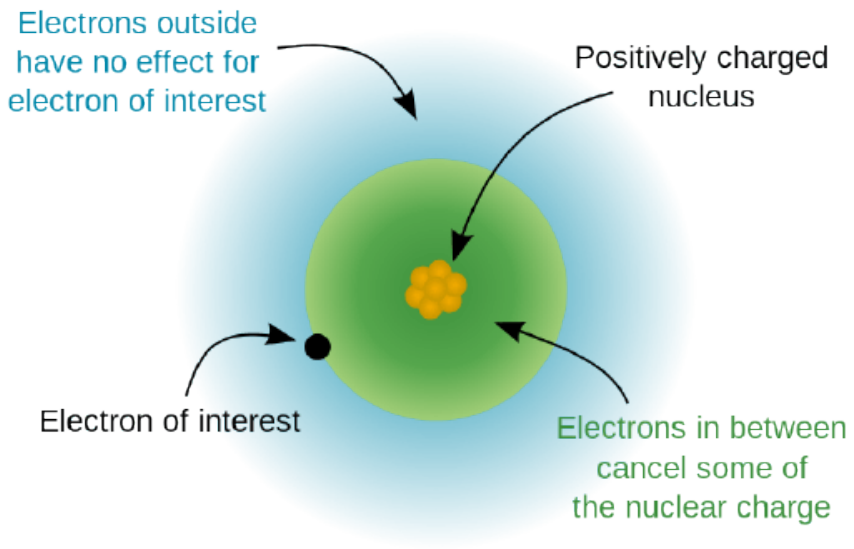


Figure 2.2.4.3. Diagram illustrating effective nuclear charge according to Slater's rules.

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 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 available at the end of this section.

"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.

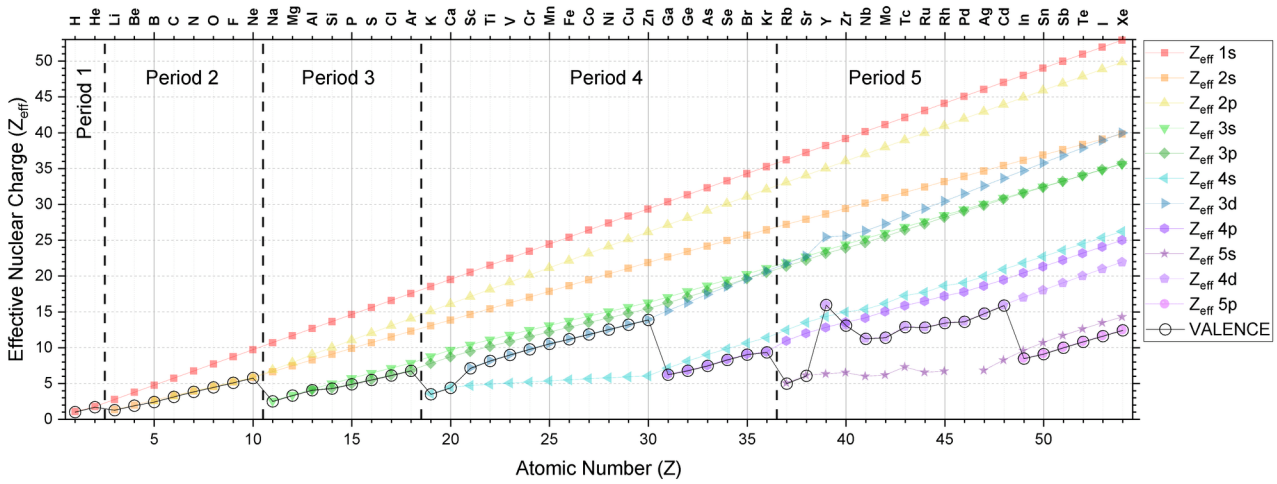


Figure 2.2.4.5: The Z* values for electrons in each subshell of the first 54 elements (H to Xe). Each subshell is plotted as a different series (see legend) and the valence shell is highlighted by a solid black line with open circles. (Kathryn Haas; CC-NC-BY-SA)

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 available at the end of this section.

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Answers

Exercises

(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.

(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!

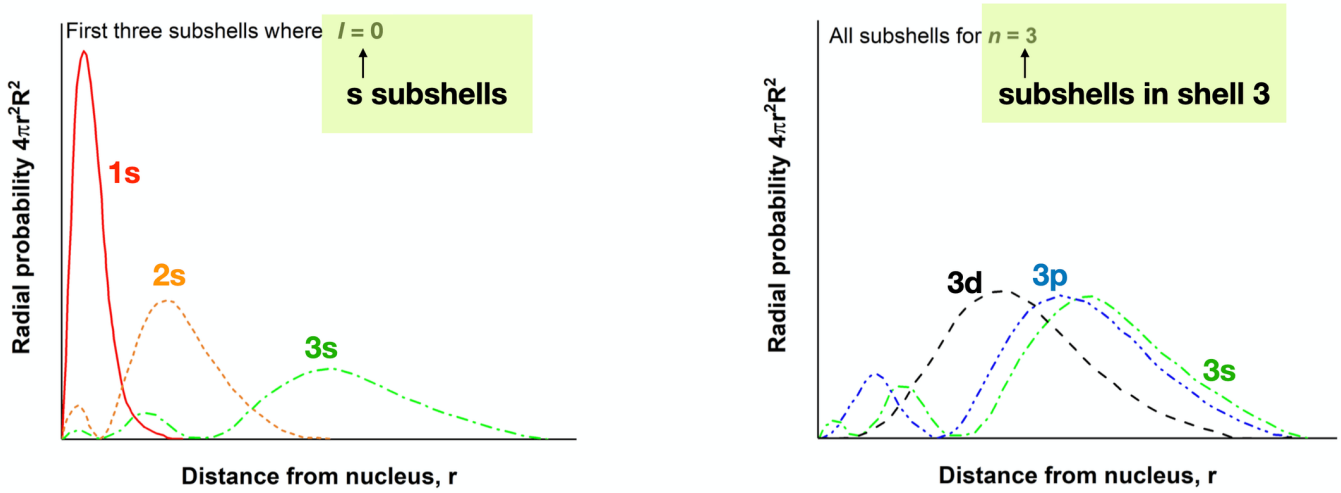
(c) The 2p orbital is lower in energy than 3s; this is because 2p is still significantly closer to the nucleus on average and experiences a stronger Z*. (Penetration is not the only consideration!)

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.

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.

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.

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



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.

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*.

Exercise 2.2.4.1

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 $Z* \approx 8.85$!

Exercise 2.2.4.2

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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2.3: 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

1. Russo, Steve, and Mike Silver. Introductory Chemistry. San Francisco: Pearson, 2007.
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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.
5. Kots, John C. et. al, *Chemistry & Chemical Reactivity*, 5th Edition, 2003, Thomson Learning Inc, pg. 305-309.

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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.

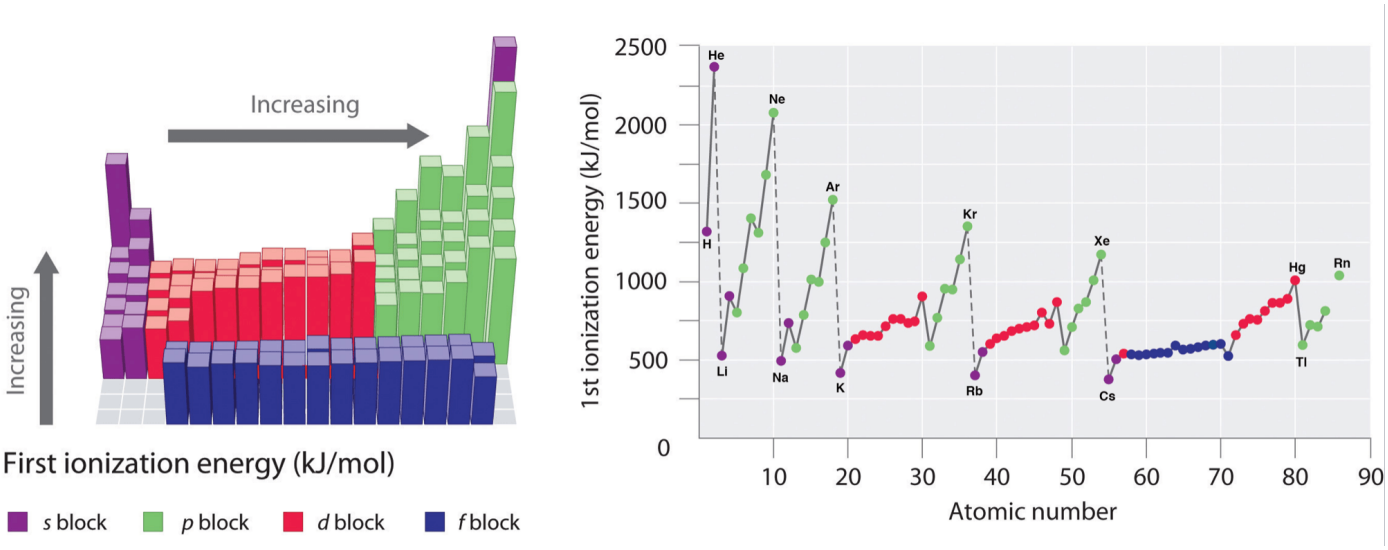


Figure 2.3.1.1: Graph showing the First Ionization Energy of the Elements. Left: ionization energies are mapped onto the periodic table, where the magnitude of ionization energy is depicted as a bar graph. Right: the first ionization energy is plotted against atomic number. In both panels the elements 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!

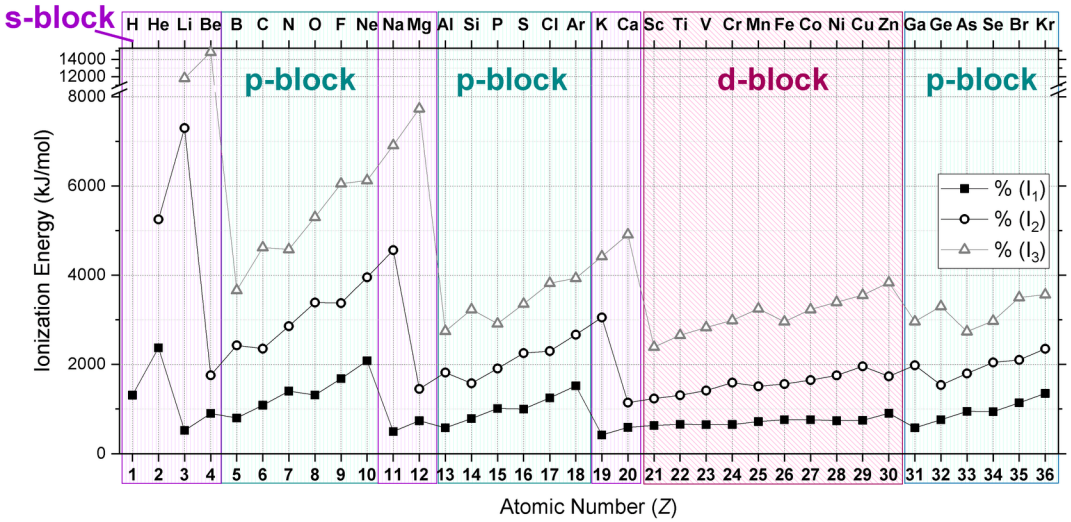


Figure 2.3.1.2. The first (I_1), second (I_2), and third (I_3) ionization energies plotted for elements with Z = 1 to 36 (H to Kr). The position of each element in its atomic form is indicated as s- p- or d-block. (CC-BY-NC-SA; Kathryn Haas)

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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.

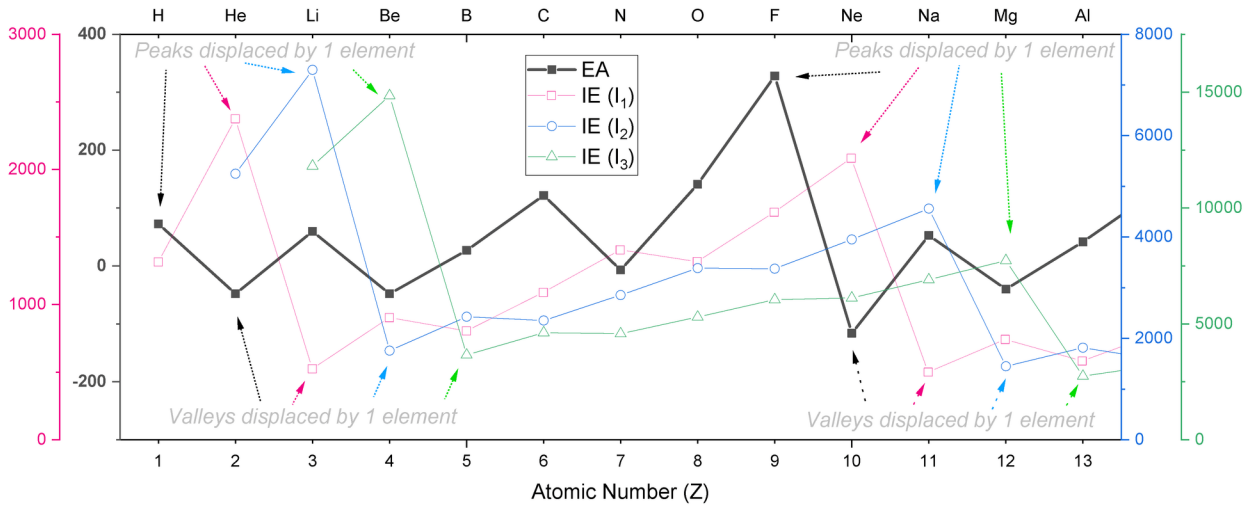


Figure 2.3.2.1. A plot of electron affinity (the zeroth ionization energy) is overlaid on plots of the first (I_1), second (I_2), and third (I_3) ionization energies. Each plot is shown using separate y-axes. Trends in EA are similar to those in ionization energies, except that the peaks and valleys 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.

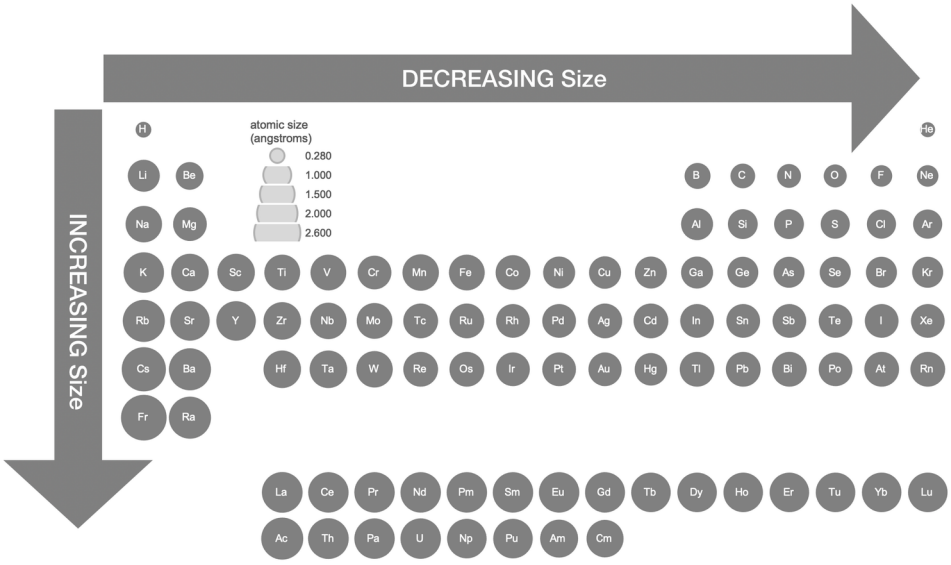


Figure 2.3.3.1. *Atomic Radii Calculated from Crystalographic Data. Data from Cordero, Beatriz, Veronica Gomez, Ana E. Platero-Prats, Marc Reves, Jorge Echeverria, Eduard Cremades, Flavia Barragan, and Santiago Alvarez. "Covalent Radii Revisited." Dalton Transactions, no. 21 (2008): 2832–38. doi:10.1039/b801115j.*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

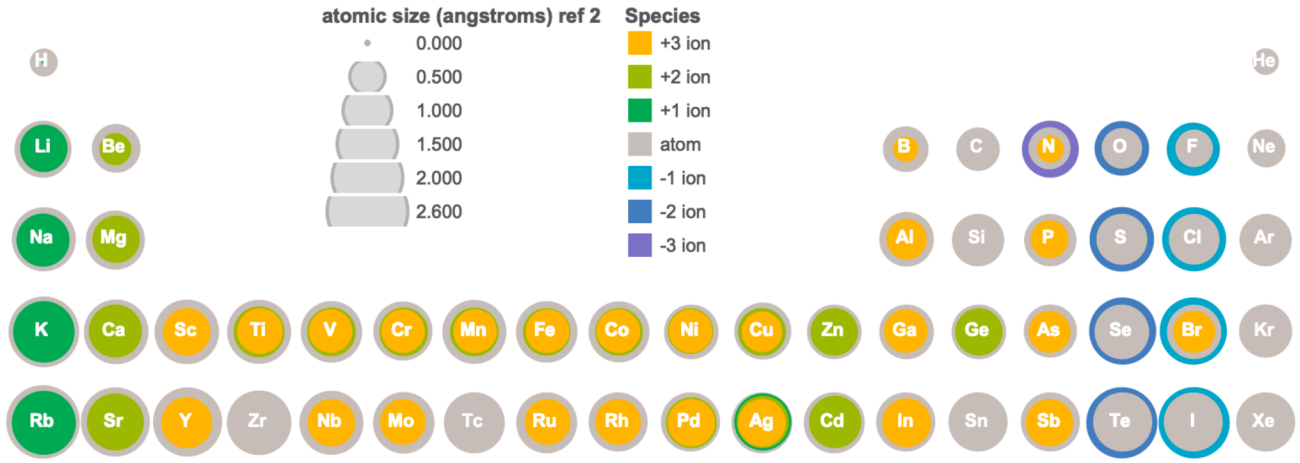


Figure 2.3.3.2. This figure illustrates relative size of atoms and ions of the first four periods of the periodic table. Atomic radius is indicated by grey circles. Radius of cations is shown in green (+1), lime (+2), and yellow (+3) circles. Radius of anions are shown as aqua (-1), blue (-2), and purple (-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) 0.785 (+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 available at the end of this section.

Answers

Exercises

Helium (He).

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

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.

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

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

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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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.

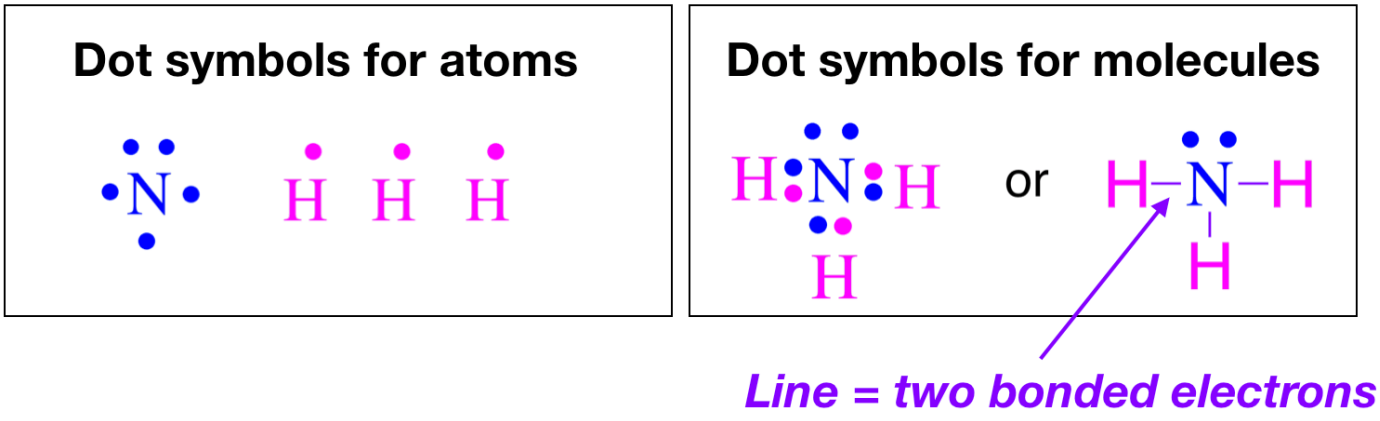


Figure 3.1.1: Lewis dot structure of atoms comprising ammonia and the dot structure of the molecule. (Kathryn Haas; CC-NC-BY-SA)

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 available at the end of this section.

Exercise 3.1.2

Draw the Lewis structures for H_2, BH_3 and BF_3.

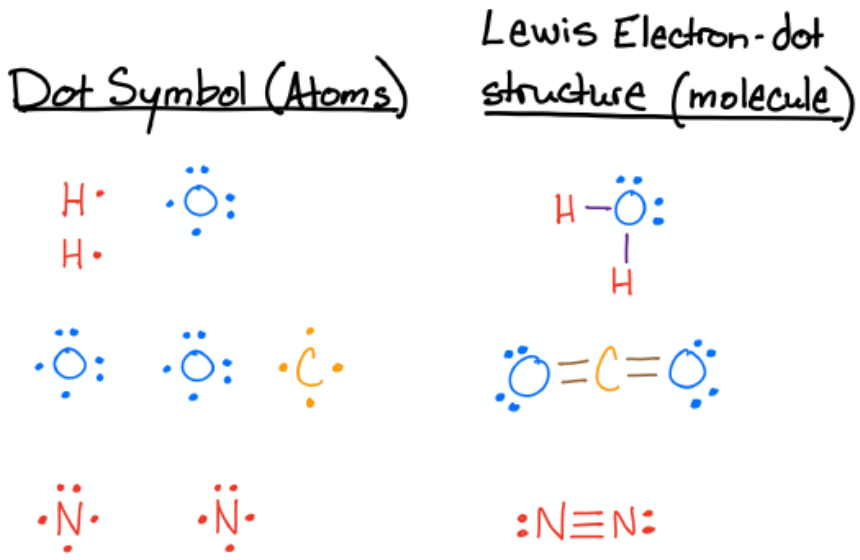
Answer available at the end of this section.

Outside Links

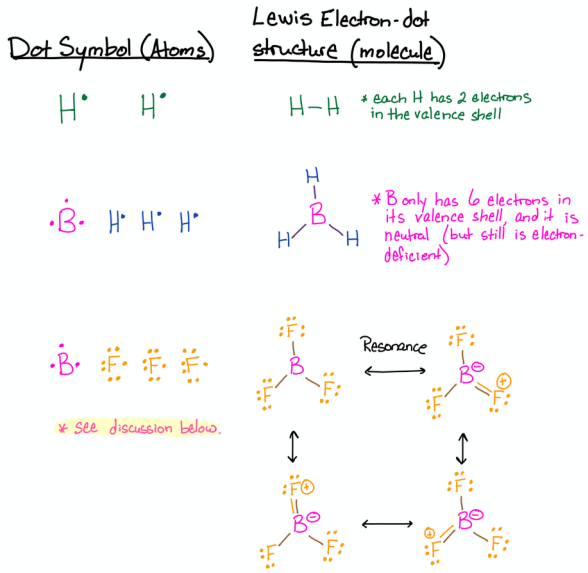
- en.Wikipedia.org/wiki/Lewis_structures
- http://www.ausetute.com.au/lewisstr.html
- cost.georgiasouthern.edu/chem...cule/lewis.htm

Answers

Exercise 3.1.1



Exercise 3.1.2



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).

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3.1.1: Resonance

Learning Objectives

- To understand the concept of resonance.

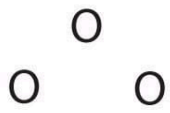
Resonance structures are a set of two or more Lewis Structures that collectively describe the electronic bonding of a single polyatomic species including fractional bonds and fractional charges. Resonance structures are capable of describing delocalized electrons that cannot be expressed by a single 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 (O_3), an allotrope of oxygen with a V-shaped structure and an O–O–O angle of 117.5°.

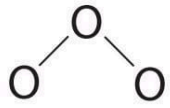
Ozone (O_3)

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



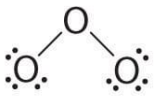
2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

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



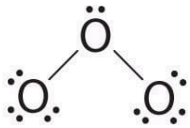
with 14 electrons left over.

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:

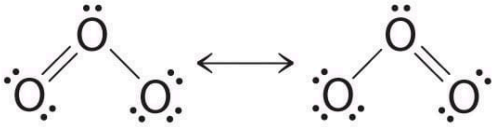


6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons—but which one? Depending on which one we choose, we obtain either



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:



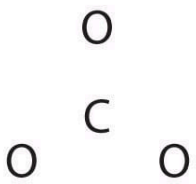
The double-headed arrow indicates that the actual electronic structure is an *average* of those shown, not that the molecule oscillates between the two structures.

> 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.

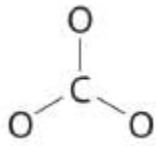
1. Because carbon is the least electronegative element, we place it in the central position:



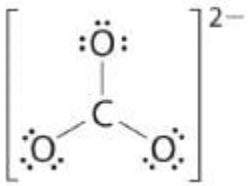
The three oxygens are drawn in the shape of a triangle with the carbon at the center of the triangle.

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:



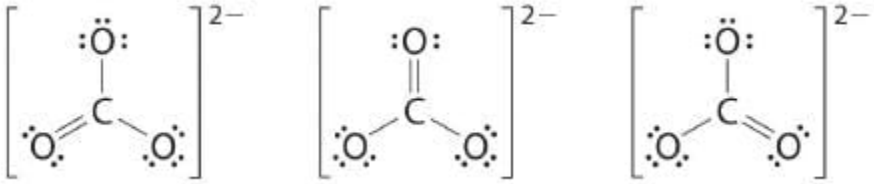
4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the –2 charge:



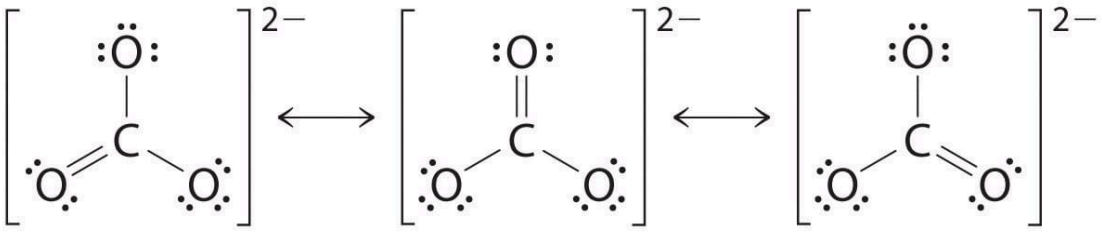
The Lewis dot structure has a central carbon that is bonded to 3 oxygens. Each oxygen has 3 lone pairs. The molecule is inside square brackets and has a charge of minus 2.

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:



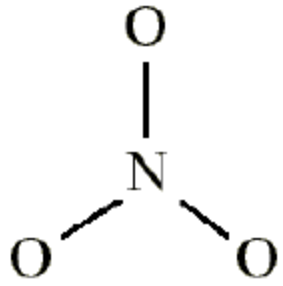
The resonance structure includes all three Lewis dot structures with double headed arrows between them.

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

The Nitrate (NO_3^-) ion

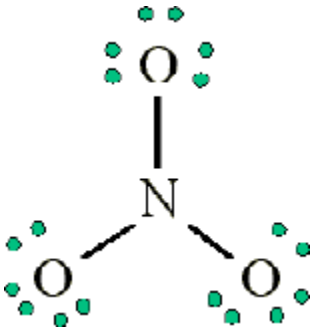
1. Count up the valence electrons: (1*5) + (3*6) + 1(ion) = **24** electrons

2. Draw the bond connectivities:

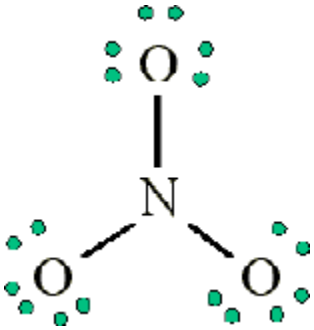


The three oxygens are drawn in the shape of a triangle with the nitrogen at the center of the triangle.

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

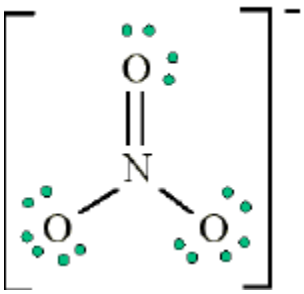


4. Place any leftover electrons (24-24 = **0**) on the center atom:



5. Does the central atom have an octet?

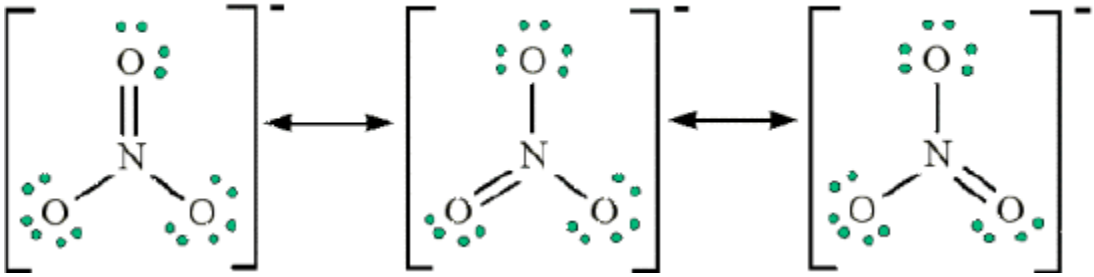
- **NO**, it has 6 electrons
- Add a multiple bond (first try a double bond) to see if the central atom can achieve an octet:



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 NO_3^- ion to be somewhat shorter than a single bond.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

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

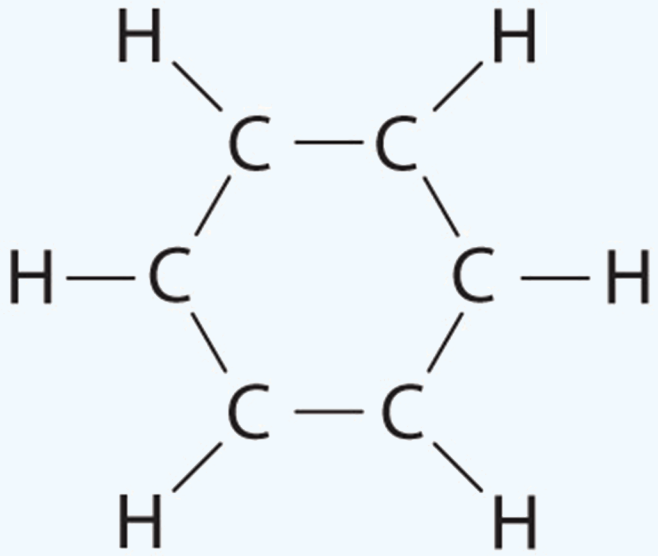
Asked for: resonance structures

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.

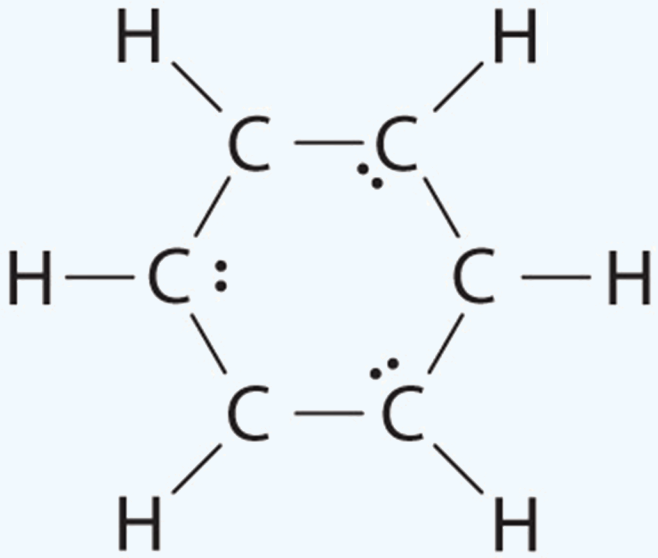
Solution:

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:



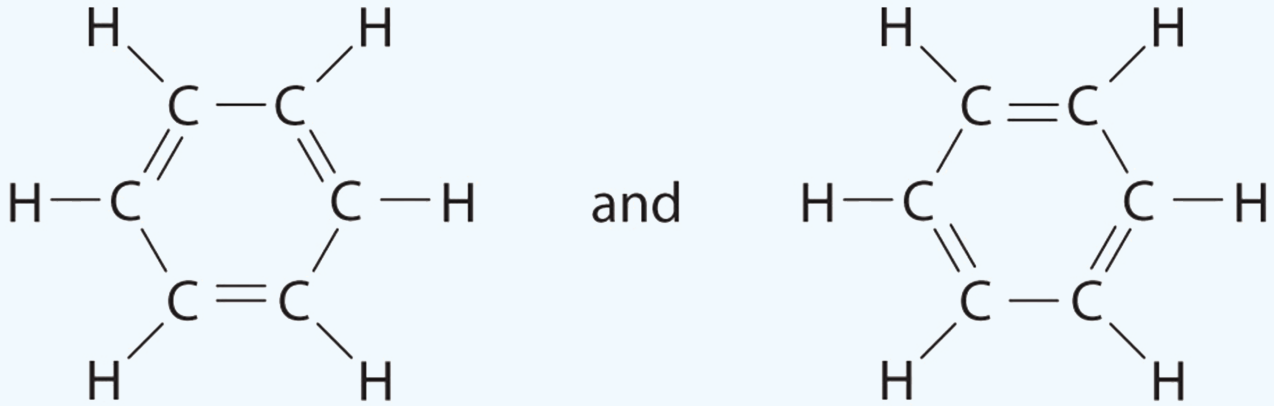
Each carbon atom in this structure has only 6 electrons and has a formal charge of +1, but we have used only 24 of the 30 valence electrons.

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

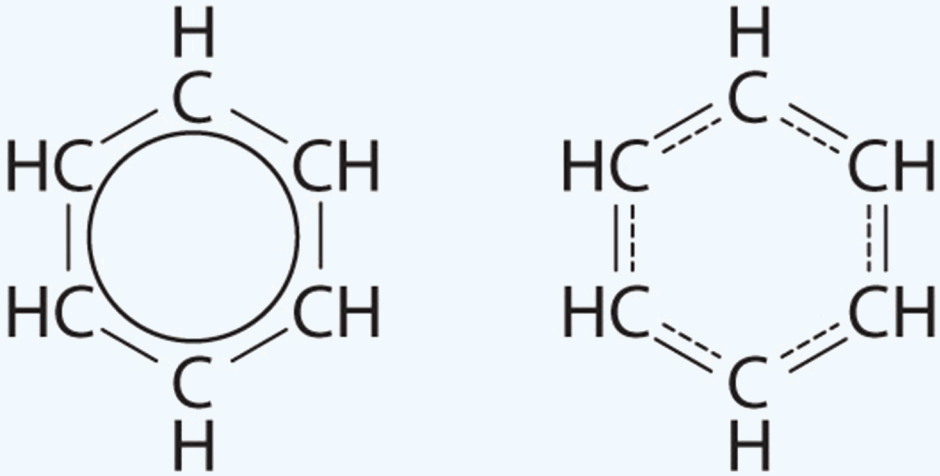


Three carbon atoms now have an octet configuration and a formal charge of –1, while three carbon atoms have only 6 electrons and a formal charge of +1. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of electrons and a formal charge of 0, by making three C=C double 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 available at the end of this section.

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.

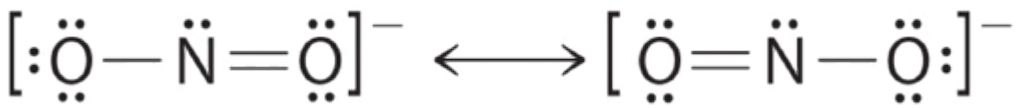
Resonance structures is a mechanism that allows us to use all of the possible resonance structures to try to predict what the actual form of the molecule would be. Single bonds, double bonds, triple bonds, +1 charges, -1 charges, these are our limitations in explaining the structures, and the true forms 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.

Answers

Exercise 3.1.1.1**: Nitrite Ion**



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.

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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 ($\mathrm{SF_6}$).

Answer available at the end of this section.

Exercise 3.1.2.1

Draw the Lewis structure for chlorine trifluoride ($\mathrm{ClF_3}$.

Answer available at the end of this section.

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.

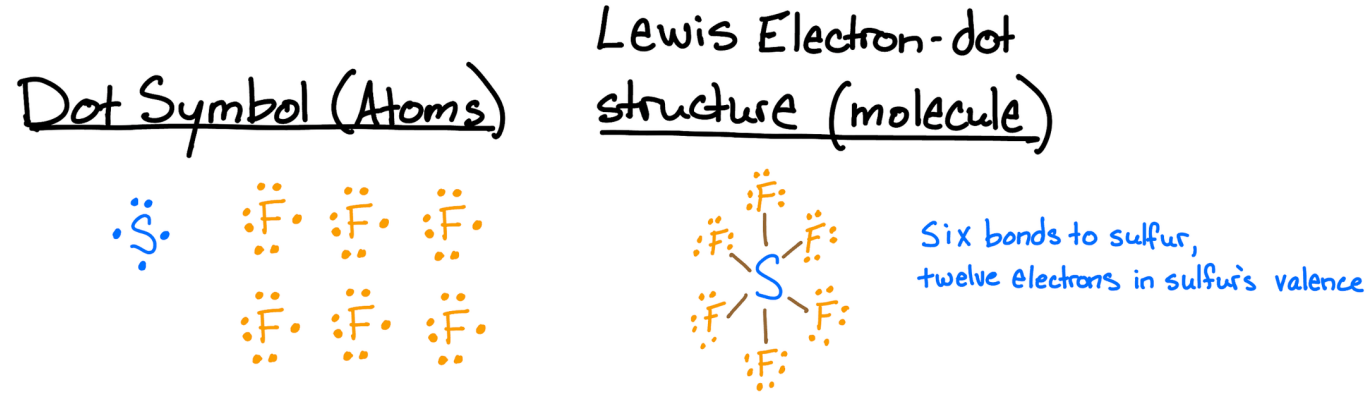
> Bonding theories can only be judged by their predictions.

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.

Answers

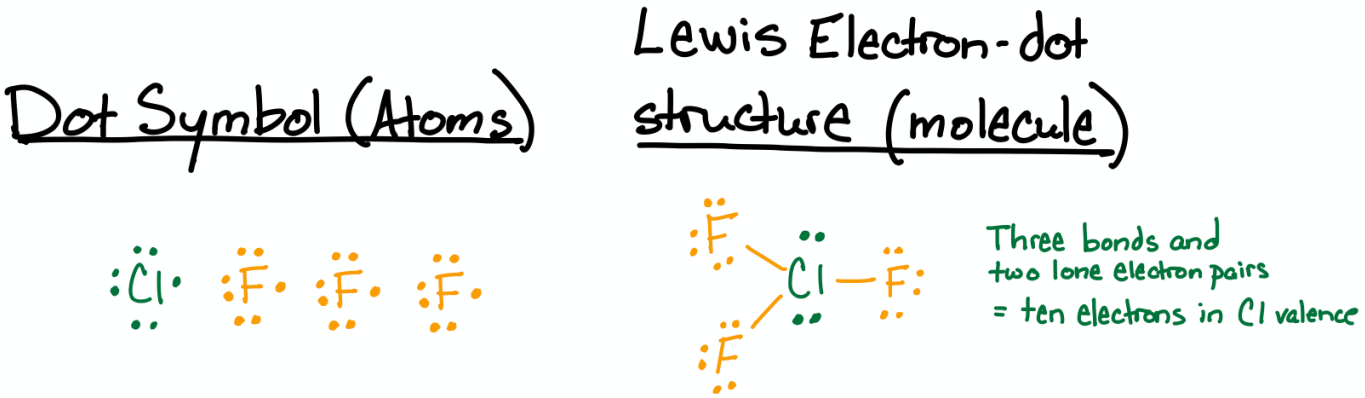
Exercise 3.1.2.1

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

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.



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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.

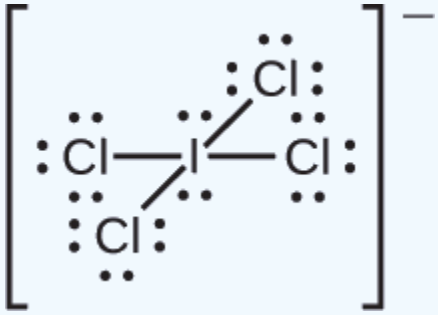
We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen ion $\mathrm{ICl_4^-}$.

Solution

We divide the bonding electron pairs equally for all $\mathrm{I{-}Cl}$ 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:



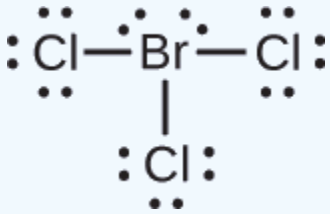
Answer available at the end of this section.

Example: Calculating Formal Charge from Lewis Structures

Assign formal charges to each atom in the interhalogen molecule $\mathrm{BrCl_3}$.

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 $\mathrm{BrCl_3}$ 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 $\mathrm{NCl_3}$.

Answer available at the end of this section.

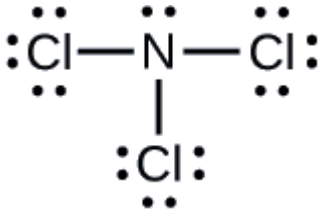
Answers

Exercise 3.1.3.1

C –1, O +1

Exercise 3.1.3.2

N: 0; all three Cl atoms: 0



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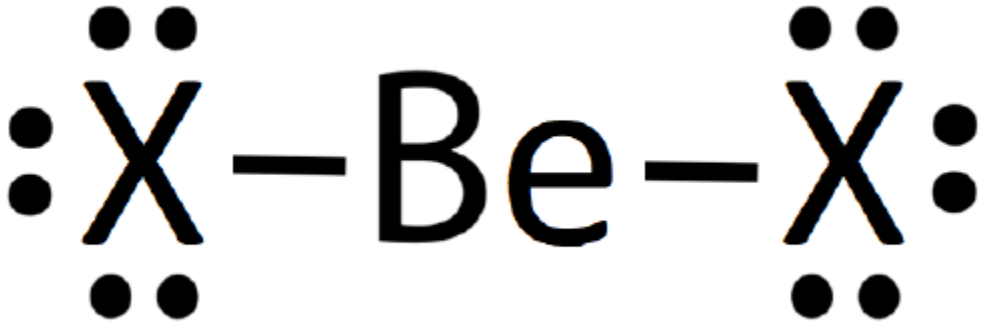
- 7.5: Formal Charges and Resonance by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

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 $\mathrm{BeX_2}$, where X is one of the halogens, F or Cl.



Each of the structures above would predict a linear geometry for the $\mathrm{BeX_2}$ 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 $\mathrm{BeCl_2}$ at very high temperatures).

It turns out that the monomer of $\mathrm{BeX_2}$ 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 $3.1.4.1$.

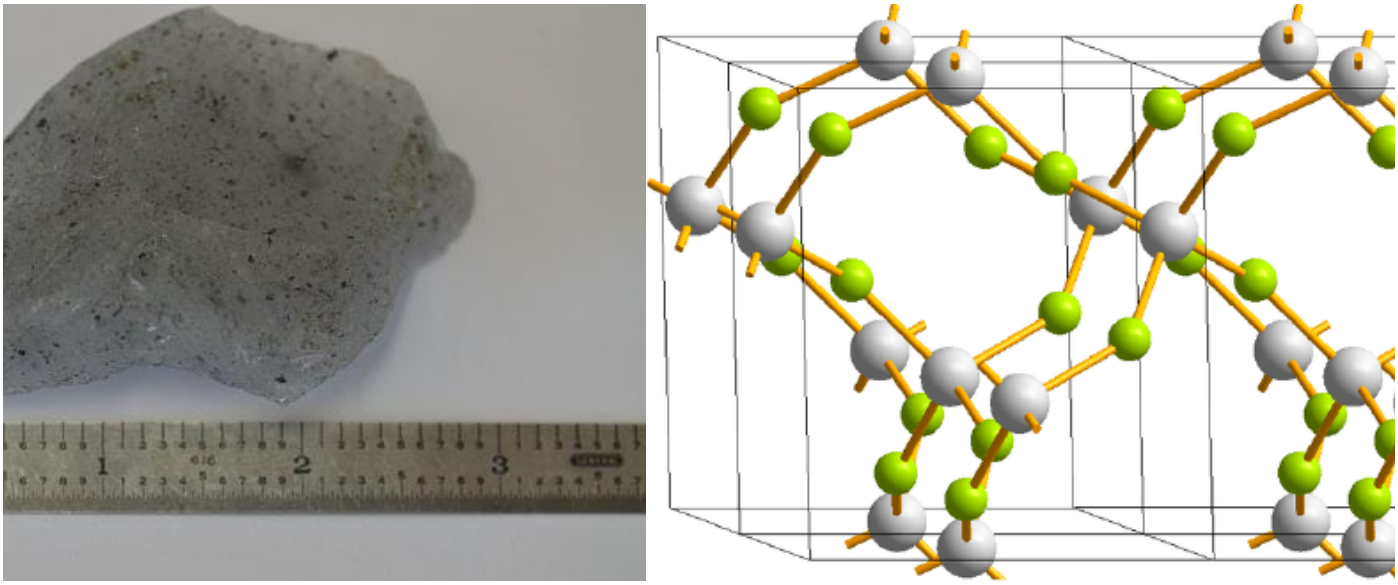


Figure 3.1.4.1: (left) A nugget of beryllium fluoride obtained from Materion. Black spots are carbon (CC BY-SA 3.0; Bckelleher via Wikipedia). (right) BeF2 structure (CC BY-SA 3.0 Unported; Materialscientist via Wikipedia)

In the liquid phase, $\mathrm{BeF_2}$ 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, $\mathrm{BeF_2}$ exists as a monomer with linear geometry and a bond length of 1.43 Å, consistent with a double bond between Be and F.

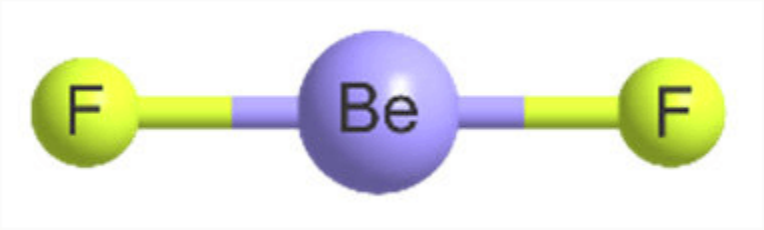


Figure 3.1.4.2: Geometries of $\mathrm{BeF_2}$. (CC BY; Ibon Alkorta and Anthony C. Legoe via Inorganics)

$\mathrm{BeCl_2}$

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

In the gas phase, $\mathrm{BeCl_2}$ 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 $\mathrm{BH_3}$ and $\mathrm{BF_3}$ were described in Exercise 3.1.2, and are drawn again below for convenience.

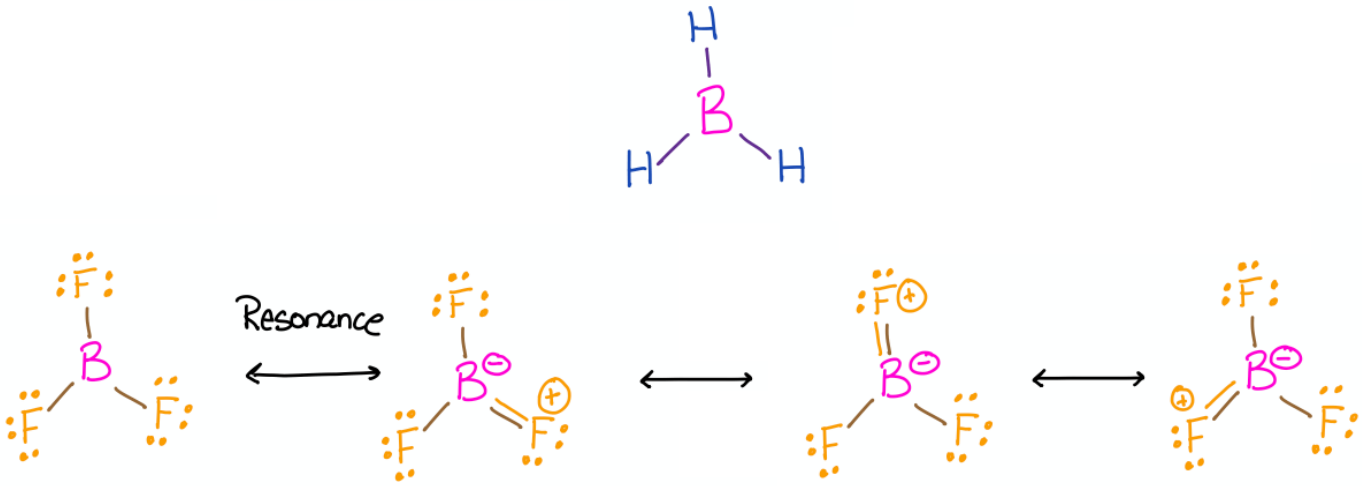


Figure 3.1.4.2: Lewis structures of BH_3 and BF_3. (Kathryn Haas; CC-NC-BY-SA)

Boron trihalides

Boron trihalides, like BF_3, have properties that are largely predicted by Lewis structures and VSEPR theory. The Lewis structure for 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 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 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 (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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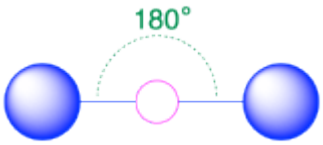
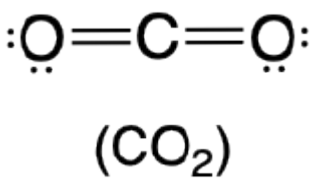
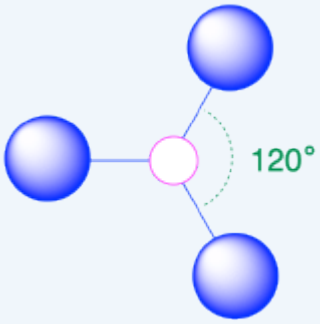
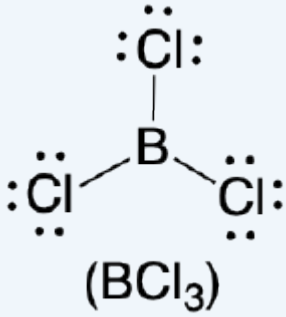
3.2: Valence Shell Electron-Pair Repulsion

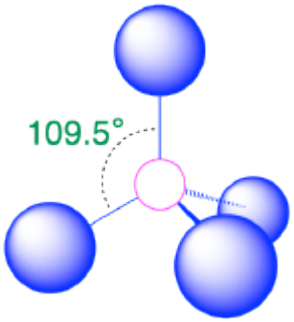
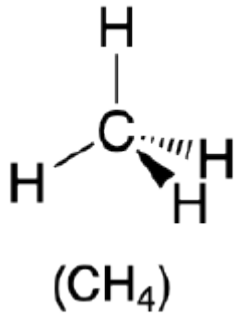
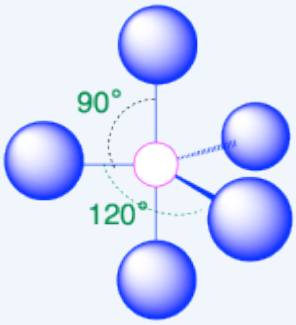
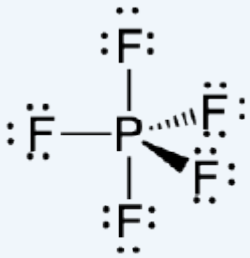
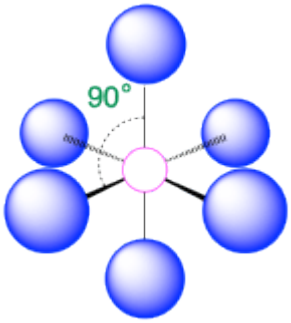
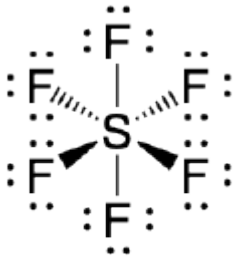
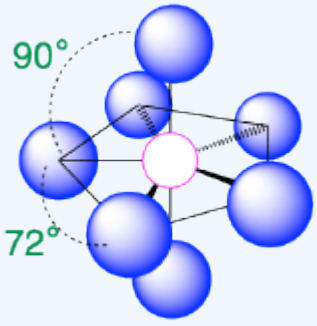
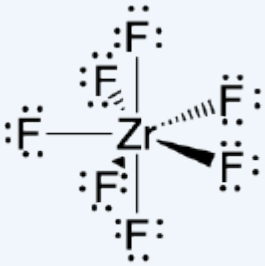
Introduction to VSEPR

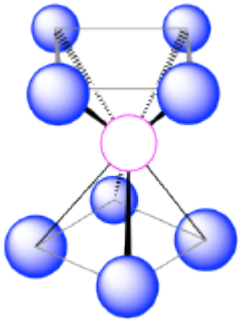
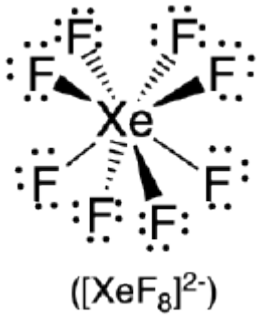
The **Valence Shell Electron Repulsion (VSEPR)** model can predict the structure of most molecules and polyatomic ions in which the central atom is a nonmetal; it also works for some structures in which the central atom is a metal. VSEPR builds on Lewis electron dot structures (discussed in Section 3.1); 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 $\mathbf{AX}_m\mathbf{E}_n$ 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.

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°	 (CO_2)
3	trigonal plane		120°	 (BCl_3)

Groups around central atom (*m* + *n*)	Geometry Name	Geometry Sketch	Predicted bond Angle	Example
4	tetrahedron		109.5°	 (CH_4)
5	trigonal bipyramid		90° and 120°	 (PF_5)
6	octahedron		90°	 (SF_6)
7	pentagonal bipyramid		90° and 72°	 ($[ZrF_7]^{3-}$)

Groups around central atom (m + n)	Geometry Name	Geometry Sketch	Predicted bond Angle	Example
8	square antiprism		70.5°, 99.6° and 109.5°	 ($[XeF_8]^{2-}$)

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 BeH2 available at the end of this section.

Answer CO2 available at the end of this section.

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 BCl3 available at the end of this section.

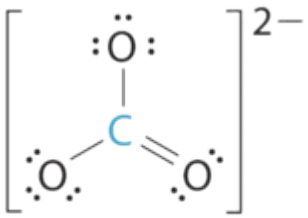
2. There are three groups around the central atom and all are single bonds. The structure is designated as AX_3.

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

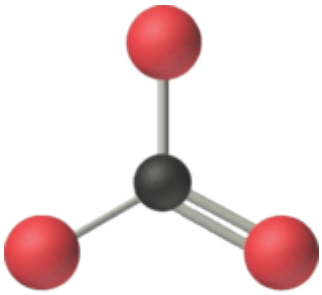


Lewis structure

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.

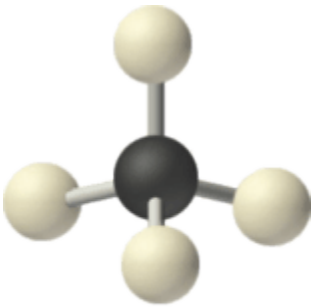
Answer CH4 available at the end of this section.

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°.

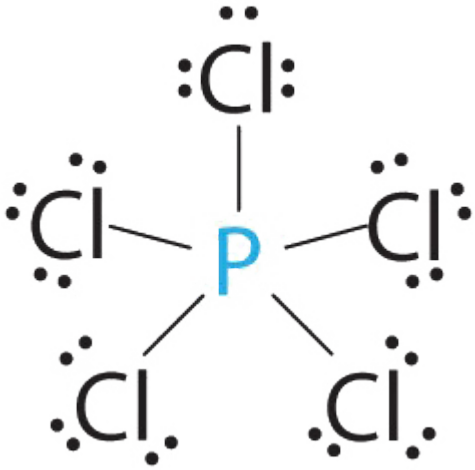
4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Table 3.2.1).



Molecular geometry
(tetrahedral)

Answer PCl_5

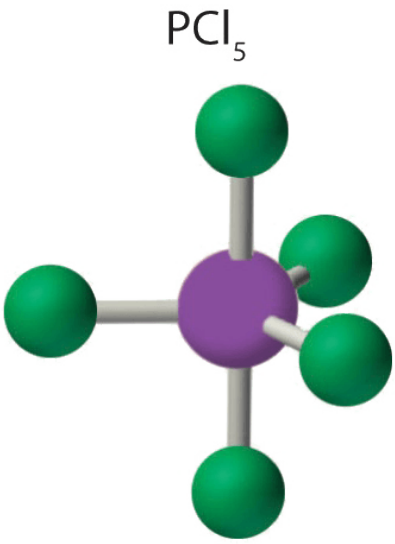
1. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron structure of PCl_5 is



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

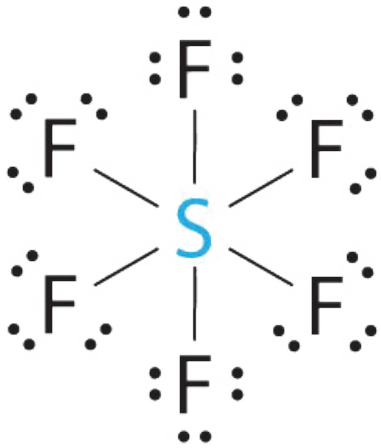
3. The structure that minimizes repulsions is a *trigonal bipyramid*, which consists of two trigonal pyramids that share a base (Table 3.2.1).

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



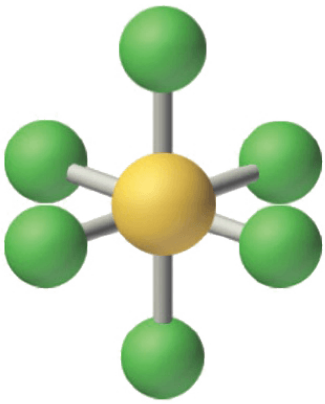
Lewis structure

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

2. There are six electron groups around the central atom, each a bonding pair. We see from Figure 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.

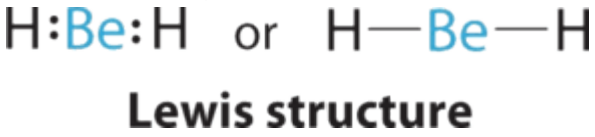


Molecular geometry
(octahedral)

Answers

Exercise 3.2.1

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

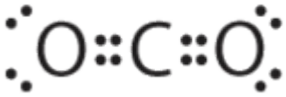


Lewis structure

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*.

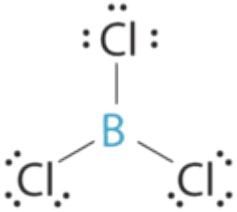
Exercise 3.2.1

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



Exercise 3.2.2

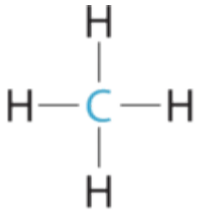
1. The central atom, boron, contributes three valence electrons, and each chlorine atom contributes seven valence electrons. The Lewis electron structure is



Lewis structure

Exercise 3.2.3

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

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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 $\mathbf{AX_mE_n}$, 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.

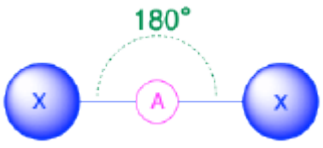
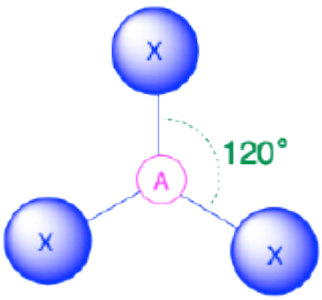
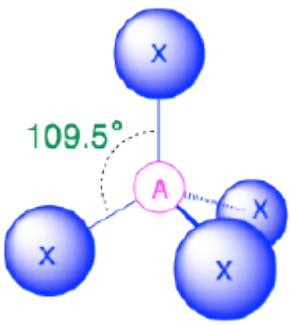
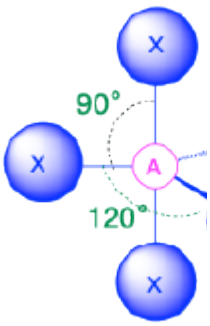
When one or more of the groups is a lone pair of electrons (non-bonded electrons), the experimentally-observed geometry around an atom is slightly different than in the case where all groups are bonds. The actual bond angles are similar, but not exactly the same, as those predicted based on the *total 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:

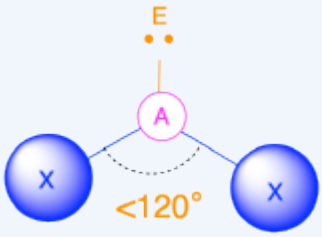
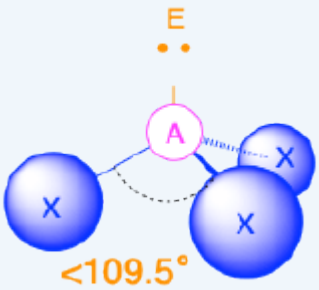
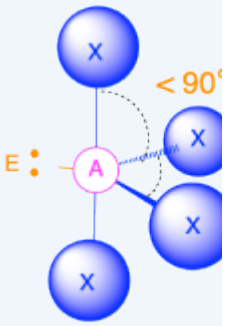
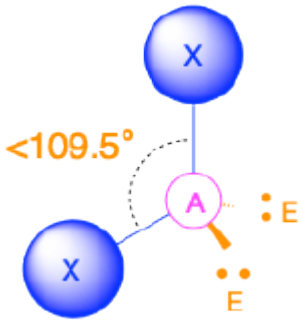
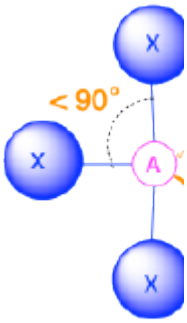
Trend in bond angles:

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) elec

	Electron Groups (*m* + *n*)			
	2 (steric number = 2)	**3** (steric number = 3)	**4** (steric number = 4)	**5** (steric number
Parent Geometry (**0 lone pairs**) **AX_m**	 **AX_2**, linear 180°	 **AX_3**, trig. plane 120°	 **AX_4**, tetrahedron 109.5°	 **AX_5**, trig. bipyra 90°, 120°

	Electron Groups (m + n)			
	2 (steric number = 2)	3 (steric number = 3)	4 (steric number = 4)	5 (steric number
1 lone pair **AX_mE_1**		 **AX_2E_1**, bent <120°	 **AX_3E_1**, trig. pyramid <109.5°	 **AX_4E_1**, see-s <90°, <120°
2 lone pairs **AX_mE_2**			 **AX_2E_2**, bent <109.5°	 **AX_3E_2**, T-sha <90°

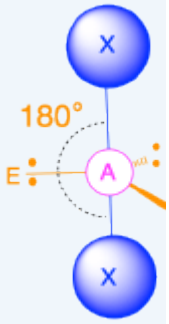
	Electron Groups (m + n)			
	2 (steric number = 2)	3 (steric number = 3)	4 (steric number = 4)	5 (steric number
3 lone pairs **AX_mE_3**				 **AX_2E_3**, linea 180°

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.

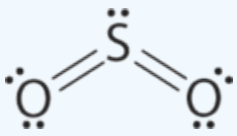
Three Electron Groups (m + n = 3)

(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)

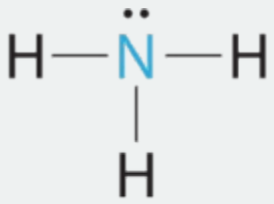
(Steric number = 4) In the case that there are four electron groups around a central atom, those groups will lie approximately 109.5° from one another in space. This results in an electronic geometry that is approximately **tetrahedral**. There are three different molecular geometries that are possible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

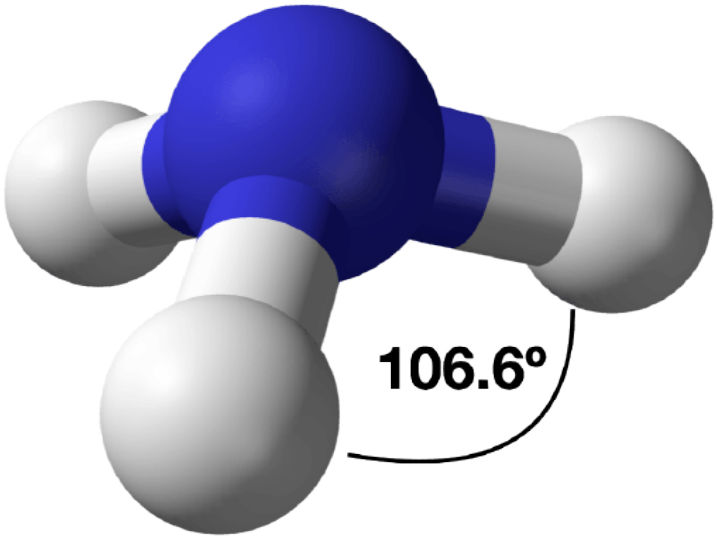
1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure



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

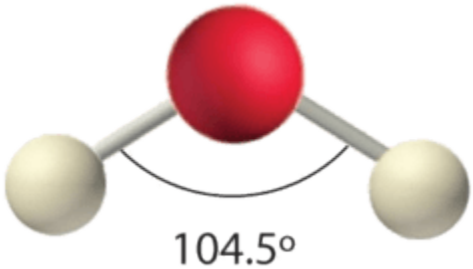
1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure



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)

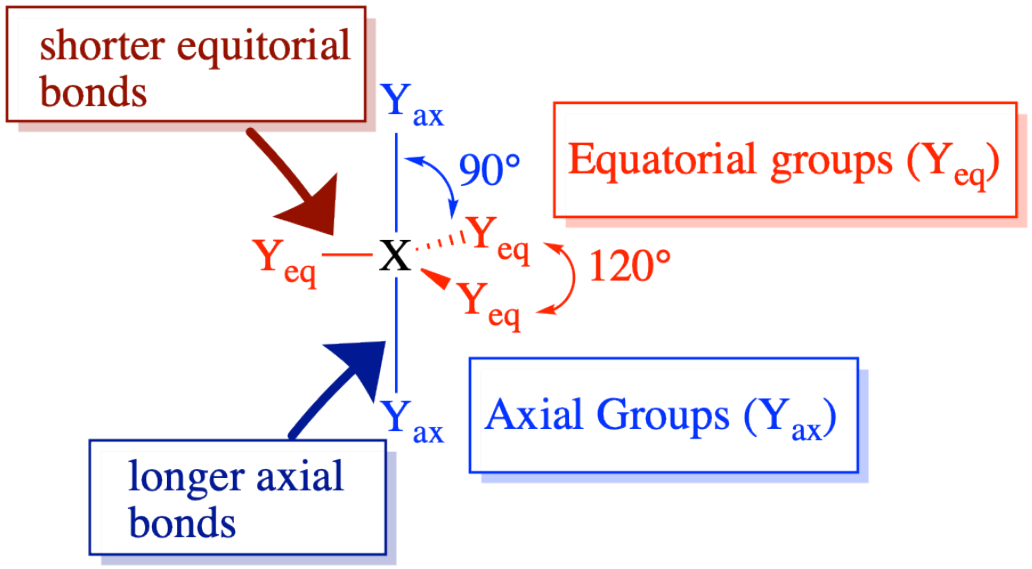


Figure: Trigonal pyramidal molecules (steric number 5) possess different bond angles and lengths for axial (ax) and equatorial (eq) pendant atoms. (CC-BY-NC-SA; Kathryn Haas).

(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.

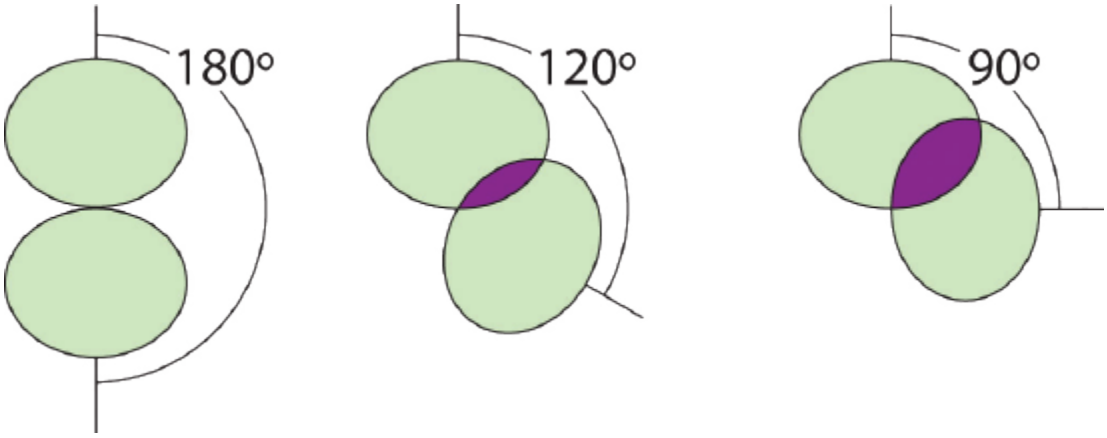
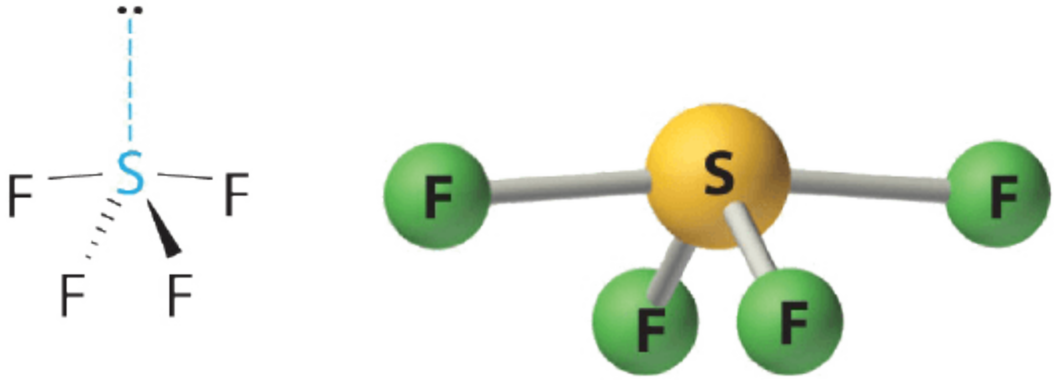


Illustration of the Area Shared by Two Electron Pairs versus the Angle between Them

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

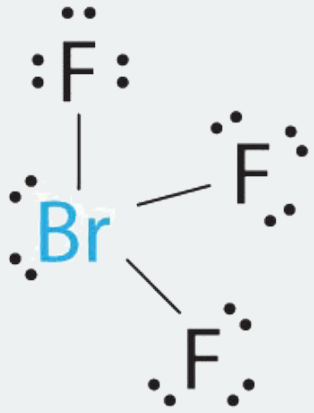
4. With four nuclei and one lone pair of electrons, the molecular structure is based on a trigonal bipyramid with a missing equatorial vertex; it is described as a *seesaw*. The F_{axial}–S–F_{axial} angle is 173° rather than 180° because of the lone pair of electrons in the equatorial plane.



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

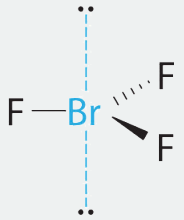


Lewis structure

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

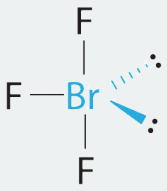
2. There are five groups around the central atom, three bonding pairs and two lone pairs. We again direct the groups toward the vertices of a trigonal bipyramid.

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°:



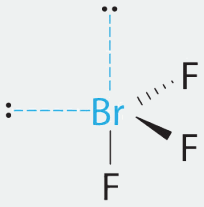
Lone pairs axial

(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.

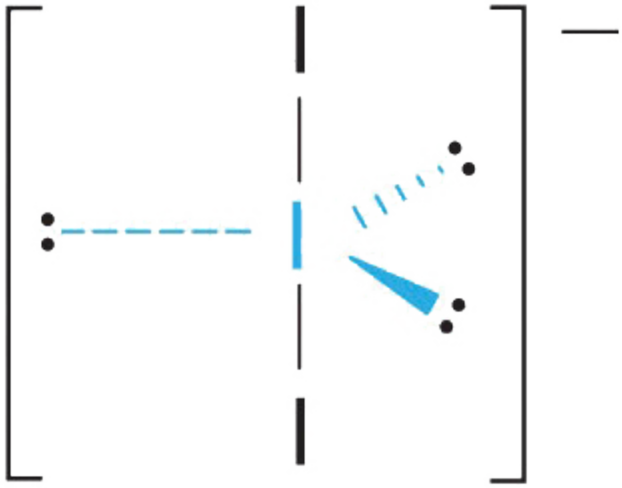
AX_2E_3 Molecules: I_3^-

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



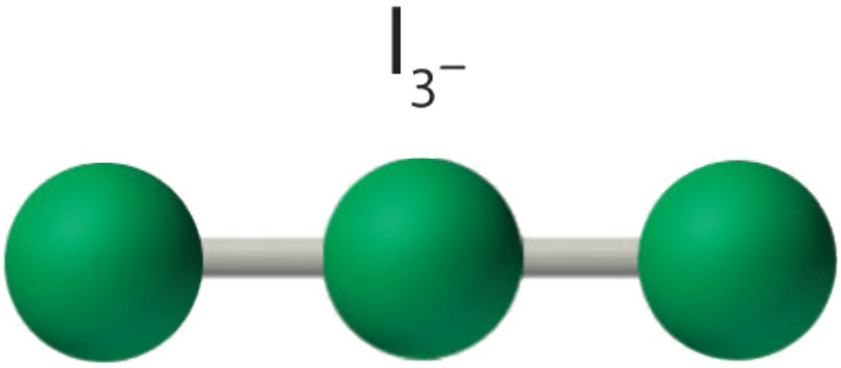
2. There are five electron groups about the central atom in I_3^-, two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

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.



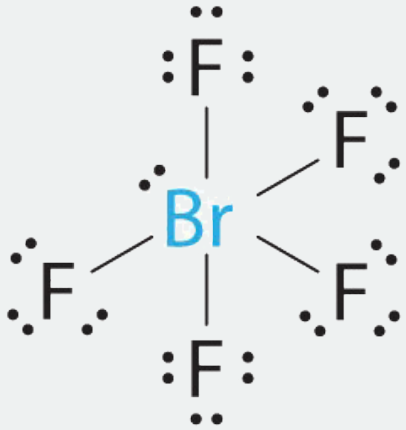
Six Electron Groups (m + n = 6)

(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

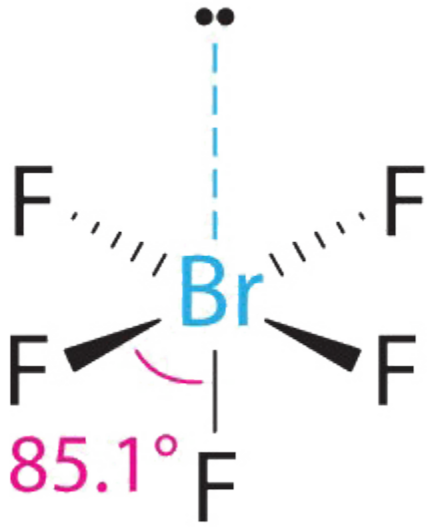
1. The central atom, bromine, has seven valence electrons, as does each fluorine, so the Lewis electron structure is



Lewis structure

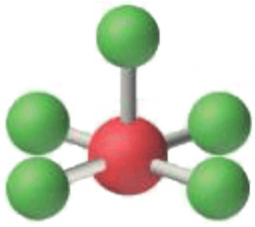
With its expanded valence, this species is an exception to the octet rule.

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.

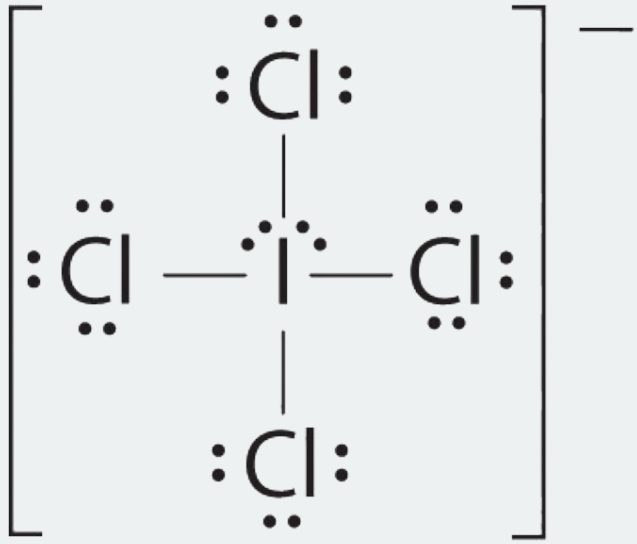
4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is *square pyramidal*. The F_{axial}–B–$F_{equatorial}$ angles are 85.1°, less than 90° because of LP–BP repulsions.



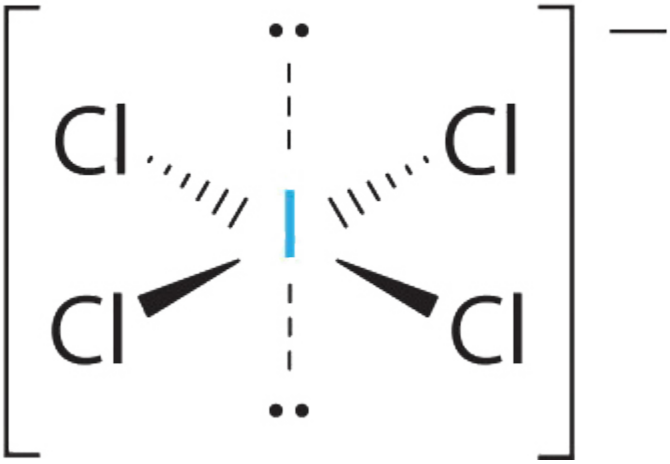
Molecular geometry
(square pyramidal)

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



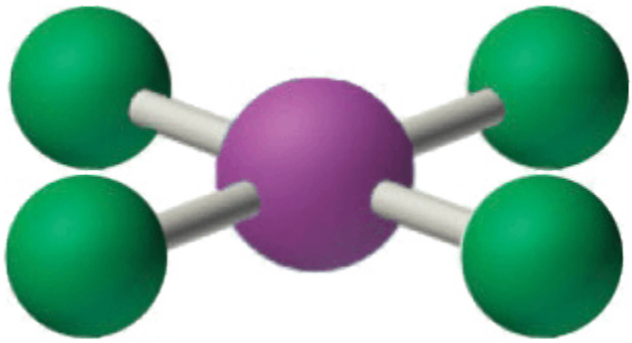
2. There are six electron groups around the central atom, four bonding pairs and two lone pairs. The structure that minimizes LP–LP, LP–BP, and BP–BP repulsions is



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

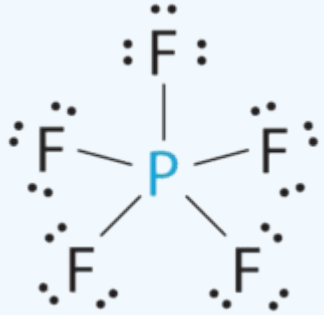
Strategy:

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



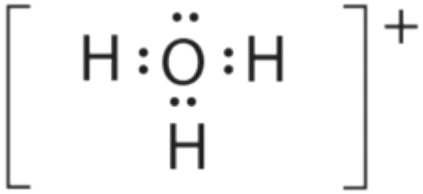
B There are five bonding groups about phosphorus. The structure that minimizes repulsions is a trigonal bipyramid.

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.



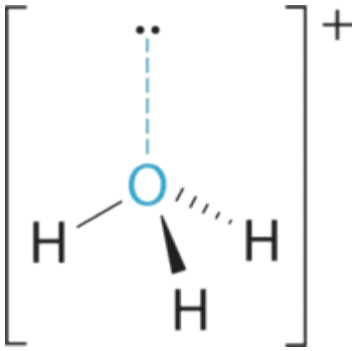
- **A** The central atom, O, has six valence electrons, and each H atom contributes one valence electron. Subtracting one electron for the positive charge gives a total of eight valence electrons, so the Lewis electron structure is



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 available at the end of this section.

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 Example3.2.1.1.

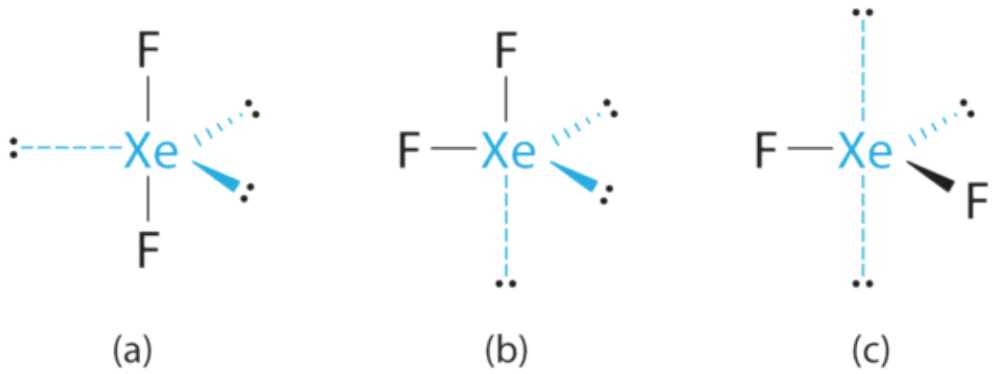
Solution:

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:



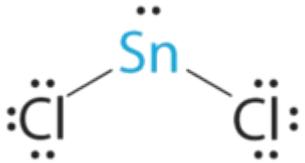
Interactions

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 available at the end of this section.

Answers

Exercise 3.2.1.1

trigonal pyramidal

octahedral

linear

Exercise 3.2.1.2

trigonal planar

square planar

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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.

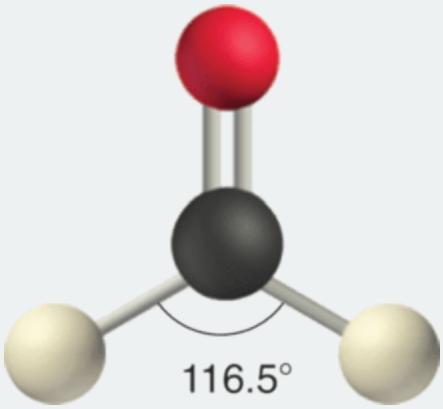
Double and triple bonds are more repulsive than single bonds

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

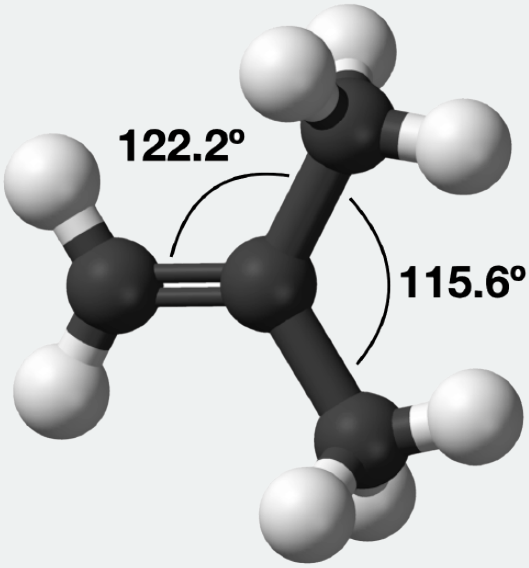
CH_2O

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

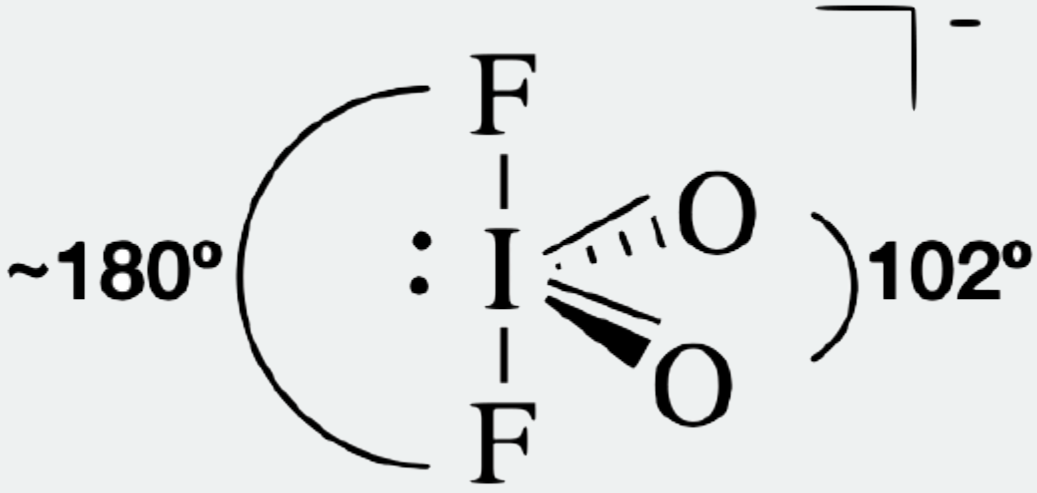
In general, we expect that a lone pair has slightly greater repulsive force than a multiple bond, and that a multiple bond has slightly greater repulsive force than a single bond. The **order of expected repulsive force** is:

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

Examples3.2.2.1

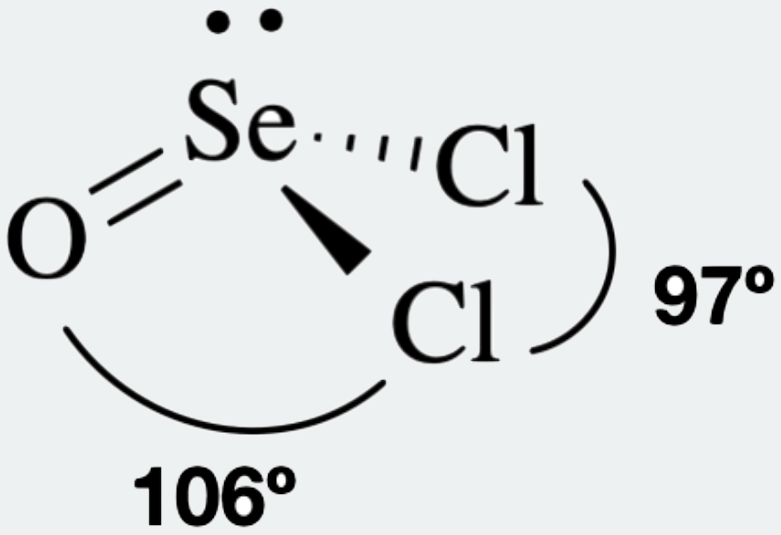
$IO_2F_2^-$

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 available at the end of this section.

Answer b available at the end of this section.

Answer c available at the end of this section.

Answer d available at the end of this section.

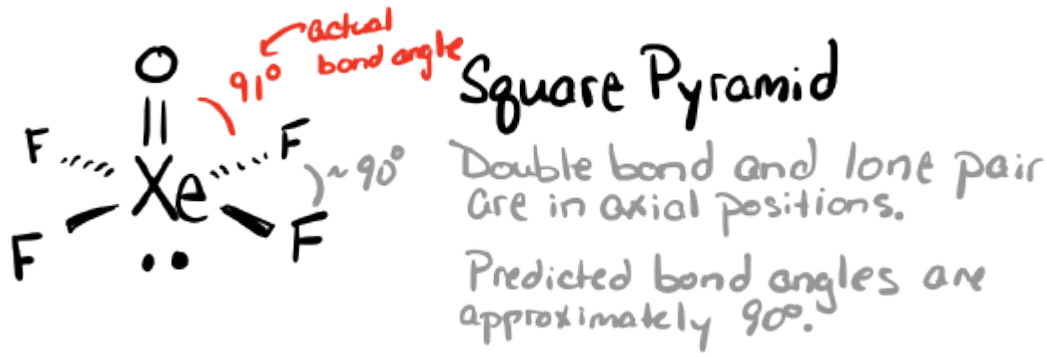
References

- Miessler, G.; Fischer, P.J.; Tarr, D. (2014). Inorganic Chemistry. New Jersey: Prentice-Hall. pp. 55

Answers

Exercise 3.2.2.1

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).



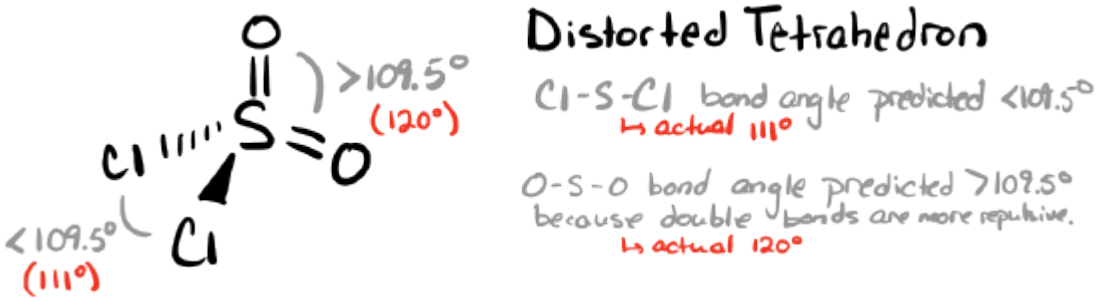
Exercise 3.2.2.1

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°.*



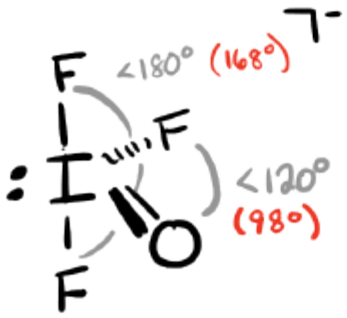
Exercise 3.2.2.1

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.



Exercise 3.2.2.1

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°.



Distorted see saw

Lone pair and double bond in equitorial positions.

Predicted bond angles:

F-I-O <120° / actual 98°

F_{axial}-I-F_{axial} <180° / actual 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?

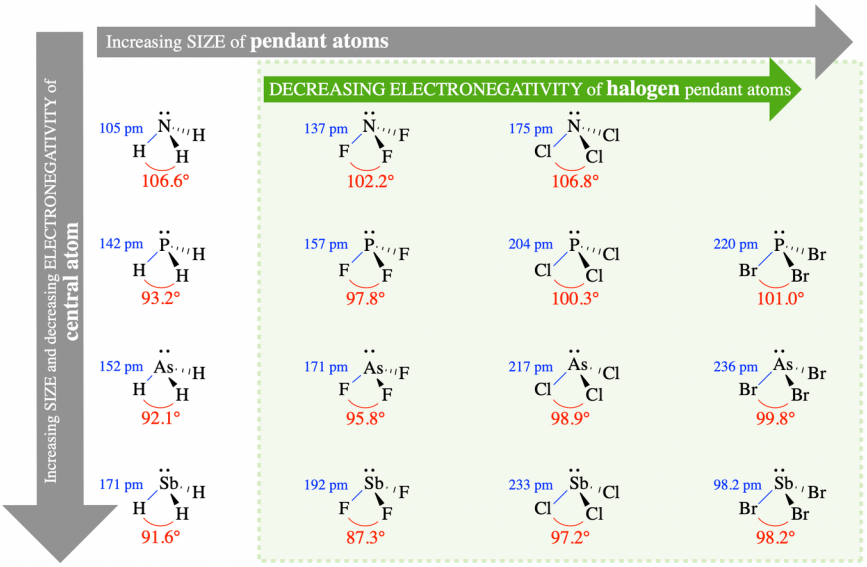


Figure 3.2.3.2: Several molecules with trigonal pyramidal electronic geometry are shown arranged according to size of the central atom (increasing size of central atom from top to bottom) and pendant atom (increasing size of pendant atoms from left to right). Bond angles and bond lengths are indicated.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

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 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).

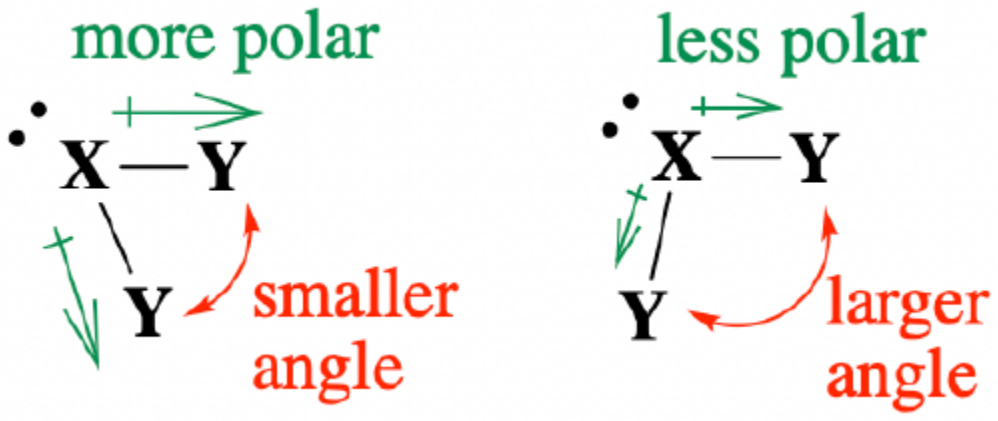


Figure 3.2.3.3. When electron pairs are distributed away from the central atom, repulsions are decreased, allowing smaller bond angles. (Kathryn Haas; CC-NC-BY-SA)

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) available at the end of this section.

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?

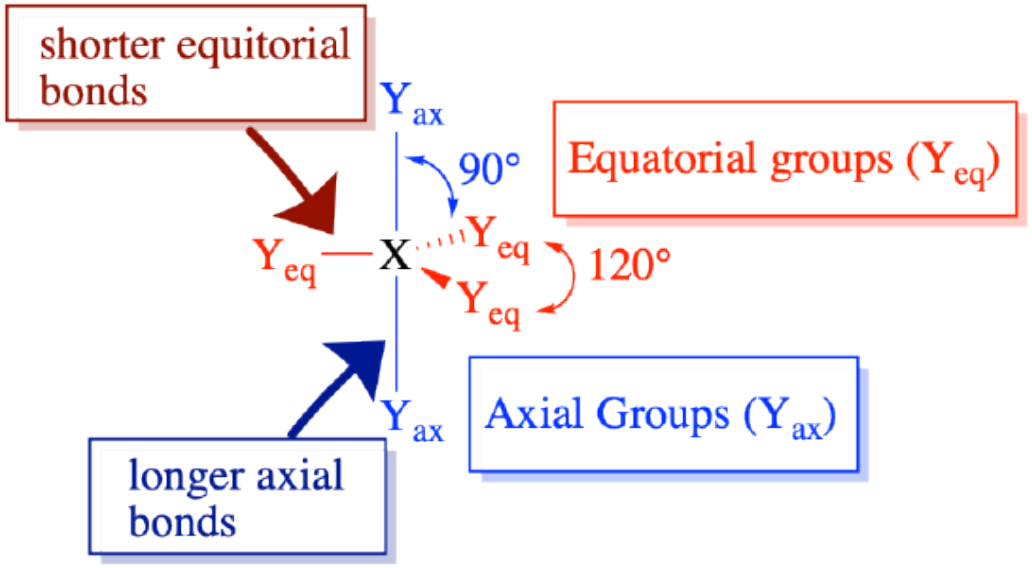
a. $N(CH_3)_3$ has an C-N-C bond angle of 110.9°, while $N(CF_3)_3$ has a bond angle of 117.9°.
b. The X-S-X bond angles in molecules of the form $SO_2(X)_2$ are: $SO_2(OH)_2$ 101.3°; $SO_2(CF_3)_2$ 102.0°; $SO_2(CH_3)_2$ 102.6°.

Answer (a) available at the end of this section.

Answer (b) available at the end of this section.

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

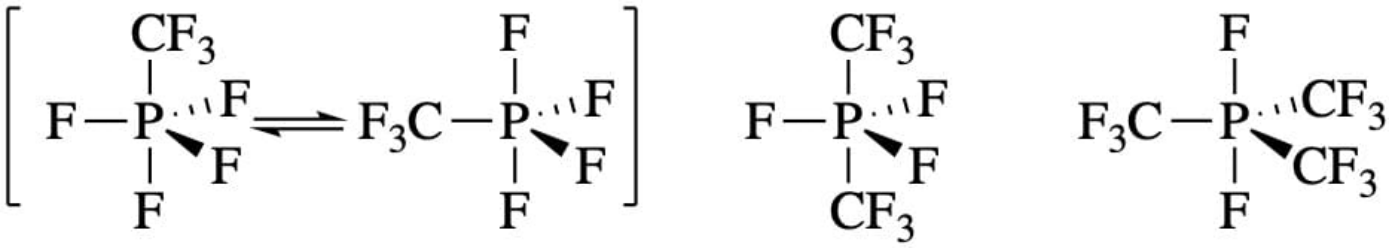
Some examples of molecule that demonstrate the equatorial preference of less electronegative groups are below. Predict (draw) their structures.

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) available at the end of this section.

Answer (b) available at the end of this section.

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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Acknowledgment

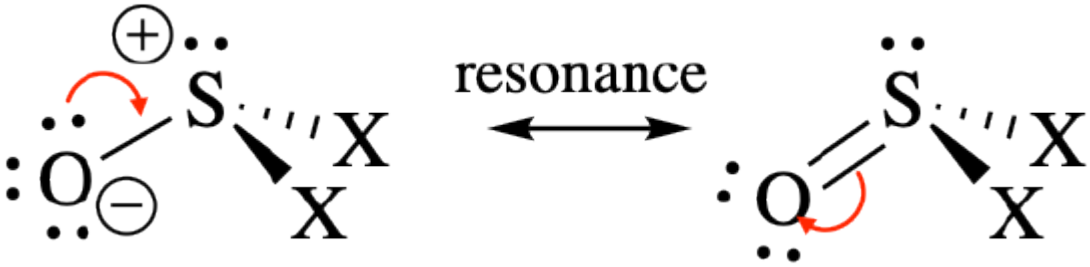
- Matthew Salem (UC Davis) (Pauling Electronegativity)
- Introduction to Inorganic Chemistry Wikibook (https://chem.libretexts.org/Bookshel..._Bond_Strength)

- Curated or created by Kathryn Haas

Answers

Exercise 3.2.3.1

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.

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.

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°).

Exercise 3.2.3.2

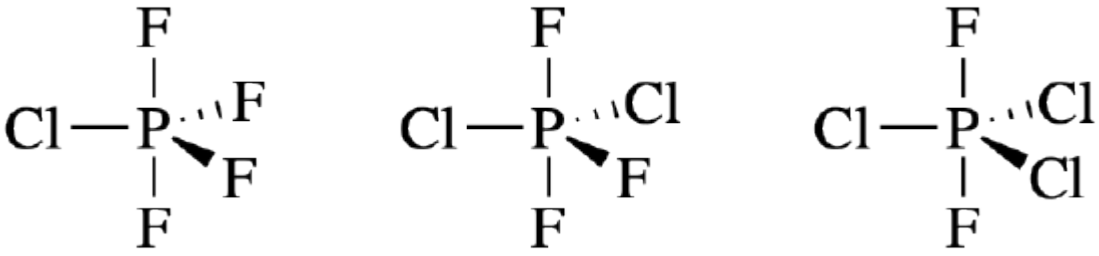
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Exercise 3.2.3.2

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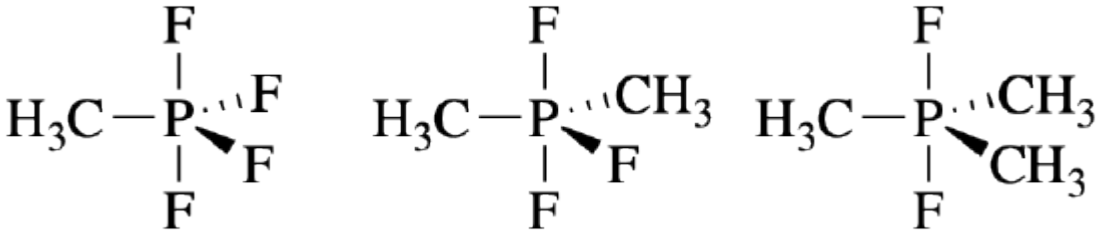
Exercise 3.2.3.3

Cl is less electronegative than F; thus we expect Cl to have stronger preference for the equatorial positions.



Exercise 3.2.3.3

CH_3, an electron donating group, is less electronegative than F. We expect CH_3 to have a stronger preference for the equatorial positions.



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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, $\mathrm{PF_4}^+$ and $\mathrm{PF_3O}$ have almost identical $\mathrm{F-F}$ distances of 238 and 237 pm, respectively. As expected from VSEPR, the $\mathrm{F-P-F}$ bond angle in $\mathrm{PF_4}^+$ is 109.5°. The $\mathrm{F-P-F}$ bond angle in $\mathrm{PF_3O}$ (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 $\mathrm{PF_4}^+$ and 154 pm in $\mathrm{PF_3O}$.

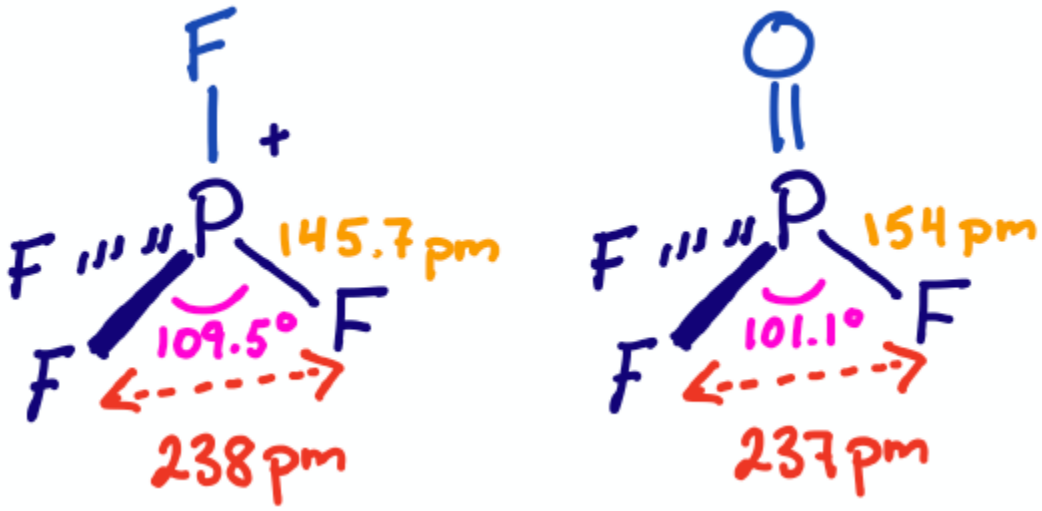


Figure 3.2.4.1: The molecular structures of $\mathrm{PF_4}^+$ and $\mathrm{PF_3O}$. The distances between neighboring F atoms are similar in the two molecules, while bond lengths and angles differ. The $\mathrm{PF_4}^+$ ion has a $\mathrm{P-F}$ bond length of 145.7 pm, an $\mathrm{F-P-F}$ bond angle of 109.5°, and a distance of 238 pm between neighboring F atoms. The $\mathrm{PF_3O}$ molecule has a $\mathrm{P-F}$ bond length of 154 pm, an $\mathrm{F-P-F}$ 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 .

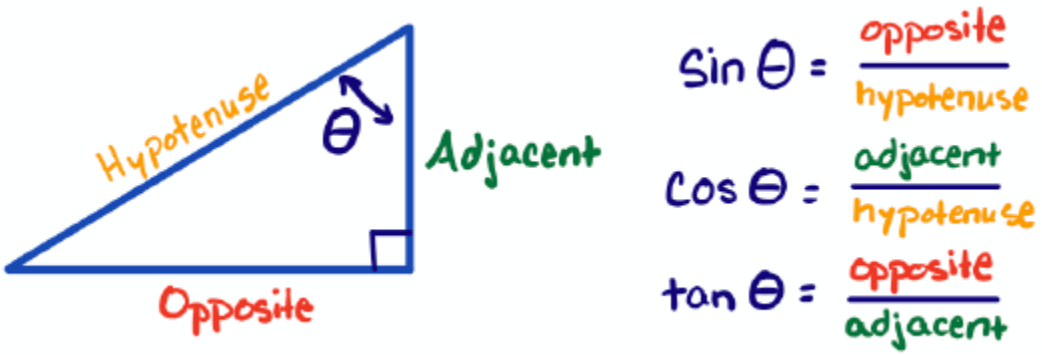


Figure 3.2.4.2: Visual depiction of SOA-CAH-TOA. (CC-BY-NC-SA; Kathryn Haas)

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.

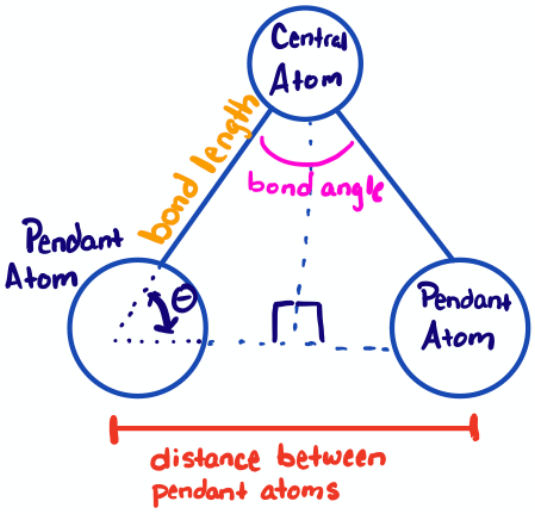


Figure 3.2.4.1: Illustration of how right angle trigonometry can be applied to determine bond angle, bond length, or distance between neighboring atoms: any bond angle can be divided into two right angles where the bond length is the hypotenuse, the distance between neighbors is twice the opposite side, 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?

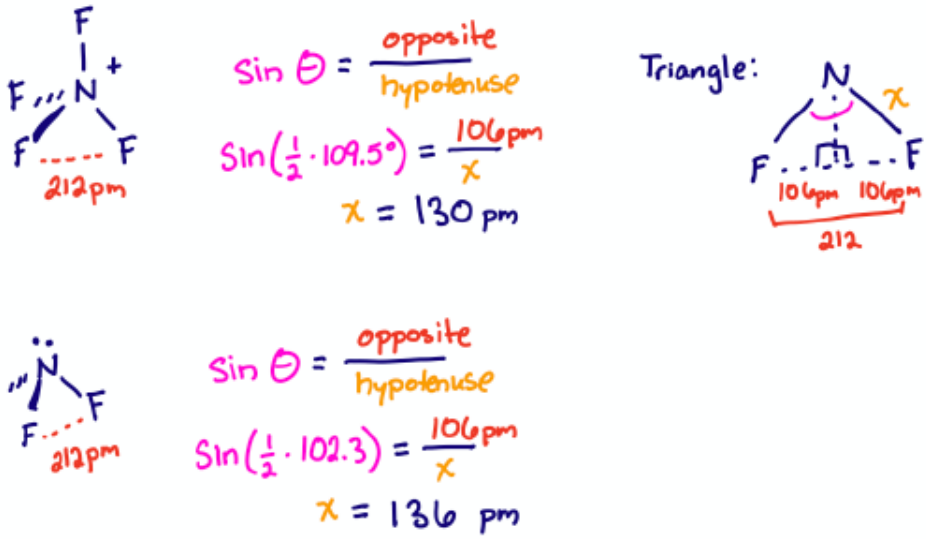
Answer available at the end of this section.

Sources and Resources

- https://en.Wikipedia.org/wiki/LCP_th...ieNyholm1957-3

Answers

Exercise 3.2.4.1



The actual measured bond lengths are 130 pm for NF_4^+ and 136.5 pm for NF_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 i^{th} charge, and
- $\vec{r}_i$ is the vector representing the position of i^{th} charge.

The dipole moment acts in the direction of the vector quantity. An example of a polar molecule is $\mathrm{H_2O}$. Because of the lone pair on oxygen, the structure of $\mathrm{H_2O}$ 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.

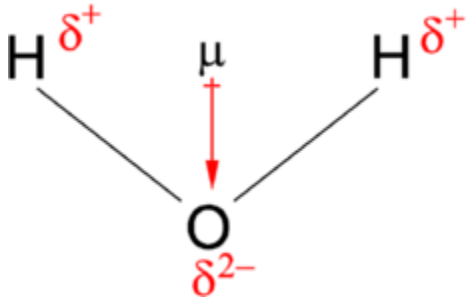


Figure 3.3.1: Dipole moment of water. The convention in chemistry is that the arrow representing the dipole moment goes from positive to negative. Physicist tend to use the opposite orientation.

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).

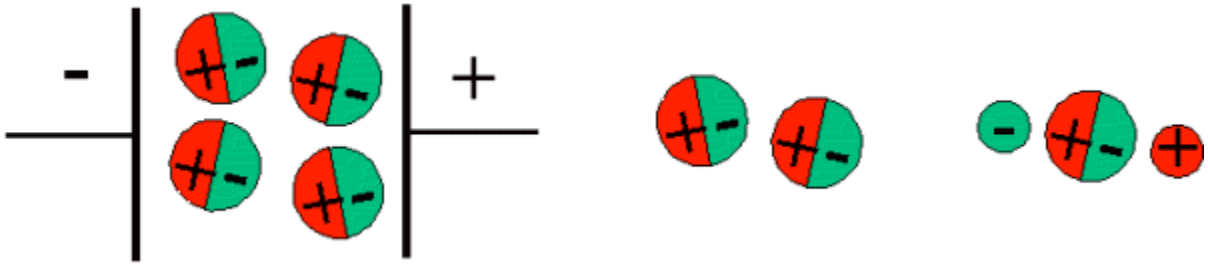


Figure 3.3.2: Polar molecules align themselves in an electric field (left), with respect to one another (middle), and with respect to ions (right)

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.

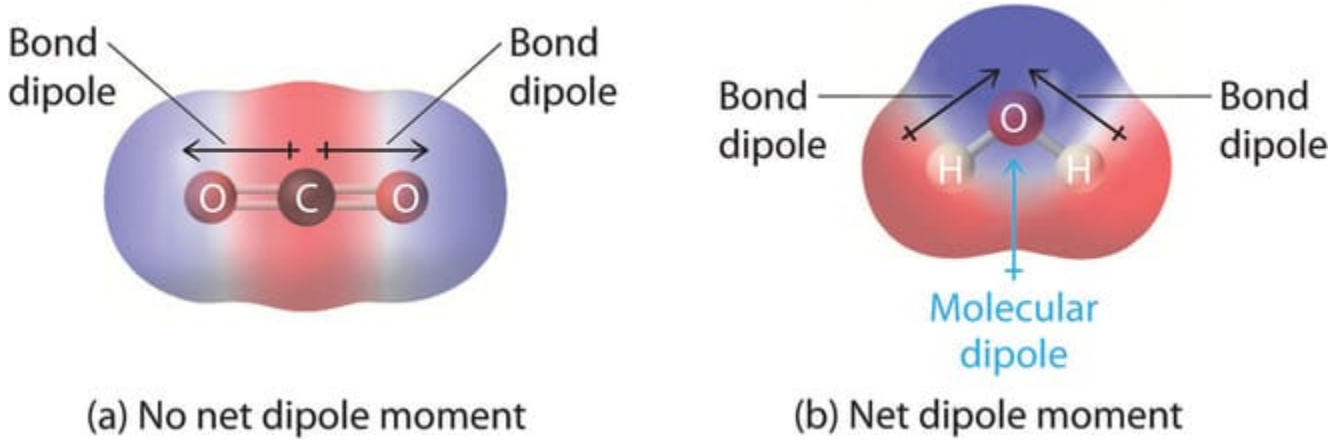


Figure 3.3.3: Charge distributions of CO_2 and H_2O\). Blue and red colored regions are negatively and positively signed regions, respectively. (CC BY-SA-NC 3.0; anonymous)

A good example of a nonpolar molecule that contains polar bonds is carbon dioxide (Figure $3.3.3a$). 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.

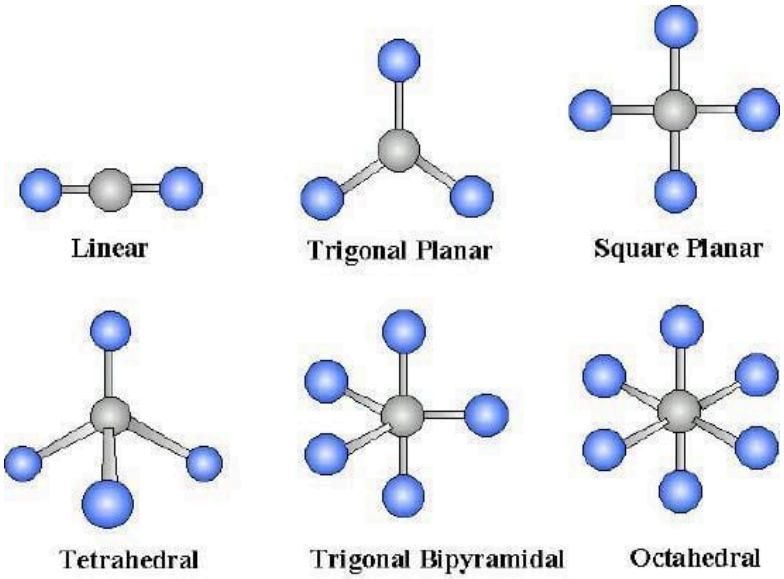
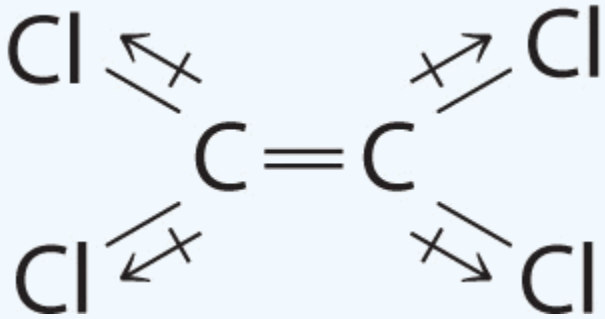


Figure 3.3.4: Molecular geometries with exact cancellation of polar bonding to generate a non-polar molecule ($\mu = 0$)

Example 3.3.3: C_2Cl_4

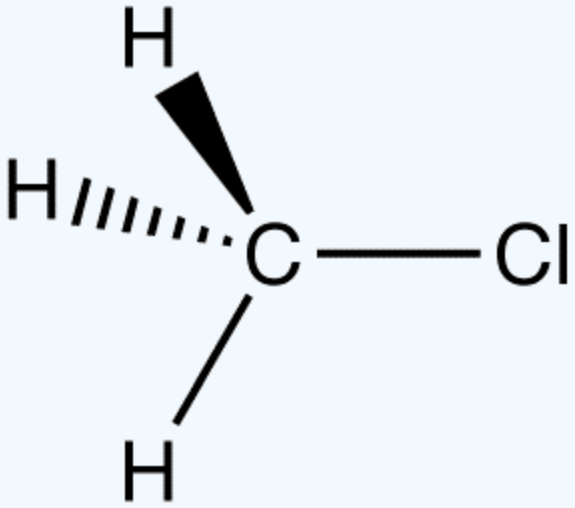
Although the C–Cl bonds are rather polar, the individual bond dipoles cancel one another in this symmetrical structure, and $Cl_2C{=}CCl_2$ does not have a net dipole moment.



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.

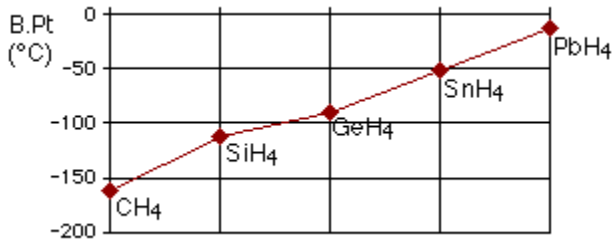


Figure 1: Boiling points of group 14 elemental halides.

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.

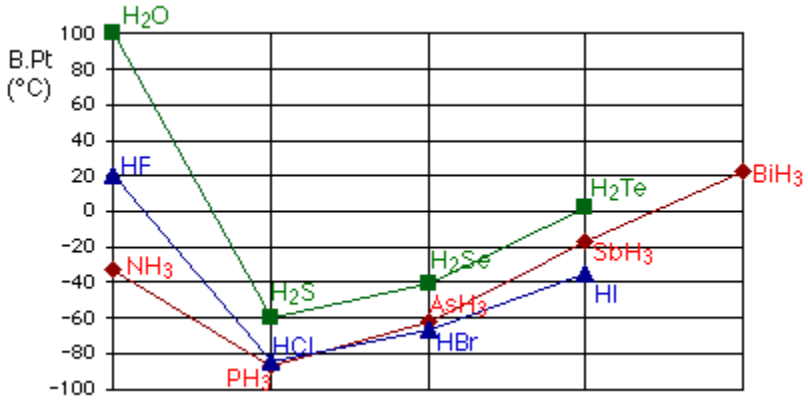


Figure 2: Boiling points of group 15-17 elemental halides.

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:

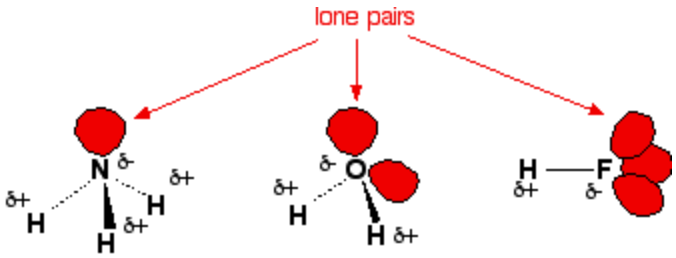


Figure 3: The lone pairs responsible for hydrogen bonding in NH_3, H_2O, and HF. The solid line represents a bond in the plane of the screen or paper. Dotted bonds are going back into the screen or paper away from you, and wedge-shaped ones are coming out towards you.

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.

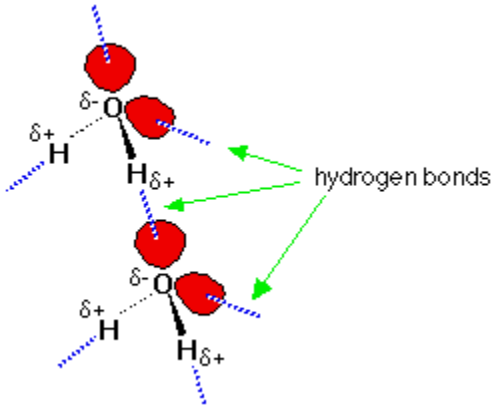


Figure 4: Hydrogen bonding in water

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.

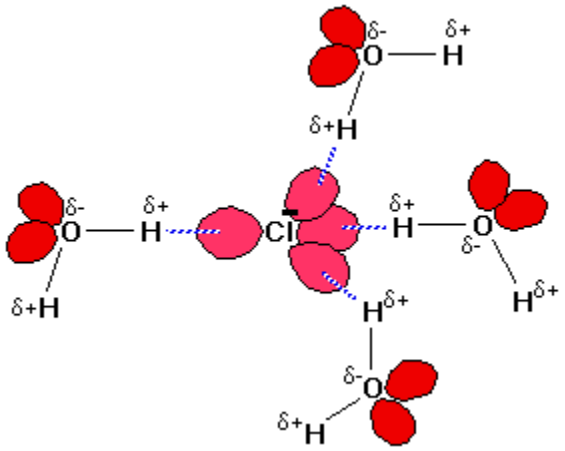


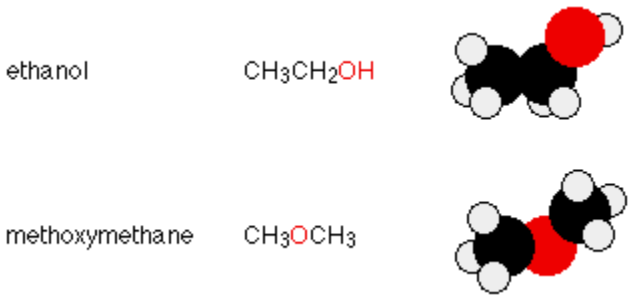
Figure 5: Hydrogen bonding between chloride ions and water.

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, CH_3CH_2-O-H, and methoxymethane, CH_3-O-CH_3, both have the same molecular formula, 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.

pentane	$CH_3CH_2CH_2CH_2CH_3$	B.Pt: 36.3°C
butan-1-ol	$CH_3CH_2CH_2CH_2OH$	B.Pt: 117°C
2-methylpropan-1-ol	$CH_3CH(CH_3)CH_2OH$	B.Pt: 108°C

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.

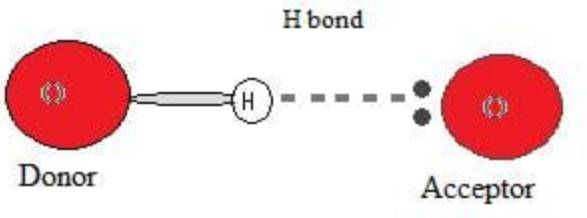
Hydrogen bonding in organic molecules containing nitrogen

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

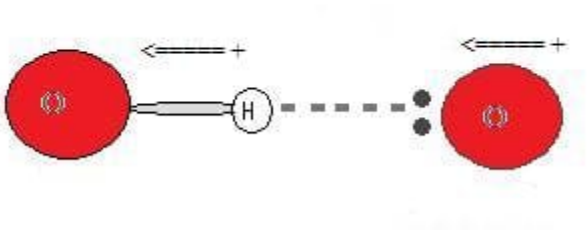
In order for a hydrogen bond to occur there must be both a hydrogen donor and an acceptor present. The donor in a hydrogen bond is usually a strongly electronegative atom such as N, O, or F that is covalently bonded to a hydrogen bond.

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)

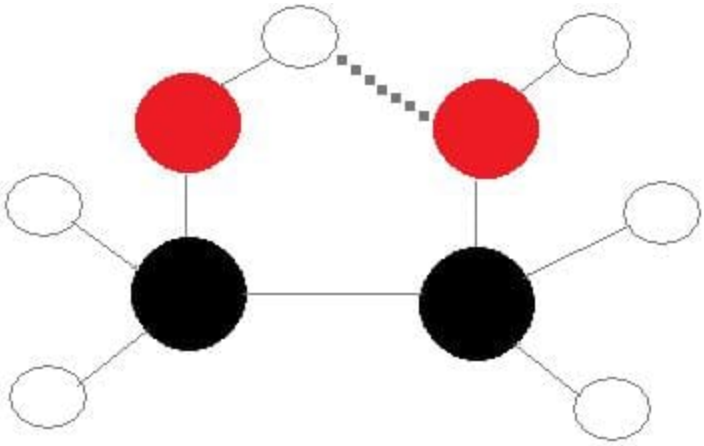


Types of hydrogen bonds

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

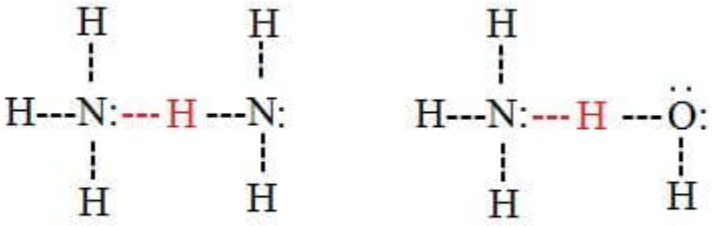
Intramolecular hydrogen bonds are those which occur *within* one single molecule. This occurs when two functional groups of a molecule can form hydrogen bonds with each other. In order for this to happen, both a hydrogen donor a hydrogen acceptor must be present within one molecule, and they must be 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

Compound	Molar Mass	Normal Boiling Point
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.

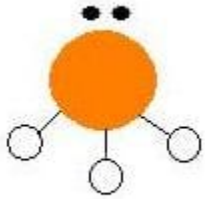
On Viscosity

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.

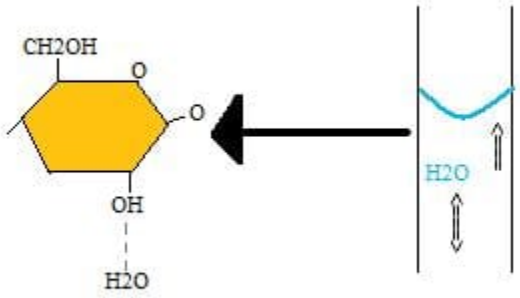


Hydrogen Bonding in Nature

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.
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4: SYMMETRY AND GROUP THEORY

4.1: Symmetry Elements and Operations

4.2: Point Groups

4.2.1: Groups of Low and High Symmetry

4.2.2: Other Groups

4.3: Properties and Representations of Groups

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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.

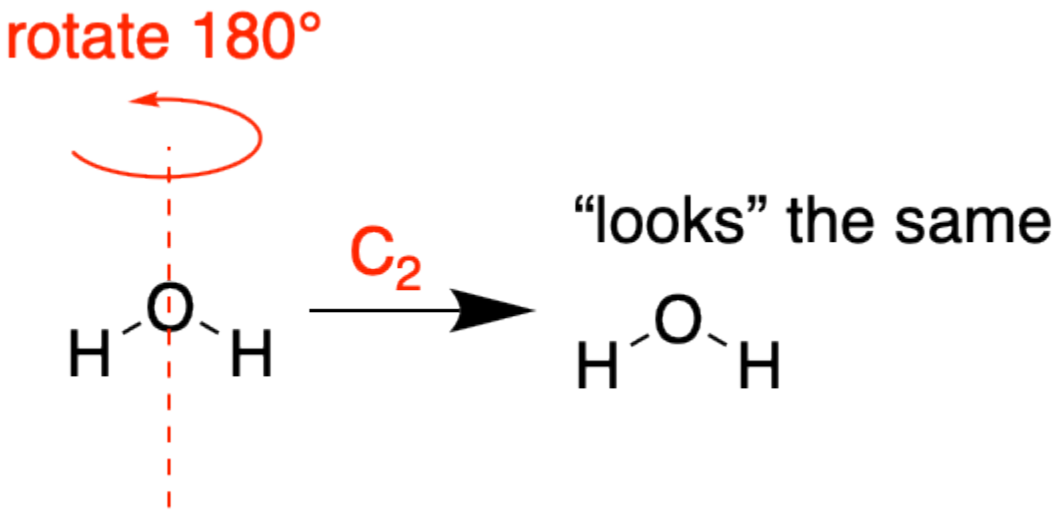


Figure 4.1.1: An example of a symmetry operation is a 180° rotation where the resulting position is indistinguishable from the original. A 180° rotation is called a C_2 operation; the axis of rotation is the symmetry element. (Kathryn Haas; CC-NC-BY-SA)

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 $(360/n)^o$	C_n
Symmetry plane	reflection in the plane	σ
Inversion center	inversion of a point at (x,y,z) to (-x,-y,-z)	*i*
Improper axis	rotation by $(360/n)^o$, followed by reflection in the plane perpendicular to the rotation axis	S_n

Symmetry Operations and Elements

Identity (E)

All molecules have the identity element. The identity operation is doing nothing to the molecule (it doesn't rotate, reflect, or invert...it just is).

Proper Rotation and Proper Axis (C_n)

A "proper" rotation is just a simple rotation operation about an axis. The symbol for any proper rotation or proper axis is $C_{(360/n)}$, where n is the degree of rotation. Thus, a 180° rotation is a C_2 rotation around a C_2 axis, and a 120° rotation is a C_3 rotation about a C_3 axis.

> **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.

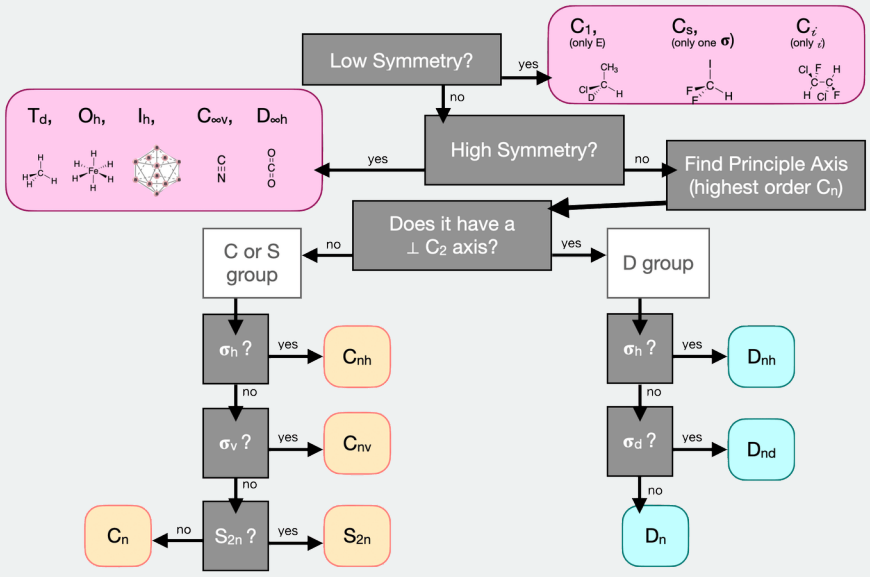


Figure 4.2.1: Decision tree for determining a molecule's point group (CC-BY-NC-SA; Kathryn Haas)

Example 4.2.1

Find the point group of benzene (C_6H_6).

Answer available at the end of this section.

See Also

Symmetry Gallery

Answers

Example 4.2.1

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.

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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

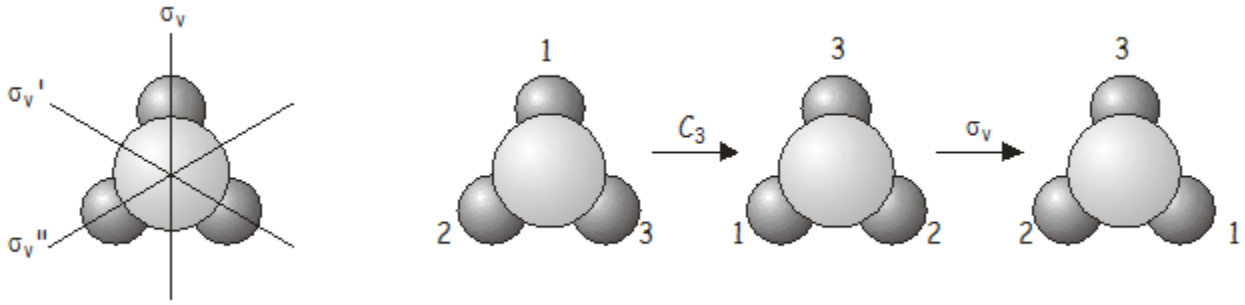
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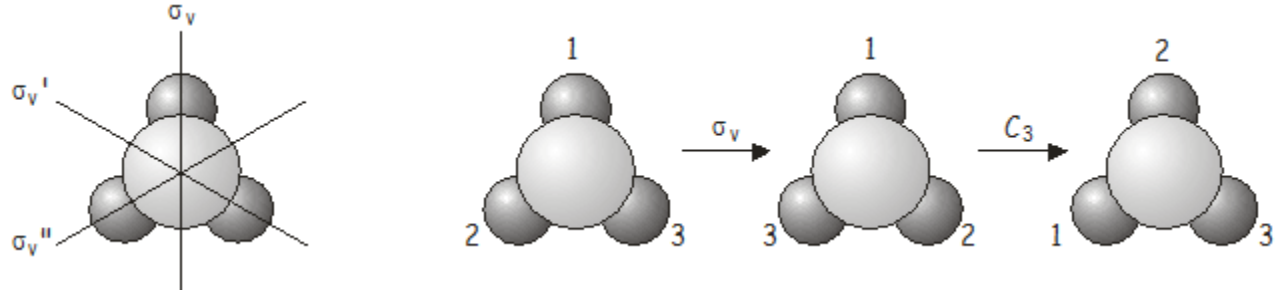
4.3: Properties and Representations of Groups

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}.

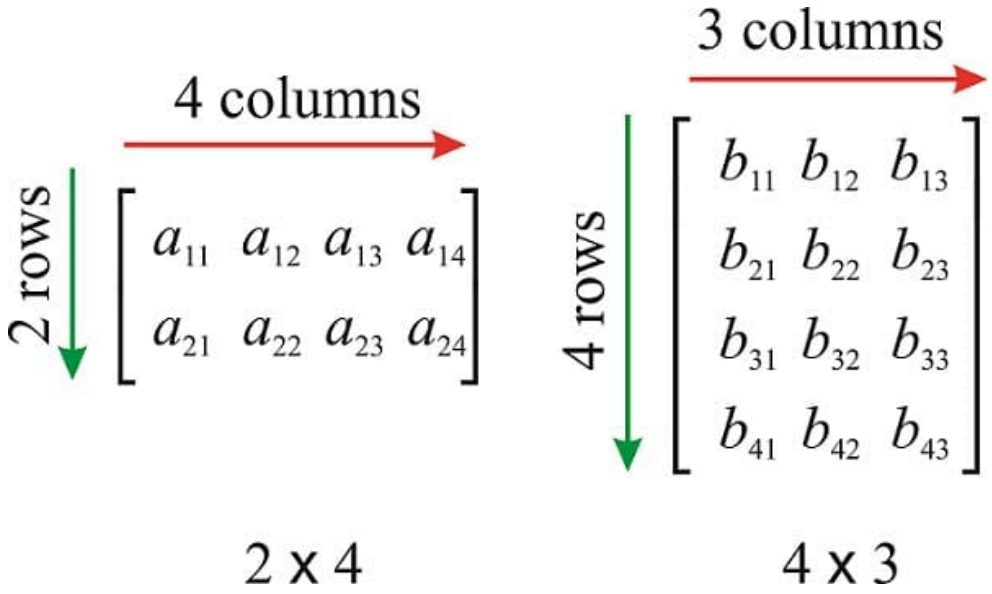


Figure 4.3.1.1: Matrices of different dimensions

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:

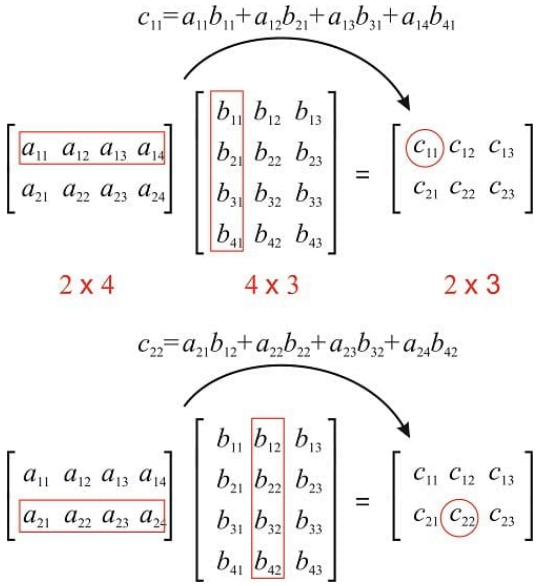


Figure 4.3.1.1: Matrix multiplication

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]).

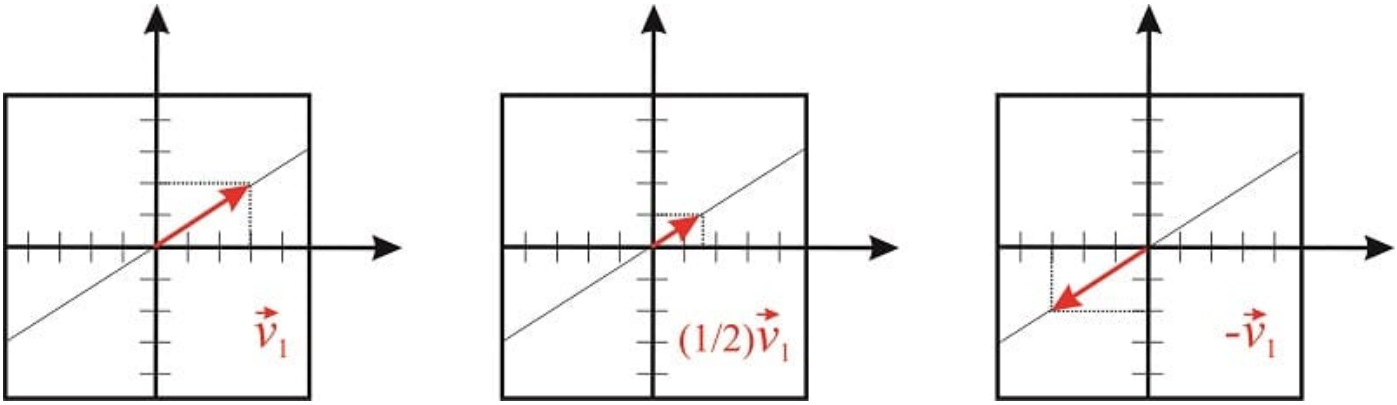


Figure 4.3.1.2: Multiplication of a vector by a scalar

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 $4.3.1.3$).

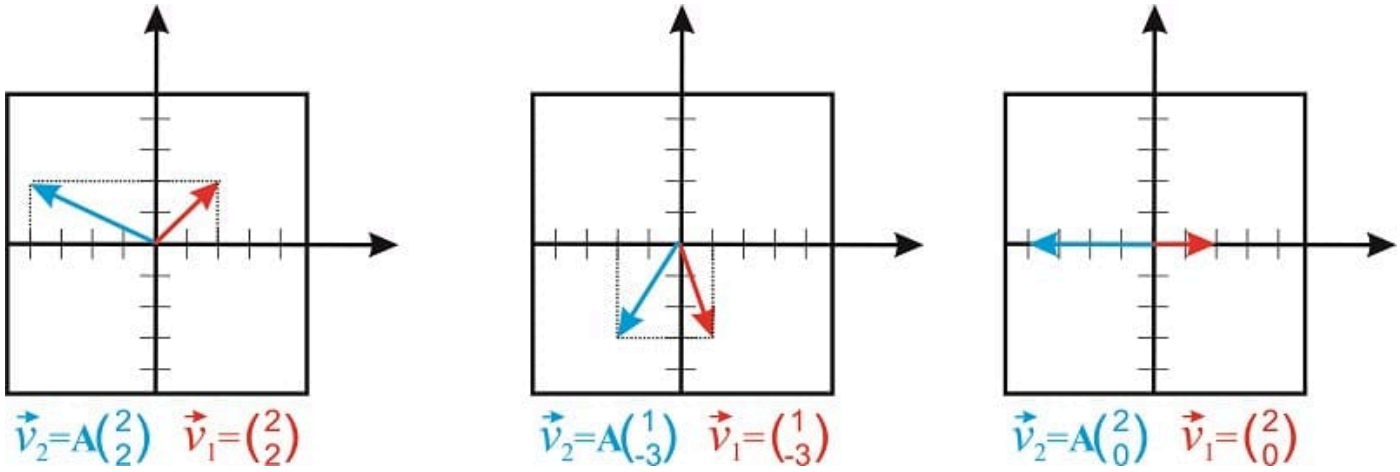


Figure $4.3.1.3$: Multiplication of a vector by a square matrix

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:

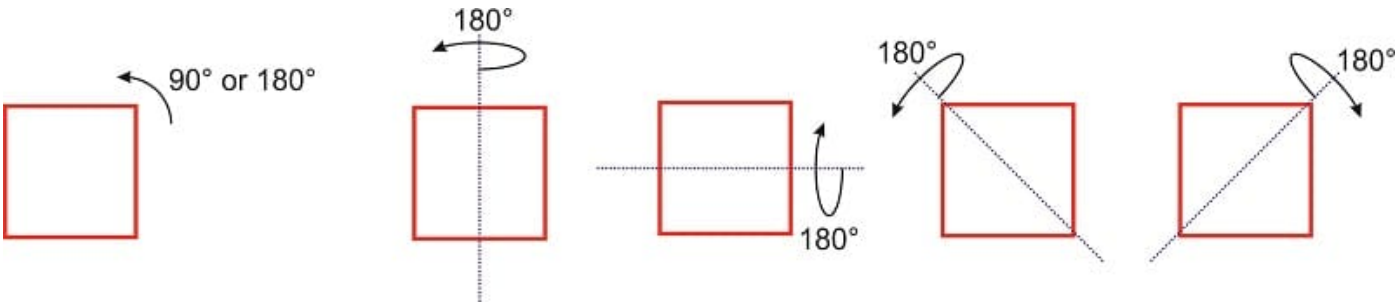


Figure $4.3.2.1$: Symmetry operations performed on a square

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.

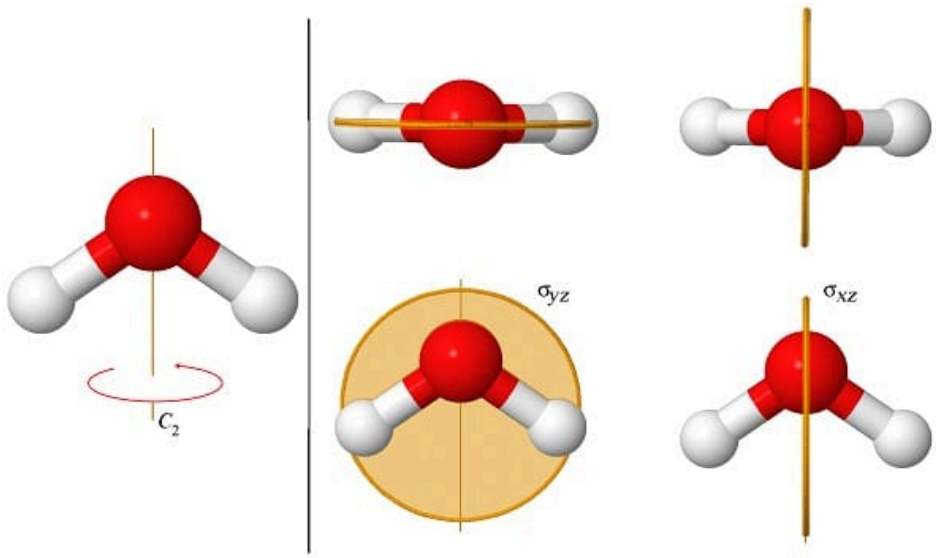


Figure 4.3.2.2: The symmetry elements of the molecule of water

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.

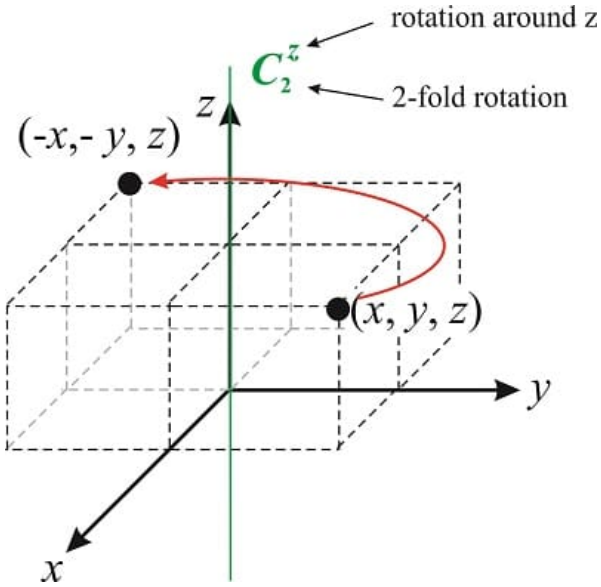


Figure 4.3.2.3: A 2-fold rotation around the z-axis

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 $\hat{\sigma}_{xz}$:

$$\sigma_{xz}(x, y, z) = (x, -y, z)$$

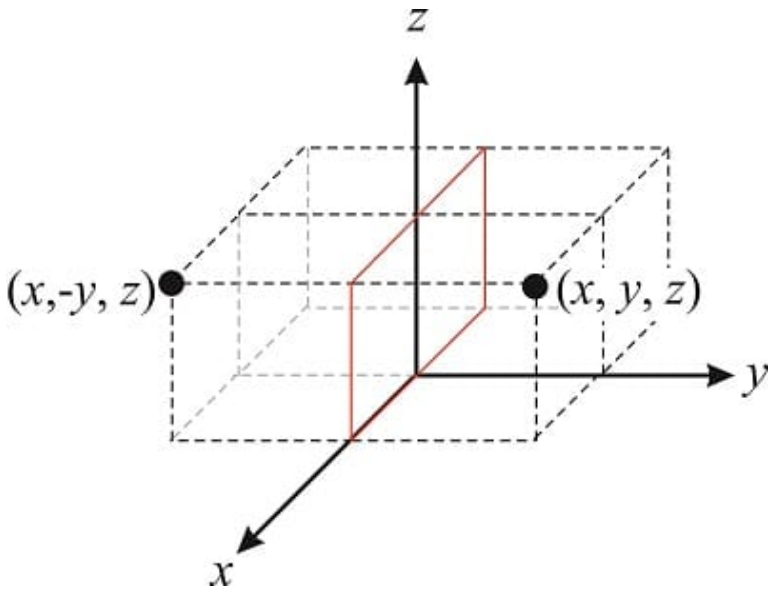


Figure 4.3.2.3: A reflection through the xz plane

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 available at the end of this section.

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 available at the end of this section.

Reducible and Irreducible Representations

Let us now go back and look in more detail at the transformation matrices of the C_{2v} point group that we derived above. If we look at the matrices carefully we see that they all take the same block diagonal form (a square matrix is said to be **block diagonal** if all the elements are zero except for a set of submatrices lying along the diagonal).

$$E = \begin{pmatrix} [1] & 0 & 0 \\ 0 & [1] & 0 \\ 0 & 0 & [1] \end{pmatrix}, C_2 = \begin{pmatrix} [-1] & 0 & 0 \\ 0 & [-1] & 0 \\ 0 & 0 & [1] \end{pmatrix}, \sigma'_{v(xz)} = \begin{pmatrix} [1] & 0 & 0 \\ 0 & [-1] & 0 \\ 0 & 0 & [1] \end{pmatrix}, \sigma_{v(yz)''} = \begin{pmatrix} [-1] & 0 & 0 \\ 0 & [1] & 0 \\ 0 & 0 & [1] \end{pmatrix}$$

All the non-zero elements become 1x1 matrices that each represent individual x, y, z coordinates. In other words, the element a_{11} represents x, a_{22} represents y, and a_{33} represents z. The matrix elements for x from each transformation matrix combine to form an irreducible representation of the C_{2v} point group. Likewise, the matrix elements for y combine to form a second irreducible representation, and the same is true for z elements. These irreducible representations are shown below:

C_{2v}	E	C_2	σ_v	σ_v'	Coordinate Used
	1	-1	1	-1	x
	1	-1	-1	1	y
	1	1	1	1	z
Γ	3	-1	1	1	

The irreducible representations add to form the reducible representation, Γ. This Γ, which is the set of 3x3 matrices, can be reduced to the set of 1x1 matrices of the irreducible representations. The irreducible representations cannot be reduced further,

hence their name.

Sources & Attribution

- Parts of this page was adapted from Matrices (click here) (Symmetry Operators), contributed by Marcia Levitus, Associate Professor (Biodesign Institute) at Arizona State University.
- Parts of this page were adapted from Reductions of Representations, contributed by

  Claire Vallance (University of Oxford)

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Answers

Exercise 4.3.2.1

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 $\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$.

Exercise 4.3.2.1

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

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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:

$$\begin{aligned} x' &= x\cos\theta + y\sin\theta \\ y' &= -x\sin\theta + y\cos\theta \end{aligned}$$

For a C_3 rotation counterclockwise through 120° (or $\frac{2\pi}{3}$):

$$\begin{aligned} x' &= x\cos(2\pi/3) + y\sin(2\pi/3) &&= -\tfrac{1}{2}x - \tfrac{\sqrt{3}}{2}y \\ y' &= -x\sin(2\pi/3) + y\cos(2\pi/3) &&= \tfrac{\sqrt{3}}{2}x - \tfrac{1}{2}y \end{aligned}$$

The transformation matrices for symmetry operations of C_{3v} are as follows:

$$E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \; C_3 = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \; \sigma'_{v(xz)} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

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):

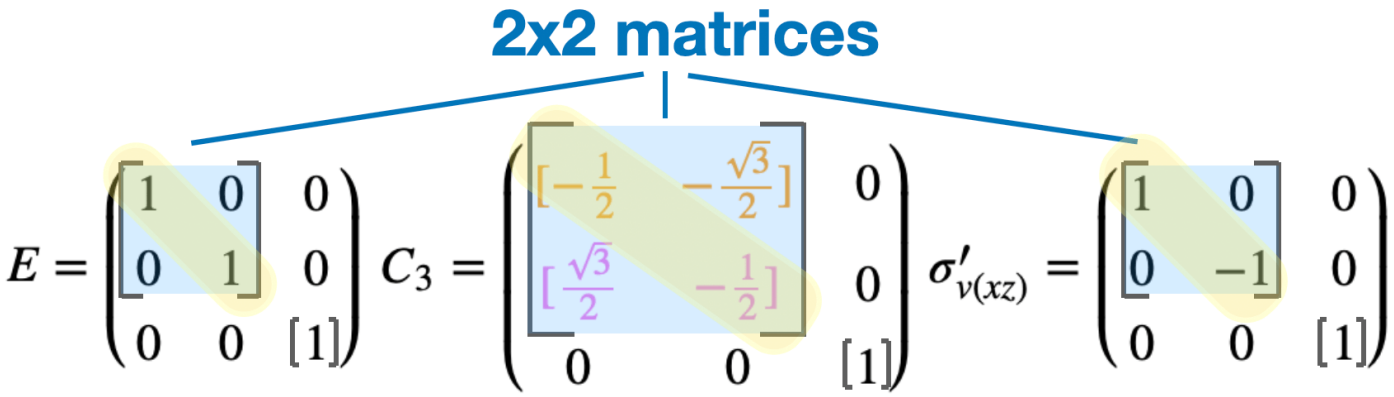


Figure 4.3.3.1: The C_3 transformation matrix contains off-diagonal entries, and therefore it cannot be block diagonalized as 1x1 matrices. However, the first two lines can be diagonalized as a 2x2 and the last line as a 1x1 matrix. (CC-BY-NC-SA; Kathryn Haas)

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.

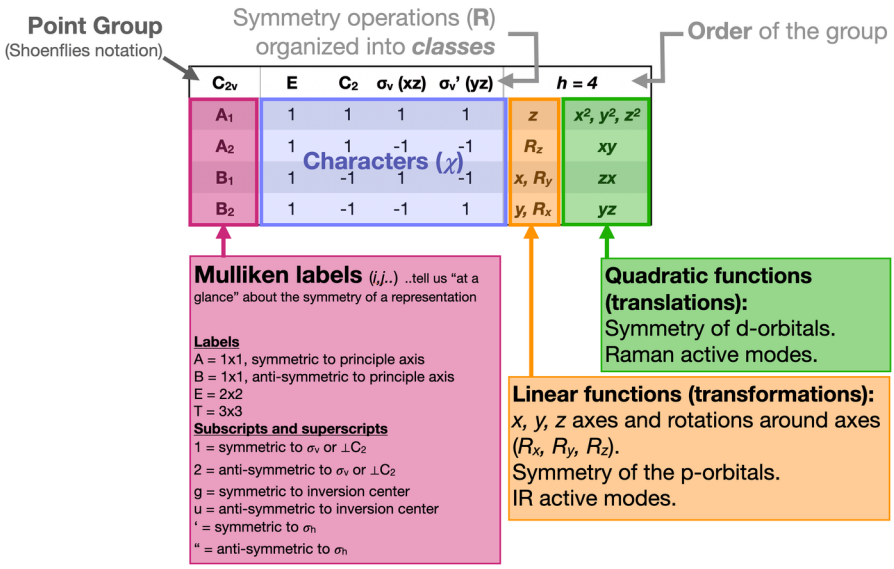


Figure 4.3.3.2: Visual summary of the sections of a character table and their meaning. (CC-BY-NC-SA; Kathryn Haas)

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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.

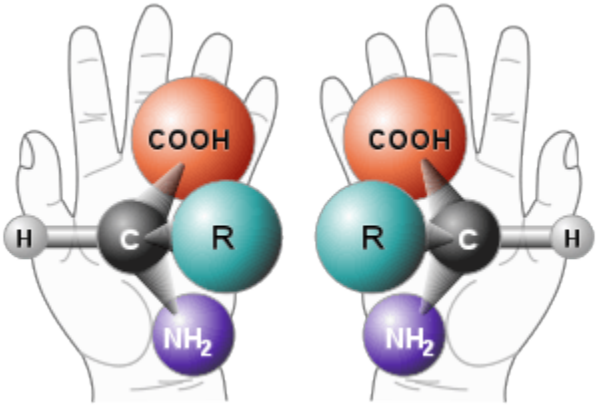


Figure 4.4.1.1: Two enantiomers of an amino acid (with side chain R).

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.

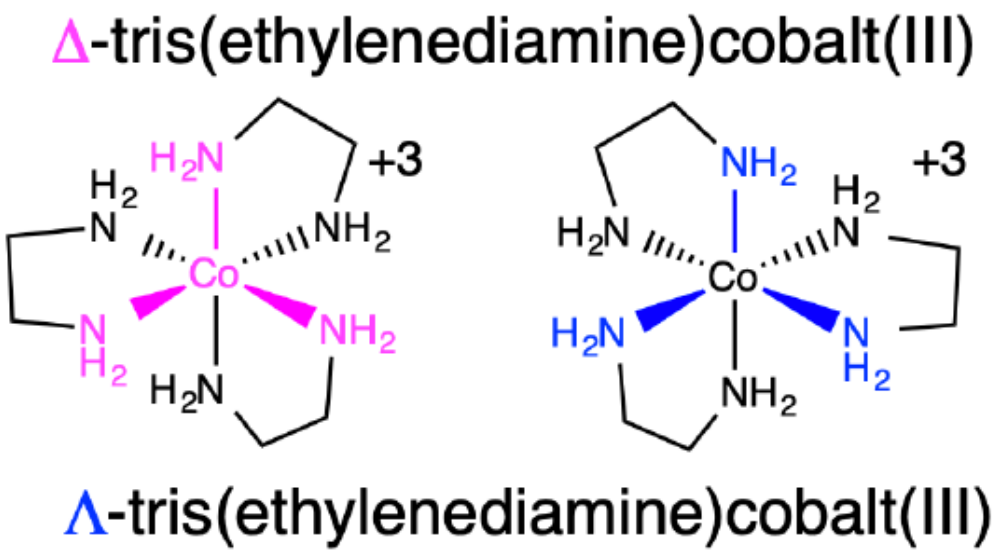


Figure 4.4.1.2: Two chiral enantiomers of tris(ethylenediamine)coalt(III).

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.

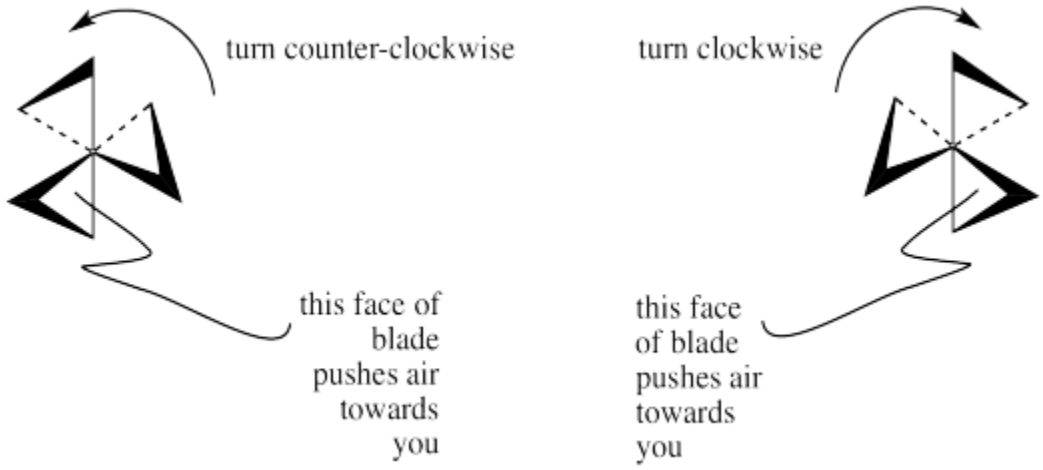


Figure 4.4.1.3: Another way of thinking about the chirality of the two chiral enantiomers of tris(ethylenediamine)coalt(III) shown in Figure 4.4.1.2. This figure was taken from Structure and Reactivity in Organic, Biological, and Inorganic Chemistry.

Exercise 4.4.1.1

Which point groups are possible for chiral molecules?

Answer available at the end of this section.

Answers

Exercise 4.4.1.1

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 $\mathrm{H_2O}$?

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 $\mathrm{H_2O}$? (click to see answer)

$\mathrm{H_2O}$ has the following operations: E, C_2, σ_v, σ_v'. The point group is C_{2v}.

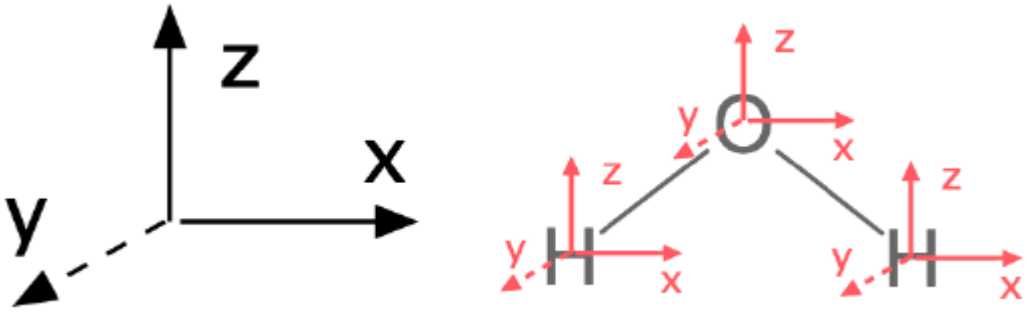


Figure 4.4.2.1: The first step to finding normal modes is to assign a consistent axis system to the entire molecule and to each atom. (CC-BY-SA; Kathryn Haas)

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 ($\theta = 0^\circ$) are assigned a value of $\cos(0^\circ) = 1$, while those that are moved into the negative of themselves (rotated or reflected to $\theta = 180^\circ$) are assigned $\cos(180^\circ) = -1$. 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 $\cos(0^\circ) = 1$, 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 ($\cos(0^\circ) = 1$), while the x and y axes are inverted ($\cos(180^\circ)$). 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:

$$\#\text{ of } i = \frac{1}{h}\sum(\#\text{ of operations in class}) \times (\chi_\Gamma) \times (\chi_i) \tag{4.4.2.2}$$

In other words, the number of irreducible representations of type i is equal to the sum of the number of operations in the class $\times$ the character of the Γ_{modes} $\times$ the character of i, and that sum is divided by the order of the group (h).

Using equation 4.4.2.2, we find that for all normal modes of H_2O:

$$\Gamma_{modes} = 3A_1 + 1A_2 + 3B_1 + 2B_2. \tag{4.4.2.3}$$

Notice there are 9 irreducible representations in Equation 4.4.2.3. 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 4.4.2.3.

Derive the nine irreducible representations of Γ_{modes} for H_2O, expression 4.4.2.3.

Hint available at the end of this section.

Answer available at the end of this section.

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 4.4.2.3, and therefore the vibrational degrees of freedom can be found by:

$$H_2O \text{ vibrations} = (3A_1 + 1A_2 + 3B_1 + 2B_2) - \text{Rotations} - \text{Translations} \tag{4.4.2.4}$$

But which of the irreducible representations are ones that represent rotations and translations? The symmetry of rotational and translational degree modes can be found by inspecting the right-hand columns of any character table. Rotational modes correspond to irreducible representations that include R_x, R_y, and R_z in the table, while each of the three translational modes has the same symmetry as the x, y and z axes. For a non-linear molecule, subtract three rotational irreducible representations and three translational irreducible representations from the total Γ_{modes}.

In the specific case of water, we refer to the C_{2v} character table:

C_{2v}	E	C_2	σ_v	σ_v'	$h = 4$	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

In C_{2v}, translations correspond to B_1, B_2, and A_1 (respectively for x, 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 three 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 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.

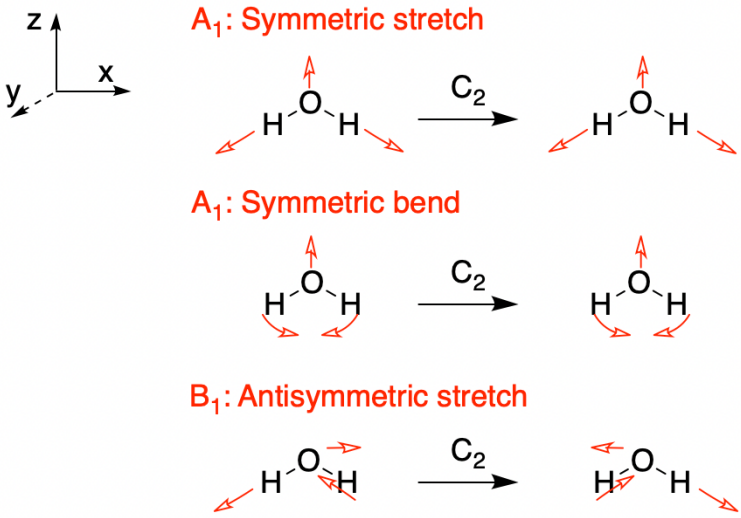


Figure 4.4.2.2: Illustration of the vibrational motions of water. The antisymmetric stretch has B_1 symmetry, while the symmetric stretch and symmetric bend both have A_1 symmetry. (Click here to see animation) (CC-BY-NC-SA; Kathryn Haas)

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 available at the end of this section.

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.

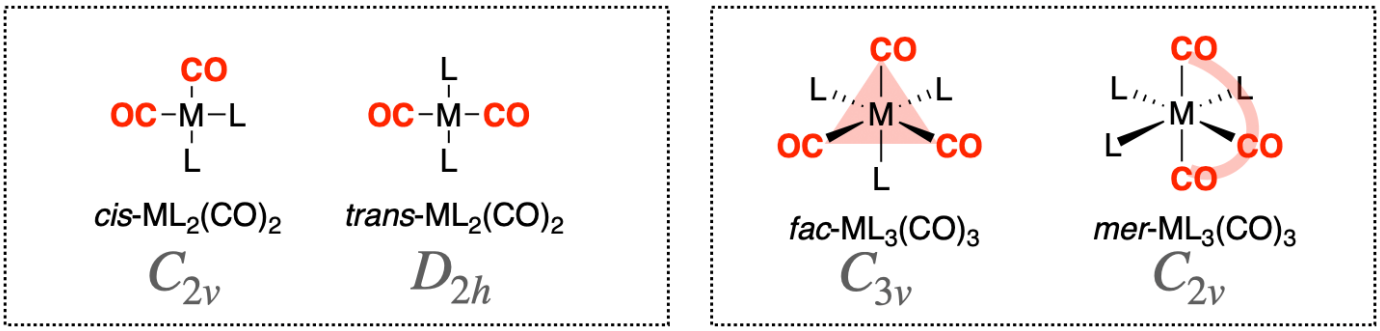


Figure 4.4.2.3: Cis- and *trans*- isomers of square planar metal dicarbonyl complexes ($ML_2(CO)_2$) are shown in the left box. *Mer*- and *fac*- isomers of octahedral metal tricarbonyl complexes ($ML_3(CO)_3$) are shown in the right box. The point group for each of the general structures is also shown. (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}.



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 $\Gamma_{trans-CO}$.



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:



(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:



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 available at the end of this section.

Answers

Exercise 4.4.2.1: Derive the irreducible representation in equation 4.4.2.3.

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 4.4.2.2.

C_{2v}	$1E$	$1C_2$	$1\sigma_v$	$1\sigma_v'$	$h=4$	
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz

In the C_{2v} point group, each class has only one operation, so the number of operations in each class (from equation 4.4.2.2) is 1 for each class. This has been explicitly added to the character table above for emphasis.

Exercise 4.4.2.1: Derive the irreducible representation in equation 4.4.2.3.

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 $B_2 = \frac{1}{4}[(1\times 9\times 1)+((-1)\times(-1)\times 1)+((-1)\times 3\times 1)+(1\times 1\times 1)] = 2B_2$

Exercise 4.4.2.2

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

(4.4.2.6)

.

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.

Exercise 4.4.2.3

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:



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:



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.

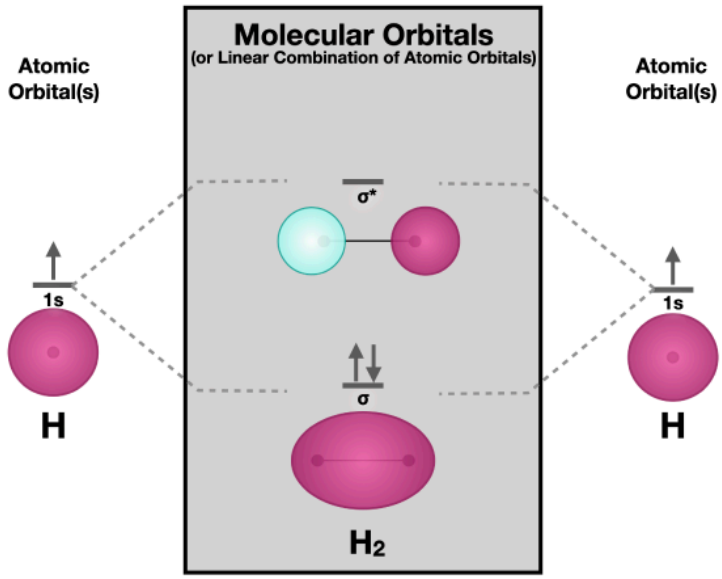
5. Why is important to find symmetry in molecules?

Symmetry tells us about bonding for that molecule.

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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).

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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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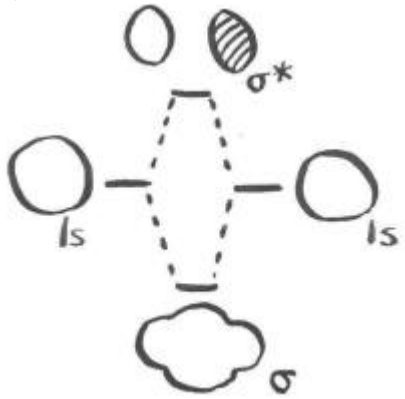
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5.1.1: Molecular Orbitals from s Orbitals

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

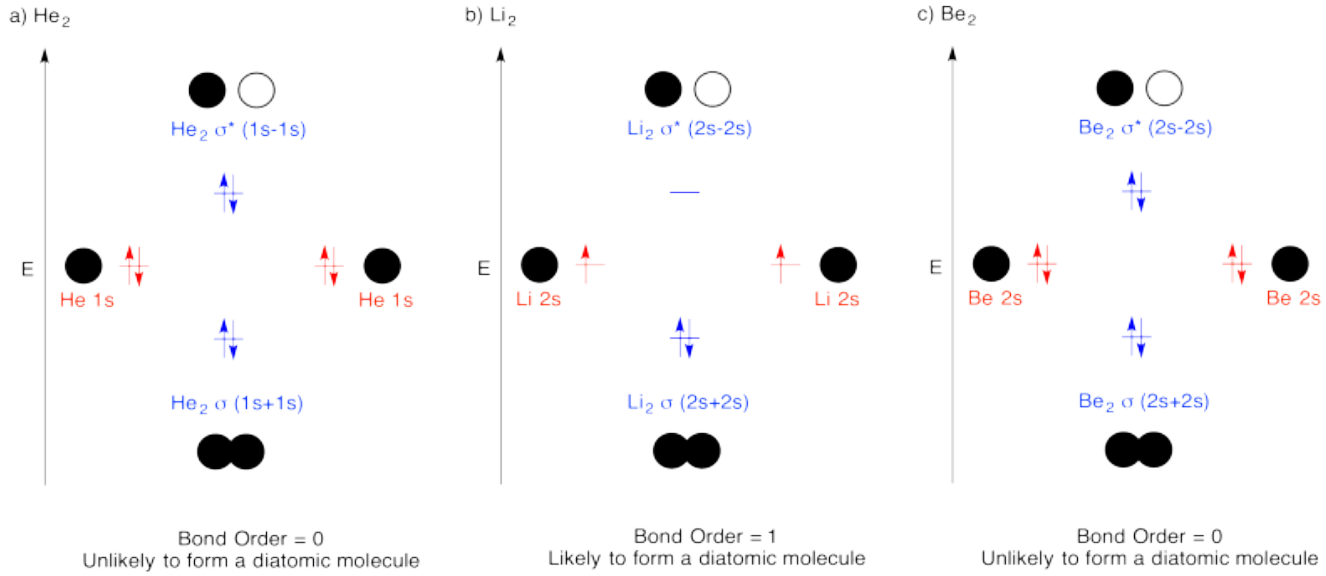
Construct molecular orbital diagrams for the following diatomic species and discuss the likelihood of bond formation in each case.

a. He_2.
b. Li_2.
c. Be_2.

Answer available at the end of this section.

Answers

Exercise 5.1.1.1



Bond Order = 0
Unlikely to form a diatomic molecule

Bond Order = 1
Likely to form a diatomic molecule

Bond Order = 0
Unlikely to form a diatomic molecule

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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.

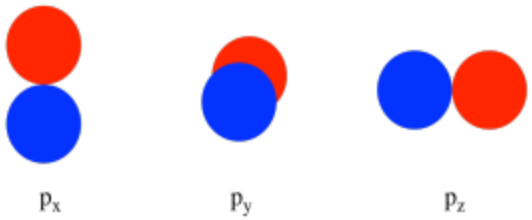
Orbitals interact most easily with other orbitals that have the same element of symmetry. For now, we can simplify and say that orbitals on one atom only interact with the same type of orbitals on the other atom.

- 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.

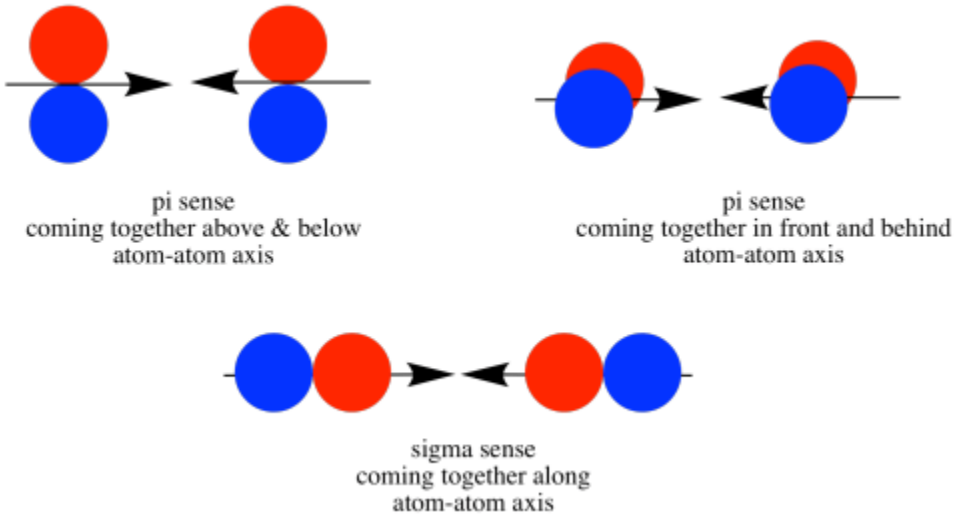
Another complication here is that the s and p orbitals do not start out at the same energy level. When the orbitals mix, one combination goes up in energy and one goes down. Does the s antibonding combination go higher in energy than the combinations from p orbitals? Do the p bonding combinations go 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.

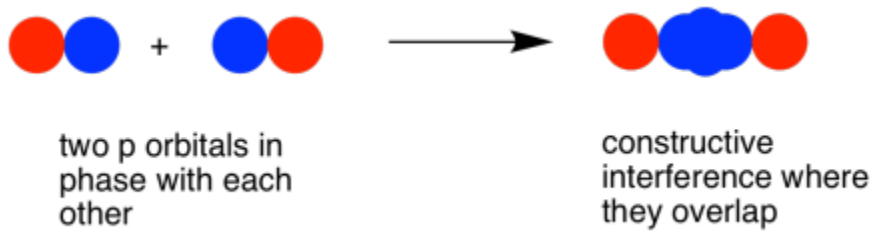


We first need to define one axis as lying along the N-N bond. It does not really matter which one. We arbitrarily say the N-N bond lies along the z axis. The p_z orbitals have a different spatial relationship to each other compared to the p_y and p_x. The p_z orbitals lie along the bond axis, whereas the p_y and p_x are orthogonal to it.

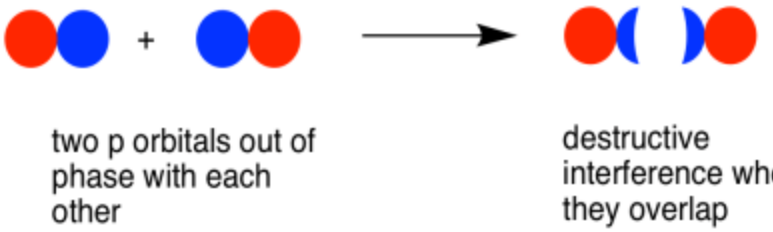


As the nitrogen atoms are brought together, one lobe on one p_z orbital overlaps strongly with one lobe on the other p_z orbital. The other lobes point away from each other and do not interact in any obvious way.

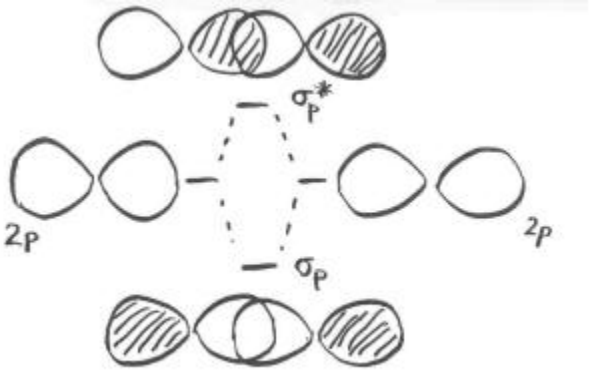
As with the s orbital, the p_z orbitals can be in-phase or out-of-phase. The in-phase combination results in constructive interference. (Here, "in-phase" means the lobes that overlap are in-phase; for that to happen the two p orbitals are actually completely out-of-phase with each other mathematically, 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.

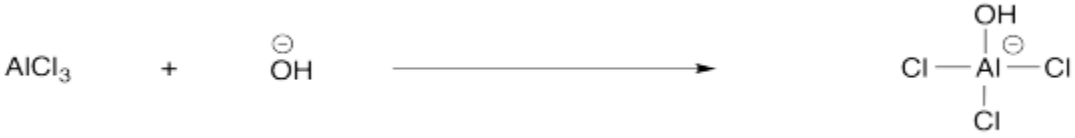
Exercise 5.1.2.2

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 available at the end of this section.

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.

- Draw the orbital from the base (hydroxide) that is likely to donate its electrons.
- Draw the orbital from the acid (aluminum chloride) that is likely to accept electrons.
- Complete the MO mixing diagram of these two orbitals:

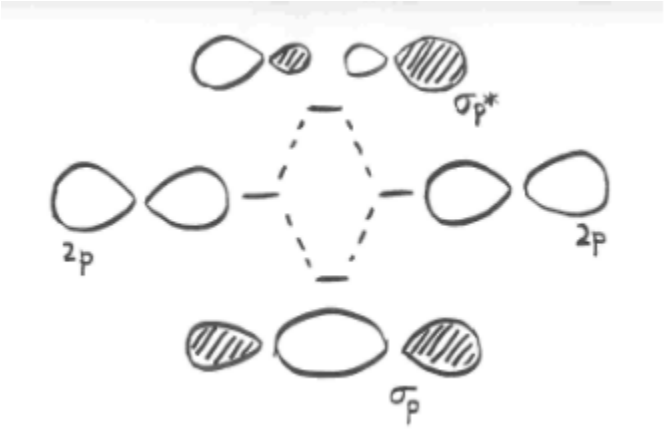
- Label the electron donating orbital
- Label the electron accepting orbital
- Populate the MO mixing diagram with electrons

o Draw a cartoon showing each reactant and product MO that contributes to the bonding interaction.

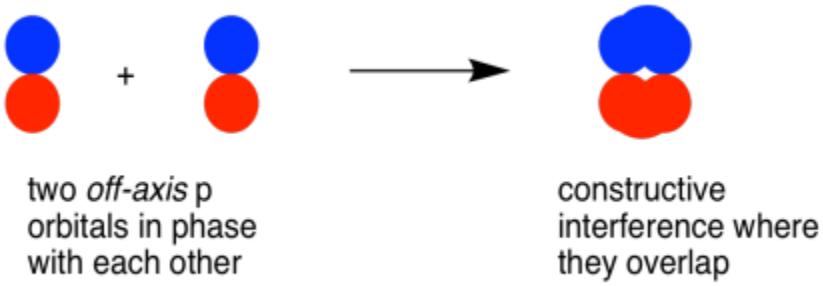
Answer available at the end of this section.

Pi-bonding with p-orbitals

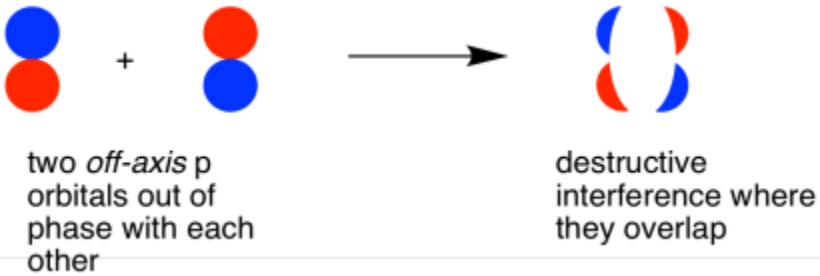
Earlier, we saw that p orbitals that lie along the same axis can interact to form bonds.



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.

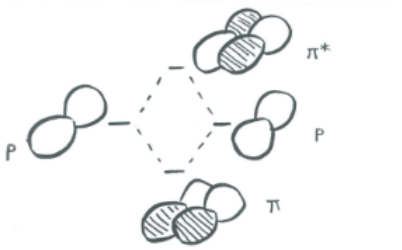


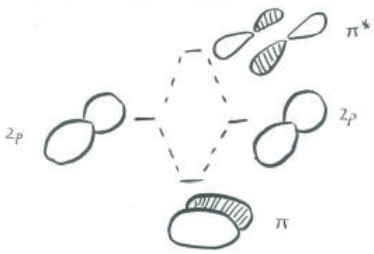
They could also make an out-of-phase combination, as shown below.



- 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.

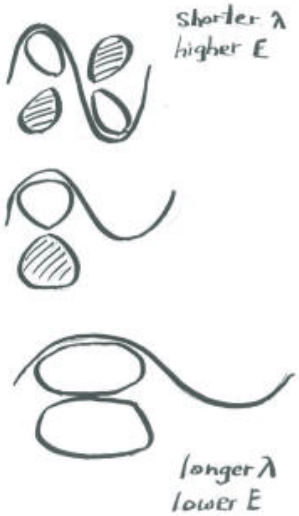
The illustration above is for one set of p orbitals that are orthogonal to the bond axis. The second picture shows the result of the constructive (or destructive) interference. A similar picture could be shown for the other set of p orbitals.



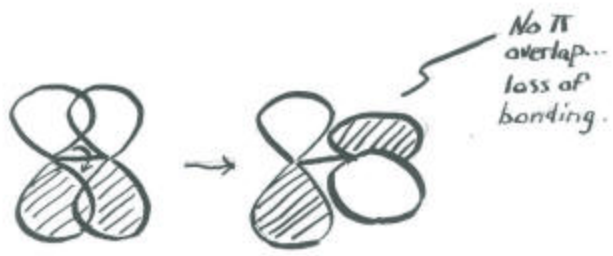


In a main group diatomic species like dinitrogen, one p orbital lying along the bond axis can engage in s bonding. The two p orbitals orthogonal to the bond axis can engage in p bonding. There will be both bonding and antibonding combinations.

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 available at the end of this section.

Exercise 5.1.2.5

The combinations of _____ atomic orbitals leads to π orbitals.

Draw pictures.

Answer available at the end of this section.

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 available at the end of this section.

Exercise 5.1.2.7

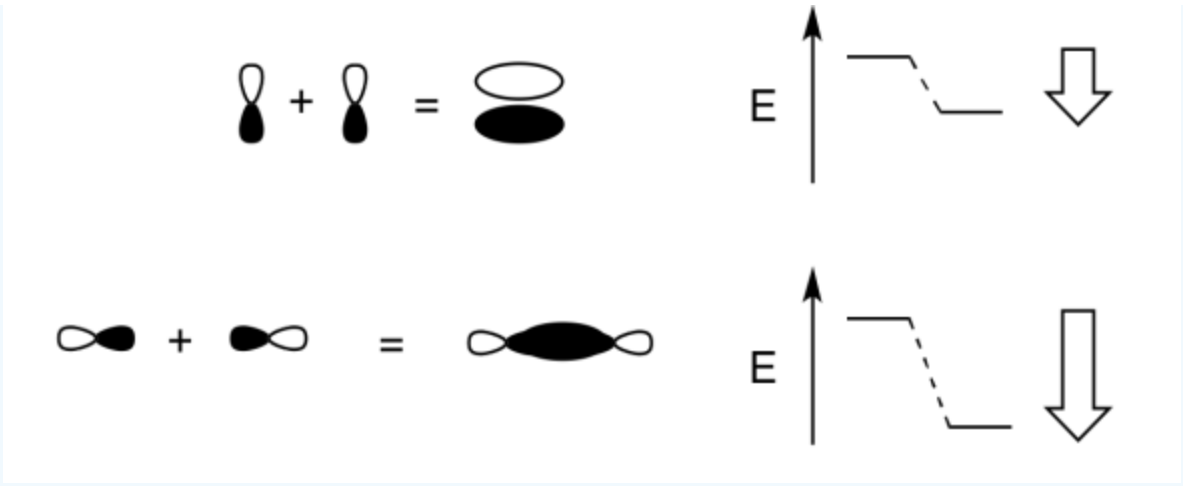
Why would a *core* 1s orbital not interact with a *valence* 2s orbital?

Hint: Why is a Li_2O bond stronger than a K_2O bond?

Answer available at the end of this section.

Exercise 5.1.2.8

Add a few words to explain the ideas conveyed in these drawings.



Answer available at the end of this section.

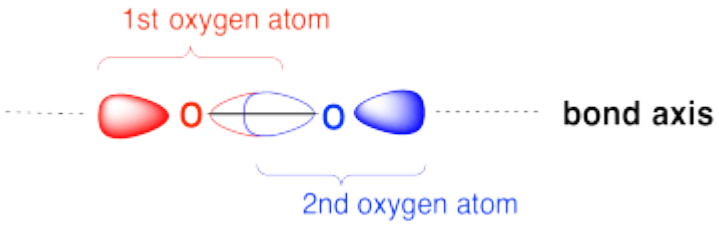
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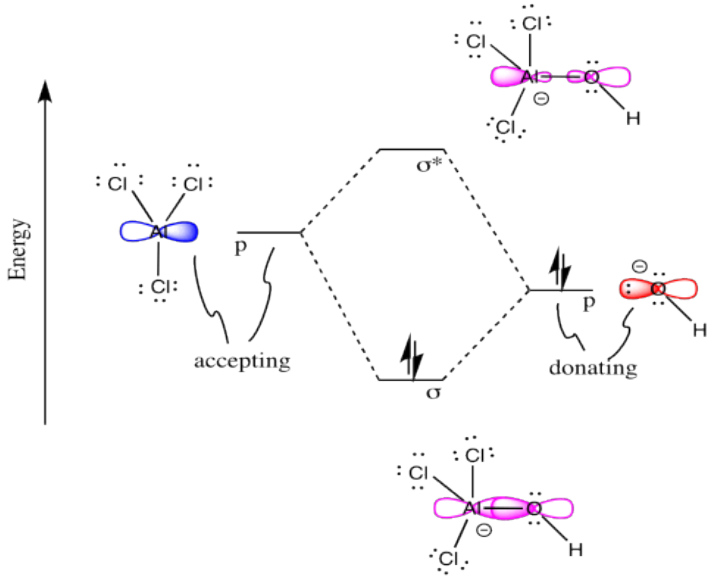
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Answers

Exercise 5.1.2.2

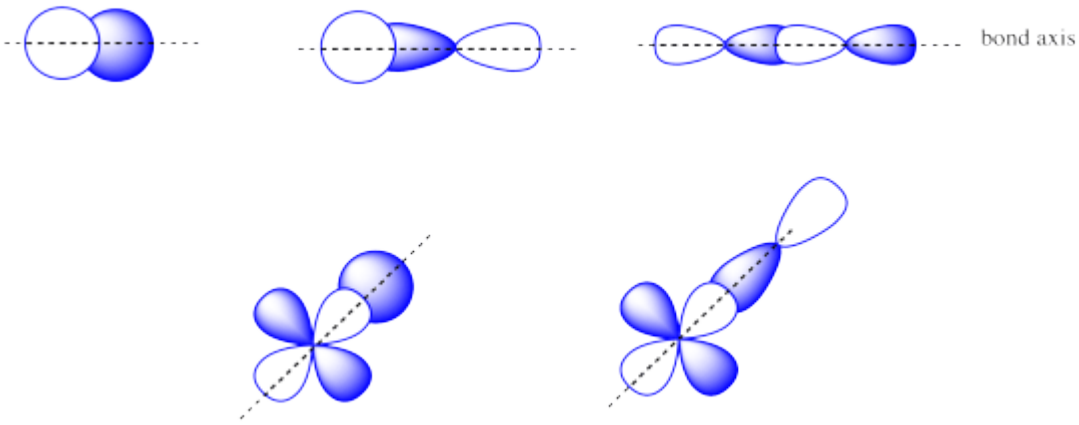


Exercise 5.1.2.3



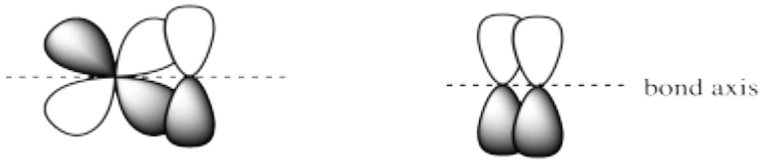
Exercise 5.1.2.4

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 side by side p + p or p + d atomic orbitals leads to π orbitals.



Exercise 5.1.2.6

e) σ*

Exercise 5.1.2.7

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

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.

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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.

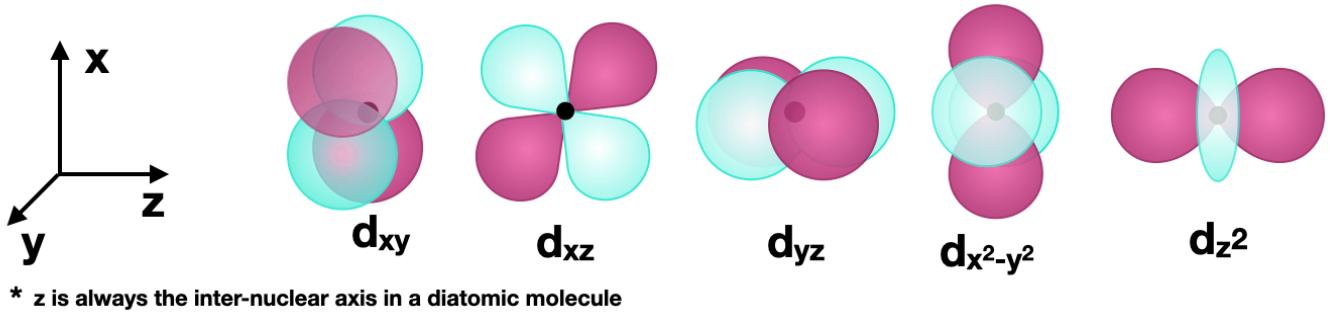


Figure 5.1.3.1: The five $3d$ orbitals are shown. The orientation of the axes is consistent and the z axis is horizontal for convenience in drawing bonding along the z axis (see examples below). (CC-BY-SA; Kathryn Haas)

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.

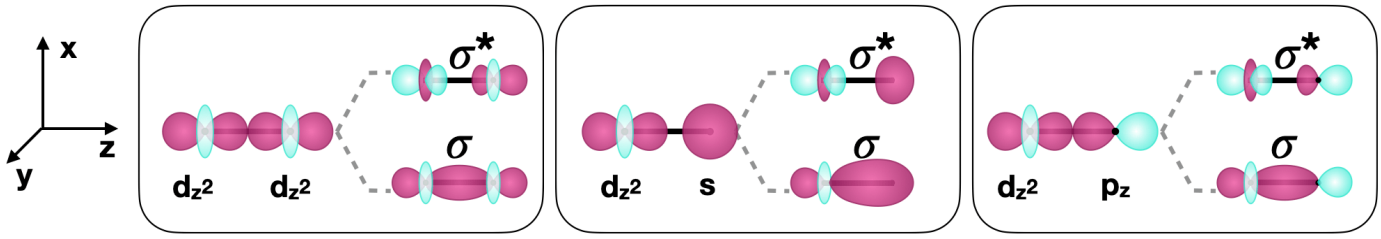


Figure 5.1.3.2: Selected examples of σ bonds involving d orbitals along the z internuclear axis (shown as a bold horizontal line) between two atoms. (CC-BY-SA; Kathryn Haas)

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.

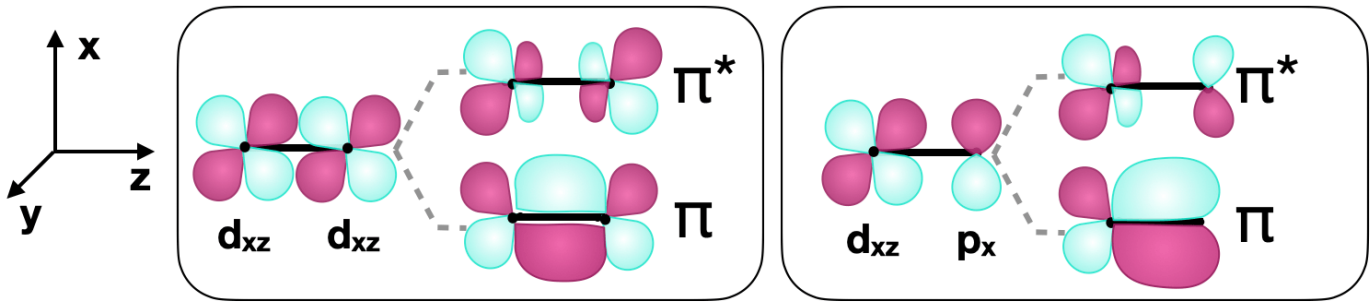


Figure 5.1.3.3: Selected examples of π bonds involving d orbitals along the z internuclear axis (shown as a bold horizontal line) between two atoms. (CC-BY-SA; Kathryn Haas)

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).

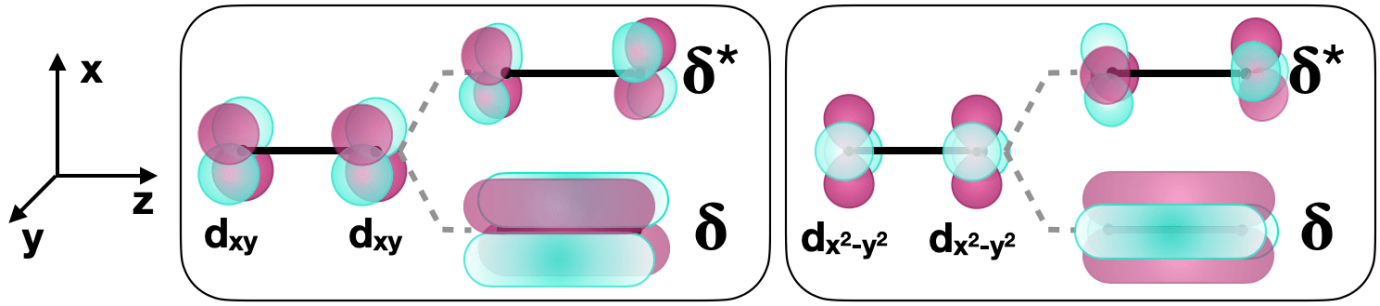


Figure 5.1.3.4: Selected examples of δ bonds involving d orbitals along the z internuclear axis (shown in bold horizontal line) between two atoms. (CC-BY-SA; Kathryn Haas)

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.

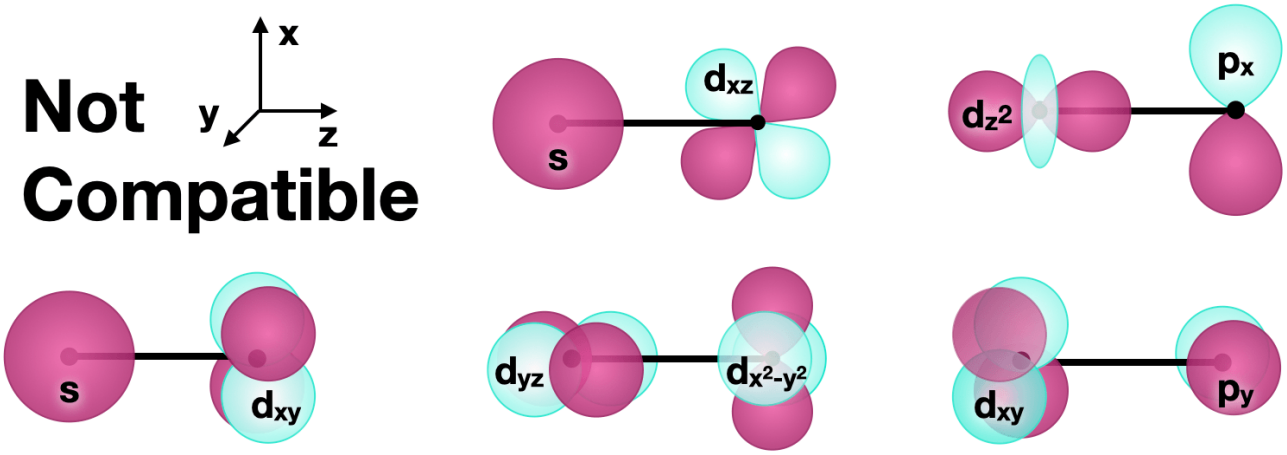


Figure 5.1.3.5: Several incompatible pairs of orbitals. (CC-BY-SA; Kathryn Haas)

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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).

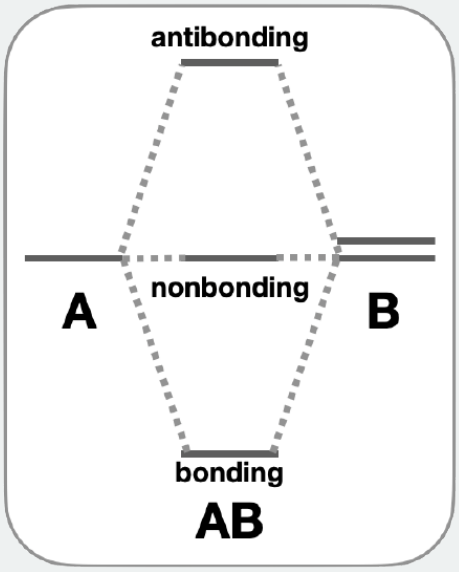


Figure 5.1.4.1. This figure illustrates the most common case for three atomic orbitals that combine to form three molecular orbitals; formation of one low-energy bonding, one high-energy antibonding, and one intermediate energy non-bonding molecular orbital. (CC-BY-NC-SA, Kathryn Haas)

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.

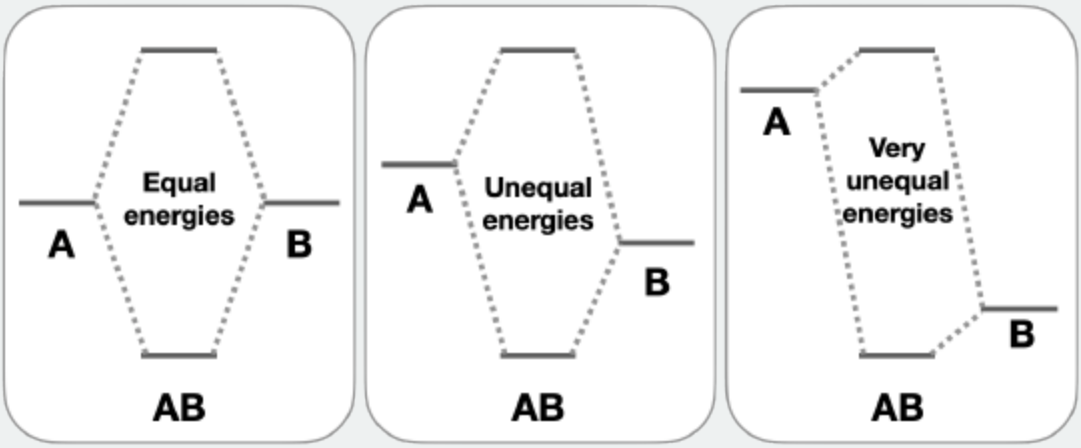


Figure 5.1.4.2. This figure illustrates how relative energies of atomic orbitals result in molecular orbitals that are more or less favorable. The greater the energy difference between atomic orbitals and the bonding molecular orbital, the more eneretically favorable it is for bonding to occur. (CC-BY-NC-SA, Kathryn Haas)

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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!

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

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.

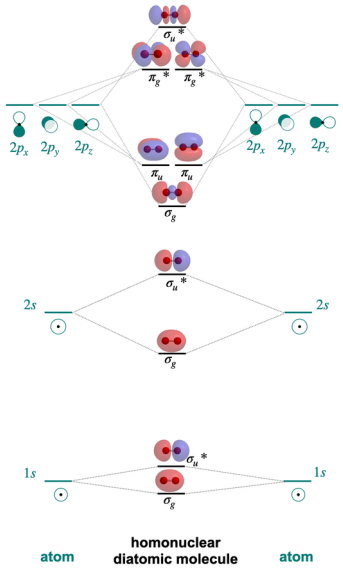


Figure 5.2.1.1: A generic molecular orbital diagram for a homonuclear diatomic molecule of second-row elements assuming no orbital mixing (interactions are formed by orbitals of the same energy from each atom). (CC-BY-NC-SA, Kathryn Haas)

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!

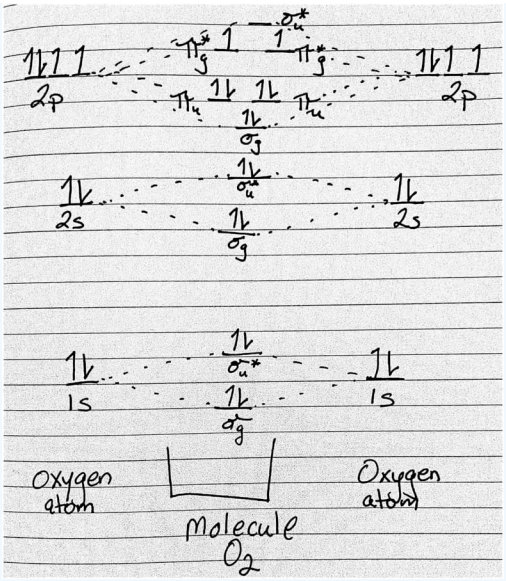


Figure 5.2.1.2: Hand-drawn molecular orbital diagram for dioxygen. (CC-BY-SA; Kathryn Haas)

Exercise 5.2.1.1

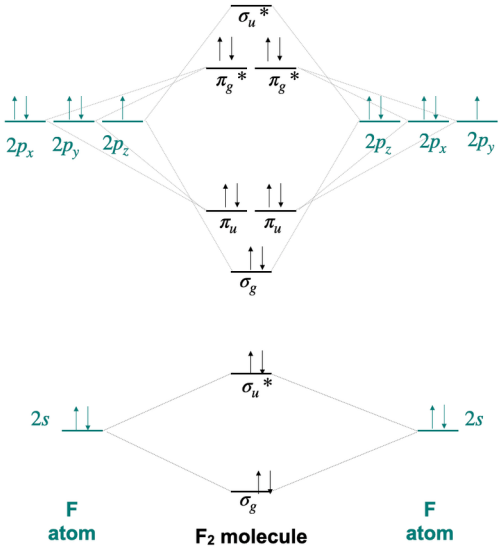
Draw the molecular orbital diagram for F_2; be sure to label your orbitals with the appropriate symmetry and count your orbitals to make sure that the total number of atomic orbitals and molecular orbitals is the same. As a shortcut, include only the valence orbitals and electrons. What is the bond order? Is the molecule diamagnetic or paramagnetic?

Answer available at the end of this section.

Answers

Exercise 5.2.1.1

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.

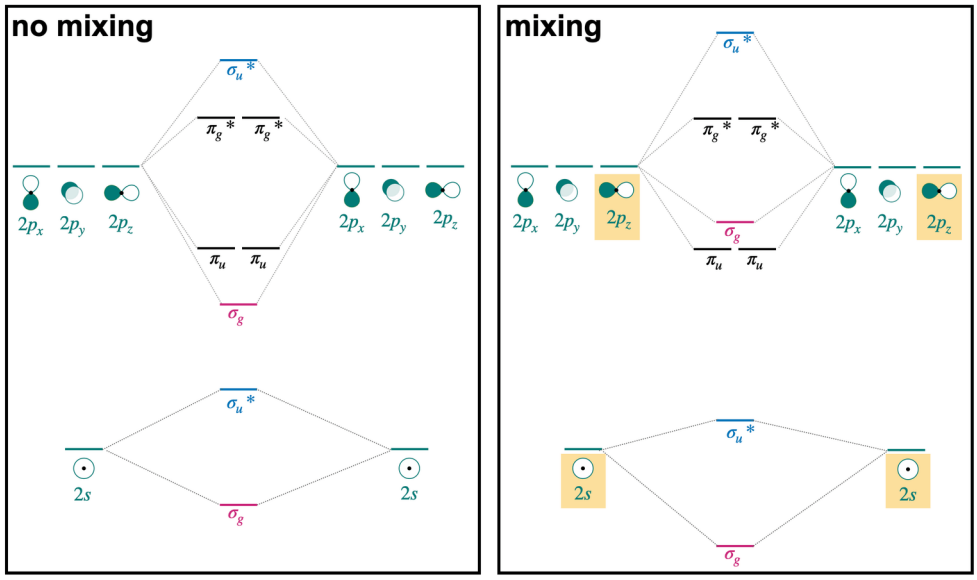


Figure $5.2.2.1$: Mixing of orbitals with like symmetry affects the energies of molecular orbitals. The simplified case where no mixing occurs is shown on the left. The effects of mixing are shown on the right. The σ_g orbitals of like symmetry are highlighted in fuschia and the σ_u^* orbitals of like 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

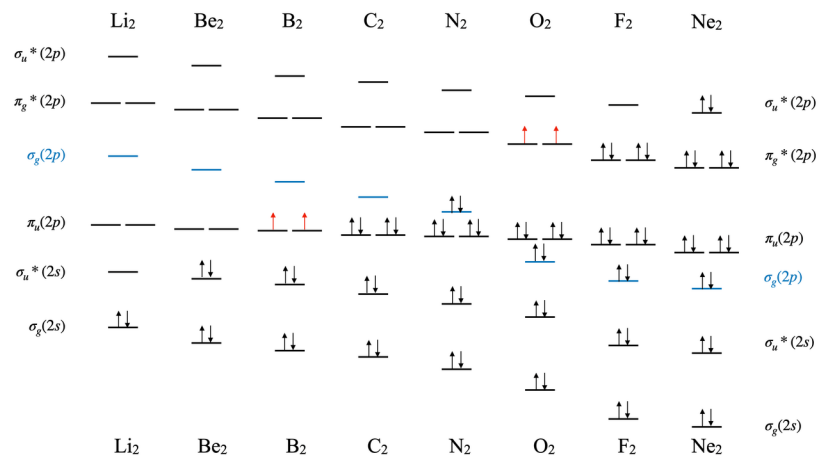
Draw the complete molecular orbital diagrams for H_2 and for He_2. Include sketches of the atomic and molecular orbitals.

Answer available at the end of this section.

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 available at the end of this section.

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 available at the end of this section.

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 (N_2). The shortest bond distance is at N_2 due to its high bond order of 3. From N_2 to F_2 the bond distance increases despite the fact that atomic radius decreases.

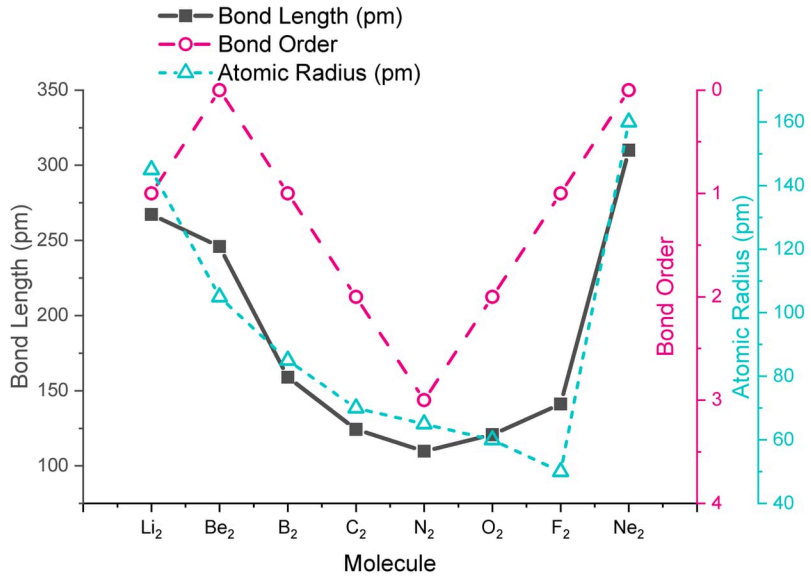


Figure 5.2.3.2: Overlayed plots of bond length (black squares), bond order (pink circles), and atomic radius (teal triangles) versus atomic number for second period homonuclear diatomic molecules. (CC-BY-NC-SA; Kathryn Haas)

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.

Answers

Exercise 5.2.3.1

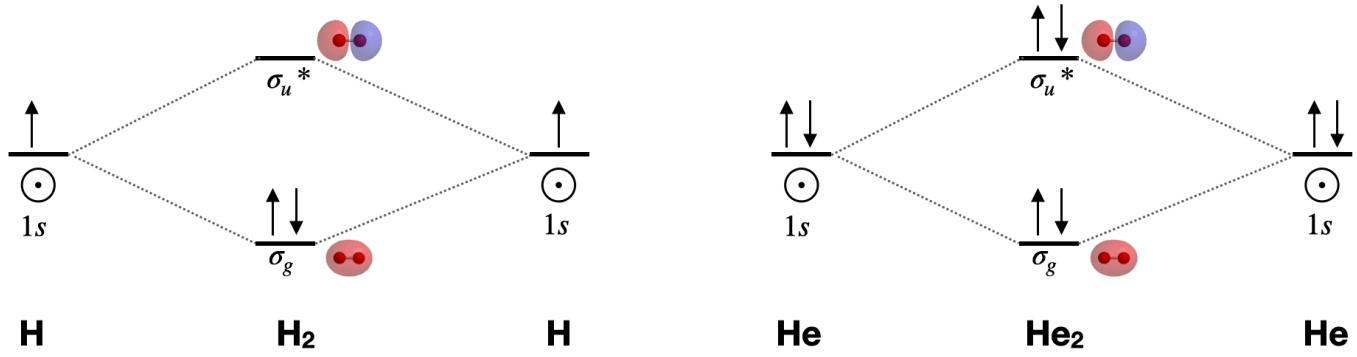


Figure for Exercise 5.2.3.1: Molecular orbital diagrams for dihydrogen and dihelium. Molecular orbital surfaces calculated using Spartan software. (CC-BY-NC-SA; Kathryn Haas)

A complete molecular orbital diagram includes all atomic orbitals and molecular orbitals, their symmetry labels, and electron filling.

Exercise 5.2.3.2

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.

Bond order $= \frac{1}{2}\left[\left(\begin{array}{c}\text{8 electrons in}\\ \text{valence bonding orbitals}\end{array}\right) - \left(\begin{array}{c}\text{4 electrons in}\\ \text{valence antibonding orbitals}\end{array}\right)\right]$

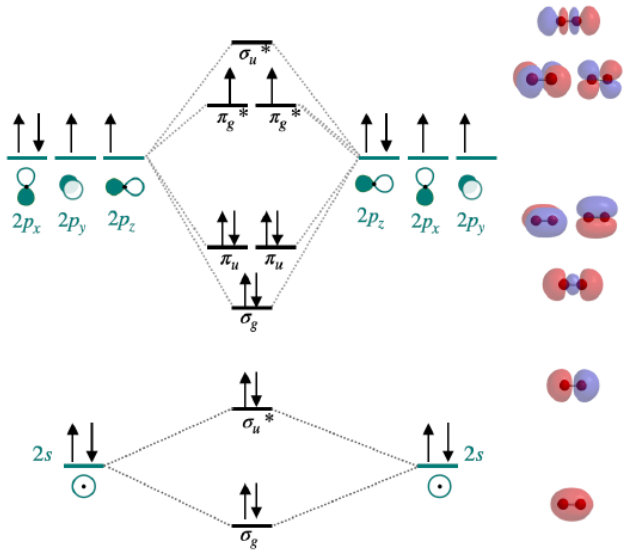


Figure for Exercise 5.2.3.2. Molecular orbital diagram of O_2. (CC-BY-NC-SA, Kathryn Haas)

Exercise 5.2.3.3**: The Peroxide Ion**

This diagram looks similar to that of 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.

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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).

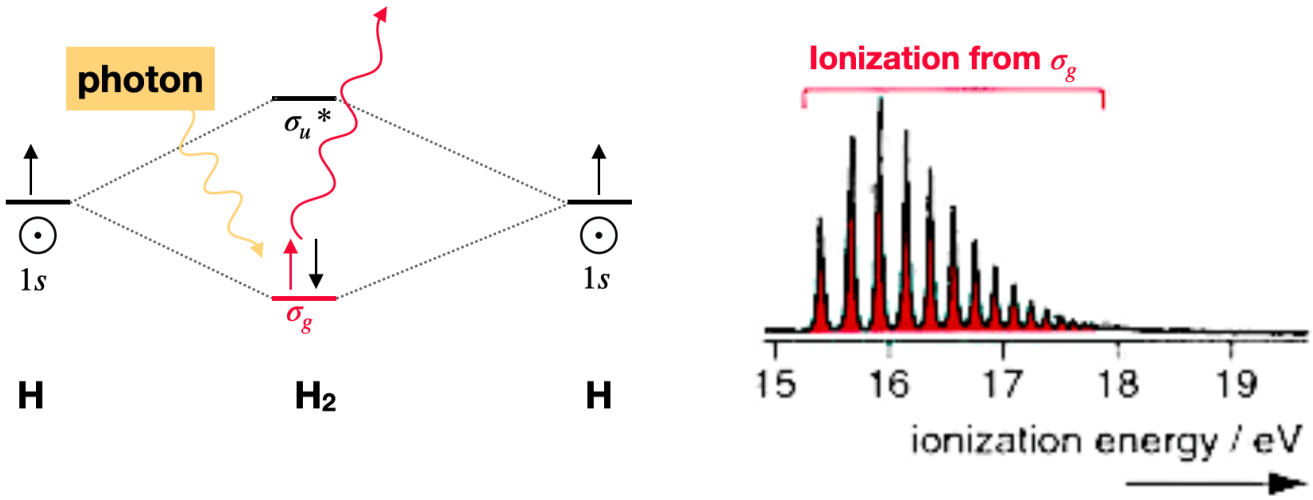


Figure $5.2.4.1$: The molecular orbital diagram and photoelectron spectrum of dihydrogen. (CC-BY-NC-SA; Libretexts)

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.

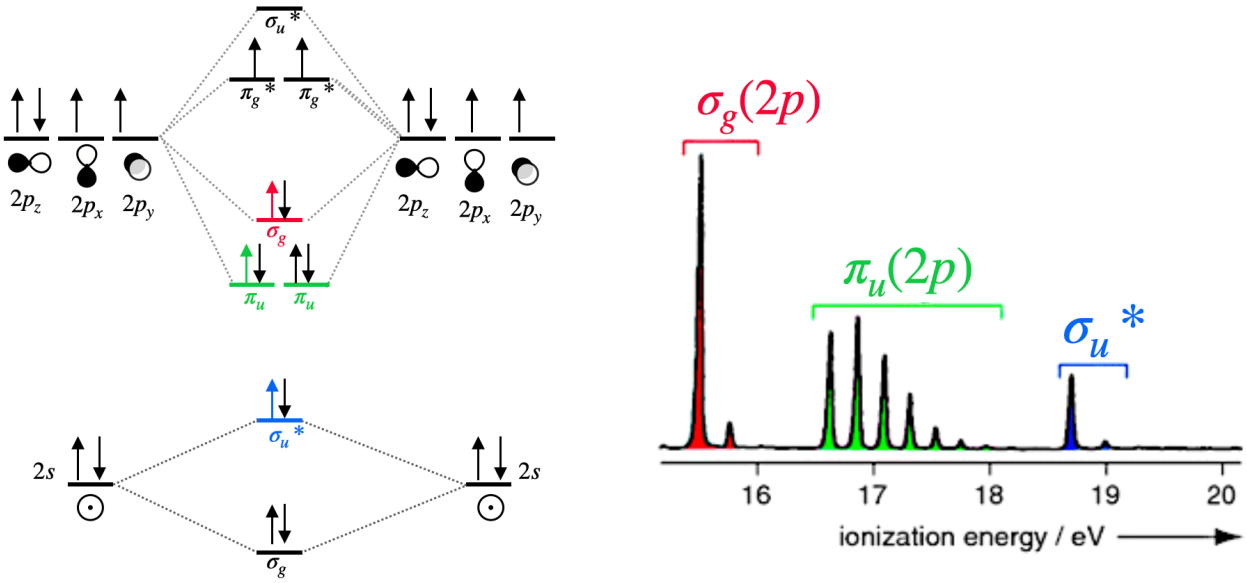


Figure 5.2.4.2: The molecular orbital diagram and photoelectron spectrum of dinitrogen. (CC-BY-NC-SA; Libretexts)

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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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.



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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.

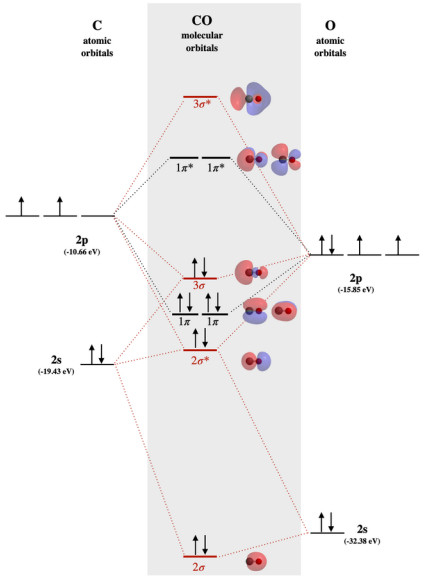
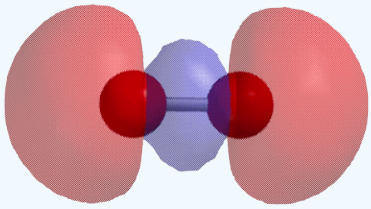


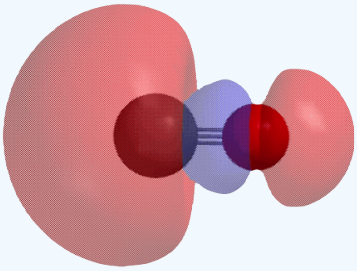
Figure $5.3.2.1$: Molecular orbital diagram of carbon monoxide. The labeling of molecular orbitals in this diagram follows a convention by which orbitals are given serial names according to the type of orbital (σ, π, etc.). The lowest energy orbitals of any type are assigned a value of 1 and higher energy 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 available at the end of this section.

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.

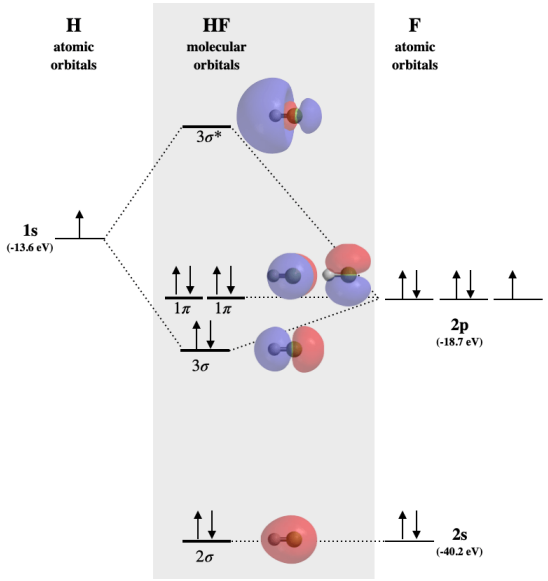


Figure 5.3.2.2: Molecular Orbital diagram of hydrogen fluoride. Molecular orbitals calculated using Spartan software. (Kathryn Haas, CC-BY-NC-SA)

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 available at the end of this section.

Answers

Exercise 5.3.2.1

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 $2p_z$.

Exercise 5.3.2.2

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 $3s$ orbital (-5.2 eV) is significantly higher in energy than the chlorine valence orbitals. The chlorine $3s$ 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 $3s$; still, the energy difference is large enough to make bonding weak. The Na $3s$ orbital combines with Cl $3p_z$ to form the molecular orbitals labeled 4σ and $4\sigma^*$ 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 $4\sigma^*$ 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.

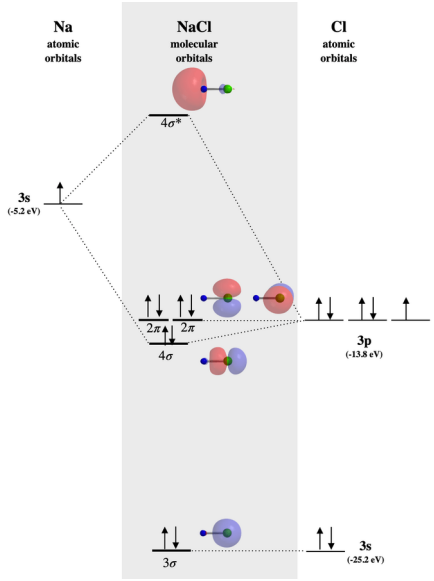


Figure $5.3.3.1$: The molecular orbital diagram for sodium chloride. Molecular orbital surfaces calculated using Spartan software indicate almost no covalent nature of bonding. (CC-BY-NC-SA, Kathryn Haas)

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 available at the end of this section.

Answers

Exercise 5.3.3.1

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 $3\sigma^*$

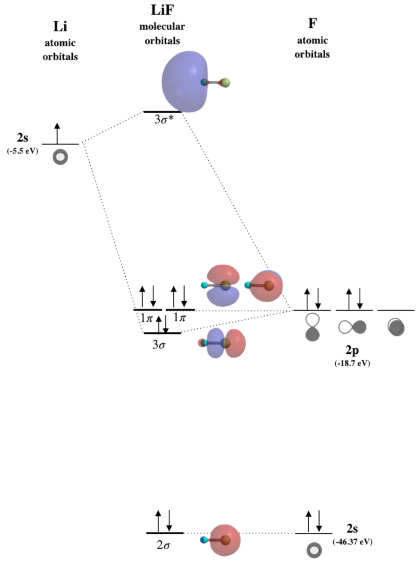


Figure for Exercise 5.3.3.1: Molecular orbital diagram for the ionic compund, LiF. (CC-BY-NC-SA, Kathryn Haas)

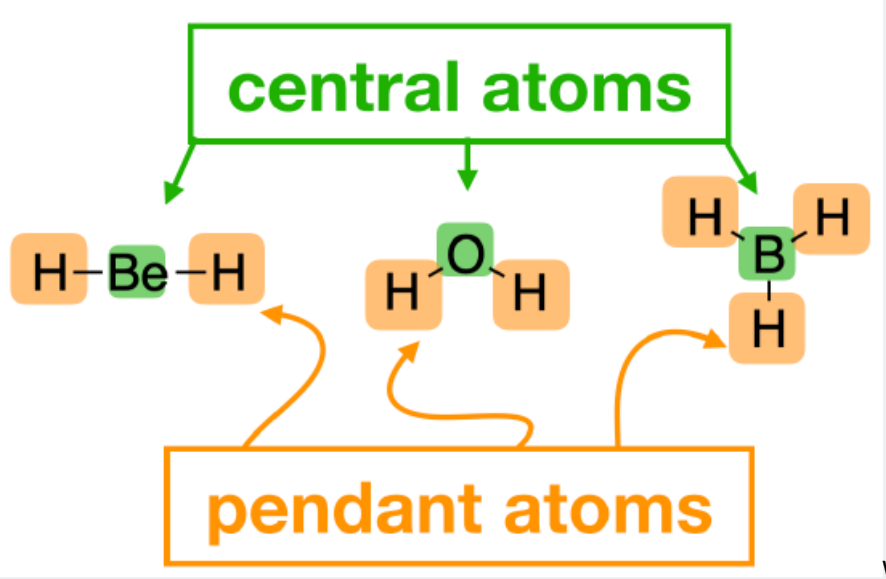
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5.4: LARGER (POLYATOMIC) MOLECULES

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 $5.4.1.1$).

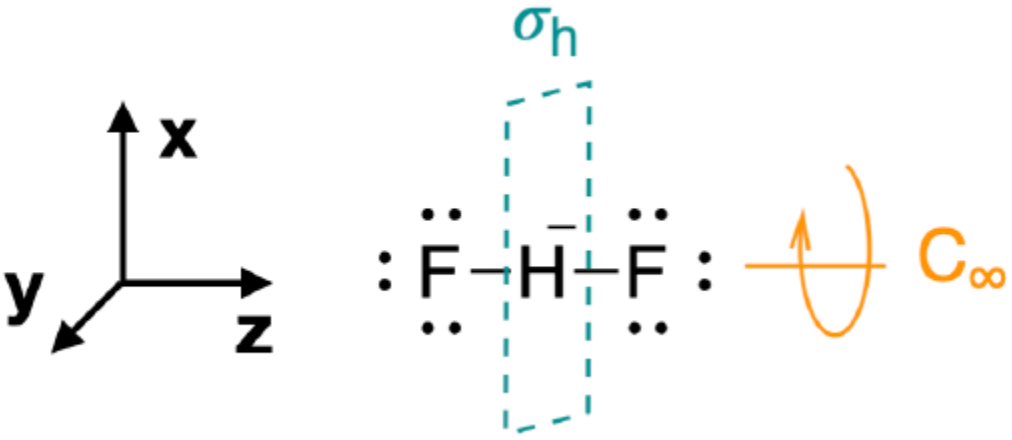


Figure $5.4.1.1$: The [FHF]$^-$ anion belongs to the $D\infty_h$ point group. (CC-BY-NC-SA; Kathryn Haas)

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 $5.4.1.2$.

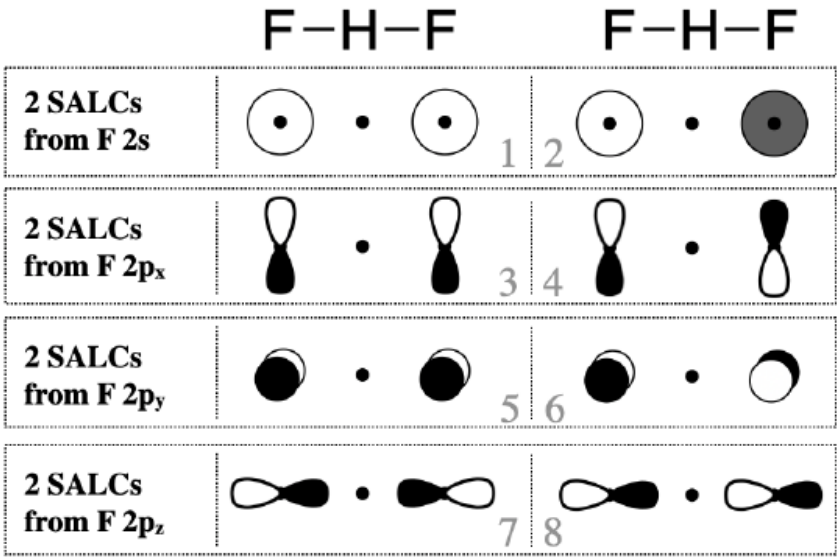


Figure 5.4.1.2: Eight SALCs from the valence orbitals of two fluorine atoms. (CC-BY-NC-SA; Kathryn Haas)

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.

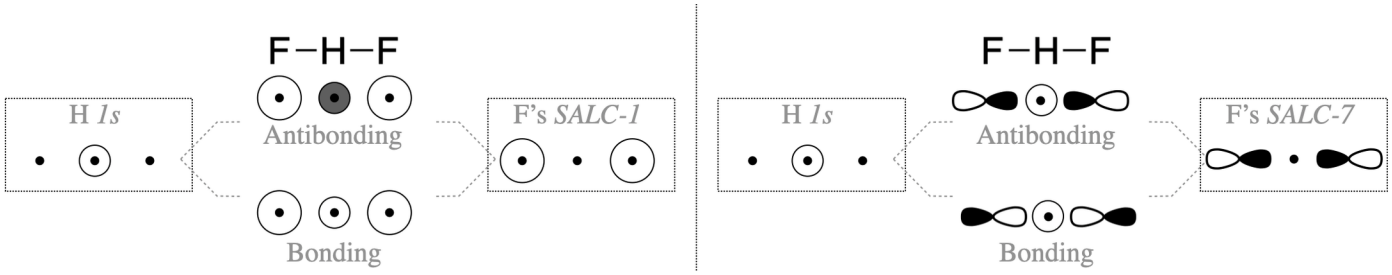


Figure 5.4.1.3: Combinations of a central H $1s$ orbital with the group orbitals, SALC-1 and SALC-7 from Figure 5.4.1.2, to create bonding and antibonding interactions. (CC-BY-NC-SA; Kathryn Haas)

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-H-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.

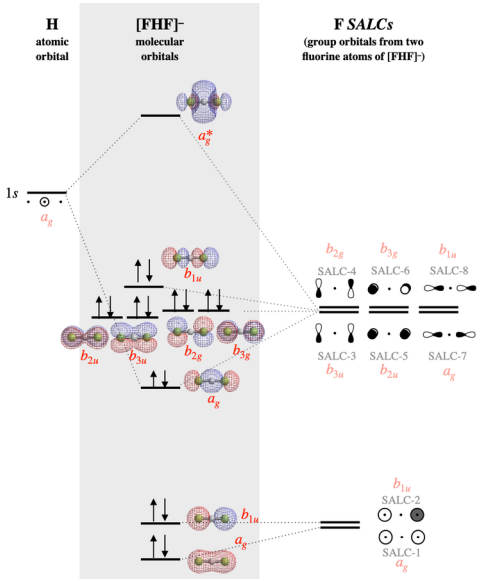
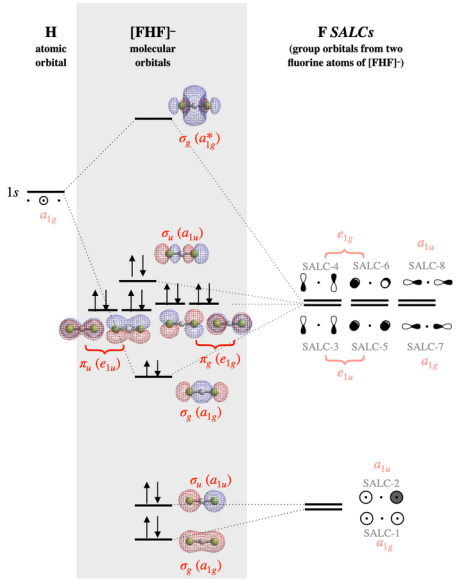


Figure 5.4.1.4:The molecular orbital diagram for $[F\text{-}H\text{-}F]^-$. The molecular orbital surfaces and relative energy levels were calculated using Spartan software. SALCs are labeled according to numbers assigned in Figure 5.4.1.2. The symmetry of each SALC and orbital under the D_{2h} **point 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 $[F\text{-}H\text{-}F]^-$. 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 $1s$ 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.

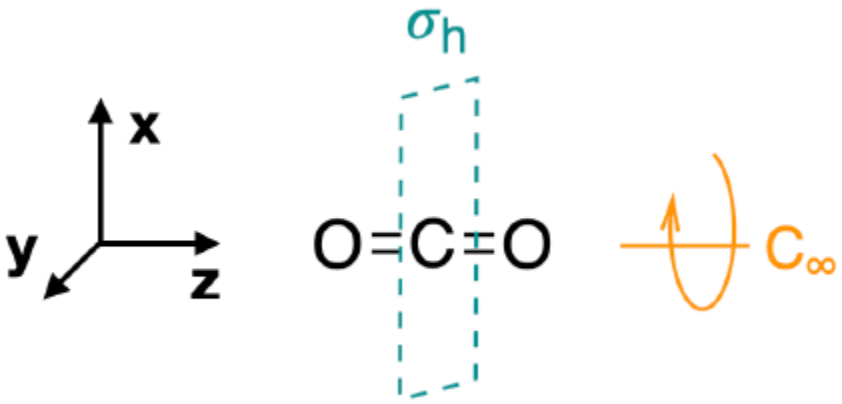


Figure $5.4.2.1$: CO_2 belongs to the $D_{\infty h}$ point group. (CC_BY-NC-SA; Kathryn Haas)

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:



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 $\times$ the character of the Γ_{modes} $\times$ the character of i, and that sum is divided by the order of the group (h).

Using either approach results in the following eight irreducible representations ($2A_g + 2B_{1u} + B_{2g} + B_{3u} + B_{3g} + B_{2u}$):



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.

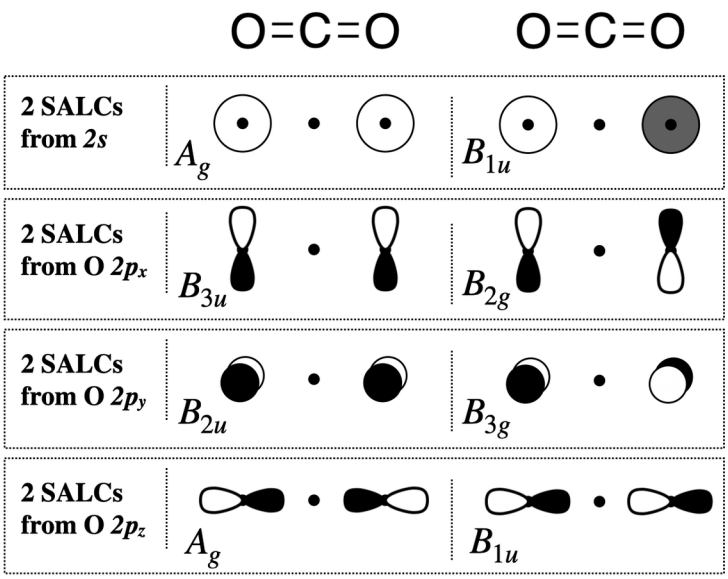


Figure 5.4.2.2: SALCs from the valence orbitals of oxygen atoms in CO_2. (CC-BY-NC-SA; Kathryn Haas)

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:

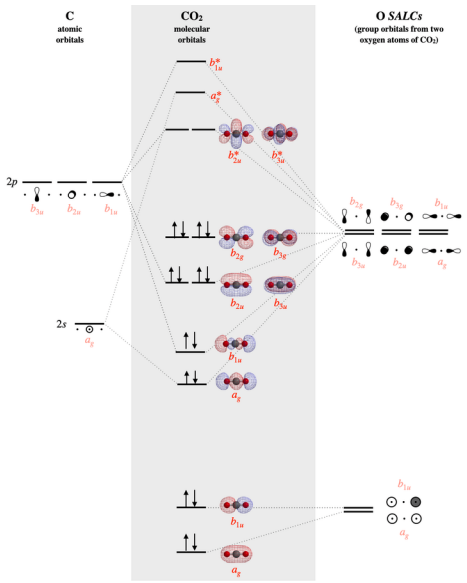


Figure 5.4.2.3: Molecular orbital diagram for carbon dioxide. (CC-BY-NC-SA; Kathryn Haas)

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.

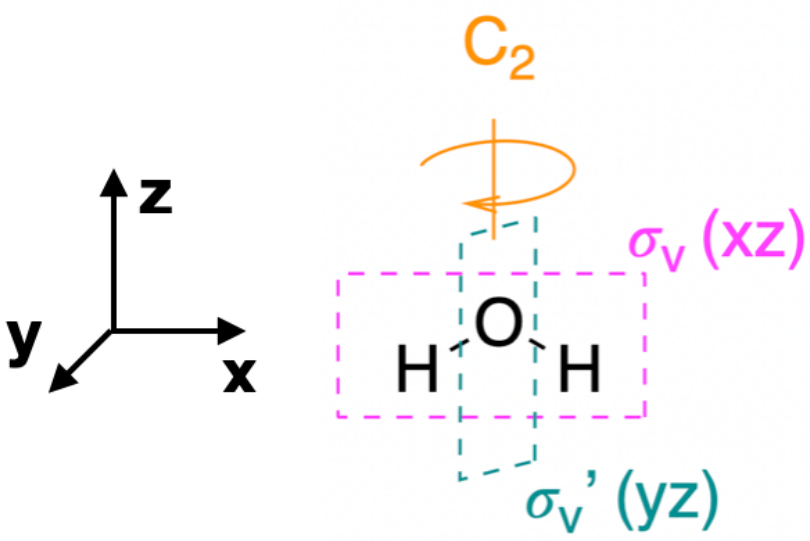


Figure 5.4.3.1: The water molecular is in the C_{2v} point group. (CC-BY-NC-SA; Kathryn Haas)

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:

[redacted]

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.

[redacted]

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.*

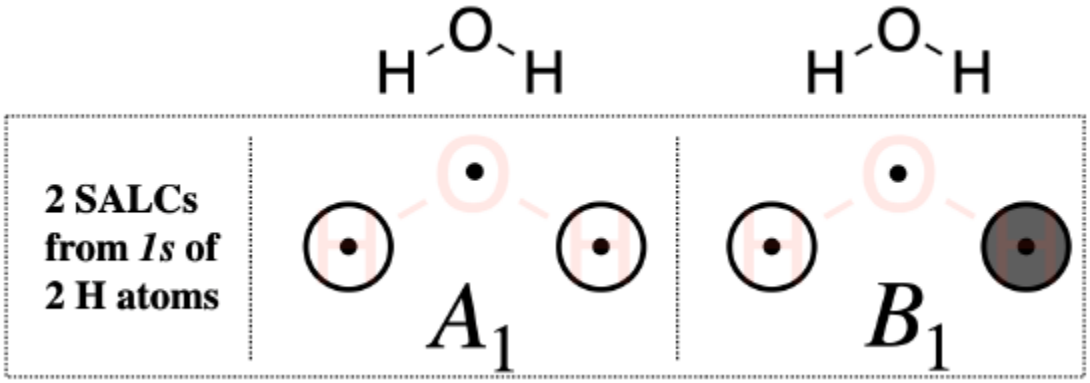


Figure 5.4.3.2: Sketch of the A_1 and B_1 hydrogen SALCs of water. (CC-BY-NC-SA; Kathryn Haas)

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 available at the end of this section.

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:

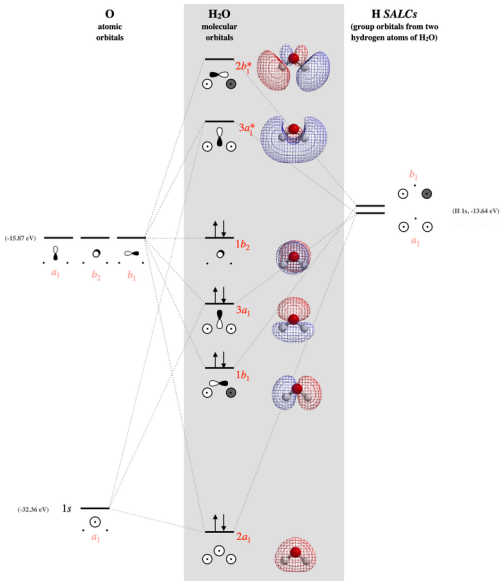


Figure 5.4.3.3: The molecular orbital diagram of water. Molecular orbital surfaces calculated using Spartan software. The surface of the $3a_1^*$ orbital has been trimmed. (CC-BY-NC-SA; Kathryn Haas)

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.

$$\Psi = c_{oxygen}\left(\psi_{oxygen}\right) + c_{SALCs}\left(N(\psi_{H_a} \pm \psi_{H_b})\right)$$

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 $5.4.3.3$).



Answers

Exercise $5.4.3.1$

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5.4.4: NH_3

Construct SALCs and the molecular orbital diagram for $\mathrm{NH_3}$

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.

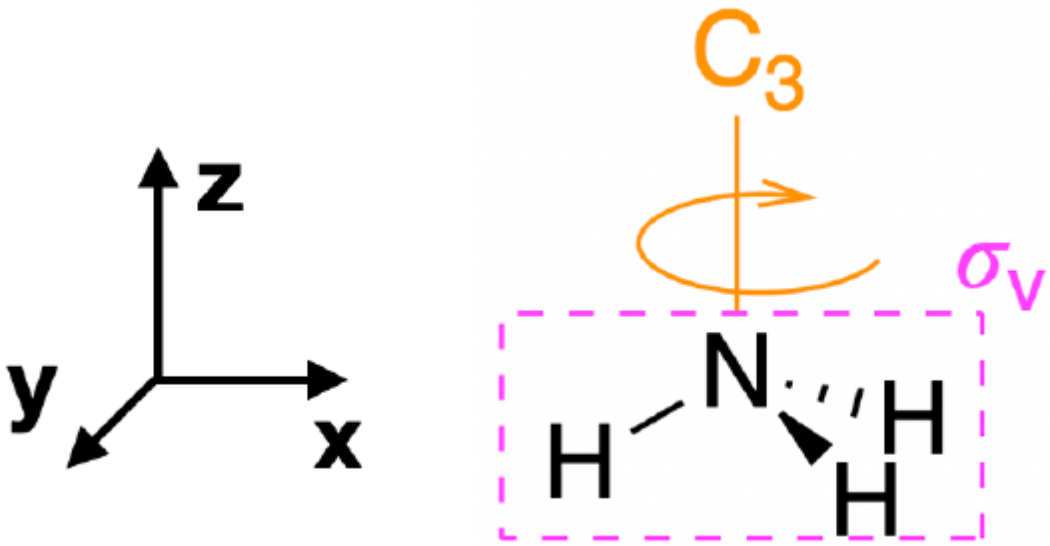


Figure 5.4.4.1: The ammonia molecule is in the C_{3v} point group. (CC-BY-NC-SA; Kathryn Haas)

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:

[redacted]

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.

[redacted]

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).

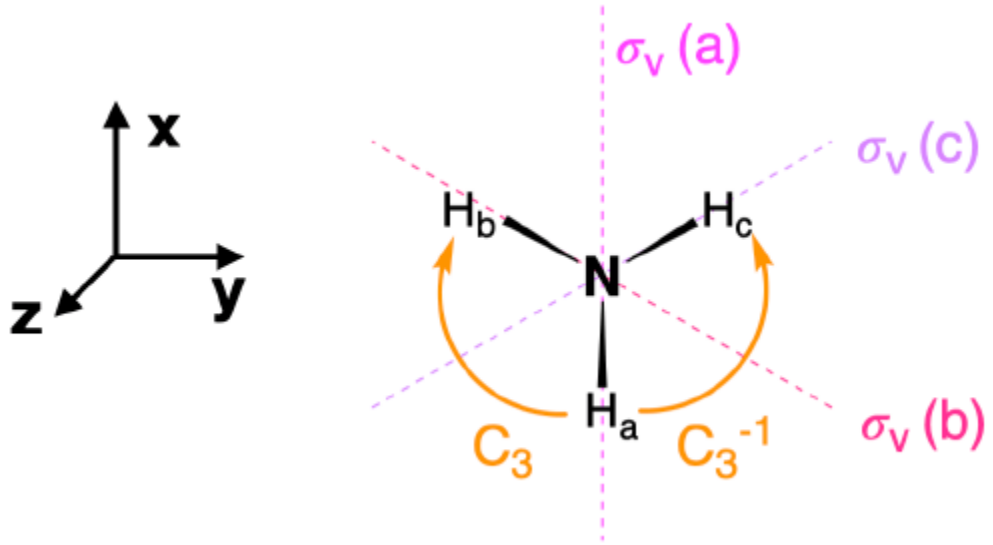


Figure 5.4.4.2: The three H's in NH_3 are chemically identical, but we can distinguish them using labels for the purpose of applying the projection operator method. In this figure, we have placed the z axis along the principal C_3 axis and placed the x axis colinear with one H. Each of the three H atoms 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.

[redacted] (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.

[redacted] (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.

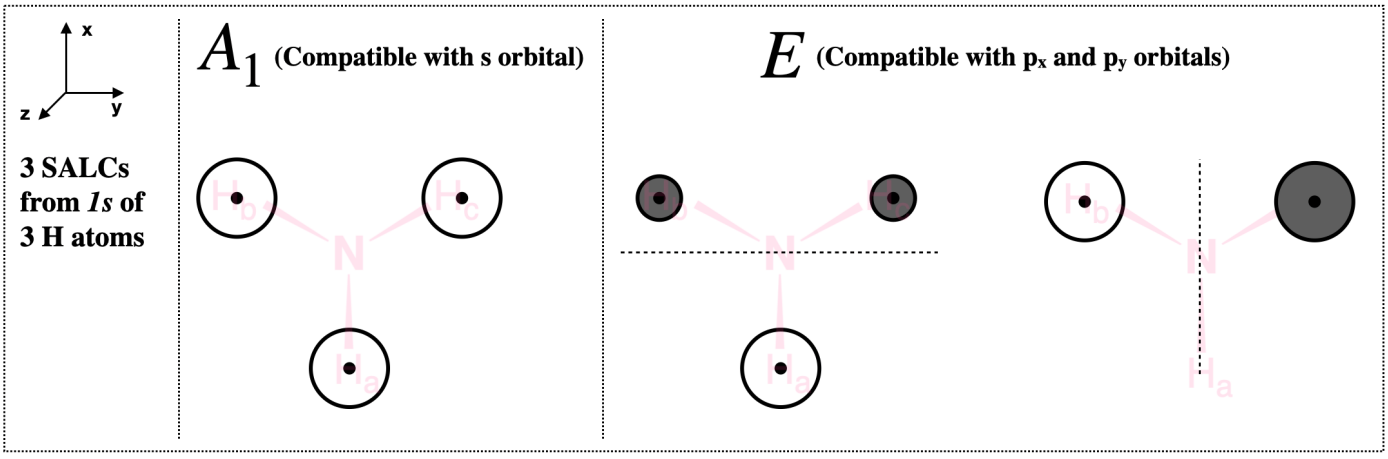


Figure 5.4.4.3: Sketches of H SALCs of ammonia from the perspective of the C_3 axiz (z axis). The A_1 SALC is shown at the left, while two degenerate SALCs with E symmetry are shown on the right. Nodes for E group orbitals are shown as dashed lines. (CC-BY-NC-SA; Kathryn Haas)

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.

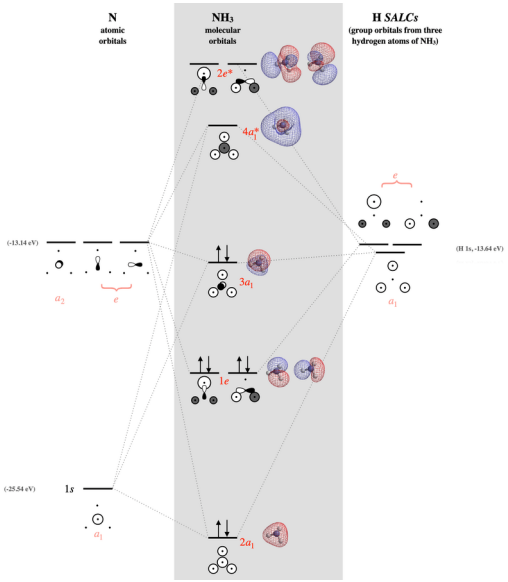


Figure 5.4.4.4: The molecular orbital diagram of ammonia. Molecular orbitals surfaces calculated using Spartan software. (CC-BY-NC-SA; Kathryn Haas)

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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 $\mathrm{CO_2}$

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.

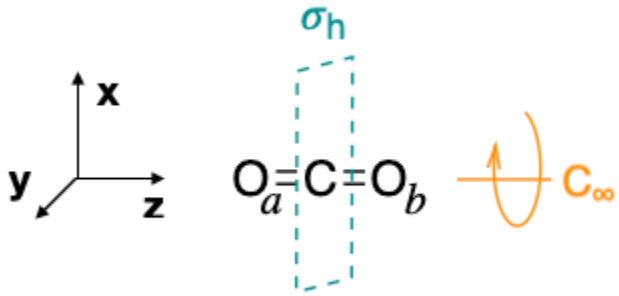


Figure 5.4.5.1: The structure of carbon dioxide with pendant oxygen atoms distinguished with labels a and b. Note that we will approximate the C_∞ axis as a C_2 axis to simplify the process of finding the SALCs. (CC-BY-SA; Kathryn Haas)

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.

[redacted]

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.



(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 $4\mathrm{O}_a + 4\mathrm{O}_b$ 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 $4\mathrm{O}_a - 4\mathrm{O}_b$ 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:



(5.4.5

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 .

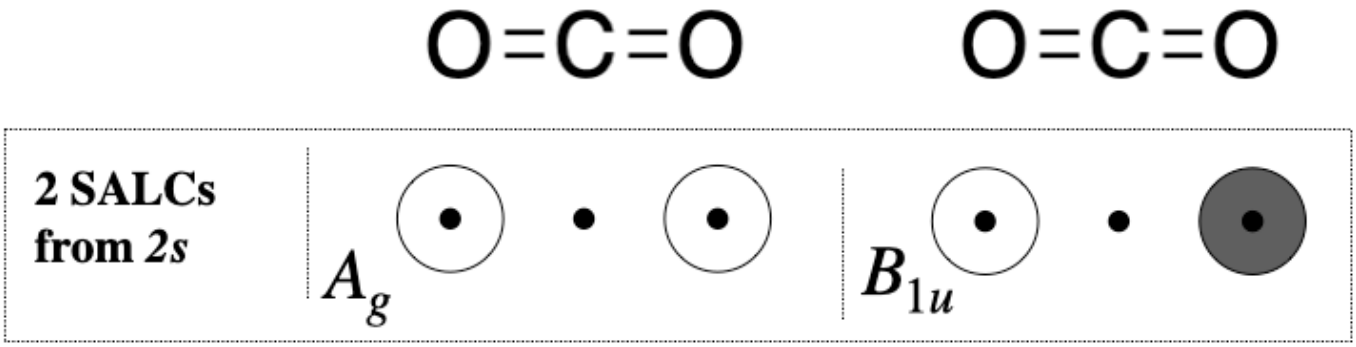


Figure $5.4.5.2$: SALCs derived from two oxygen $2s$ orbitals from carbon dioxide. Compare to Section 5.4.2. (CC-BY-SA; Kathryn Haas)

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).



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).

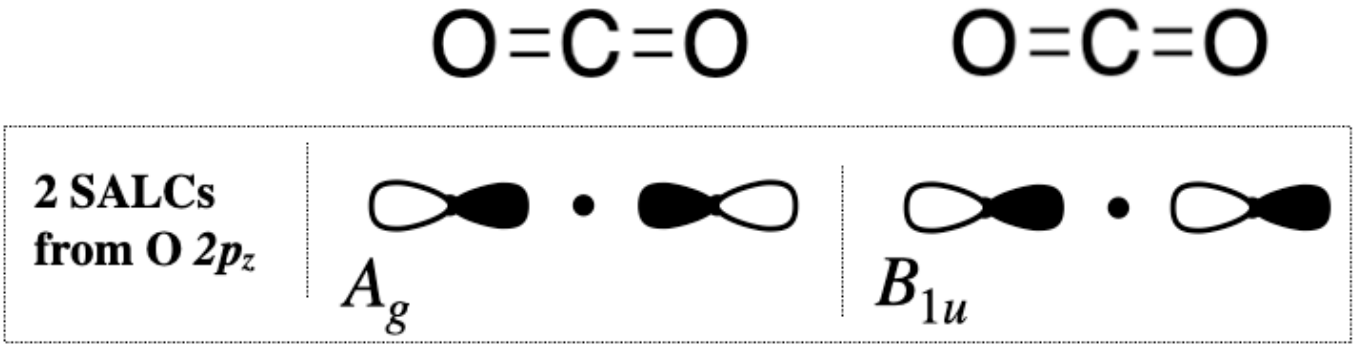


Figure $5.4.5.3$: SALCs derived from two oxygen $2p_z$ orbitals from carbon dioxide. Compare to Section 5.4.2. (CC-BY-SA; Kathryn Haas)

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.

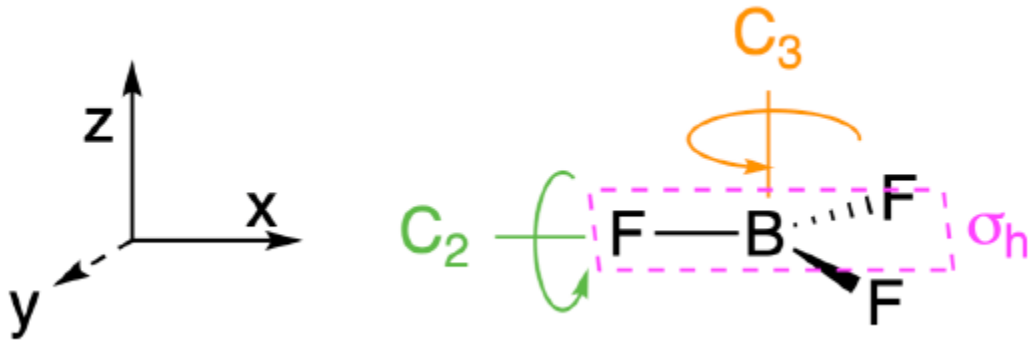


Figure 5.4.6.1: The molecule is in the D_{3h} point group. (CC-BY-NC-SA; Kathryn Haas)

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.

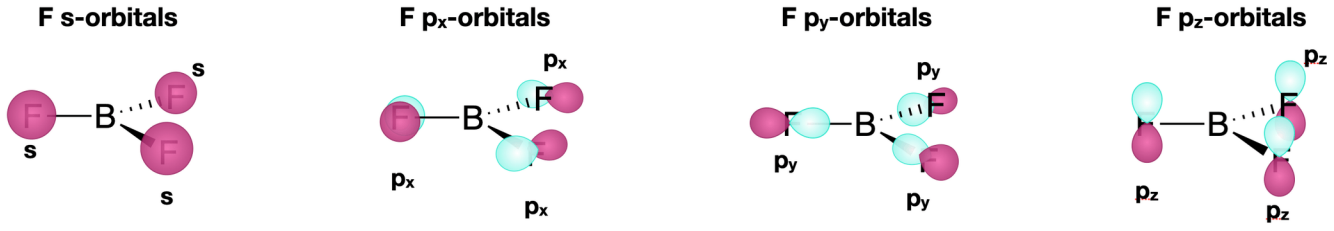


Figure 5.4.6.2: Individual sets of pendant fluorine atomic orbitals will create separate sets of SALCs. (CC-BY-SA; Kathryn Haas)

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).

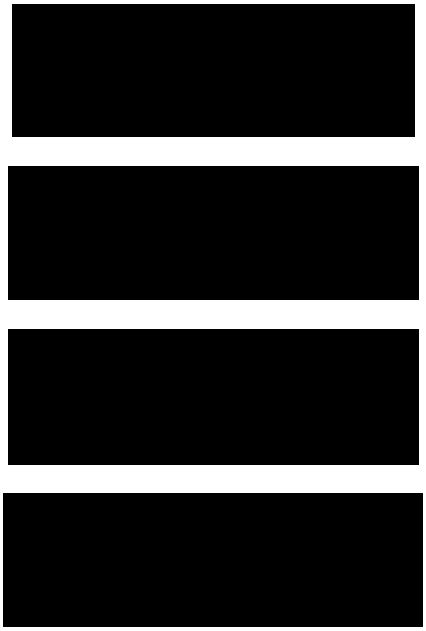
- For the set of s orbitals: perform the operation for each class in the character table. Each s orbital is assigned a value depending on whether it moves or not: assign a value of 1 if it remains in place during the operation, or 0 (zero) if it moves out of its original place.
- for each set of p orbitals: 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:



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 each of the Γ reduces to two irreducible representations under the D_{3h} point group; in each case one is singly degenerate (A) and the other doubly degenerate (E). This equates to three SALCs for each Γ (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.



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 $2s$ and $2p$ orbitals can be found from the D_{3h} character table.

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5.5: Acid-Base and Donor-Acceptor Chemistry

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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 available at the end of this section.

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 available at the end of this section.

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 available at the end of this section.

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 available at the end of this section.

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 available at the end of this section.

Exercise 6

Which are the symmetry types of the central atom orbitals in the PCl_5 molecule?

Answer available at the end of this section.

Exercise 7

For the hypothetical $BrKr^+$ molecule: Toward which atom is the HOMO polarized? Explain briefly why.

Answer available at the end of this section.

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 available at the end of this section.

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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 available at the end of this section.

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 available at the end of this section.

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 available at the end of this section.

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 available at the end of this section.

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?
d. Based on molecular orbital pictures, how easily do you think dioxygen could be reduced to peroxide (through the addition of two electrons)?

Answer available at the end of this section.

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 available at the end of this section.

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 available at the end of this section.

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 available at the end of this section.

Exercise 5.P.9

Make drawings and notes to summarize the effect of populating antibonding orbitals.

Answer available at the end of this section.

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 available at the end of this section.

Exercise $5.P.1$

Draw the molecular orbital diagram for (NO^-).

Answer available at the end of this section.

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 available at the end of this section.

Exercise $5.P.1$

Draw the molecular orbital diagram for hydroxide ion (OH^-).

Answer available at the end of this section.

Exercise $5.P.1$

Draw the molecular orbital diagram for hydroxide fluoride (HF).

Answer available at the end of this section.

Exercise $5.P.1$

Draw the molecular orbital diagram for borane (BN).

Answer available at the end of this section.

BH3

Exercise $5.P.1$

Draw the molecular orbital diagram for $(\mathrm{FeH_6})$.

Answer available at the end of this section.

Exercise $5.P.1$

Draw the molecular orbital diagram for boron trifluoride $(\mathrm{BF_3})$.

- 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 $\mathrm{BH_3}$ in this MO diagram?

Answer available at the end of this section.

Answers

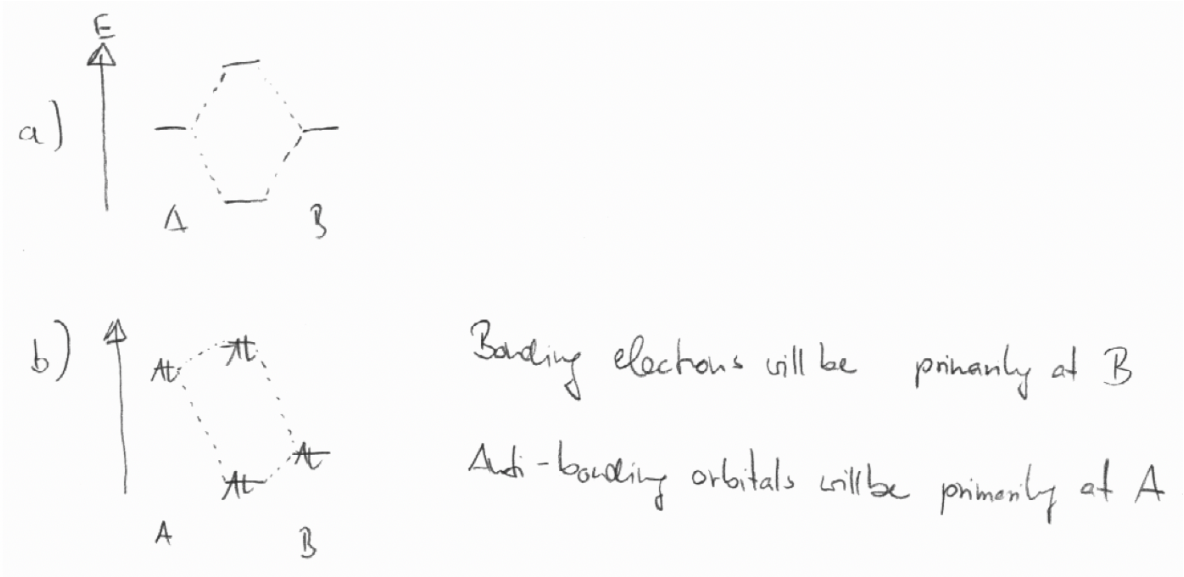
Exercise 1

a) Overlap of a small and a large orbital.

Exercise 2

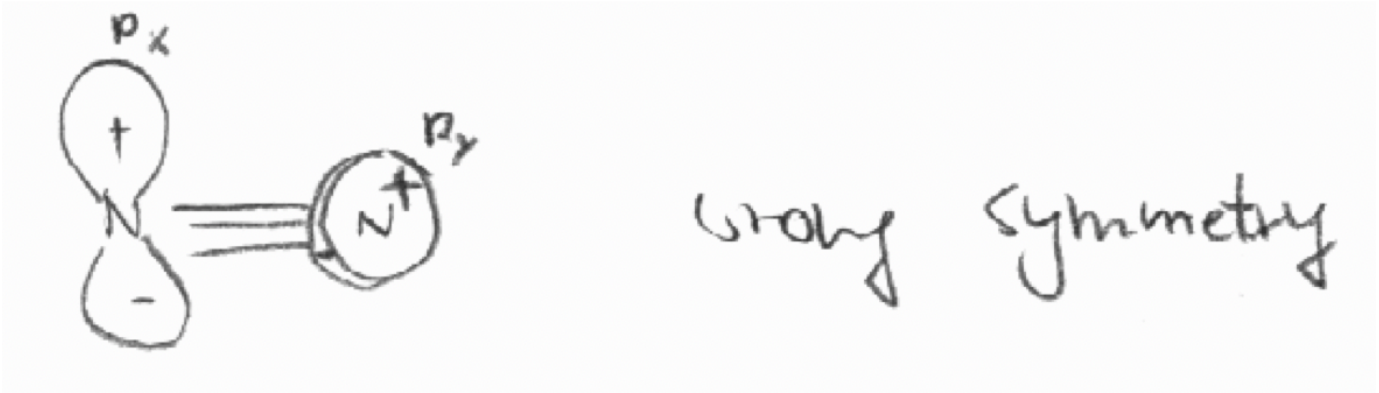
a) orbital overlap in sigma-fashion

Exercise 3

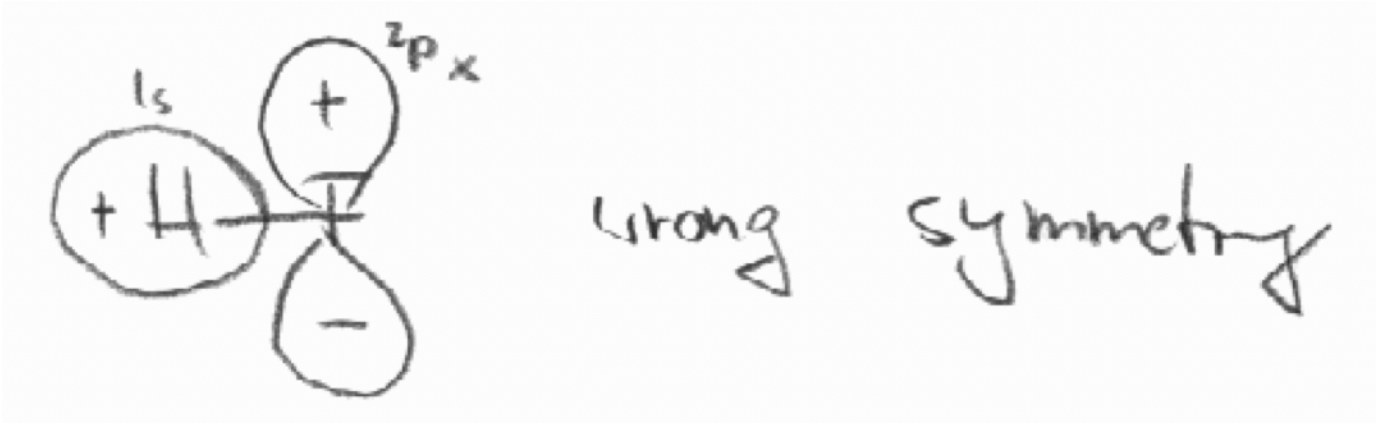


Exercise 4

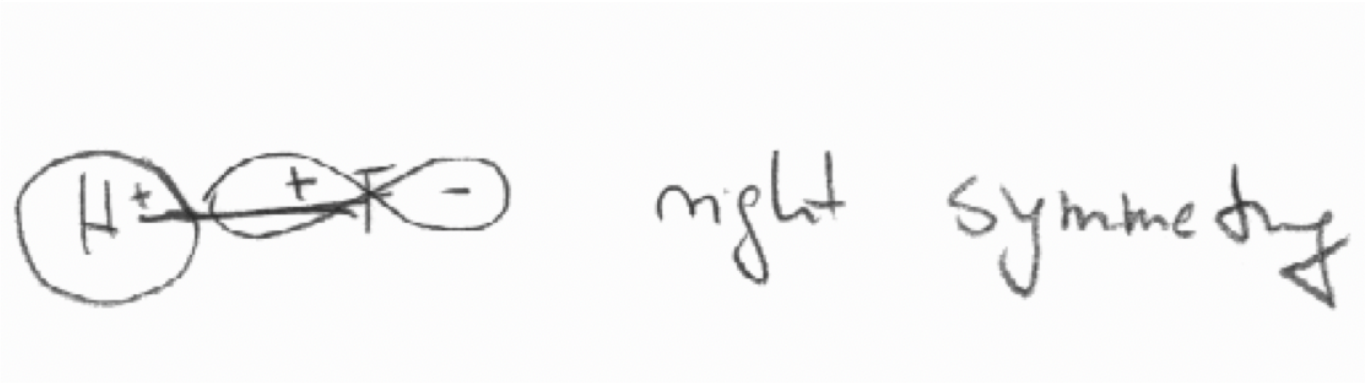
a)



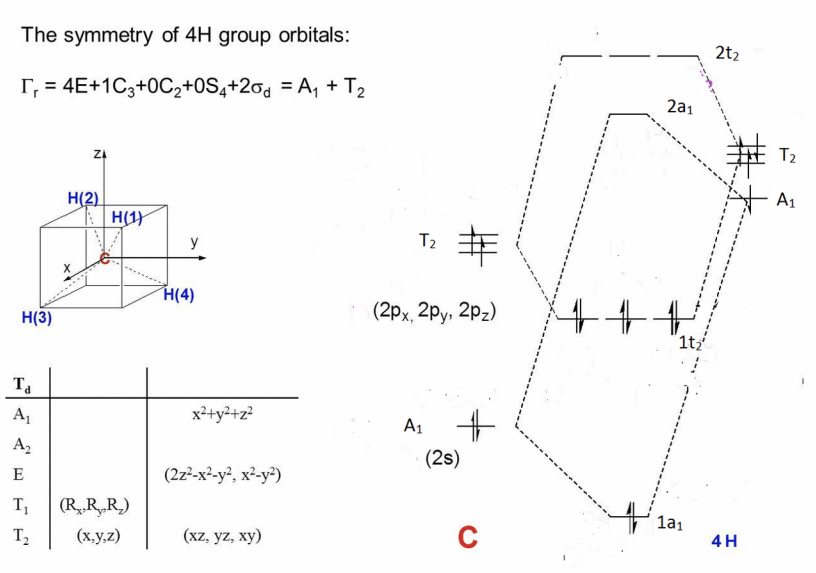
b)



c)



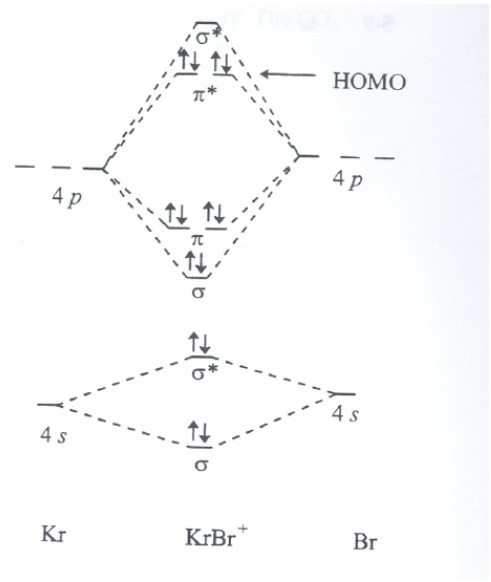
Exercise 5



Exercise 6

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'($3p_x$, $3p_y$)

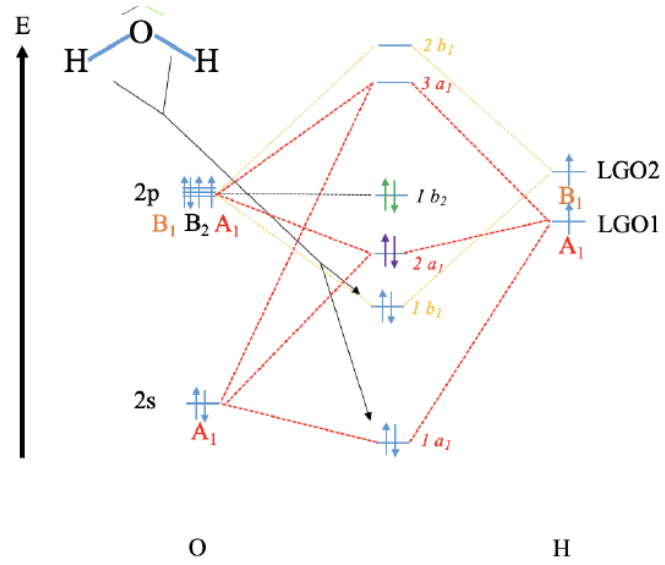
Exercise 7



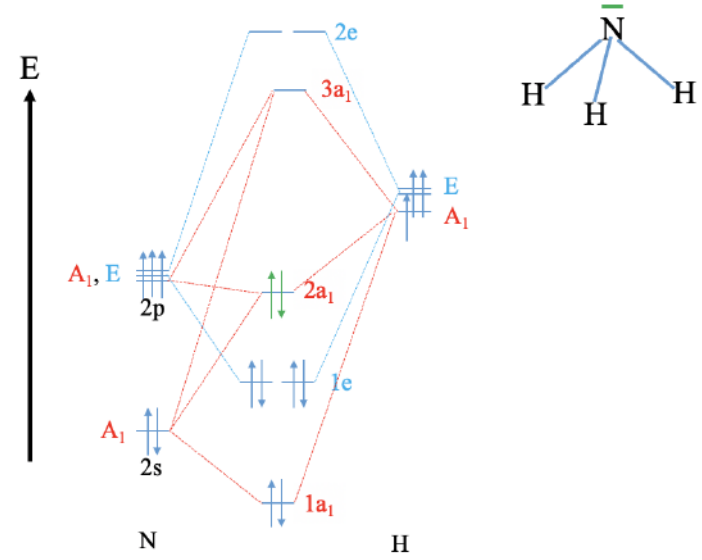
Orbital energies of Kr must be somewhat lower than the ones of Br because the electrons experience higher effective nuclear charge (Z_{eff} increases within a period). This means that the antibonding HOMO is polarized towards Br (HOMO energetically closer to 4p(Br) than 4p(Kr)).

Exercise 8

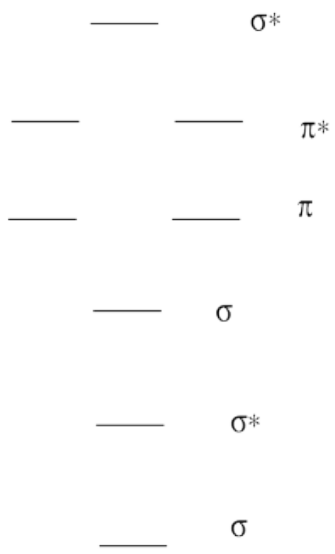
Water



NH_3



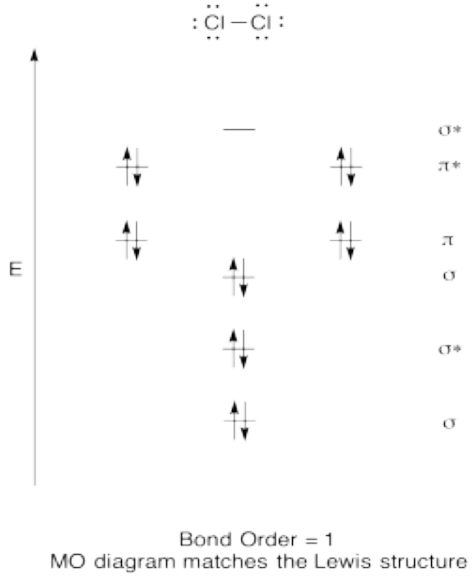
Exercise $5.P.1$



Exercise $5.P.2$

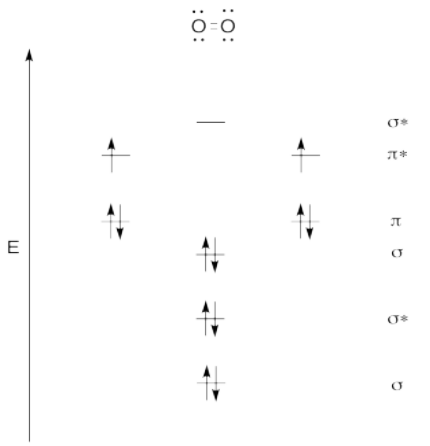
- Count the valence electrons on the molecule. That's the number of valence electrons on each atom, adjusted for any charge on the molecule. (eg C_2^{2-} has 10 valence electrons: 4 from each carbon -- that's 8 -- and two more for the 2- charge).
- Fill electrons into the lowest energy orbitals first.
- Pair electrons after all orbitals at the same energy level have one electron.

Exercise $5.P.3$



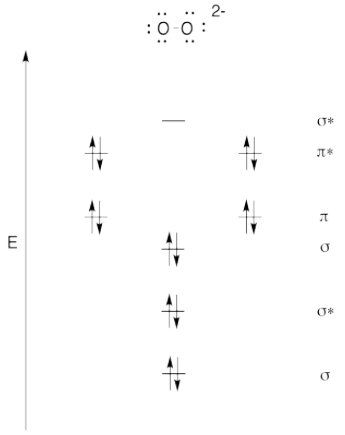
Bond Order = 1
MO diagram matches the Lewis structure

Exercise $5.P.4$



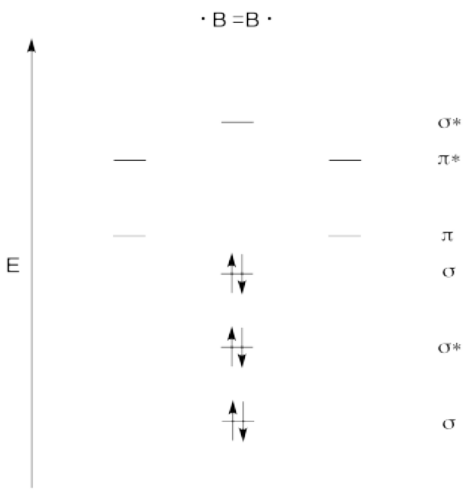
Bond Order = 2
MO diagram indicates two unpaired electrons and therefore does not match the Lewis structure. Based on the MO diagram oxygen would be paramagnetic and would be attracted to a magnetic field

Exercise $5.P.5$



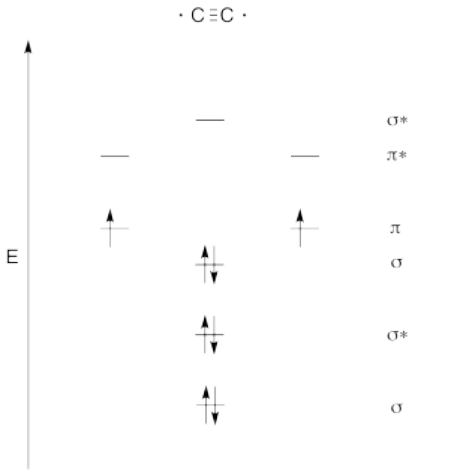
Bond Order = 1
MO diagram matches the Lewis structure. Both predict a Bond Order of 1 and 6 lone pairs of electrons. The addition of two electrons to O_2 to O_2^{2-} would be possible.

Exercise $5.P.6$



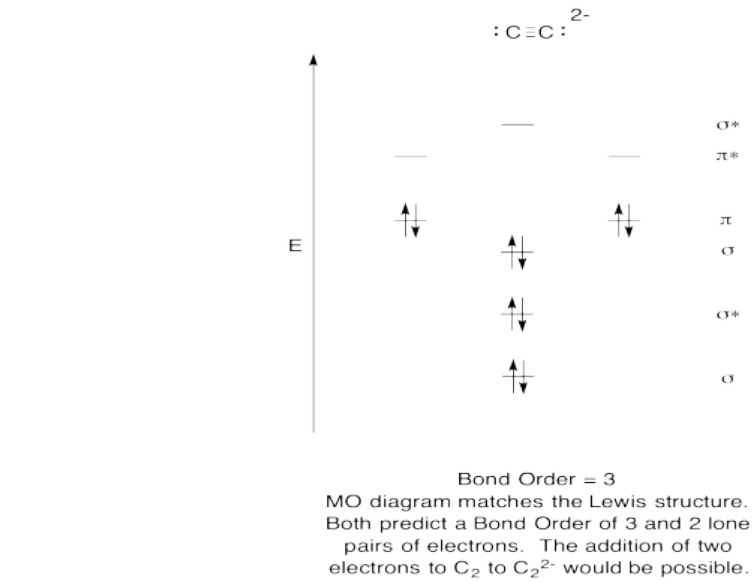
Bond Order = 1
Boron-Boron bonding should be possible

Exercise $5.P.7$



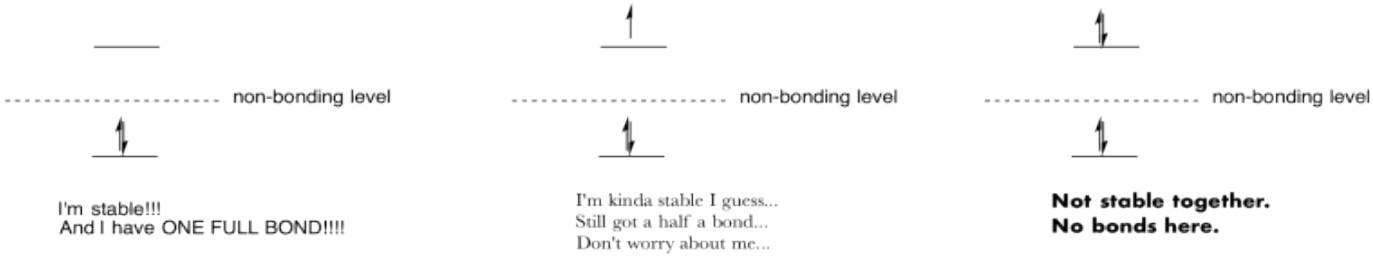
Bond Order = 2
MO diagram does not match the Lewis structure.
However, the MO diagram does concur about the
2 unpaired electrons.

Exercise $5.P.8$



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 $5.P.9$



I'm stable!!!
And I have ONE FULL BOND!!!!

I'm kinda stable I guess...
Still got a half a bond...
Don't worry about me...

Not stable together.
No bonds here.

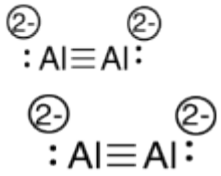
Exercise $5.P.10$

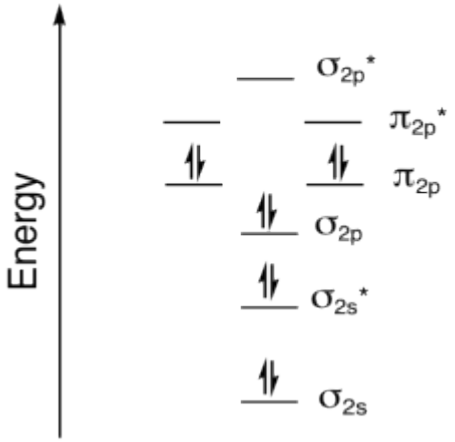
a) Na, because Na has a lower ionization potential (and a lower electronegativity) than Al.

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-





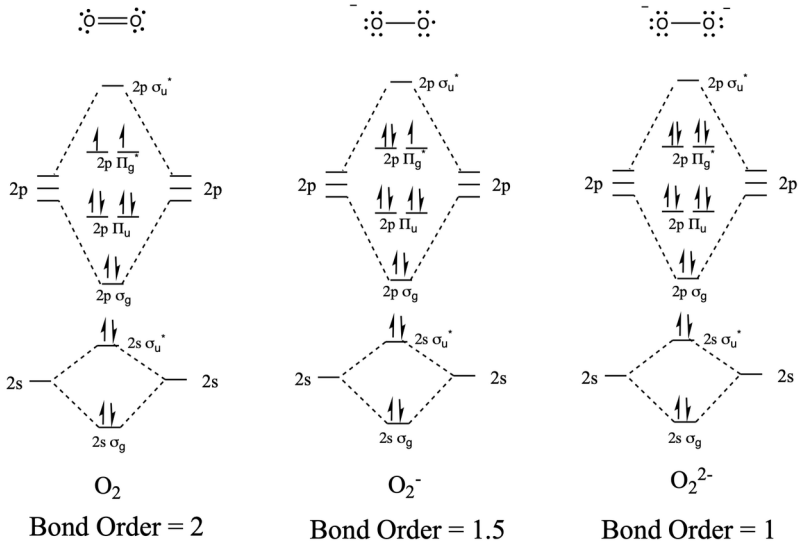
g) bond order $= \frac{(\#bonding\ e^- - \#antibonding\ 3^-)}{2} = \frac{8-2}{2} = 3$

Exercise $5.P.1$

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Exercise $5.P.1$

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 $5.P.1$

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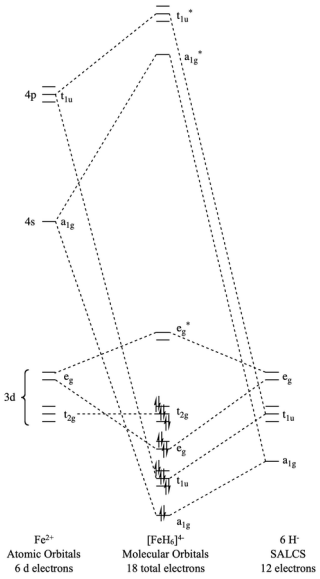
Exercise $5.P.1$

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Exercise $5.P.1$

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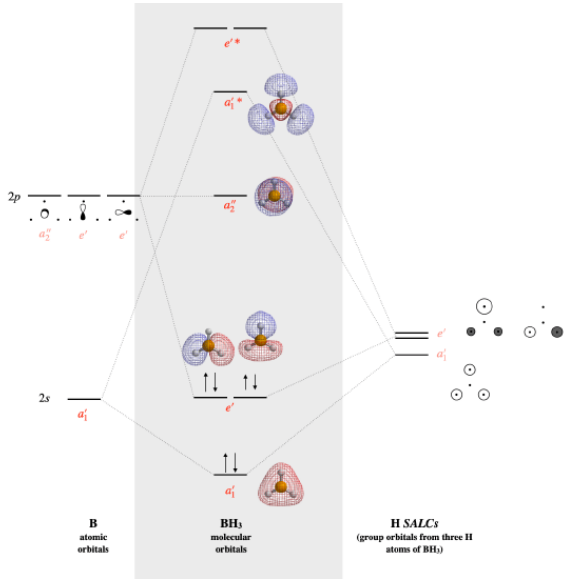
Exercise $5.P.1$



Exercise $5.P.1$

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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6: ACID-BASE AND DONOR-ACCEPTOR CHEMISTRY

6.1: Acid-Base Models as Organizing Concepts

6.2: Arrhenius Concept

6.3: Brønsted-Lowry Concept

6.3.1: Brønsted-Lowry Concept

6.3.2: Rules of Thumb for thinking about the relationship between Molecular Structure and Brønsted Acidity and Basicity*

6.3.3: The acid-base behavior of binary element hydrides is determined primarily by the element's electronegativity and secondarily by the element-hydrogen bond strength

6.3.4: Brønsted-Lowry Superacids and the Hammett Acidity Function

6.3.5: Thermodynamics of Solution-Phase Brønsted Acidity and Basicity

6.3.6: Thermodynamics of Gas Phase Brønsted Acidity and Basicity

6.3.7: The Acidity of an Oxoacid is Determined by the Electronegativity and Oxidation State of the Oxoacid's Central Atom*

6.3.8: High Charge-to-Size Ratio Metal Ions Act as Brønsted Acids in Water

6.3.9: The Solvent System Acid Base Concept

6.3.10: Acid-Base Chemistry in Amphoteric Solvents and the Solvent Leveling Effect

6.3.11: Non-nucleophilic Brønsted-Lowry Superbases

6.4: Lewis Concept and Frontier Orbitals

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.

6.4.2: All other things being equal, electron withdrawing groups tend to make Lewis acids stronger and bases weaker while electron donating groups tend to make Lewis bases stronger and acids weaker

6.4.3: The electronic spectra of charge transfer complexes illustrate the impact of frontier orbital interactions on the electronic structure of Lewis acid-base adducts

6.4.4: Substances' solution phase Lewis basicity towards a given acid may be estimated using the enthalphy change for dissociation of its adduct with a reference acid of similar hardness.

6.4.5: In the boron trifluoride affinity scale, the enthalphy change on formation of an adduct between the base and boron trifluoride is taken as a measure of Lewis basicity.

6.4.6: Lewis base strength may also be estimated by measuring structural or energy changes upon formation of a Lewis acid-base complex, as illustrated by efforts to spectroscopically assess the strengths of halogen bonds

6.4.7: Bulky groups weaken the strength of Lewis acids and bases because they introduce steric strain into the resulting acid-base adduct.

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.

6.5: Intermolecular Forces

6.5.1: Host-Guest Chemistry and π-π Stacking Interactions

6.5.2: Hydrogen bonds may be considered as a special type of Lewis acid-base interaction in which a Lewis acid hydrogen ion is shared between Lewis bases

6.6: Hard and Soft Acids and Bases

6.6.1: Quantitative Measures of Hardness, Softness, and Acid-Base Interactions from a Hard Soft Acid-Base Principle Perspective Involve Orbital Energies and/or Apportioning Acid-Base Bonding in Terms of Electrostatic and Covalent Factors

6.6.2: Hard-Hard and Soft-Soft preferences may be explained and quantified in terms of electrostatic and covalent and electronic stabilization on the stability of Lewis acid-base adducts

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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

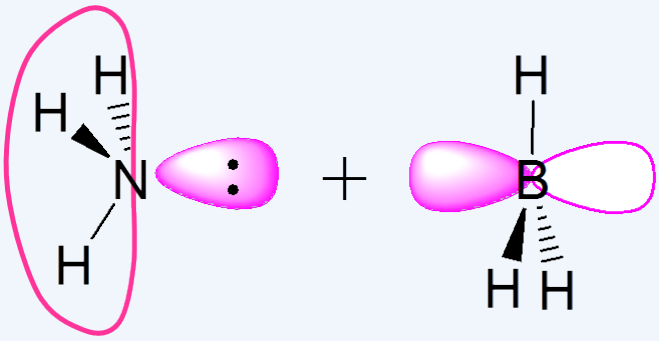
The concept of acids and bases is often associated with the movement of hydrogen ions from one molecule or ion to another. However, a host of acid-base concepts have been developed to help chemists organize and make sense of a wide range of reactions (Table 6.1).

Table 6.1. Summary of major acid-base models.

Definition	Theoretical paradigm and notable features.	Acid	Base	Illustrative sam
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^+	$\underset{acid}{HCl} + \underset{base}{NH_3} \rightarrow \underset{conj.\ acid}{NH_4^+} + \underset{conj.\ base}{Cl^-}$ $\underset{acid}{HOAc} + \underset{base}{NH_3} \rightarrow \underset{conj.\ acid}{NH_4^+} + \underset{conj.\ base}{OAc^-}$ $\underset{amphoteric}{2\ H_2O} \rightarrow \underset{conj.\ acid}{H_3O^+} + \underset{conj.\ base}{OH^-}$

Definition	Theoretical paradigm and notable features.	Acid	Base	Illustrative sam
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	$\underset{acid}{SbF_5} + \underset{base}{BrF_3} \rightarrow \underset{conj.\ base}{SbF_6^-} + \underset{conj.\ acid}{BrF_2^+}$ $\underset{amphoteric}{2\ BrF_3} \rightarrow \underset{conj.\ acid}{BrF_2^+} + \underset{conj.\ base}{BrF_4^-}$

Definition	Theoretical paradigm and notable features.	Acid	Base	Illustrative sam
Lewis (1923)	Envisions acid-base reactivity in terms of electron pair donation. Encompasses the Arrhenius , Brønsted-Lowry, Lux-Flood, and Solvent System definitions and readily integrates with molecular orbital descriptions of chemical reactivity in Frontier orbital theory.	Accepts an electron pair	Donates an electron pair	$:\underset{base}{NH_3} + \underset{acid}{BF_3} \rightarrow H_3N + BF_3$
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	$:\underset{base}{NH_3} + \underset{acid}{BH_3} \rightarrow \underset{adduct}{H_3N-BH_3}$ $\underset{acid}{Fe^{2+}} + \underset{base}{Zn^0} \rightarrow Fe^0 + Zn^{2+}$

Definition	Theoretical paradigm and notable features.	Acid	Base	Illustrative sam
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: Arrhenius Concept

The Arrhenius acid-base concept defines acids and bases in terms of how they affect the amount of hydronium ions, $\mathrm{H_3O^+}$, (and by extension hydroxide ions, $\mathrm{OH^-}$) in aqueous solutions. Simply, in the Arrhenius definition an acid is a substance that increases the concentration of hydronium ions when it is dissolved in water. This typically occurs when the acid dissociates by loss of a proton to water according to the general equation:

$$\mathrm{HA\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq)} \tag{6.2.1}$$

where A is the deprotonated form of the acid. For example, what hydrochloric and acetic acid, $\mathrm{CH_3CO_2H}$, have in common is that both increase the amount of hydronium ion when they are dissociated in solution.

$$\mathrm{HCl\,(aq) + H_2O\,(l) \longrightarrow H_3O^+\,(aq) + Cl^-\,(aq)}$$
$$\mathrm{CH_3CO_2H\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + CH_3CO_2{}^-\,(aq)}$$

In terms of the Arrhenius definition, the major difference between hydrochloric and acetic acid is that hydrochloric acid dissociates completely in solution to yield stoichiometric amounts of $\mathrm{H_3O^+}$, while acetic acid only partially dissociates. Acids like HCl that completely dissociate in water are classified as strong in the Arrhenius definition, while those like acetic acid that do not are classified as weak.

Although all weak acids incompletely dissociate, the extent of dissociation can vary widely. The relative strengths of weak Arrhenius acids is conveniently expressed in terms of the equilibrium constant for their acid dissociation reaction, K_a.

$$K_a = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

The pK_a values for selected weak acids are given in Table $6.2.1$.

Table $6.2.1$: Values of K_a, pK_a, K_b, and pK_b for selected monoprotic acids.

Acid	HA	K_a	pK_a	A^-	K_b	pK_b
sulfuric acid (2nd ionization)	HSO_4^-	1.0×10^{-2}	1.99	SO_4^{2-}	9.8×10^{-13}	12.01
hydrofluoric acid	HF	6.3×10^{-4}	3.20	F^-	1.6×10^{-11}	10.80
nitrous acid	HNO_2	5.6×10^{-4}	3.25	NO_2^-	1.8×10^{-11}	10.75
formic acid	HCO_2H	1.78×10^{-4}	3.750	HCO_2^-	5.6×10^{-11}	10.25
benzoic acid	$C_6H_5CO_2H$	6.3×10^{-5}	4.20	$C_6H_5CO_2^-$	1.6×10^{-10}	9.80
acetic acid	CH_3CO_2H	1.7×10^{-5}	4.76	$CH_3CO_2^-$	5.8×10^{-10}	9.24
pyridinium ion	$C_5H_5NH^+$	5.9×10^{-6}	5.23	C_5H_5N	1.7×10^{-9}	8.77
hypochlorous acid	$HOCl$	4.0×10^{-8}	7.40	OCl^-	2.5×10^{-7}	6.60
hydrocyanic acid	HCN	6.2×10^{-10}	9.21	CN^-	1.6×10^{-5}	4.79
ammonium ion	NH_4^+	5.6×10^{-10}	9.25	NH_3	1.8×10^{-5}	4.75
water	H_2O	1.0×10^{-14}	14.00	OH^-	1.00	0.00
acetylene	C_2H_2	1×10^{-26}	26.0	HC_2^-	1×10^{12}	–12.0
ammonia	NH_3	1×10^{-35}	35.0	NH_2^-	1×10^{21}	–21.0
***The number in parentheses indicates the ionization step referred to for a polyprotic acid.**						

As can be seen from the table the K_a values for weak acids are less than one (otherwise they would not be weak) and vary over many orders of magnitude. Consequently it is customary to tabulate acid ionization constants as pK_a values:

$$pK_a = -\log K_a$$

Because pK_a values essentially place the K_a values on a negative base ten logarithmic scale, the stronger the weak acid, the lower its pK_a. Weak acids with larger K_a values will have lower pK_a values than weaker acids with smaller K_a. Moreover, each unit increase or decrease in the pK_a corresponds to a tenfold increase or decrease in the corresponding K_a.

While Arrhenius acids increase the concentration of $\mathrm{H_3O^+}$ in aqueous solution, Arrhenius bases decrease $\mathrm{H_3O^+}$. Strong bases do this stoichiometrically. Most are hydroxide salts of alkali metals or quaternary ammonium salts that dissociate completely when dissolved in water:

$$\mathrm{MOH\,(aq) \longrightarrow M^+\,(aq) + OH^-\,(aq)}$$

This added hydroxide decreases the concentration of H_3O^+ by shifting the water autoionization equilibrium towards water.

$$\mathrm{2\,H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)}$$

In contrast, most weak bases react with water to produce an equilibrium concentration of hydroxide ion according to the base dissociation reaction

$$\mathrm{B\,(aq) + H_2O\,(l) \rightleftharpoons BH^+\,(aq) + OH^-\,(aq)}$$

in which B is the weak base. The ionization constant for this reaction, called the **base ionization constant** or K_b, is typically used as a measure of a weak base's strength.

Because both hydroxide and hydronium ion are products of water autoionization, the concentrations of hydronium ion and hydroxide ion in aqueous solution will vary reciprocally with one another. This means that Arrhenius acids can be recognized as substances that decrease the hydroxide concentration and Arrhenius bases as substances that increase it.

Since the Arrhenius acid-base concept is concerned about the state of the water autoionization reaction, Arrhenius acids and bases may also be recognized by their effect on the solution pH. Arrhenius acids decrease the pH and Arrhenius bases will increase it.

NOTE

To qualify as an Arrhenius acid, upon the introduction to water, the chemical must cause, either directly or otherwise:

- an increase in the aqueous hydronium concentration,
- a decrease in the aqueous hydroxide concentration, or
- a decrease in the solution pH.

Conversely, to qualify as an Arrhenius base, upon the introduction to water, the chemical must cause, either directly or otherwise:

- a decrease in the aqueous hydronium concentration,
- an increase in the aqueous hydroxide concentration, or
- an increase in the solution pH.

Because the Arrhenius acid-base model defines acids and bases in terms of their impact on the state of an aqueous solution the Arrhenius concept is unable to describe reactions in nonaqueous solvents, gases, molten liquids, and the solid state. Consequently other models should be used to describe reactions involving the transfer of H^+ and other fragments in nonaqueous media.

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6.3: BRØNSTED-LOWRY CONCEPT

6.3.1: Brønsted-Lowry Concept

6.3.2: Rules of Thumb for thinking about the relationship between Molecular Structure and Brønsted Acidity and Basicity*

6.3.3: The acid-base behavior of binary element hydrides is determined primarily by the element's electronegativity and secondarily by the element-hydrogen bond strength

6.3.4: Brønsted-Lowry Superacids and the Hammett Acidity Function

6.3.5: Thermodynamics of Solution-Phase Brønsted Acidity and Basicity

6.3.6: Thermodynamics of Gas Phase Brønsted Acidity and Basicity

6.3.7: The Acidity of an Oxoacid is Determined by the Electronegativity and Oxidation State of the Oxoacid's Central Atom*

6.3.8: High Charge-to-Size Ratio Metal Ions Act as Brønsted Acids in Water

6.3.9: The Solvent System Acid Base Concept

6.3.10: Acid-Base Chemistry in Amphoteric Solvents and the Solvent Leveling Effect

6.3.11: Non-nucleophilic Brønsted-Lowry Superbases

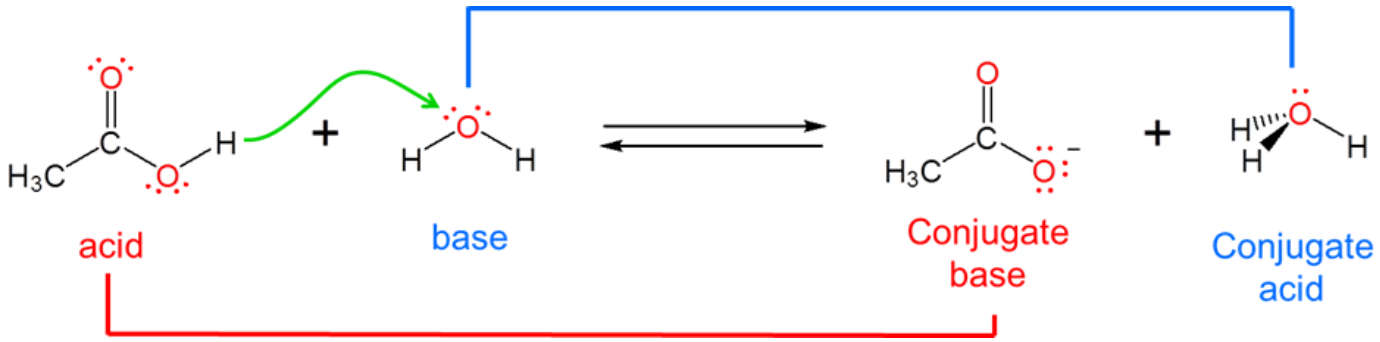
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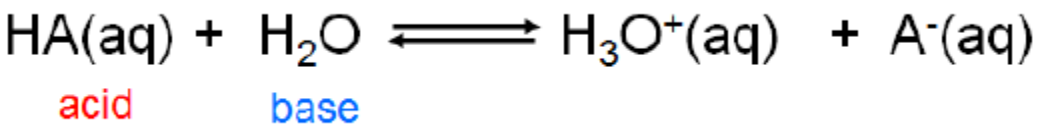
6.3.1: Brønsted-Lowry Concept

The Brønsted-Lowry acid-base concept

The Brønsted-Lowry acid-base concept overcomes the Arrhenius system's inability to describe reactions that take place outside of aqueous solution by moving the focus away from the solution and onto the acid and base themselves. It does this by redefining acid-base reactivity as involving the transfer of a hydrogen ion, H^+, between an acid and a base. Specifically, a Brønsted acid is a substance that loses an H^+ ion by donating it to a base. This means that a Brønsted base is defined as a substance which accepts H^+ from an acid when it reacts.

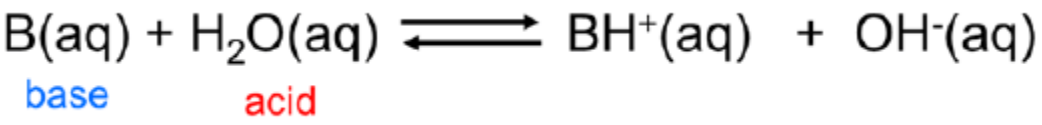


Because the Brønsted-Lowry concept is concerned with H^+ ion transfer rather than the creation of a particular chemical species, it is able to handle a diverse array of acid-base concepts. In fact, from the viewpoint of the Brønsted-Lowry concept, Arrhenius acids and bases are just a special case involving hydrogen ion donation and acceptance involving water. Arrhenius acids donate H^+ ion to water, which acts as a Brønsted base in accepting it to give H_3O^+:



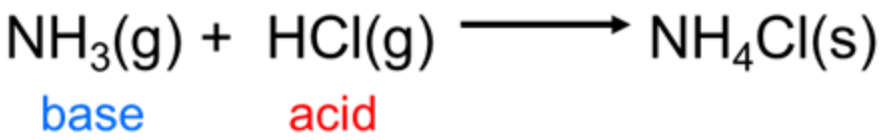
(6.3.1.1)

Similarly, Arrhenius bases act as Brønsted bases in accepting a hydrogen ion from the Brønsted acid water:



In this way it can be seen that Arrhenius acids and bases are defined in terms of their causing hydrogen ions to be donated to and abstracted from water, respectively, while Brønsted acids and bases are defined in terms of their ability to donate and accept hydrogen ions to and from anything.

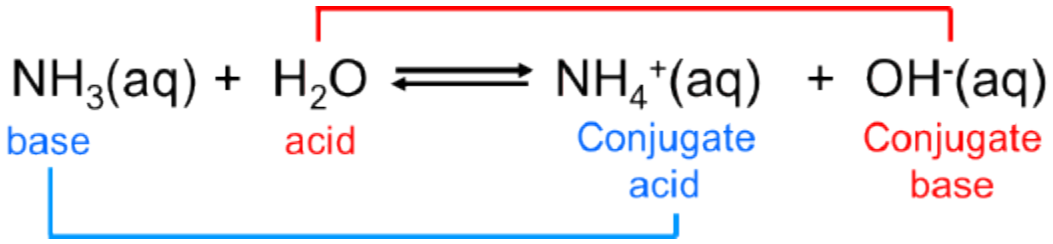
Becasue the Brønsted-Lowry concept can handle any sort of hydrogen ion transfer it readily accommodates many reactions that Arrhenius theory cannot, including those that take place outside of water, such as the reaction between gaseous hydrochloric acid and ammonia:



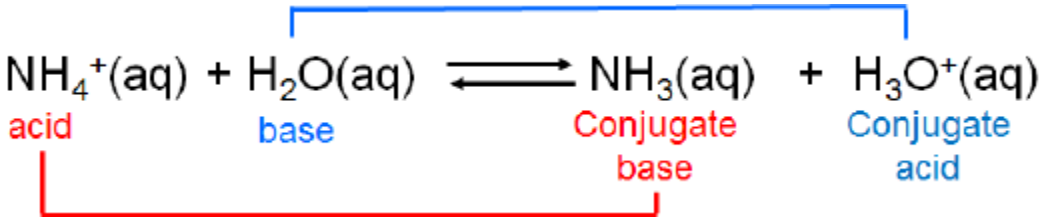
The classification of acids as strong or weak usually refers to their ability to donate or abstract hydrogen ions to or from water to give H_3O^+ and OH^-, respectively, *i.e.,* their Arrhenius acidity and basicity. However, acids and bases may be classified as strong and weak under the Brønsted-Lowry definition based on whether they completely transfer or accept hydrogen ions; it is just that in this case it is important to specify the conditions under which a given acid or base acts strong or weak. For example, acetic acid acts as a weak acid in water but is a strong acid in triethylamine, since in the latter case it completely transfers a hydrogen ion to triethylamine to give triethylammonium acetate. Alternatively, the acidity or basicity of a compound may be specified using a thermodynamic scale like the Hammett acidity.

Conjugate Acids and Bases

By redefining acids and bases in terms of hydrogen ion donation and acceptance, the Brønsted-Lowry system makes it easy to recognize that when an acid loses its hydrogen ion it becomes a substance that is capable of receiving it back again, namely, a base. Consider, for example, the base dissociation of ammonia in water. When ammonia acts as a Brønsted base and receives a hydrogen ion from water, ammonium ion and hydroxide are formed:

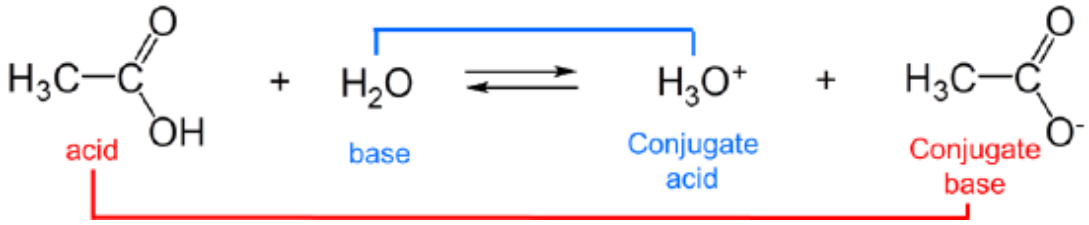


The ammonium ion is itself a weak acid that can undergo dissociation:

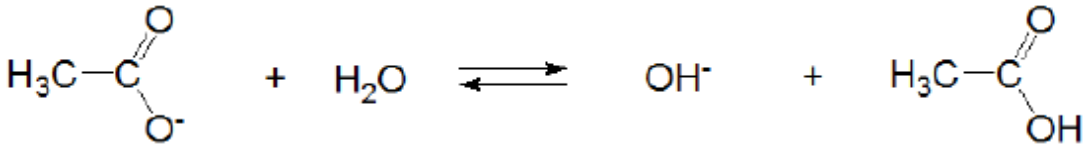


In this case ammonia and ammonium ion are acid-base conjugates. In general acids and bases that differ by a *single ionizable hydrogen ion* are said to be conjugates of one another.

The strengths of conjugates vary reciprocally with one another, so the stronger the acid the weaker the base and vice versa. For example, in water, acetic acid acts as a weak Brønsted acid:



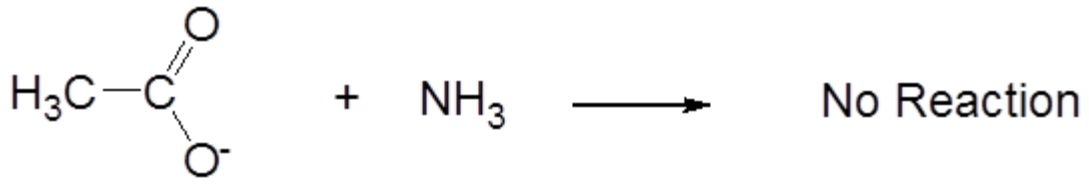
and acetic acid's conjugate base, acetate, acts as a weak Brønsted base.



However, in liquid ammonia acetic acid acts as a strong Brønsted acid:



while its conjugate base, acetate, is neutral.

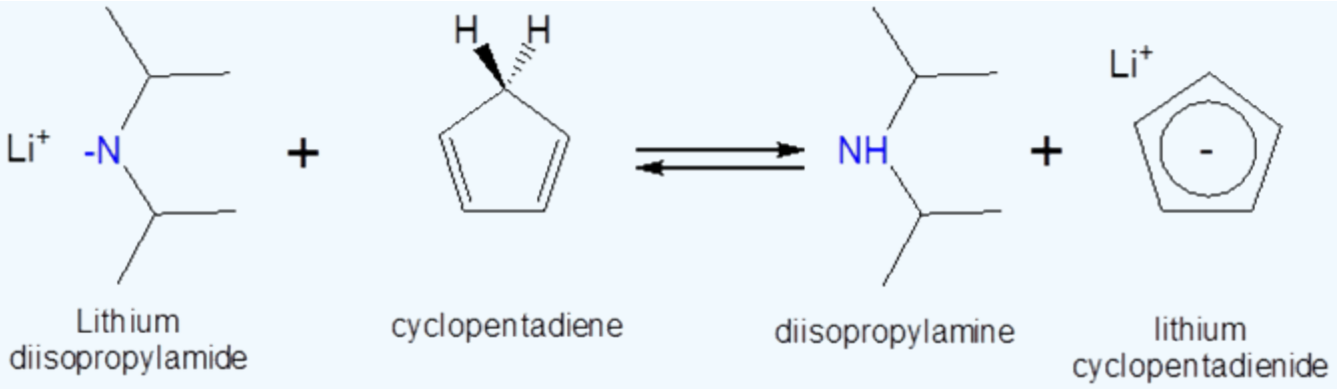


The reciprocal relationship between the strengths of acids and their conjugate bases has several consequences:

1. Under conditions when an acid or base acts as a weak acid or base its conjugate acts as weak as well. Conversely, when an acid or base acts as a strong acid or base its conjugate acts as a neutral species.
2. When a Brønsted acid and base react with one another, the equilibrium favors formation of the weakest acid-base pair. That is why the acid-base reaction between acetic acid and ammonia in liquid ammonia proceeded to give the weak acid ammonium ion and neutral acetate. This consequence is particularly important for understanding the behavior of acids and bases in nonaqueous solvents, as illustrated by the following example.

Example 6.3.1.1

Can a solution of lithium diisopropylamide in heptane be used to form lithium cyclopentadienide? The pK_a of cyclopentadiene and diisopropylamine are ~15 and 40, respectively, and the proposed reaction is as follows:



Solution: available at the end of this section.

Answers

Example 6.3.1.1

Since cyclopentadiene is a stronger acid than diisopropylamine (the stronger the acid the lower the pK_a) the equilibrium will favor protonation of the diisopropylamine by cyclopentadiene. Consequently addition of a heptane solution of lithium diisopropylamide to monomeric cyclopentadiene should give lithium cyclopentadienide.

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6.3.2: Rules of Thumb for thinking about the relationship between Molecular Structure and Brønsted Acidity and Basicity*

Because the acidity of a given substance depends on the interplay between the relatively large values of its proton affinity and the energy associated with solvation of an acid's conjugate base, it can sometimes be difficult to estimate the strength of an acid in a given solvent in the absence of detailed computations. Nevertheless a variety of simple ideas may be used to roughly estimate the relative strengths of acids. These should never be substituted for a detailed consideration of solvation but can serve as useful aids when thinking about trends and designing new Brønsted acids and bases.

Four main factors should be considered when thinking about the relationship between molecular structure and Brønsted acidity and basicity

Some simple factors that it can be helpful to consider when thinking about the strength of a given acid or base are:

1. Bond strength effects

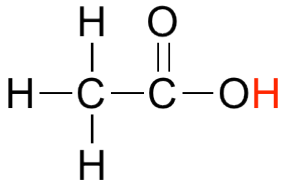
The weaker the bond to the ionizable hydrogen, the stronger the acid. Strongly bonded hydrogen ions are difficult to remove, weakly bonded ones much less so.

2. Inductive effects

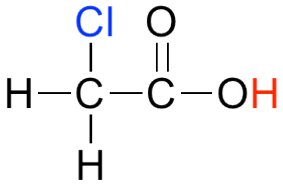
Inductive effects involve the donation or withdrawal of electrons from an atom by a group connected to it through bonds. **Electron donating groups** increase the electron density while **electron withdrawing groups** decrease it. Atoms or groups that withdraw electron density away from a center increase its acidity while those which donate electrons to the center decrease its acidity. The reasons for this follow from the heterolytic bond cleavage of acid ionization:

$$E-H \rightarrow E:^{-} + H^{+}$$

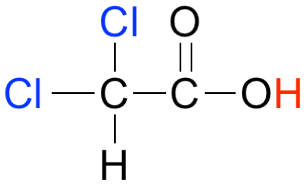
- When a bond to hydrogen is more polarized away from the H (more like $^{-\delta}E-H^{\delta+}$) it is easier to cleave off the hydrogen ion from that E-H bond. This may be seen from how the pK_a values of acetic acid and its mono-, di-, and tri-chlorinated derivatives decreases with the extent of chlorination of the methyl group.



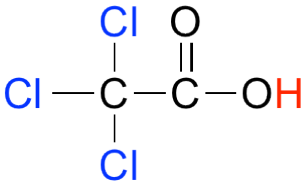
$pK_a = 4.8$



$pK_a = 2.8$



$pK_a = 1.3$



$pK_a = 0.64$

- Polarized E-H bonds also make for stronger Brønsted acids because the resulting $E:^{-}$ conjugate base is more stable.

This leads to the third major factor that should be considered when thinking about acid strength.

3. Electronegativity Effects, Especially as Seen Using the Conjugate Base Principle

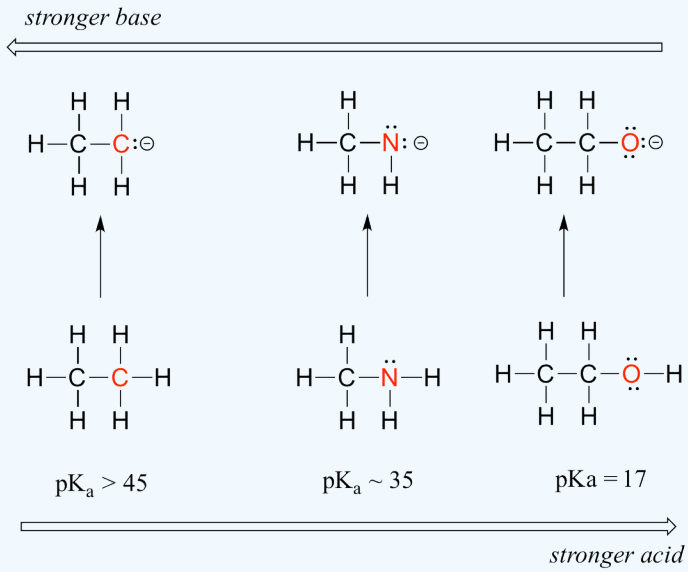
The more stable the acid's conjugate base, the stronger the Brønsted acid. All reactions are in theory reversible, and so when considering the propensity of an acid to donate hydrogen ions, it can be helpful to look at the reverse of hydrogen ion donation, namely, protonation of the acid's conjugate base. If deprotonation of the acid gives a very stable conjugate base then deprotonation of the acid will be more favorable.

Two factors determine the stability of an acid's conjugate base.

- Conjugate bases in which a small amount of charge is on a large atom, spread over a large number of atoms, and on electronegative atoms tend to be more stable. Conjugate bases in which a small amount of charge is spread over a large number of electronegative atoms are especially stable. That is why magic acid, a mixture of HF and SbF_5, is so acidic: the single negative charge on its conjugate base is spread over six F atoms and on Sb in SbF_6^-.

- Groups which tend to inductively polarize E-H bonds also tend to stabilize the conjugate base formed when that bond ionizes. In general, the more electronegative an atom, the better able it is to bear a negative charge. All other things being equal, weaker bases have negative charges on more electronegative atoms; stronger bases have negative charges on fewer electronegative atoms. This is apparent from how inductive effects lead to an increase in the acidity of E-H bonds as the electronegativity of the element to which the acidic hydrogen is bound increases from left to right across a row of the periodic table. This horizontal periodic trend in acidity and basicity is apparent from the homologous series below:

Horizontal periodic trend in acidity and basicity



Notice how the inductive polarization of the E-H bond, which results in greater acidity, contributes to the greater stability of the conjugate base. For the case above, look at where the negative charge ends up in each conjugate base. In the conjugate base of ethane, the negative charge is borne by a carbon atom, while on the conjugate base of methylamine and ethanol the negative charge is located on a nitrogen and an oxygen, respectively. Remember that electronegativity also increases as we move from left to right along a row of the periodic table, meaning that oxygen is the most electronegative of the three atoms, and carbon the least.

Thus, the methoxide anion is the most stable (lowest energy, least basic) of the three conjugate bases, and the ethyl carbanion anion is the least stable (highest energy, most basic). Conversely, ethanol is the strongest acid, and ethane the weakest acid.

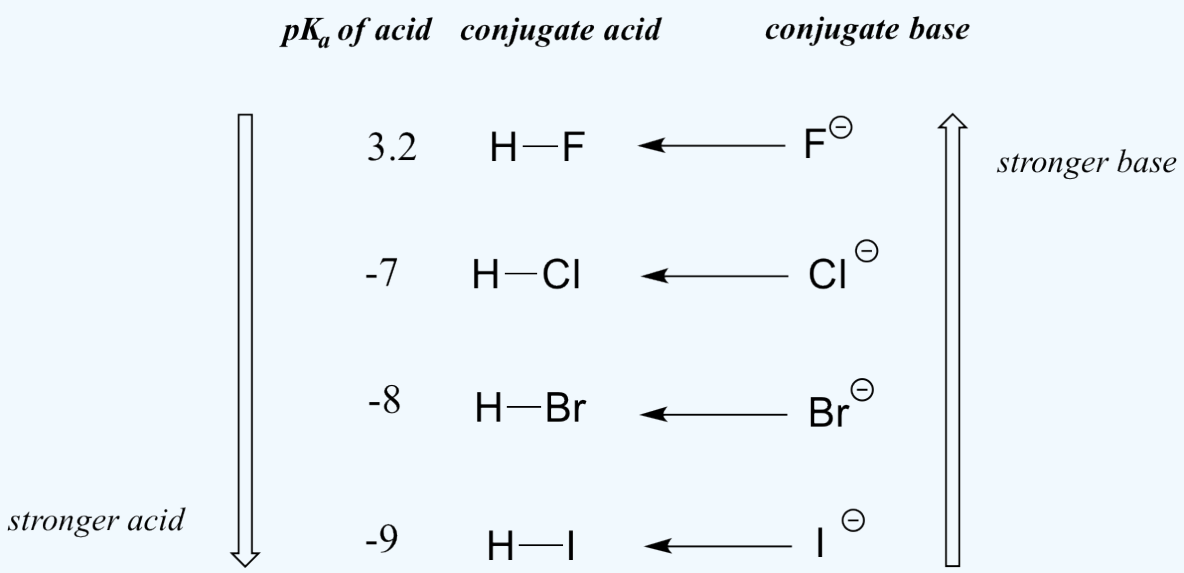
4. Size effects on Bond Strength and Charge Delocalization

There are two classes of size effects to be considered:

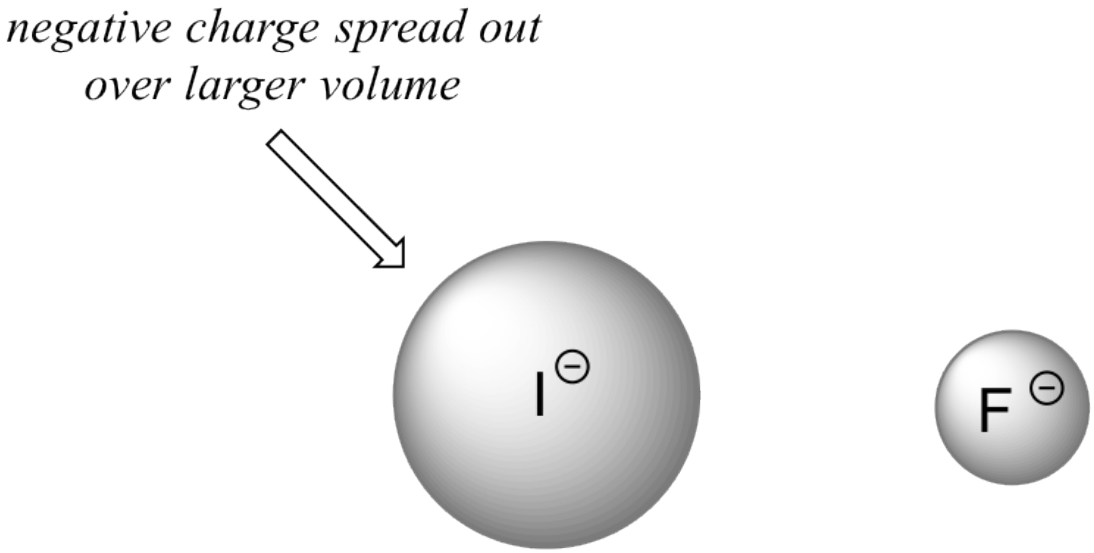
a. The larger the atom to which a H is bound in an E-H bond, the weaker the bond and the stronger the acid.
b. Increased charge delocalization with increasing size. Electrostatic charges, whether positive or negative, are more stable when they are 'spread out' over a larger area. The greater the volume over which charge is spread in the acid's conjugate base, the more stable that base and the stronger the acid.

The impact of size effects are readily seen in the increase in acidity of the hydrogen halides, as illustrated by the vertical periodic trend in acidity and basicity below:

Vertical periodic trend in acidity and basicity



On going vertically down the halogen group from F to I the H-X bond strength decreases in the acid, making it easier to ionize, while the charge becomes more diffuse in the resultant X^- ion, making the conjugate base more stable.

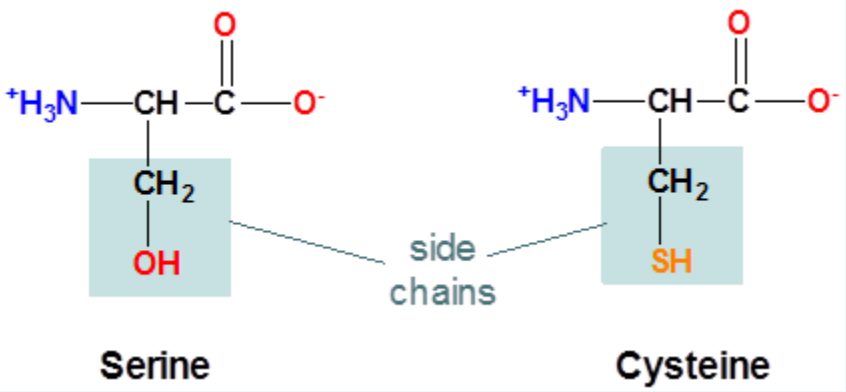


The increase in the acidity of the hydrogen halides down a group suggests that size effects are more important than inductive effects. In the case of the hydrogen halides, because fluorine is the most electronegative halogen element, we might expect fluoride to also be the least basic halogen ion. But in fact, it is the *least* stable, and the most basic! It turns out that when moving vertically in the periodic table, the *size* of the atom trumps its electronegativity with regard to basicity. The atomic radius of iodine

is approximately twice that of fluorine, so in an iodide ion, the negative charge is spread out over a significantly larger volume.

Exercise

The structure of the amino acids serine and cysteine are shown below. Which do you expect will have the more acidic side chain?



Answer available at the end of this section.

Contributors and Attributions

Stephen M. Contakes (Westmont College),

* who expanded this section from a combination of

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https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Book%3A_Organic_Chemistry_with_a_Biological_Emphasis_(Soderberg)/Chapter_07%3A_Organic_compounds_as_acids_and_base/7.3%3A_Structural_effects_on_acidity_and_basicity

Answers

Exercise

Cysteine, since the cysteine side chain possesses an ionizable S-H bond while serine's side chain possesses an ionizable O-H bond. Since S is larger than O, cysteine's S-H bond will be weaker than serine's O-H bond, and the cysteine side chain's thiolate conjugate base more stable than the serine side chain's alkoxide conjugate base. In fact, the side chain pK_a of cysteine is 8.3 while serine is considered to be nonionizable under physiological conditions.

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6.3.3: The acid-base behavior of binary element hydrides is determined primarily by the element's electronegativity and secondarily by the element-hydrogen bond strength

The compounds formed between the elements and hydrogen are called binary hydrides. All such compounds can in principle act as Brønsted acids in reactions with a suitably strong base. However, as the electronegativity decreases down a group and increases from left to right across the periodic table, the acidity of binary hydrides increases. In fact, on the left side of the periodic table the hydrides of extremely electropositive alkali and alkaline earth metals are not acidic but basic. They are perhaps best considered to be ionic salts of the hydride ion (H^-). Consequently substances such as NaH and CaH_2 tend to act as Brønsted bases in their reactions.

$$NaH\,(s) + H_2O\,(l) \longrightarrow Na^+\,(aq) + OH^-\,(aq) + H_2\,(g)$$

$$CaH_2\,(s) + 2\,H_2O\,(l) \longrightarrow Ca^{2+}\,(aq) + 2\,OH^-\,(aq) + 2\,H_2\,(g)$$

On the right side of the periodic table the binary hydrides of the nonmetals exhibit appreciable acidity.

$$HBr\,(aq) + H_2O\,(l) \longrightarrow H^+\,(aq) + Br^-\,(aq)$$

For this reason the binary nonmetal hydrides are termed acidic hydrides. Nevertheless not all are equally acidic. The dilute aqueous acid ionization constants for these hydrides are given in Figure 6.3.3.1. As can be seen from the constants in Figure 6.3.3.2, the ability of the hydrides to transfer a hydrogen to water increases across a period and down a group.

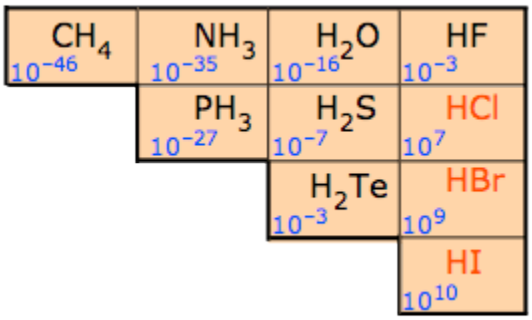


Figure 6.3.3.1: The acid ionization constants of nonmetal hydrides increase across a period and down a group. (CC BY-NC 3.0; Stephen Lower via Chem1)

These trends are largely due to changes in the electronegativity and size of the nonmetal atom:

1. Foing across a period, the acid strength increases as there is an increase in electronegativity and the molecule gets more polar, with the hydrogen getting a larger partial positive charge. This makes it easier to heterolytically cleave the E-H bond to produce a stable anion.

$$E - H \rightarrow E:^- + H^+$$

2. Going down a group, the acid strength increases because the bond strength decreases as a function of increasing size of the nonmetal, and this has a larger effect than the electronegativity. In fact HF is a weak acid because it is so small that the hydrogen-fluorine bond is so strong that it is difficult to break. Remember, the weaker the bond, the stronger the acid strength. This is further illustrated in Table 6.3.3.1, where the weakest bond has produced the strongest acid.

Table 6.3.3.1 Acid strength as function of bond energy

Relative Acid Strength	HF	<<	HCl	<	HBr	<	HI
H–X Bond Energy (kJ/mol)	570		432		366		298
K_a	10^{-3}		10^{7}		10^{9}		10^{10}

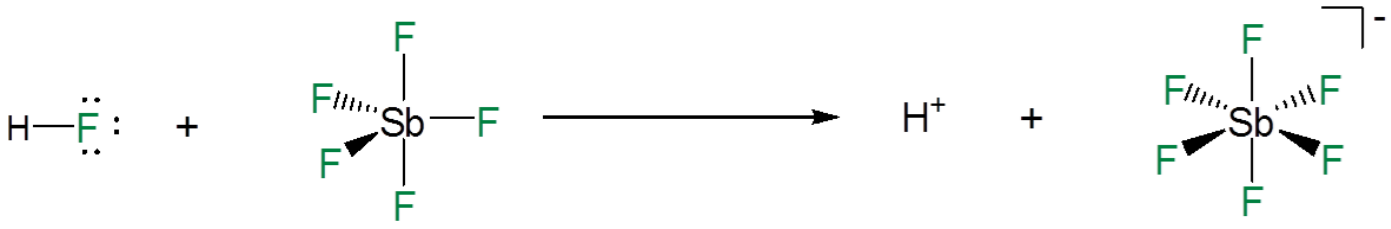
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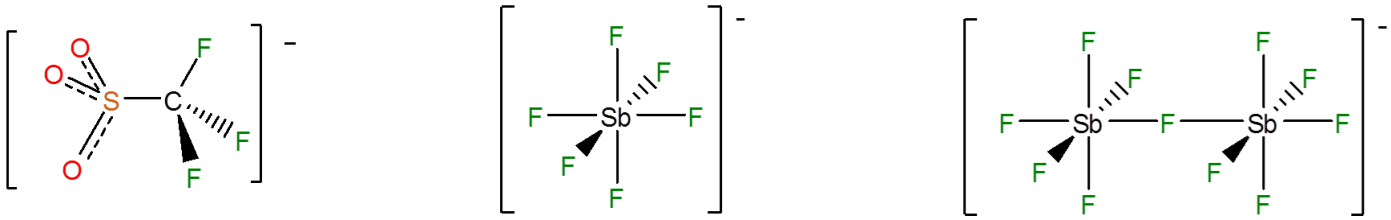
6.3.4: Brønsted-Lowry Superacids and the Hammett Acidity Function

Acids with an acidity greater than that of sulfuric acid are termed superacids.

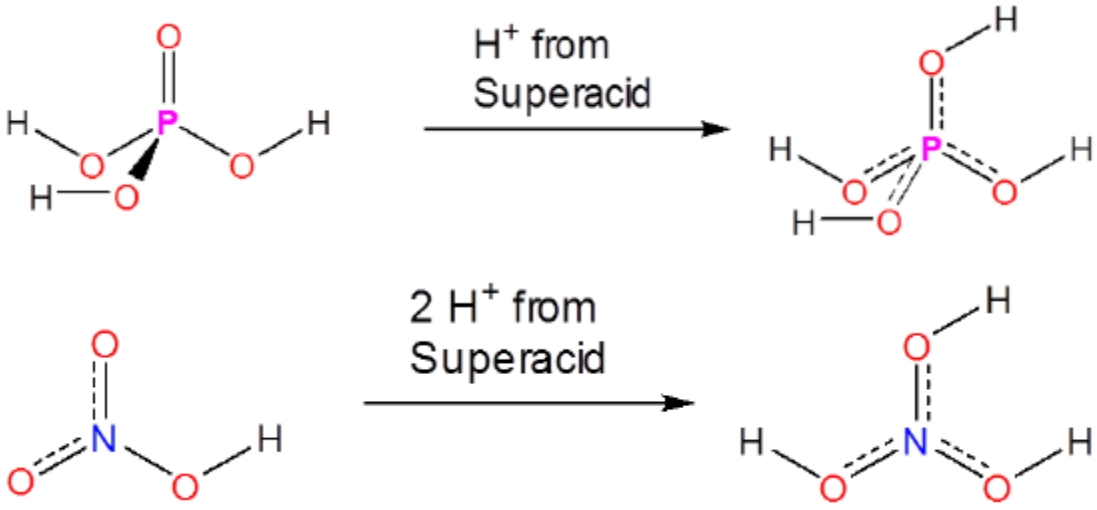
Superacids are able to dissociate completely because when they do so they give an extremely stable anion in which the residual negative charge is distributed among multiple electronegative atoms. For example, in mixtures of HF and antimony pentaflouride the dissociation of a hydrogen ion from the HF is promoted by the formation of a Lewis acid-base adduct between the HF flouride and $\mathrm{SbF_5}$.

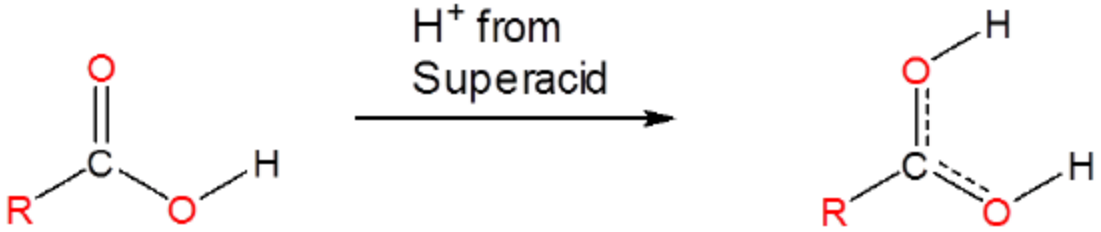


This gives extremely stable anions like $\mathrm{SbF_6^-}$ and $\mathrm{Sb_2F_{11}^-}$, in which a single negative charge is delocalized among many electronegative groups and atoms; of these, CF_3 and F are particularly common.



Superacids are able to protonate species that would otherwise act as neutral or even acidic species in water or aprotic media. Phosphoric, nitric, carboxylic, and other ordinary acids are all protonated when dissolved in superacids:





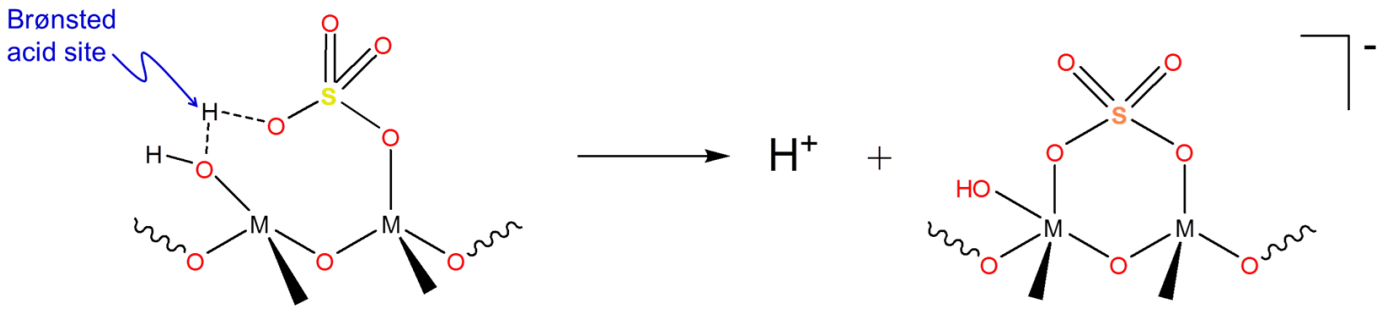
However, superacids also protonate many species that are not usually considered to have acid base properties. Even alkanes can be protonated and, in fact, superacids are used to generate carbocations in a variety of synthetic applications. They do this by protonating alkanes to give unstable species which then decompose to carbocations in further reactions. For example, mixtures of $\mathrm{SbF_5}$ and $\mathrm{FSO_3H}$ called **Magic Acid** can even protonate methane, which gives a $\mathrm{CH_5}^+$ cation:

$$\mathrm{F_5Sb + FSO_3H + CH_4 \longrightarrow F_5Sb{-}OSO_2F^- + CH_5}^+$$

which subsequently decomposes to give an ordinary carbocation

$$\mathrm{CH_5}^+ \longrightarrow \mathrm{CH_3}^+ + \mathrm{H_2}$$

Since liquid superacids are extremely corrosive and can be costly to separate from reaction mixtures, solid superacids are used industrially instead. The main use for these solid superacids is to generate carbocations for use in hydrocarbon isomerization and alkylation chemistry. Many solid superacids consist of sulfuric acid/sulfates attached to a metal oxide surface to give structures similar to that shown below:



\[]\

These structures exhibit Hammett acidity parameters in the superacid range. However, the mechanism by which these solid superacids generate carbocations isn't entirely clear since they contain both Brønsted acid sites (at OH) and Lewis acid sites (at M) that could be involved in the carbocation generation process.

The Hammett Acidity Function

The acid ionization constants typically used to measure weak acids' acidity are only valid in dilute aqueous solutions. A more general measure of acidity that in principle is valid for any acid is the Hammett acidity function. The **Hammett acidity function,** H_o**,** is analogous to the pH used to describe the acidity of aqueous solutions but instead refers to the pure acid:

$$pH = -\log(A_{\mathrm{H^+}}) \qquad \text{(for dilute aqueous solutions)}$$

$$H_o = -\log(A_{\mathrm{H^+}}) \qquad \text{(for pure acids)}$$

where $\mathrm{A_{H^+}}$ is the activity of $\mathrm{H^+}$, which in many dilute solutions is approximately equal to the hydrogen ion concentration (that is why the pH is often defined in terms of [H^+].

At first glance it may seem that the Hammett acidity function is simply a generalization of the pH concept for use in nonaqueous solutions. This is especially so since in water the the pH and H_o do refer to the same quantity. However, the hydrogen ion of the Hammett acidity function is more than a generalization of the pH concept. Its real genius lies in that A_{H^+} does not necessarily represent an actual chemical species of identity H^+ but rather an acid's ability to protonate weak indicator bases, B, specifically

via the reaction:

$$\mathrm{H^+ + B \rightleftharpoons BH^+}$$

This reaction gives the weak acid BH^+ which can ionize in the reaction that is the reverse of that above:

$$\mathrm{BH^+ \rightleftharpoons B + H^+}$$

The extent of this ionization will depend on A_{H^+} according to

$$K_{ion} = \frac{[\mathrm{BH^+}]}{A_{\mathrm{H^+}}[B]}$$

Taking the negative logarithm of both sides and rearranging gives the Henderson-Hasselbach equation for the indicator base, B:

$$-K_{ion} = -\log A_{\mathrm{H^+}} - \log \frac{[\mathrm{BH^+}]}{[\mathrm{B}]}$$

which can be rearranged to give

$$pK_{ion} = H_o - \log \frac{[\mathrm{BH^+}]}{[\mathrm{B}]}$$

or

$$H_o = pK_{ion} - \log \frac{[\mathrm{BH^+}]}{[\mathrm{B}]}$$

From this it is apparent that H_o represents an acid's ability to donate a hydrogen ion, as measured in terms of its ability to shift the equilibrium between B and $\mathrm{BH^+}$ towards $\mathrm{BH^+}$. More negative values of H_o correspond to stronger Brønsted acids with a greater hydrogen ion transfer ability while less negative ones indicate weaker Brønsted acidity.

The value of H_o has been experimentally determined for a number of strong acids by measuring the ratio of $\mathrm{BH^+}$ to B using weakly basic aromatics like 2,4,6-trinitroaniline, various nitrotoluenes, and triflouromethylbenzene as the indicator base, B. Some of these Hammett acidity parameters are shown in Table $6.3.4.1$.

As can be seen from table $6.3.4.1$, sulfuric acid has a Hammett acidity of -12. Since superacids are defined as acids with greater Brønsted acidity than pure sulfuric acid this means that superacids have $(H_o < -12)$.

Table $6.3.4.1$: Hammett Acidity for selected strong acids. a. Difficult to estimate reliably. b. Depends on the SF_5 to FSO_3H ratio.

Acid	H_o
Sulfuric acid, $\mathrm{H_2SO_4}$	-12
Perchloric Acid, $\mathrm{HClO_4}$	-13.0
Triflic acid (triflouromethanesulfonic acid), $\mathrm{CF_3SO_3H}$	-14.6
Flourosulfonic acid, $\mathrm{FSO_3H}$	-15.6
Magic Acid, $\mathrm{F_5Sb{-}{-}{-}FSO_3H}$	-24 to -21[a]
Fluoroantimonic acid, $\mathrm{SbF_5{-}{-}{-}FH}$	-24 to -21[a,b]

References

1. Gillespie, R. J.; T. E. Peel, T. E.; Robinson, E.A. *J. Am. Chem. Soc.* 1971, *93(20)*, 5083-5087.
2. Gillespie, R. J.; T. E. Peel, T. E. *J. Am. Chem. Soc.*, 1973, 95(16), 5173-5178.3.
3. Olah, George A. *Superacid chemistry, 2nd ed.* Hoboken, N.J.: Wiley. 2009.

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6.3.5: Thermodynamics of Solution-Phase Brønsted Acidity and Basicity

The behavior of Brønsted-Lowry acids and bases in solution is heavily influenced by solvation

This is particularly true in aqueous systems in which the energies and entropies of hydration can be quite significant. Consider the enthalpy and entropy changes for the dissociation of a number of acids in dilute aqueous solution at 25°C as given in Table 6.3.5.1.

Table 6.3.5.1: Thermochemical parameters for acid dissociation of selected inorganic acids.[1,2]

Acid	ΔS° (J/mol-K)	$-T \times \Delta S^\circ$ (kJ/mol)	ΔH° (kJ/mol)	ΔG° (kJ/mol)	K_a (calcd. from ΔG°)
HF	-102	30	-16	14	6.8×10^{-4}
HCl	-35	10	-57	-47	10^{8}
HBr	-13	4	-65	-61	10^{10}
HI	11	-3	-62	-65	10^{11}
HClO	-95.4	28.4	13.9	42.3	4×10^{-8}
$HClO_2$	-86.6	25.8	-14.6	11.2	1.1×10^{-2}
$H_3PO_4 \rightarrow H^+ + H_2PO_4^-$	-66.9	20.0	-7.9	12.1	7.9×10^{-3}
$CH_3CO_2H \rightarrow H^+ + CH_3CO_2^-$	-92.4	27.5	-0.4	27.1	1.8×10^{-5}

As can be seen from the data in Table 6.3.5.1, the major driving force for dissociation of inorganic acids is the enthalpy of dissociation, which is exothermic for all of the acids listed except very weakly acidic $HClO$. In contrast, the entropy term usually disfavors dissociation since it is negative for all acids except weakly polar HI (for which it contributes little to the overall free energy of dissociation). The situation is exactly reversed in the case of acetic acid, CH_3CO_2H, for which the enthalphly of dissociation is small and the entropy is the dominant contributor to the free energy.

Further insight into the factors which govern Brønsted acid strength in aqueous solution may be gained by examining the relative contributions of heterolytic H-A bond breaking and hydration to the enthalpy of dissociation. This is done using the thermodynamic cycle depicted in Figure 6.3.5.1.

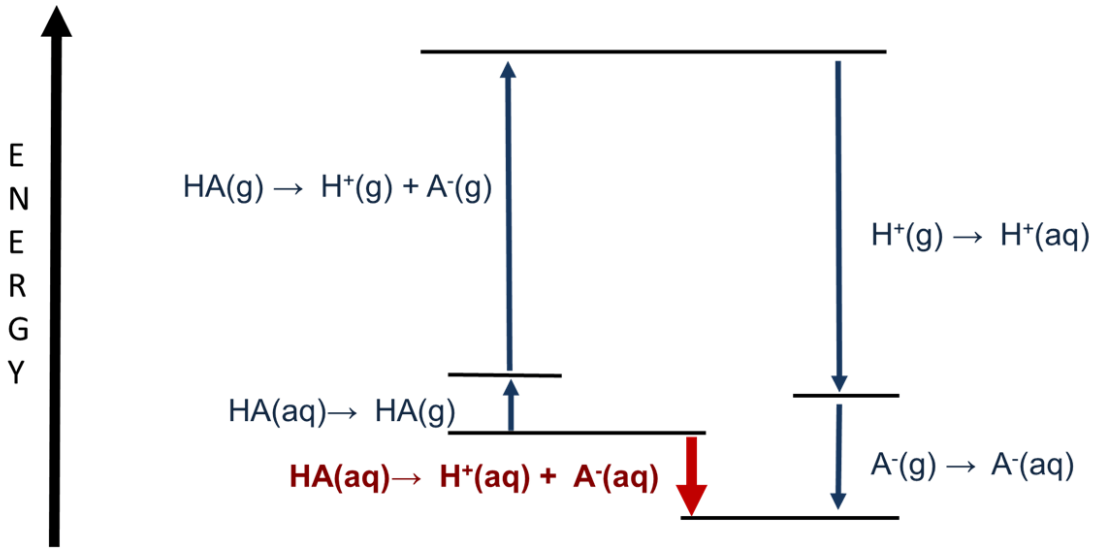


Figure 6.3.5.1: Thermodynamic cycle showing the contributions of gas phase bond dissociation and solvation to the enthalpy of acid dissociation. This scheme is more than just a way to think about the relative importance of the various contributions ot the acid dissociation enthalpy, though. Since weak acid ionization is incomplete it can be difficult to determine the enthalpy of ionization for weak acids directly. In these cases it can be easier to determine the gas phase bond dissociation energy (proton affinity) and solvation energies and then calculate the acid ionization enthalpy using Hess' Law.

As can be seen from Figure 6.3.5.1, while most of the process involves solvation energies, the heterolytic bond dissociation enthalpy is also a major factor in determining the acid dissociation enthalpy. The heterolytic bond dissociation energy step is a gas phase Brønsted acid base reaction:

$$\mathrm{HA\,(g) \longrightarrow H^+\,(g) + A^-\,(g)}$$

Consequently it will be important to consider gas phase acidity before examining the thermodynamics of acid ionization further.

References

1. The data for inorganic acids is compiled from or calculated from data compiled in Dasent, W. E. Inorganic Energetics: An Introduction, 2nd ed. Cambridge University Press, 1982, pp. 168-170.
2. The data for acetic acid is calculated from the data given in Meissler, G.L.; Fischer, P.J.; Tarr, D.A. Inorganic Chemistry, 5th ed. Pearson, 2014, pg. 175.

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6.3.6: Thermodynamics of Gas Phase Brønsted Acidity and Basicity

Proton Affinity and Gas Phase Acidity/Basicity Describe Thermodynamic Aspects of Hydrogen Ion Transfer

Defining acidity in terms of hydrogen ion donation and acceptance within the Brønsted-Lowry acid base concept allows for the understanding of acidity and basicity in a variety of liquid, solid, and gaseous media. The latter are particularly important for understanding the thermodynamics of hydrogen ion donation and acceptance since the energies of gas phase species are uninfluenced by solvation factors. These reactions are perhaps best thought of in terms of the association of a hydrogen ion and a base, B.

Formally the gas phase **proton affinity (PA)** of B is defined as the negative of the enthalpy change for the its association with hydrogen:

$$\mathrm{H^+\,(g) + B\,(g) \rightleftharpoons BH^+\,(g)} \tag{6.3.6.1}$$

where ΔH_{rxn} is the Proton Affinity of B.

However, it is simpler to think about the PA in terms of the reverse reaction of Equation 6.3.6.1, which describes the dissociation of $\mathrm{BH^+}$:

$$\mathrm{BH^+\,(g) \rightleftharpoons H^+\,(g) + B\,(g)}$$

where ΔH_{rxn} is the PA of B and is also the **heterolytic bond dissociation enthalpy,** from which it can be seen that the proton affinity is just the enthalpy for heterolytic cleavage of the $\mathrm{H{-}B}$ bond.

The **absolute or gas phase basicity (GB)** of B is the negative of the Gibb's free energy change for the same reaction:

$$\mathrm{H^+\,(g) + B\,(g) \rightleftharpoons BH^+\,(g)}$$

where $\Delta\ G_{rxn}$ is the negative of the Absolute or Gas phase basicity of B.

Again, it is simpler to think about the GB of B as the free energy change upon heterolytic dissociation of the $\mathrm{B{-}H}$ bond in $\mathrm{BH^+}$:

$$\mathrm{BH^+\,(g) \rightleftharpoons H^+\,(g) + B\,(g)}$$

where ΔG_{rxn} is the Absolute or Gas phase basicity of B and is also the **free energy for heterolytic bond dissociation**.

Because both PA and GB values correspond to heterolytic bond dissociation, more positive values of the PA and GB correspond to higher thermodynamic affinity between B and $\mathrm{H^+}$.

Note that the **gas phase acidity (GA)** is a very similar quantity to the gas phase basicity, being defined for an acid of formula HA as the Gibb's free energy change for:[††]

$$\mathrm{HA\,(g) \rightleftharpoons H^+\,(g) + A^-\,(g)}$$

where ΔG_{rxn} is the Absolute or Gas phase acidity of HA.

Since $\mathrm{A^-}$ and B are just both convenient shorthand notations for a Brønsted base gas phase acidity and gas phase basicity, both refer to ionization of a gas phase acid. The quantities only differ in that gas phase acidities correspond to ionization of a neutral acid, HA, while gas phase basicities correspond to ionization of a monocationic base, $\mathrm{BH^+}$. For many purposes this difference may be ignored.

Gas phase proton affinities and acidities/basicities have been determined for a large number of species and are available through

the NIST chemistry webbook. Selected values are given in Table 6.3.6.1. As can be seen from the data in Table 6.3.6.1, typical proton affinity and gas phase acidity values fall between 600 and 1750 kJ/mol, with proton affinities being slightly larger by 20-50 kJ/mol.

Table 6.3.6.1: Gas phase proton affinity and acidity values for selected species. Data are taken from the NIST Chemistry Webbook. When more than one value is available, the number presented below represents the average of those reported (after rejection of outliers at the 90% confidence interval using a G-test).

Base	Proton Affinity (kJ/mol)	Gas Phase Acidity (kJ/mol)
hexafluorobenzene C_6F_6	648	
H_2O	691	
benzene	750	
NH_3	854	819
aniline	882	851
pyridine	930	898
triethylamine	982	951
ClO_4^-	1238	1201
ClO_3^-	1310	1284
I^-	1313	1293
Br^-	1349	1328
NO_3^-	1368	1330
Cl^-	1390	1367
NO_2^-	1424	1396
ClO_2^-	1488	1461
$anilide^-$	1537	1506
F^-	1555	1524
CH_3O^-	1573	1570
O^-	1601	1576
$H:^-$	1675	1649
$NH_2:^-$	1686	1656
$FCH_2:^-$	1734	1676
$CH_3CH_2:^-$	1758	1723

Proton Affinity and Gas Phase Acidity/Basicity Data are Consistent with Expected Acidity Trends but also Illuminate the Role of Solvation and Dissociation Entropy in Solution Phase Acid-Base Behavior

Two lessons may be derived from gas phase acidity and proton affinity data:

1. The gas phase proton affinities and acidities of neutral and anionic bases are large, positive, and strongly disfavor acid ionization. As shown in Figure 6.3.3.1, acid ionization is driven by the high solvation energy of the hydrogen ion ($\Delta H^o = -1091$ $\mathrm{kJ/mol}$) with smaller contributions from solvation of the acid's conjugate base.
2. Trends in gas phase proton affinities and acidities indicate the importance of solvation for acid-base behavior in solution. As can be seen from the data in Table 6.3.6.1, water is a very weak base in the gas phase. In fact, water's proton affinity is

even lower than the proton affinity of the conjugate bases of most strong acids. This means that transfer of hydrogen ion from most strong acids to water is endothermic in the gas phase. For instance, for

$$\mathrm{HCl\,(g) + H_2O\,(g) \longrightarrow H_3O^+\,(g) + Cl^-\,(g)} \qquad \Delta H = +699 kJ/mol$$

In other words, based on the thermodynamics of hydrogen ion transfer in the gas phase, most strong Brønsted acids should not act as Brønsted acids towards water. Nevertheless they do act as strong acids. This means that the solvation energy terms in the thermodynamic cycle of Figure 6.3.3.1 (possibly assisted by entropic effects) are driving hydrogen ion transfer in solution.

This is confirmed by the values for the proton affinities and hydration energies for the hydrohalic acids given in Table 6.3.6.2 . For these acids the solvation energies for the hydrogen ion (-1130 kJ/mol) and anions (*e.g.,* for Cl^-, -363 kJ/mol) are much larger than the hydration energies of the neutral acids and contribute towards an overall exothermic enthalpy of acid dissociation in water.

Table 6.3.6.2 Contribution of heterolytic bond dissociation and hydration (hyd) energies to the enthalpy of dissociation for the hydrohalic acids.1

Acid	Proton Affinity (PA) $H-A(g) \rightarrow H^+(g) + A^-(g)$ (kJ/mol)	ΔH_{hyd} *for* HX $HX(aq) \rightarrow HX(g)$ (kJ/mol)	$\Delta\ H_{hyd}$ *for* H^+ $H^+(g) \rightarrow H^+(aq)$ (kJ/mol)	$\Delta\ H_{hyd}$ *for* X^- $X^-(g) \rightarrow X^-(aq)$ (kJ/mol)	Total (acid dissociation enthalpy) $H-A(aq) \rightarrow H^+(aq) + A^-(aq)$ (kJ/mol)
HF	+1555	+48	-1091	-524	-12
HCl	+1390	+18	-1091	-378	-61
HBr	+1349	+21	-1091	-348	-69
HI	+1313	+23	-1091	-308	-63

Although solvation plays a crucial role in determining a substance's acid-base behavior in solution, an acid's strength cannot be predicted from solvation energies alone. This is because it is difficult to predict the relative importance of the large proton affinity and conjugate base hydration enthalpy terms (and to a lesser extent the acid hydration enthalpy) in a given case. This is also illustrated by the data in Table 6.3.6.2. The hydrohalic acid bond dissociation energy and halide hydration enthalpy both decrease in magnitude by approximately the same amount on going from HCl to HI, so that the acid dissociation enthalpies remain approximately constant. While proton affinities and hydration enthalpies often change in tandem, it is not always the case that they change by similar magnitudes. This may be seen by comparing the data shown for HF with those for the other hydrohalic acids in Table 6.3.6.2. In the case of HF, the 165 kJ/mol increase in proton affinity between HCl and HF is not compensated for by the -146 kJ/mol decrease in hydration energy on going from Cl^- to F^- (due to fluorine's ability to form hydrogen bonds), leading HF to exhibit an anomalously small ionization enthalpy.

How Gas phase acidity values are measured

Gas phase acidities can be conveniently determined thermochemically relative to a standard by measuring the relative affinity of a hydrogen ion for two bases, B_1 & B_2, by using mass spectrometry to follow the equilibrium of the hydrogen ion transfer reaction:

$$HB_1^+ + B_2 \rightarrow B_1 + HB_2^+$$

The free energy change of this reaction may be found from the relative populations of HB_1^+ and HB_2^+ using mass spectrometry:

$$\Delta G = \frac{[B_1][HB_2^+]}{[HB_1^+][B_2]}$$

and the enthalpies and entropies of reaction from the temperature dependence of the free energies (since $\Delta G = \Delta H - T \times \Delta S$.

Gas phase acidity values determined from hydrogen ion transfer equilibrium values are called relative acidities. In contrast, absolute acidities are those which can be traced back to the standard forms of the elements at standard temperature and pressure. Absolute acidities can be found from relative ones as long as the absolute acidity of at least one of the bases is known. Fortunately, the absolute affinities of a number of gas phase acidity standards have been determined thermochemically. For instance, the gas phase proton affinity of H-A corresponds to the sum of the following processes:

$$H-A(g) \rightleftharpoons H(g) + A(g) \qquad \Delta H = Bond\ Dissociation\ Energy\ of\ HA,\ BDE_{HA}$$

$$H(g) \rightleftharpoons H^+(g) + e^-(g) \qquad \Delta H = Ionization\ Energy\ of\ H,\ IE_H$$

$$A(g) + e^-(g) \rightleftharpoons A^-(g) \qquad \Delta H = Electron\ Affinity\ of\ A^-,\ IE_A$$

$$HA(g) \rightleftharpoons H^+(g) + A^-(g) \qquad \Delta H_{rxn} = Proton\ affinity\ of\ A^-$$

so that

$$Proton\ Affinity\ of\ A^- = DeltaH_{rxn} = BDE_{HA} + IE_H - EA_A$$

For a more detailed explanation of how gas phase acidities are found see the gas phase ion thermochemistry page at the NIST chemistry webbook.

References

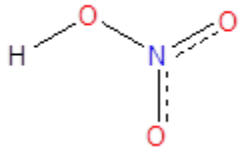
1. Proton affinities are taken from the NIST NIST Chemistry Webbook. Hydration enthalpies are from Dasent, W. E. *Inorganic Energetics: An Introduction*, 2nd ed. Cambridge University Press, 1982, pp. 168-170.

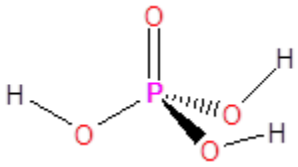
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6.3.7: The Acidity of an Oxoacid is Determined by the Electronegativity and Oxidation State of the Oxoacid's Central Atom*

Oxyacids (also known as **oxoacids**) are compounds of the general formula $\mathrm{H}_n\mathrm{EO}_m$, where E is a nonmetal or early transition metal and the acidic hydrogens are attached directly to oxygen (not E). This class of compounds includes such well-know acids as nitric acid ($\mathrm{HNO_3}$) and phosphoric acid, ($\mathrm{H_3PO_4}$).





The acidity of oxyacids follows three trends:

Trend 1: In a homologous series the acidity increases with the electronegativity of the central atom

Elements in the same group frequently form oxyacids of the same general formula. For example, chlorine, bromine, and iodine all form oxyacids of formula HOE: hypochlorous, hypobromous and hypoiodous acids. In the case of these homologous oxyacids, the acidity is largely determined by the electronegativity of the central element. Central atoms that are better able to inductively pull electron density towards themselves make the oxygen-hydrogen bond that is to be ionized more polar and stabilize the conjugate base, OE^-. Thus the acid strength in such homologous series increases with the electronegativity of the central atom. This may be seen from the data for the hypohalous acids in Table $6.3.7.1$, in which the acid strength increases with the electronegativity of the halogen so that the order of acidity is:

$$\mathrm{HClO} > \mathrm{HBrO} > \mathrm{HIO}$$

and the order of basicity is:

$$\mathrm{ClO}^- < \mathrm{BrO}^- < \mathrm{IO}^-$$

Table $6.3.7.1$: Relationship of central atom's electronegativity to acid ionization constant in the hypohalous acids.

HOX	Electronegativity of X	K_a
HOCl	3.0	4.0×10^{-8}
HOBr	2.8	2.8×10^{-9}
HOI	2.5	3.2×10^{-11}

Note that the influence of central atom electronegativity on the strength of oxyacids is exactly the opposite to that observed for the binary hydrides in Table $6.3.7.5$, for which the acidity increased down a group, giving the order of acidity:

$$\mathrm{HI} > \mathrm{HBr} > \mathrm{HCl} \gg \mathrm{HF}$$

The reason for this is that in the hydrogen halides, the bond to be broken (H-E bond) decreased in strength down the group, while in oxyacids the bond to be broken is always an O-H bond and so varies much less in strength with the electronegativity of the central atom.

Trend 2: For oxoacids of a given central atom the acidity increases with the central element's oxidation state or, in other words, the number of oxygens bound to the central atom.

Here we are looking at the trend for acids in which there are variable numbers of oxygen bound to a given central atom. An examples is the perchloric (ClO_4^-), chloric (ClO_3^-), chlorous (ClO_2^-), and hypochlous (ClO^-) acid series. In such a series, the greater the number of oxygens, the stronger the acid. This can be explained in several ways. From the viewpoint of the acid itself the key factor is again the inductive effect, in this case involving the ability of the oxygens attached to the central atom to pull on electron density across the OH bond. This is seen from the charge density diagram for the chlorine oxoacids shown in Figure 6.3.7.1, in which the partial positive charge on the acidic hydrogen increases with the number of oxygens present.

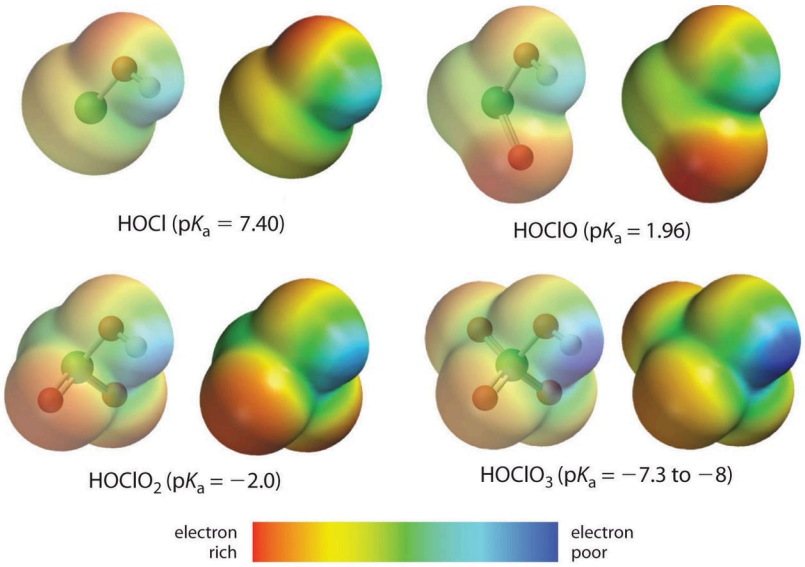


Figure 6.3.7.1: Increasing the number of oxygens increases K_a, as evidenced by the decreased electron density on the acidic hydrogen (which is most blue in $HClO_4$). Note, $K_a = 10^{-pK_a}$, and so the larger the pK_a, the smaller the K_a. (CC BY-SA-NC; anonymous)

The increase in oxoacid acidity with the number of oxygens bound to the central atom may also be seen by considering the stability of the conjugate oxyanion. That the stability of the conjugate base increases with the number of oxygens may be seen from the charge distribution diagrams and Lewis bonding models for the chlorine oxyanions shown in figure 6.3.7.2. As the negative charge is spread over more oxygen atoms it becomes increasingly diffuse.

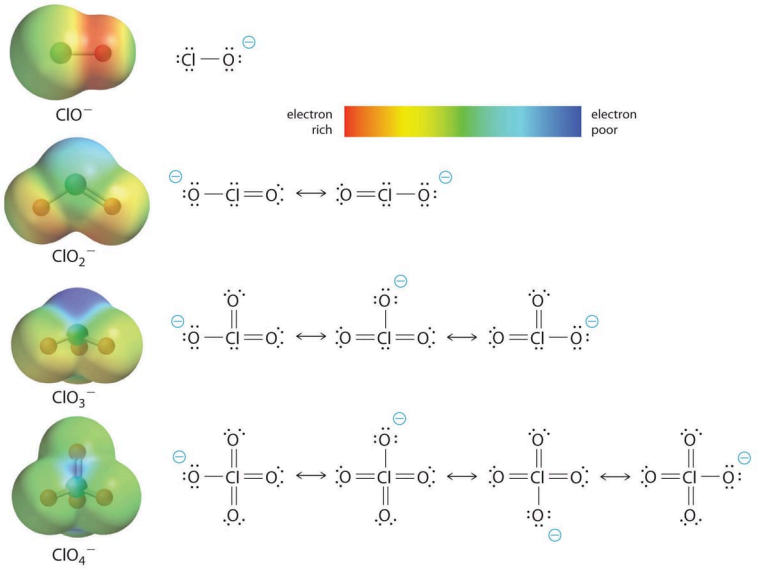


Figure 6.3.7.2: Increased diffusion of charge in chlorine oxyanions with increasing number of oxygens. The larger the ion the more dispersed the charge and thus the less the charge density, making the perchlorate the most stable anion in the series. Even the simplistic treatment of bonding depicted in the resonance structures correctly shows an increased dispersion of the charge density. (CC BY-SA-NC 3.0; anonymous)

Exercise 6.3.7.1

Sulfur and selenium both forms oxoacids of formula $\mathrm{H_2EO_3}$, where E is either S or Se. These are called sulfurous and selenous acid, respectively. Which oxoacid would you expect to be more acidic: selenous acid or sulfurous acid?

Answer available at the end of this section.

Trend 3: For polyprotic oxoacids the acidity decreases as each successive proton is removed

Oxoacids with multiple O-H bonds are called **polyprotic** since they can donate more than one hydrogen ion. In this case hydrogen ions are removed in successive ionization reactions. Examples include phosphoric and carbonic acid:

$$\begin{aligned}
\mathrm{H_3PO_4} &\rightleftharpoons \mathrm{H^+ + H_2PO_4^-} & pK_{a1} &= 2.2\\
\mathrm{H_2PO_4^-} &\rightleftharpoons \mathrm{H^+ + HPO_4^{2-}} & pK_{a2} &= 7.2\\
\mathrm{HPO_4} &\rightleftharpoons \mathrm{H^+ + PO_4^{3-}} & pK_{a3} &= 12.4\\
\mathrm{H_2CO_3} &\rightleftharpoons \mathrm{H^+ + HCO_3^-} & pK_{a1} &= 3.6\\
\mathrm{HCO_3^-} &\rightleftharpoons \mathrm{H^+ + CO_3^{2-}} & pK_{a1} &= 10.3
\end{aligned}$$

The dissociation constants for successive ionization constants decrease by about five orders of magnitude between successive hydrogen ions. This is reflected in Linus Pauling's rules for oxoacids and their oxyanions:

Pauling's Rules

1. The pK_a for an oxyacid of general formula $\mathrm{E(OH)_q(O)_p}$ is given by
$$pK_a = 8 - 5 \times p \tag{6.3.7.1}$$
2. As an oxoaxid undergoes successive ionizations the pK_a increases by five each time (i.e., K_a decreases 10,000-fold).

The central theme of Pauling's Rules is that the more oxygens there are on the central atom, the more resonance structures that

can be constructed for the conjugate base, which increases its stability and increases the acidity of the acid. However, as the acids successively ionize, they have fewer resonance structures. Pauling's Rules are phenomenological (i.e., not based on a theoretical framework). However, as empirical rules, they often work quite well, but it should be borne in mind that they are approximate.

Exercise 6.3.7.2: How well do Pauling's rules for oxoacids work?

Calculate the theoretical pK_a values for phosphoric and carbonic acid and their dissociation produces and compare the results with the experimental pK_a values.

Answer available at the end of this section.

Answers

Exercise 6.3.7.1

Sulfurous acid should be more acidic. Since sulfur is more electronegative than selenium sulfur will polarize OH bonds to a greater extent, making them more acidic. This prediction is borne out by a comparison of the pK_a values for the acids:

Acid	pK_{a1}	pK_{a2}
sulfurous acid, H_2SO_3	1.85	7.2
selenous acid, H_2SeO_3	2.62	8.32

Exercise 6.3.7.2**: How well do Pauling's rules for oxoacids work?**

For phosphoric acid, Pauling's rules (Equation 6.3.7.1) predict the pK_a values quite well:

- H_3PO_4: $p = 3$ and $q = 1$ and

$$pK_{a1,\text{predicted}} = 8 - 5 \times 1 = 3$$

  This is slightly greater than the observed value of 2.2.
- $H_2PO_4^-$:

$$pK_{a2,\text{predicted}} = pK_{a1,\text{experimental}} + 5 = 7.2$$

  This is spot on with experiment.
- HPO_4^{2-}:

$$pK_{a3,\text{predicted}} = pK_{a2,\text{experimental}} + 5 = 12.2$$

  This is slightly less than the experimental value of 12.4.

For carbonic acid Pauling's rules predict pK_{a1} reasonably well, but pK_{a2} less so:

- H_2CO_3: $p = 2$, $q = 1$ and

$$pK_{a1,\text{predicted}} = 8 - 5 \times 1 = 3$$

  This is slightly lower than the observed value of 3.6.
- HCO_3^-:

$$pK_{a2,\text{predicted}} = pK_{a1,\text{experimental}} + 5 = 8.6$$

  This is 1.7 units less than the experimental value of 10.3.

In some cases discrepancies between experimental pK_a values and those predicted by Pauling's rules suggest that structural rearrangements may be taking place upon ionization or else that the reported pK_a values do not really represent the ionization in question because they do not fully account for all the equilibria taking place in solution. In the case of carbonic acid, however, the reason for the discrepancy between the predicted and experimental pK_{a2} values is not entirely clear.

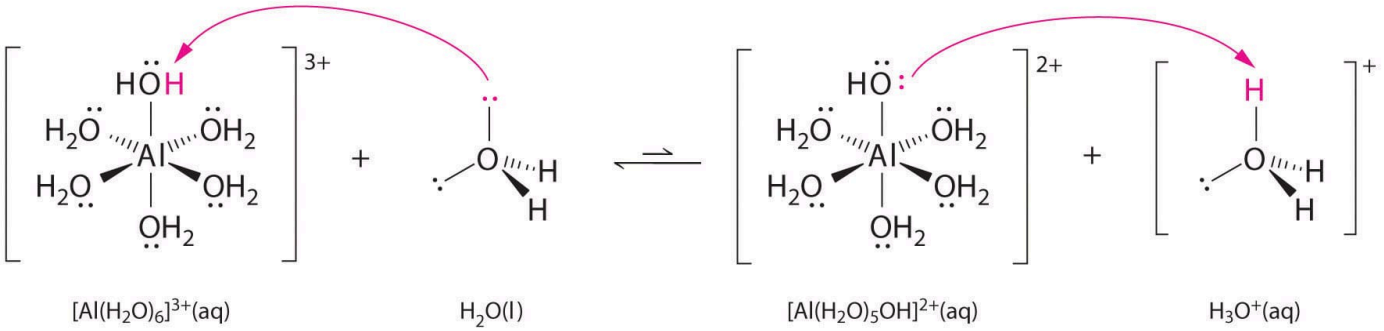
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6.3.8: High Charge-to-Size Ratio Metal Ions Act as Brønsted Acids in Water

Metal Ions Act as Acids by Polarizing Bound Water Molecules Called Aqua Ligands

Aqueous solutions of simple salts of metal ions can also be acidic, even though a metal ion cannot donate a proton directly to water to produce H_3O^+. Instead, a metal ion can act as a Lewis acid and interact with water, a Lewis base, by coordinating to a lone pair of electrons on the oxygen atom to form a hydrated metal ion.



A water molecule coordinated to a metal ion is more acidic than a free water molecule for two reasons. First, repulsive electrostatic interactions between the positively charged metal ion and the partially positively charged hydrogen atoms of the coordinated water molecule make it easier for the coordinated water to lose a proton.

Second, the positive charge on the Al^{3+} ion attracts electron density from the oxygen atoms of the water molecules, which decreases the electron density in the $\mathrm{O{-}H}$ bonds, as shown in Figure $6.3.8.5b$. With less electron density between the O atoms and the H atoms, the $\mathrm{O{-}H}$ bonds are weaker than in a free H_2O molecule, making it easier to lose an H^+ ion. This is shown schematically in Figure $6.3.8.1$.

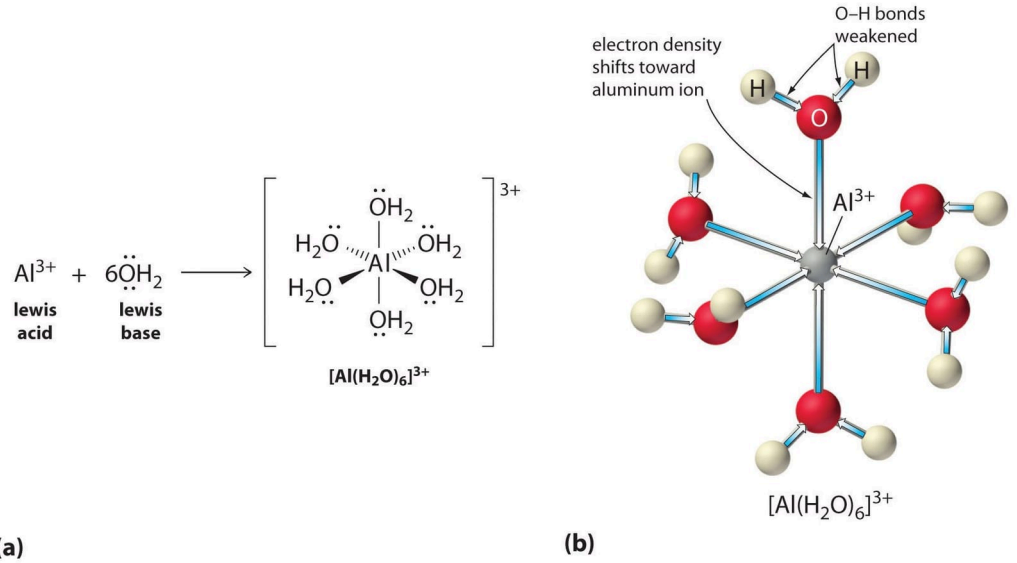


Figure $6.3.8.1$: Effect of a Metal Ion on the Acidity of Water (a) Reaction of the metal ion Al^{3+} with water to form the hydrated metal ion is an example of a Lewis acid–base reaction. (b) The positive charge on the aluminum ion attracts electron density from the oxygen atoms, which shifts electron density away from the O–H bonds. The decrease in electron density weakens the O–H bonds in the water molecules and makes it easier for them to lose a proton. (CC BY-NC-SA 3.0; anonymous)

The acidity of a given metal ion largely depends on its charge to size ratio and electronegativity, although in some cases hardness and ligand field effects also play a role.

The magnitude of this effect depends on the following factors, of which the first two are generally considered the most important (Figure 6.3.8.2):

The charge on the metal ion

A divalent ion (M^{2+}) has approximately twice as strong an effect on the electron density in a coordinated water molecule as a monovalent ion (M^{+}) of the same radius.

The radius of the metal ion

For metal ions with the same charge, the smaller the ion, the shorter the internuclear distance to the oxygen atom of the water molecule and the greater the effect of the metal on the electron density distribution in the water molecule.

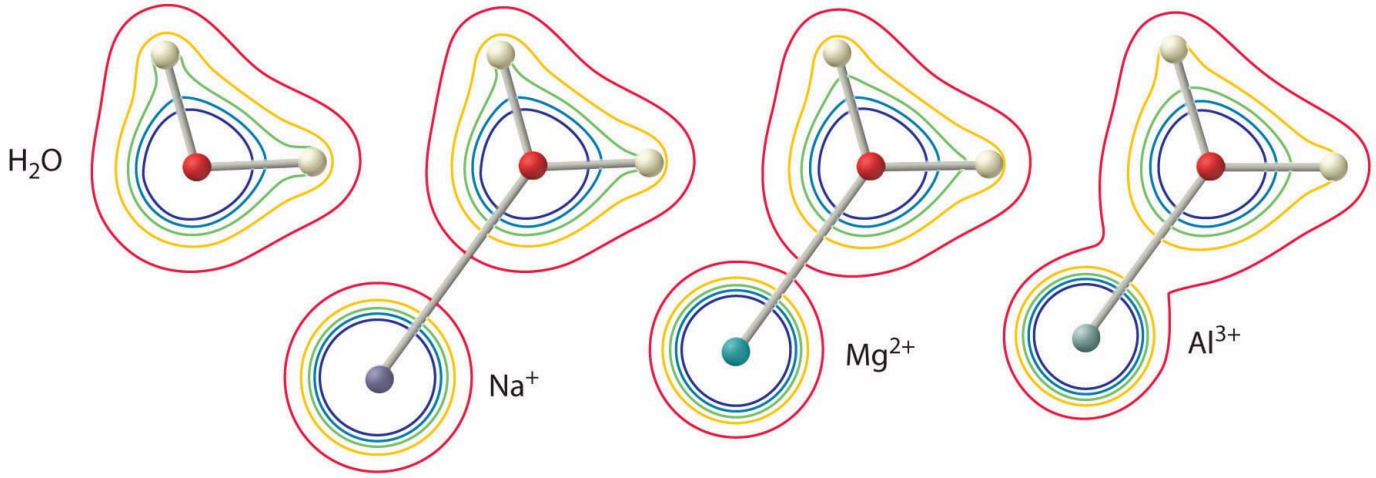


Figure 6.3.8.2: The effect of the charge and radius of a metal ion on the acidity of a coordinated water molecule. The contours show the electron density on the O atoms and the H atoms in both a free water molecule (left) and water molecules coordinated to Na^{+}, Mg^{2+}, and Al^{3+} ions. These contour maps demonstrate that the smallest, most highly charged metal ion (Al^{3+}) causes the greatest decrease in electron density of the O–H bonds of the water molecule. Due to this effect, the acidity of hydrated metal ions increases as the charge on the metal ion increases and its radius decreases. (CC BY-NC-SA 3.0; anonymous)

The first two of these factors explain why most alkali metal cations exhibit little acidity while aqueous solutions of small, highly charged metal ions, such as Al^{3+} and Fe^{3+}, are acidic:

$$[\mathrm{Al(H_2O)_6}]^{3+}\,(\mathrm{aq}) \rightleftharpoons [\mathrm{Al(H_2O)_5(OH)}]^{2+}\,(\mathrm{aq}) + \mathrm{H}^{+}\,(\mathrm{aq}) \tag{6.3.8.1}$$

The $[\mathrm{Al(H_2O)_6}]^{3+}$ ion has a pK_a of 5.0, making it almost as strong an acid as acetic acid. Because of the two factors described previously, the most important parameters for predicting the effect of a metal ion on the acidity of coordinated water molecules are the charge and ionic radius of the metal ion.

A simple empirical equation for predicting the pK_a of metal ions in water has been proposed by Wulfsberg:[1]

$$pK_a = 15.14 - 88.16\ pm\left(\frac{Z^2}{r}\right)$$

where Z is the charge on the metal ion and r its radius. As can be seen from figure 6.3.8.3, in general the acidity of metal ions increases with $\frac{Z^2}{r}$). Nevertheless a number of ions have considerably lower pK_a values than predicted from this correlation, suggesting that the acidity of metal cations cannot be predicted using a simple electrostatic model alone.

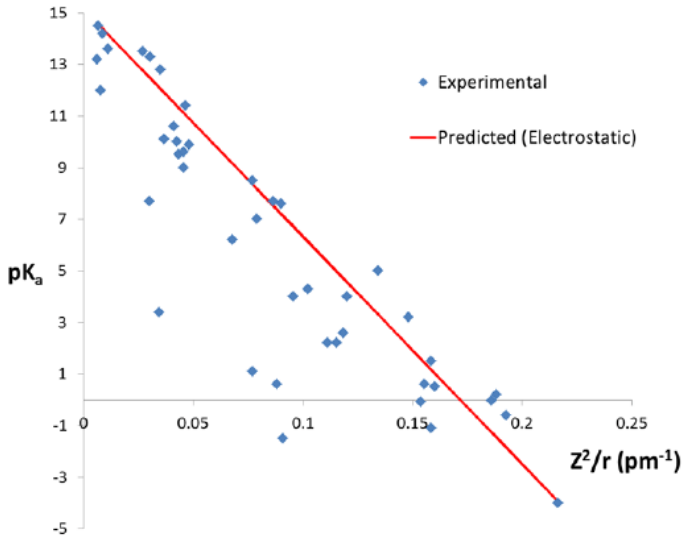


Figure 6.3.8.3: The pK_a of metal ions (♦) as a function of $\frac{Z^2}{r}$ for 43 metal ions. Drawn using radii listed in reference 1.

Although the charge-to-size ratio is the simplest and most powerful predictor of metal ion acidity in water, three additional factors also can play a role:

Electronegativity

All other things being equal, more electronegative elements are better able to withdraw electron density from a bound water ligand and consequently better at enhancing the ability of that water molecule to lose a hydrogen ion. The electrostatic model of ion acidity can be extended to account for electronegativity effects but only needs to be done so for metals with Pauling electronegativities greater than 1.5. The empirical relationship that has been proposed to account for the effect of electronegativity is:

$$pK_a = 15.14 - 88.16\left(\frac{Z^2}{r} + 0.096(\chi - 1.50)\right)$$

where r is the ion radius in pm and χ is its Pauling electronegativity. As can be seen from figure 6.3.8.4, the electronegativity term accounts for some of the deviations in metal ion acidity predicted from charge and size effects alone.

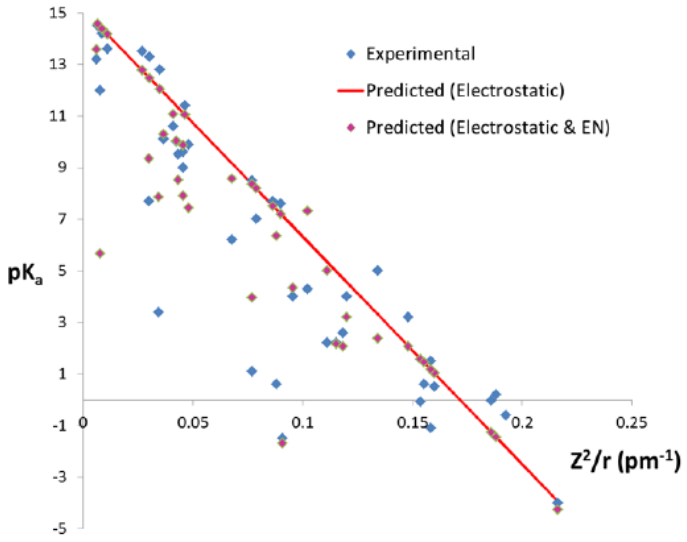


Figure 6.3.8.4: Comparison between the experimental pK_a values (♦) for 43 metal ions and those predicted empirically accounting for size and charge effects (-) and accounting for size, charge, and electronegativity effects (♦). Drawn using radii listed in reference 1.

However, there are still large deviations between the predicted and observed pK_a for a number of ions. In particular, the modified electrostatic model overestimates the pK_a of Al^{3+} and Sn^{4+} and underestimates the pK_a of Hg^{2+}, Sn^{2+}, and Tl^{3+}. While the exact reasons for these discrepancies is not entirely clear, at least some are thought to arise from the impact of the fourth factor that determines metal ion acidity.

Hardness and Softness

Cation hardness or softness is assessed according to Pearson's Hard-Soft Acid Base Principle (HSABP). In general, soft cations are more acidic than hard cations of the same charge and radius, as may be seen from the examples in Table 6.3.8.1. The greater than expected acidity of softer cations is thought to reflect the importance of covalent contributions to the metal-water bond.

Table 6.3.8.1: Comparison of the pK_a values at 25°C of hard and soft cations with approximately the same radius and charge. Based on Gutmann[2] as reported by Burgess.[3]

Cation	Classification	Radius (pm)	pK_a1
K^+	hard	1.33	14
Ag^+	soft	1.26	10
Mg^{2+}	hard	0.65	12.2
Cu^{2+}	soft	0.69	7.3
Ca^{2+}	hard	0.99	12.6
Cd^{2+}	soft	0.97	9.0
Sr^{2+}	hard	1.13	13.1
Hg^{2+}	soft	1.10	3.6

Ligand field effects

Ligand field effects involve bonding and antibonding interactions between the *d* orbitals on a transition metal and ligand orbitals. The importance of ligand field interactions on cation acidity is not well established, but ligand field interactions might influence the acidity of a hydrated metal in two cases: (a) when the ligand field stabilization of the aqua complex (metal with H_2O or OH^- bound) is greater or less than that in its conjugate base and (b) in complexes which undergo Jahn-Teller distortions that alter the metal's ability to polarize the OH bond.

References

1. Wulfsberg, G. *Principles of Descriptive Inorganic Chemistry* University Science Books, 1991, pp. 28-30.
2. (a) Gutmann, V. *Allg. Prakt. Chem.* 1970, *21,* 116. (b) Gutmann, V. *Fortschr. Chem. Forsch.* 1972, *27,* 59.
3. Burgess, J. *Metal Ions in Solution* Ellis Horwood, 1978, pg. 268.

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6.3.9: The Solvent System Acid Base Concept

The proton-centered nature of Arrhenius and Brønsted-Lowry definitions of acids and bases limits the utility of the acid-base formalism to reactions in protic solvents. A more generalizable theory is the **solvent-system** acid/base definition, which can be used to describe acid/base chemistry in non-protic solutions.

The solvent system acid-base concept generalizes the Arrhenius acid-base concept

Remember that the Brønsted-Lowry concept seeks to generalize Arrhenius acidity in ways that allow all hydrogen ion transfers to be thought of as acid-base reactions.

$$\mathrm{H_2O\,(l) + H_2O\,(l) \longrightarrow H_3O^+\,(aq) + OH^-\,(aq)}$$

Like the Brønsted-Lowry acid-base concept, the solvent system acid-base concept is a way to generalize the Arrhenius acid-base concept by focusing on cations and anions generated in any solvent that autoionizes. These include Brønsted-Lowry type autoionizations:

$$\mathrm{2\,NH_3\,(l) \rightleftharpoons {NH_4}^+ + {NH_2}^-}$$
$$\mathrm{2\,H_2SO_4\,(l) \rightleftharpoons {H_3SO_4}^+ + {HSO_4}^-}$$

However, the solvent system definition also allows for autoionizations that involve the transfer of an ion other than hydrogen. For example,

$$\mathrm{2\,SeOCl_2\,(l) \rightleftharpoons SeOCl^+ + {SeOCl_3}^-}$$
$$\mathrm{2\,BrF_3\,(l) \rightleftharpoons {BrF_2}^+ + {BrF_4}^-}$$

However, the solvent system concept does not define acidity in terms of ion transfer. Rather, like the Arrhenius concept, it defines acids and bases in terms of the impact those acids and bases have on the concentrations of cations and anions in solution (Figure 6.3.9.1).

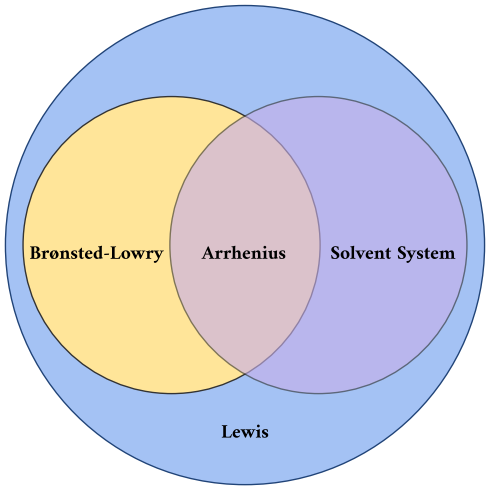


Figure 6.3.9.1: Venn diagram showing the hierarchical relationship between the major acid-base definitions. (CC BY-NC 4.0; Ümit Kaya via LibreTexts)

Definition: Solvent System Definitions of Acids and Bases

This means that under the solvent system definition:

- an acid is the solvent cation or any substance that increases the concentration of the solvent cations normally produced by solvent autoionization.
- a base is the solvent anion or any substance that increases the concentration of the solvent anions normally produced by solvent autoionization.

Note that in the solvent system concept, salts of the solvent cation are acids and salts of the solvent anion are bases. For instance, if a salt of $\mathrm{BrF_4^-}$ such as sodium tetrafluorobromate ($\mathrm{NaBrF_4}$) is added to $\mathrm{BrF_3\,(l)}$, the concentration of $\mathrm{BrF_4^-}$ increases.

The Solvent System Concept

The solvent system definition collapses to the Arrhenius definition for Brønsted acids in water. For instance, HCl is an acid in water since it increases the concentration of $\mathrm{H_3O^+}$ when it dissociates:

$$\mathrm{HCl\,(aq) + H_2O\,(l) \longrightarrow H_3O^+\,(aq) + Cl^-\,(aq)}$$

The solvent system broadens the Arrhenius definition by allowing for similar reactions in a variety of solvents. For instance, HCl also acts as an acid in liquid ammonia since it gives an $\mathrm{NH_4^+}$ ion on dissociation.

$$\underset{acid}{\mathrm{HCl}} + \mathrm{NH_3\,(l) \rightarrow NH_4^+ + Cl^-}$$

Antimony pentafluoride acts as an acid in liquid $\mathrm{BrF_3}$ since it abstracts a fluoride to give $\mathrm{BrF_2^+}$.

$$\underset{acid}{\mathrm{SbF_5}} + \mathrm{BrF_3\,(l) \rightleftharpoons SbF_6^- + BrF_2^+}$$

In contrast, the fluoride ion of potassium fluoride acts as a base, since it adds to $\mathrm{BrF_3}$ to give $\mathrm{BrF_4^-}$.

$$\underset{base}{\mathrm{KF}} + \mathrm{BrF_3\,(l) \rightleftharpoons K^+ + BrF_4^-}$$

The solvent system definition also allows for acid-base neutralization reactions. An example would be the reaction between KF and $\mathrm{SbF_5}$ in $\mathrm{BrF_3}$.

$$\underset{base}{\mathrm{KF}} + \underset{acid}{\mathrm{SbF_5}} \rightarrow \mathrm{KSbF_6}$$

although in this case it may be easier to see what is happening by writing the complete ionic form of the neutralization reaction equation.

$$\mathrm{K^+ + \underset{base}{F^-} + \underset{acid}{SbF_5} \rightarrow KSbF_6}$$

The solvent system concept allows for successive ionizations just as the Brønsted-Lowry system does. Acids like sulfuric acid can be described well under the Arrhenius, Brønsted-Lowry, and solvent system definitions.

$$\mathrm{2\,H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-}$$
$$\mathrm{HSO_4^- + H_2SO_4 \rightleftharpoons H_3SO_4^+ + SO_4^{2-}}$$

The solvent system definition also describes the autoionization of nonprotic solvents like thionyl chloride, $\mathrm{SOCl_2}$:

$$\mathrm{SOCl_2\,(l) \rightleftharpoons SOCl^+ + SOCl_3^-}$$
$$\mathrm{SOCl^+ + SOCl_2\,(l) \rightleftharpoons SO^{2+} + SOCl_3^-}$$

Successive equilibria are often useful in applying the solvent system to neutralization reactions, as may be seen in Example $6.3.9.1$.

Example 6.3.9.1

The reaction between sodium sulfite, Na_2SO_3, and thionyl chloride, $SOCl_2$, is a neutralization reaction according to the solvent system acid-base concept.

$$Na_2SO_3\,(s) + SOCl_2\,(l) \longrightarrow 2\,NaCl\,(s) + 2\,SO_2\,(g)$$

Write out the relevant equilibria and use them to explain the reaction in acid-base terms.

Solution

In the reaction shown the Na^+ just acts as a counterion. Consequently the reaction that should be considered is

$$2\,{SO_3}^{2-} + SOCl_2 \longrightarrow 2\,Cl^- + 2\,SO_2$$

A good place to start is to consider each of the species involved under the solvent-system acid-base concept by seeing if it is possible to write out ionization (or autoionization) reactions for them.

For ${SO_3}^{2-}$ these are

$$2\,{SO_3}^{2-} \rightleftharpoons \underset{acid}{SO_2} + \underset{base}{{SO_4}^{4-}}$$

$$\underset{acid}{SO_2} + 2\,\underset{base}{{SO_3}^{2-}} \rightleftharpoons \underset{acid}{\blacksquare} + \underset{base}{{SO_4}^{4-}}$$

These equations reveal that

- ${SO_3}^{2-}$ and SO_2 are amphoteric since they can act as either an acid or a base
- ${SO_4}^{4-}$ acts only as a base since it is the solvent anion
- SO^{2+} acts only as an acid since it is the solvent cation

Since ${SO_3}^{2-}$ is amphoteric, this does not resolve the issue of whether it is acting as an acid or a base. However, notice that the product of the reaction between ${SO_3}^{2-}$ and $SOCl_2$ is SO_2. This means that ${SO_3}^{2-}$ is acting as if it is following the pathway:

$$2\,{SO_3}^{2-} \rightleftharpoons SO_2 + {SO_4}^{4-}$$

The ionizations of $SOCl_2$ were already given in the main text but are also reproduced here for convenience:

$$SOCl_2\,(l) \rightleftharpoons SOCl^+ + {SOCl_3}^-$$

$$SOCl^+ + SOCl_2\,(l) \rightleftharpoons \blacksquare + {SOCl_3}^-$$

We could write an expression involving ionization of $2\,SO^{2+}$ to S^{4+} and SO_2 but that is unnecessary for solving the present problem.

The equations we have written reveal that

- $SOCl_2$ and $SOCl^+$ are amphoteric since they can act as either an acid or a base
- ${SOCl_3}^-$ acts only as a base since it is the solvent anion
- SO^{2+} acts only as an acid since it is the solvent cation

Again, since $SOCl_2$ is amphoteric this does not resolve the issue of whether it is acting as an acid or a base. However, notice that the product of the reaction between ${SO_3}^{2-}$ and $SOCl_2$ is SO_2. The only species in a reaction pathway involving $SOCl_2$ that can react to form SO_2 is SO^{2+}. This means that $SOCl_2$ is acting as if it is following the pathway:

$$2\,SOCl_2\,(l) \rightleftharpoons SOCl^+ + {SOCl_3}^-$$

$$SOCl^+ + SOCl_2\,(l) \rightleftharpoons SO^{2+} + {SOCl_3}^-$$

$$SO^{2+} + \text{base} \rightleftharpoons SO_2 + \text{the base's conjugate acid}$$

But what sort of base could react with SO^{2+} to give SO_2? The candidates in our list of bases are ${SO_4}^{4-}$, ${SO_3}^{2-}$, and SO^{2+} It must be one that donates an oxide ion, such as ${SO_4}^{4-}$. So in other words the $SOCl_2$ is following the pathway:

$$2\,SOCl_2\,(l) \rightleftharpoons SOCl^+ + {SOCl_3}^-$$
$$SOCl^+ + SOCl_2\,(l) \rightleftharpoons SO^{2+} + {SOCl_3}^-$$
$$SO^{2+} + {SO_4}^{4-} \rightleftharpoons SO_2 + {SO_3}^{2-}$$

and ${SO_3}^{2-}$ the pathway

$$2\,{SO_3}^{2-} \rightleftharpoons SO_2 + {SO_4}^{4-}$$

Adding these together gives the following net reaction:

$$3\,SOCl_2\,(l) + {SO_3}^{2-} \rightleftharpoons SO_2 + 2\,{SOCl_3}^-$$

At first glance this seems like it is not the correct equation. However, there is one acid-base reaction we are neglecting. The Cl^- product of the reaction between sodium sulfite and thionyl chloride acts as a base in thionyl chloride:

$$SOCl_2\,(l) + Cl^- \rightleftharpoons {SOCl_3}^-$$

So the net reaction above simply corresponds to the reaction between sodium sulfite and thionyl chloride with additional reactions between the product Cl^- and thionyl chloride added in. However, if a 1:1 ratio of thionyl chloride and sodium sulfate is used in the reaction, then the thionyl chloride will be consumed and the equilibrium between thionyl chloride and chloride ion shifted towards chloride, giving the desired net equation:

$$2\,{SO_3}^{2-} + SOCl_2 \longrightarrow 2\,Cl^- + 2\,SO_2$$

As Example $6.3.9.1$ illustrates, the application of the solvent system concept to the understanding of acid-base reactions in solution can be quite involved but also serves to allow chemists to apply a detailed understanding of solution chemistry to a wider variety of reactions. However, it is usually much simpler to think about solvent system neutralization reactions using the Lewis acid-base concept.

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6.3.10: Acid-Base Chemistry in Amphoteric Solvents and the Solvent Leveling Effect

Amphoteric Protic Solvents Undergo Solvent Autoionization just as Water Does

The Brønsted-Lowry concept allows for an understanding of hydrogen ion transfer chemistry in amphoteric protic solvents. Amphoteric protic solvents are those which can both accept and receive hydrogen ions. From the viewpoint of the Brønsted-Lowry concept, the acid-base chemistry in these solvents is governed by autoionization equilibria analogous to water autoionization.

$$2\,\mathrm{H_2O\,(l)} \rightleftharpoons \mathrm{H_3O^+ + OH^-} \qquad K_w = 1.0 \times 10^{-14}$$

For example, sulfuric acid ionizes according to the equation:

$$2\,\mathrm{H_2SO_4\,(l)} \rightleftharpoons \mathrm{{H_3SO_4}^+ + {HSO_4}^-} \qquad K = 4 \times 10^{-4}$$

The magnitude of the solvent autoionization constant in a given amphoteric solvent determines the amount of protonated and deprotonated* solvent present. Since sulfuric acid's autoionization constant is much larger than that of water ($K_w = 10^{-14}$), the concentrations of $\mathrm{{H_3SO_4}^+}$ and $\mathrm{{HSO_4}^-}$ present in pure sulfuric acid are ~0.02 *M*, much greater than the 10^{-7} *M* H_3O^+ and $\mathrm{OH^-}$ present in pure water.

In contrast, ammonia's autoionization constant is much less than that of water and only 10^{-14} M $\mathrm{{NH_4}^+}$ and $\mathrm{{NH_2}^-}$ are present in pure ammonia.

$$2\,\mathrm{NH_3\,(l)} \rightleftharpoons \mathrm{{NH_4}^+ + {NH_2}^-} \qquad K = 10^{-27}$$

The Solvent Leveling Effect Limits the Strongest Acid or Base that Can Exist

The conjugate acid and base of the solvent are the strongest Brønsted acids and bases that can exist in that solvent. To see why this is the case for acids, consider the reaction between a Brønsted acid (HA) and solvent (S):

$$\mathrm{HA + S \rightleftharpoons HS^+ + A^-}$$

This equilibrium will favor dissociation of whichever is a stronger acid - HA or $\mathrm{HS^+}$. If the acid is stronger it will mostly dissociate to give $\mathrm{HS^+}$, while if the solvent's conjugate acid is stronger the acid will be mostly un-ionized and remain as HA.**

Any acid significantly stronger than $\mathrm{HS^+}$ will act as a strong acid and effectively dissociate completely to give the solvent's conjugate acid ($\mathrm{HS^+}$). This also means that the relative acidity of acids stronger than $\mathrm{HS^+}$ cannot be distinguished in solvent S. This is called the **leveling effect** since the solvent "levels" the behavior of acids much stronger than itself to that of complete dissociation. For example, there is no way to distinguish the acidity of strong Arrhenius acids like $\mathrm{HClO_4}$ and HCl in water since they both completely dissociate. However, it is possible to distinguish their relative acidities in solvents that are more weakly basic than the conjugate base of the strongest† acid, since then the acids will dissociate to different extents. Such solvents are called differentiating solvents. For example, acetonitrile acts as a differentiating solvent towards $\mathrm{HClO_4}$ and HCl. Both $\mathrm{HClO_4}$ and HCl partly dissociate in MeCN, with the stronger acid $\mathrm{HClO_4}$ dissociating to a greater extent than HCl.

The leveling effect can also occur in basic solutions. The strongest Brønsted base, B, that can exist in a solvent is determined by the relative acidity of the solvent, and the base's conjugate acid, $\mathrm{BH^+}$, determines whether the base will remain unprotonated and able to act as a base in that solvent. If the solvent is represented this time as HS then the relevant equilibrium is:

$$\mathrm{B + HS \rightleftharpoons BH^+ + S^-}$$

The position of this equilibrium depends on whether B or $\mathrm{S^-}$ is the stronger base. If the solvent's conjugate base, $\mathrm{S^-}$, is stronger,

then the base B will remain unprotonated and available to act as a base. However, if B is a stronger base than $\mathrm{S^-}$, it will deprotonate the solvent to give $\mathrm{BH^+}$ and $\mathrm{S^-}$. In this way the strongest base that can exist in a given solvent is the solvent's conjugate base.

The relative strength of Brønsted bases can only be determined in solvents that are more weakly acidic than $\mathrm{BH^+}$; otherwise the bases will all be leveled to $\mathrm{S^-}$.

It is important to consider the leveling effect of protic solvents when performing syntheses that require the use of basic reagents. For instance, hydride and carbanion reagents (lithium aluminum hydride, Grignard reagents, alklyllithium reagents, etc.) cannot be used as nucleophiles in protic solvents like water, alcohols, or enolizable aldehydes and ketones. Since carbanions are stronger bases than these solvents' conjugate bases, they will instead act as Brønsted bases and deprotonate the solvent. For example if one adds n-butyllithium to water, the result (along with much heat and possibly a fire) will be butane and a solution of lithium hydroxide:

$$\mathrm{Li^+ + {}^- : CH_2CH_2CH_2CH_3 + H_2O\,(l) \longrightarrow Li^+\,(aq) + OH^-\,(aq) + CH_3CH_2CH_2CH_3\,(g)}$$

Since hydride and carbanion reagents cannot be used as nucleophiles in protic solvents like water or methanol, they are commonly sold as solutions in solvents such as hexanes (for alklyllithium reagents) or tetrahydrofuran (for Grignard reagents and $\mathrm{LiAlH_4}$).

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6.3.11: Non-nucleophilic Brønsted-Lowry Superbases

Non-Nucleophilic Organic Superbases Act as Strong Bases in Organic Solvents but Are Unreactive Towards Other Electrophiles

A variety of strong organic and inorganic bases are available for use in organic synthesis (alkyllithium reagents, diisopropyl amide derivatives, hydrides, and hydroxides). Some of these exhibit poor functional group tolerance owing to their ability to react with electrophilic functional groups. Hence there is considerable interest in the development of bases that can remove hydrogen ions from very weakly acidic organic substrates (*i.e.* like C-H bonds) without reacting with electrophilic functional groups. Classical non-nucleophilic bases used widely in organic chemistry include diisopropylethylamine (DIEA), lithium diisopropylamide (LDA), and the simple and complex ionic hydrides like $\mathrm{CaH_2}^{+2}$ and $\mathrm{LiAlH_4}$. The latter, however, are non-nucleophilic by virtue of their insolubility in organic solvents, on account of which they largely act as bases when an organic substrate interacts with the hydride at a crystal surface.

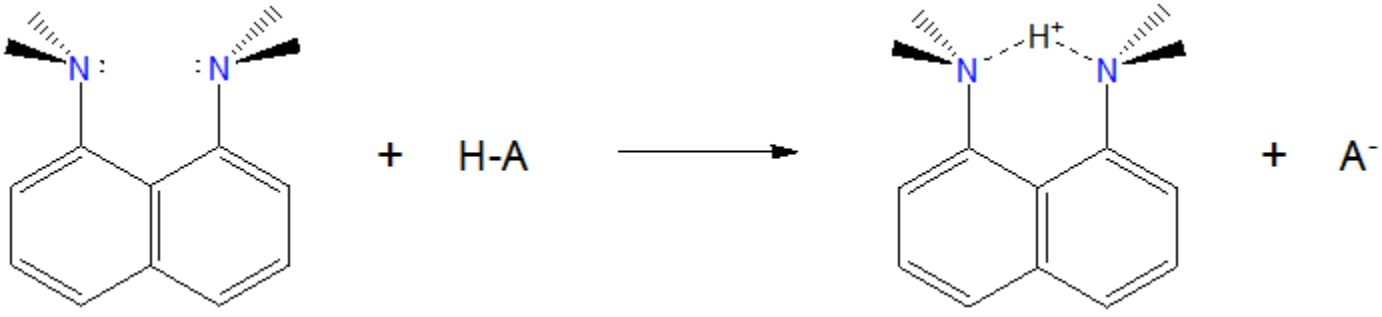
Many strong bases are called superbases in everyday usage. However, more rigorous definitions have been developed to clearly distinguish superbases from simple strong bases. Most of these use some aspect of the thermodynamics of hydrogen ion bonding by 1,8-Bis(dimethylamino)naphthalene as a delimiter between ordinary strong bases and superbases. In other words, by these criteria any base stronger than 1,8-bis(dimethylamino)naphthalene is considered a superbase. By this measure organic superbases may be defined as those having larger proton affinities than 1048 kJ/mol,[1] although most workers use defined superbases as those having a pK_a greater than 1,8-bis(dimethylamino)naphthalene's value of 12.[2]

Non-nucleophilic Organic Superbases Use Charge Delocalization, Proton Chelation, or Both to Tightly Bind Hydrogen Ion

A variety of compounds with a high affinity for hydrogen ions in organic solvents have been specifically developed as strong **non-nucleophilic organic superbases**.[3] Common classes include:

Napthalene-type proton sponges

Napthalene-type proton sponges are two basic groups held in close proximity to one another at the 1 and 8 positions of a napthalene ring. The compound 1,8-Bis(dimethylamino)naphthalene is perhaps the best known superbase of this type and is even sold by the trade name of Proton Sponge™. Its structure is shown below.



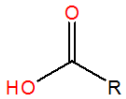
Proton sponge has the typical properties of an organic superbase. Unlike lithium diisopropylamindes and metal hydride reagents, 1,8-Bis(dimethylamino)naphthalene is only weakly basic in water. However, it possesses a very strong affinity for hydrogen ions in organic solvents.

In this case the high basicity of 1,8-Bis(dimethylamino)naphthalene is due to a combination of steric and electronic factors. First, it is a **hydrogen chelator** in that the hydrogen is held in a strong symmetric N---H---N hydrogen bond in its conjugate base. Second, the formation of that hydrogen bond relieves some of the steric strain associated with dimethyl amino groups held close

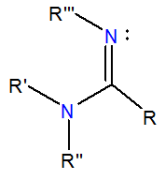
to one another at the 1 and 8 positions on the naphthalene ring.

Aminidines and Guanidenes

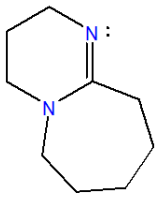
Aminidines are nitrogen derivatives of carboxylic acid derivatives. Acyclic aminidines have pK_a values ~12, similar to that of 1,8-Bis(dimethylamino)naphthalene, although cyclic aminidines are several orders of magnitude higher. For example, DBU is estimated to exhibit a pK_a value of 24.3 in MeCN.[4] Examples of aminidine superbases include the organic catalysts 1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU) and 1,5-Diazabicyclo(4.3.0)non-5-ene (DBN), and vinamidinium superbases, which bind hydrogen ion at the imine nitrogen.



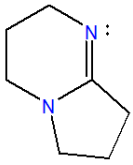
Carboxylic acid



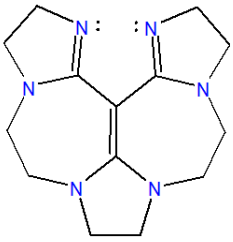
aminidene



1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU)

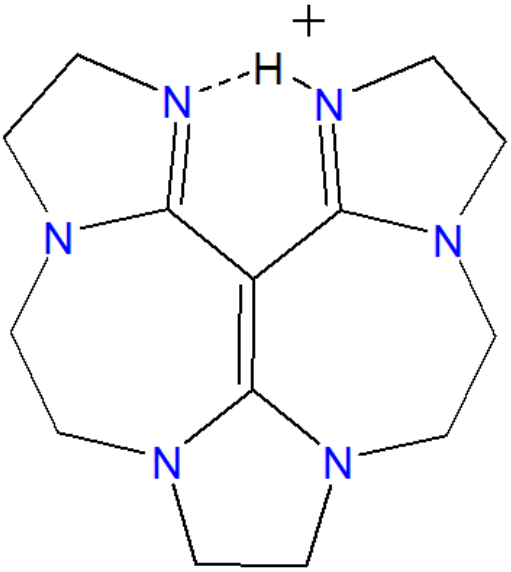


1,5-Diazabicyclo(4.3.0)non-5-ene (DBN)

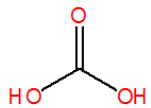


A vinamidinium superbase

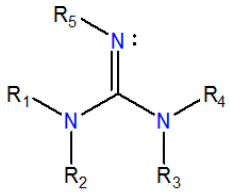
Of these the vinamidinium superbases are hydrogen ion chelators.



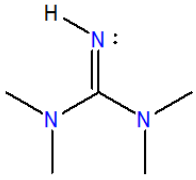
Guanidenes are nitrogen analogues of carbonate and bind hydrogen ion at a nitrogen lone pair just as aminidines do, although monomeric guanidines are slightly more basic (pK_a 13) than analogous aminidines (pK_a 12). Common classes of guanidene superbases include pentalkyl and bicyclic guanidines, shown below.



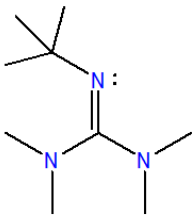
Carbonic acid



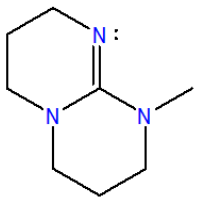
Guanidiene



1,1,3,3-Tetramethylguanidine (TMG)

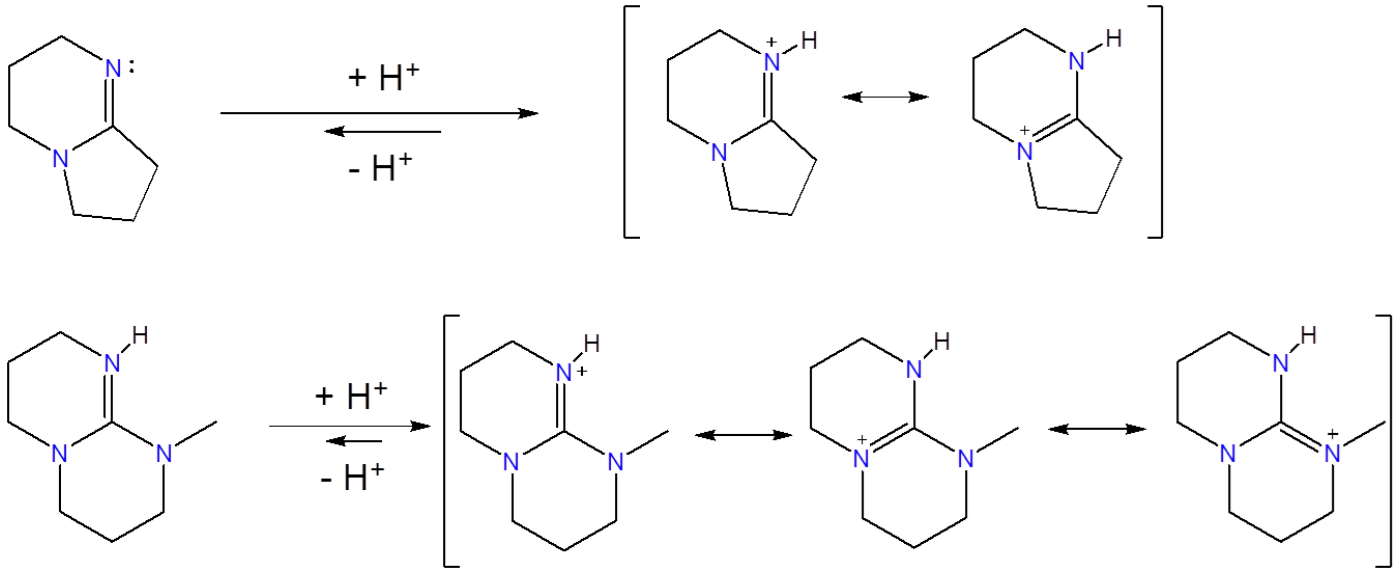


a pentalkyl guanidine superbase



a bicyclic guanidine superbase

The high basicity of aminidines and guanidines is derived from the ability of these systems to delocalize charge in the protonated form.



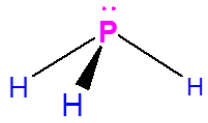
Exercise 6.3.11.1

Use the structure of protonated aminidines and guanidines to explain why guanidines are stronger bases than their aminidine analogues.

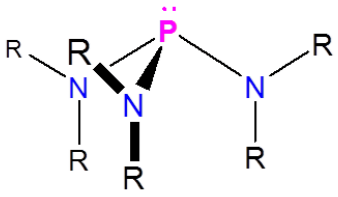
Answer available at the end of this section.

Phosphatrane-type Superbases

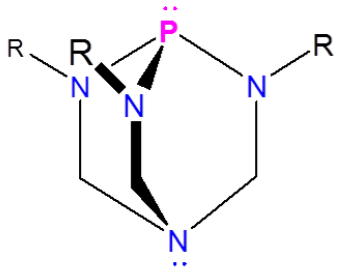
These exhibit enhanced basicity at the phosphorus atom of a special type of azaphosphine called a **proazaphosphatrane**:



phosphine

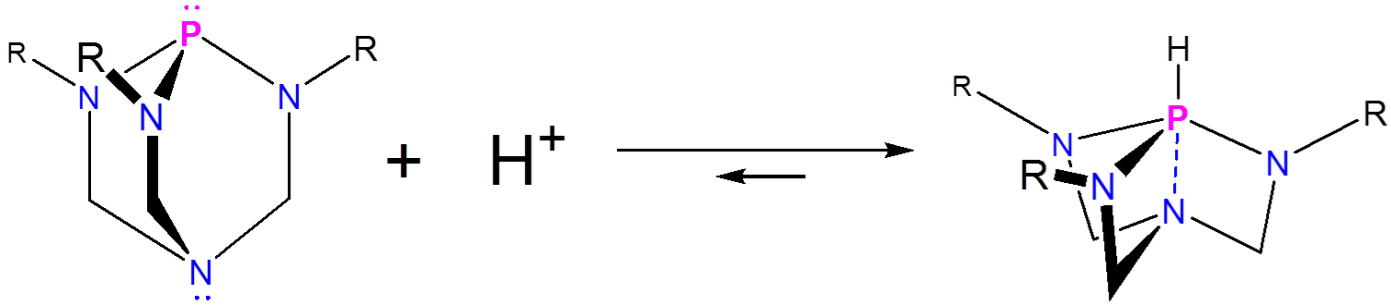


triazaphosphine



proazaphosphatrane
(Verkade-type superbase)

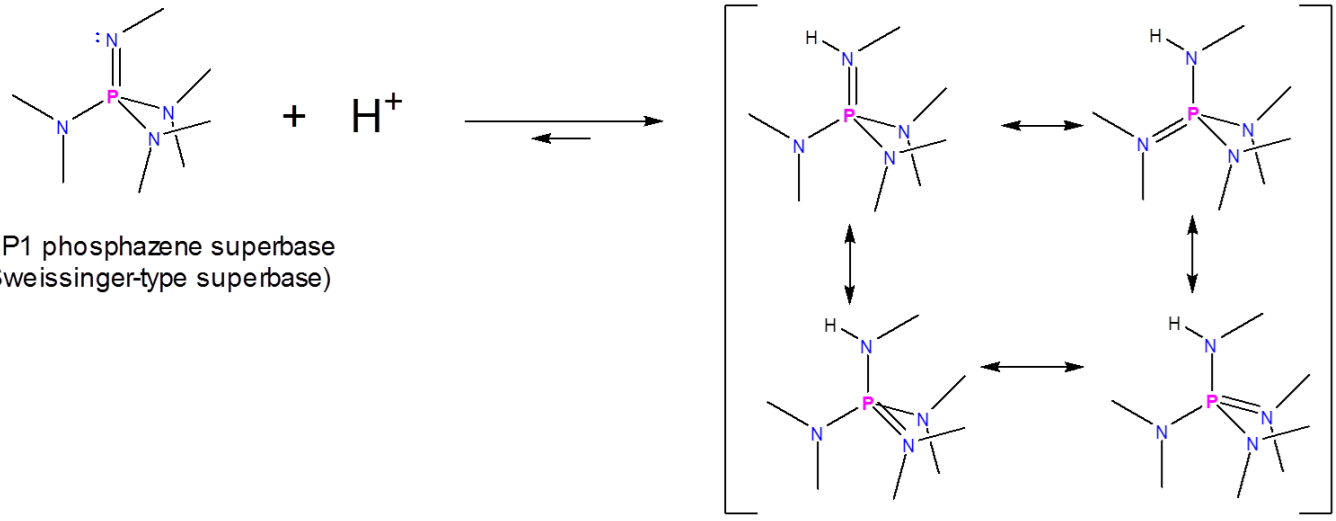
Of these the best known is Verkade's superbase, which is estimated to have a pK_a of 29 in acetonitrile,[5] meaning it is considerably more basic than aminidine and guanidine type superbases. The key to the remarkable basicity of Verkade's superbase is the ability of the proazaphosphoatrane's amine to stabilize the protonated azaphosphine through the formation of a P-N bond, giving a pseudo trigonal bipyramidal phosphorous.



These interactions are so stabilizing that the transannular amine nitrogen exhibit no basicity, even when superacids like Magic Acid are added.[6]

Phosphazene Superbases

Phosphazene superbases, also known as **Schwesinger superbases**, function similarly to aminidines and guanidines in that they bind a hydrogen ion at an imine nitrogen to give a resonance-stabilized cation. It is just that in this case the imine is that of a phosphazene and the greater resonance stabilization of the resulting cation means that they exhibit greater basicity. One phosphazene superbase has been reported to have a pK_a of 42 in acetonitrile.



The P1 phosphazene superbase
(a Sweissinger-type superbase)

References

1. Gal, J.-F.; Maria; P.-C.; Raczynska, E. D. Thermochemical aspects of proton transfer in the gas phase. *Journal of Mass Spectrometry*, 2001; 36: 699–716
2. The pK_a of 1,8-Bis(dimethylamino)naphthalene is taken from Benoit, R. L.; Lefebvre, D.; Fréchette, M., Basicity of 1,8-bis(dimethylamino)naphthalene and 1,4-diazabicyclo[2.2.2]octane in water and dimethylsulfoxide. Canadian Journal of Chemistry 1987, 65 (5), 996-1001.
3. Ishikawa, T. Superbases for Organic Synthesis: Guanidines, Amidines, Phosphazenes and Related Organocatalysts; Wiley: New York, 2009.
4. Unless otherwise noted pK_a values other than that reported for 1,8-Bis(dimethylamino)naphthalene are taken from Kaupmees, K.; Trummal, A.; Leito, I. (2014). "Basicities of Strong Bases in Water: A Computational Study". *Croat. Chem. Acta.* **87**: 385–395. doi:10.5562/cca2472
5. Kovačević, B.; Barić, D.; Maksić, Z. B., Basicity of exceedingly strong non-ionic organic bases in acetonitrile —Verkade's superbase and some related phosphazenes. New Journal of Chemistry 2004, 28 (2), 284-288.
6. Akiba, K-Y. Organic Main Group Chemistry; Wiley: New York, 2011.

Answers

Exercise 6.3.11.1

There is greater delocalization of charge in guanidinium ions. According to the resonance picture of bonding, in guanidinium ions the positive charge is delocalized over three nitrogen atoms while in amidinium ions it is only delocalized over two.

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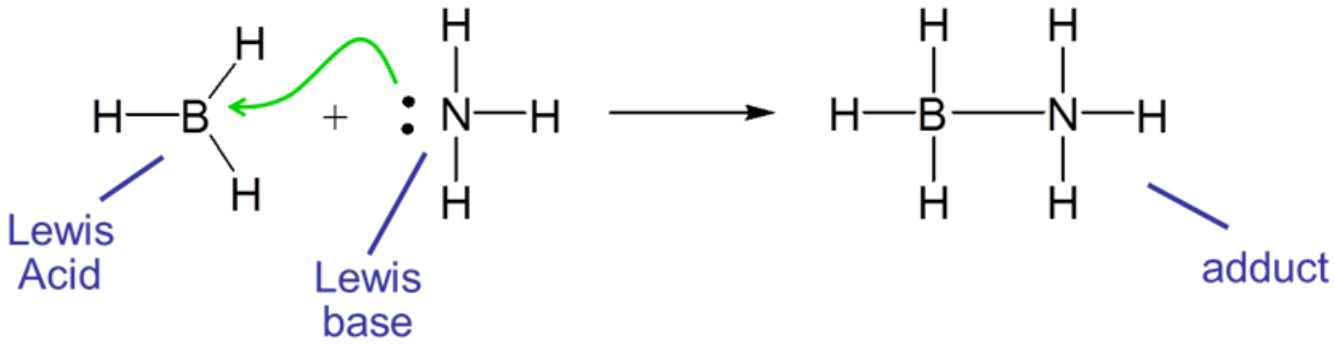
6.4: Lewis Concept and Frontier Orbitals

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.

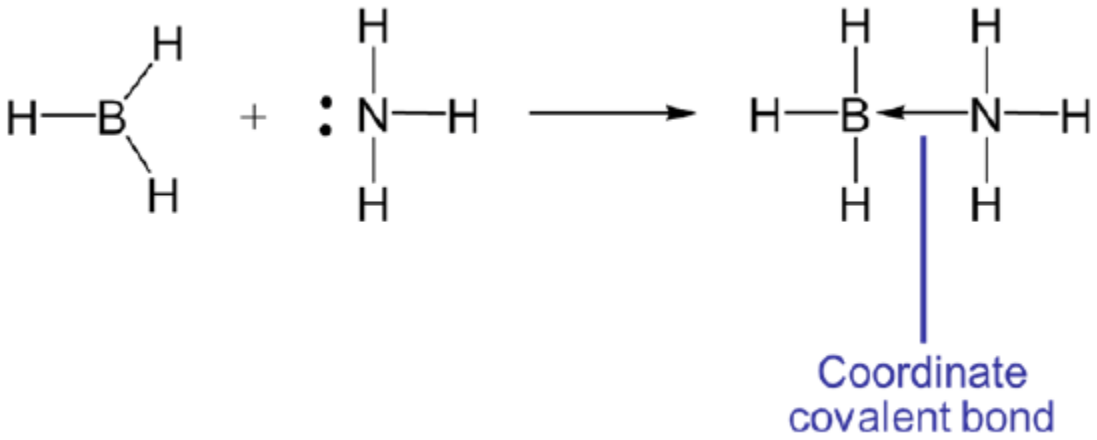
Under the Lewis definition

- **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:



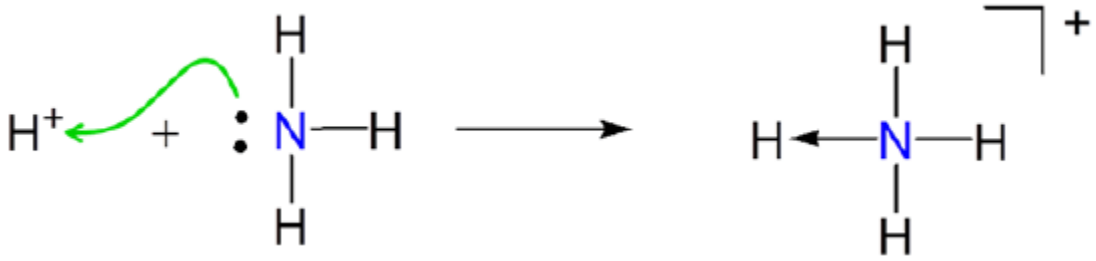
In this case the Lewis acid-base reaction results in the formation of a bond between BH_3, and NH_3. When the acid and base combine to form a larger unit, that unit is said to be an adduct, and the resulting bond is said to be a coordinate covalent or dative bond. Such coordinate covalent bonds are often 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



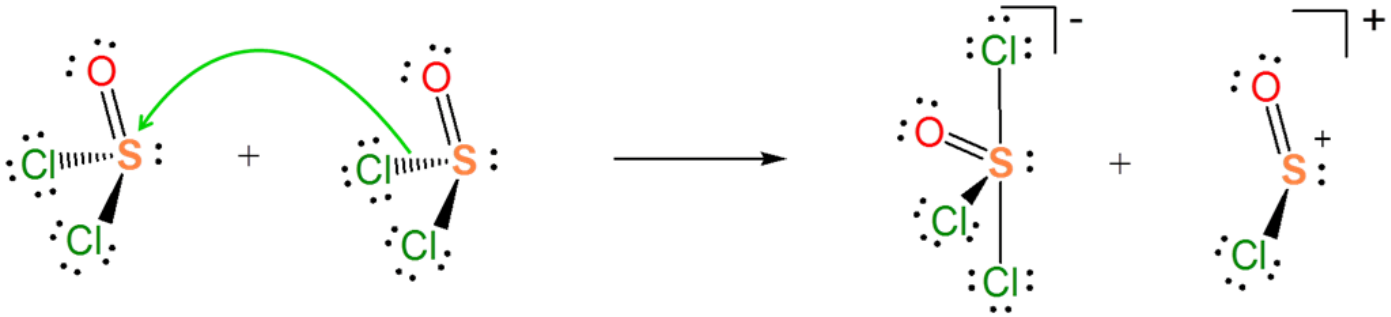
The arrow notation for the coordinate covalent bond is really just a convenient formalism - a bookkeeping tool to help keep track of where the electrons came from and where they might return if the reverse reaction occurs. In actuality a coordinate covalent bond is just an ordinary covalent bond like 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.

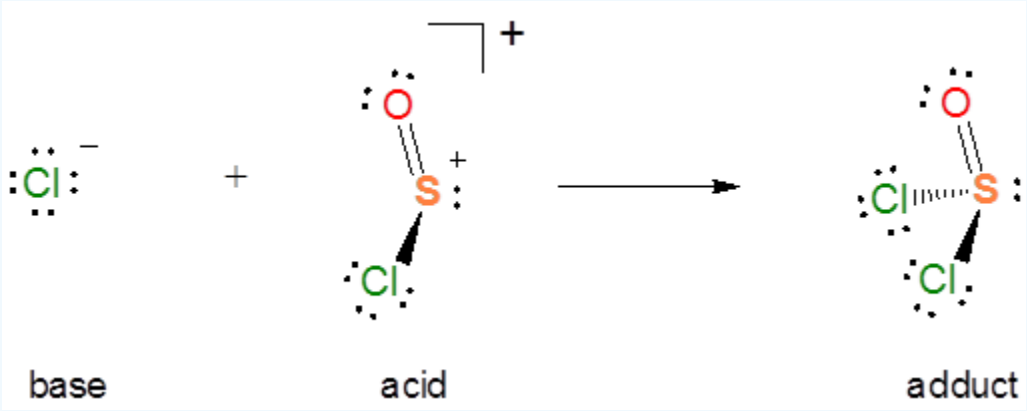


Example 6.4.1

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:

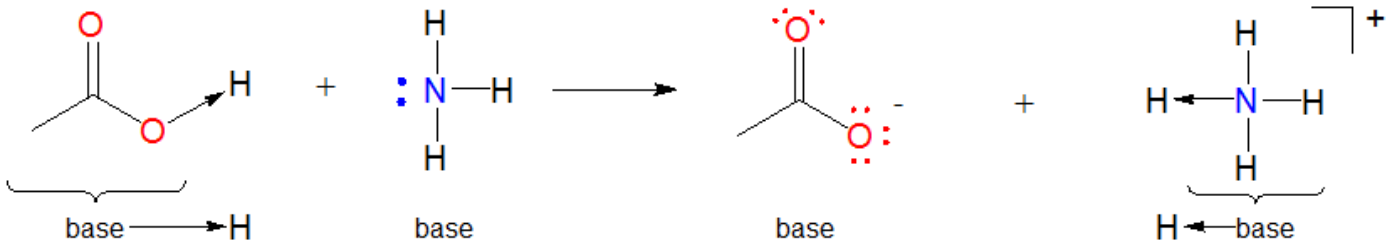


From the autoionization reaction it is also apparent that $SOCl_2$ itself acts as a Lewis acid towards the liberated Cl^-. So the autoionization reaction involves a transfer of the Cl^- base between the two Lewis acids - a Lewis acid-base displacement reaction.



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, $\mathrm{Al(OH)_3}$. In water $\mathrm{Al(OH)_3}$ can act as a Lewis acid towards OH^- ion. The reaction occurs by formation of an adduct at $\mathrm{Al(OH)_3}$'s Al^{3+} center:

$$\mathrm{Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-}$$

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 $\mathrm{Al(OH)_3}$ also acts as a Lewis base towards H^+ through the lone pairs on its hydroxide ligands.

$$\mathrm{Al(OH)_3 + 3\,H^+ + 3\,H_2O \rightarrow Al(H_2O)_6^{3+}}$$

Notice that in addition to acting as a Lewis base, in this reaction $\mathrm{Al(OH)_3}$ 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.

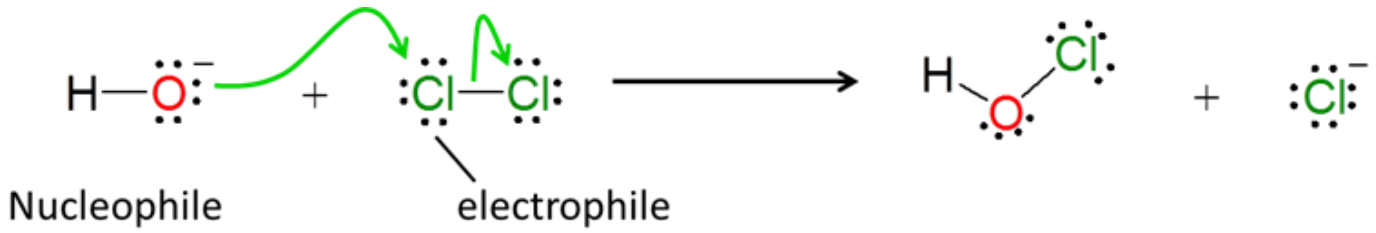
2. Acid and base strength and electrophilicity-nucleophilicity are not exactly the same thing. In many contexts where Lewis acids and bases are classified as electrophilic and nucleophilic substances, it is common to also refer to substances as being good acids or bases on the basis of their Brønsted 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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6.4.1: 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.

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 NH_3 and BH_3 involves the donation of electrons from ammonia's a_1 HOMO into BH_3's a_2'' LUMO level.

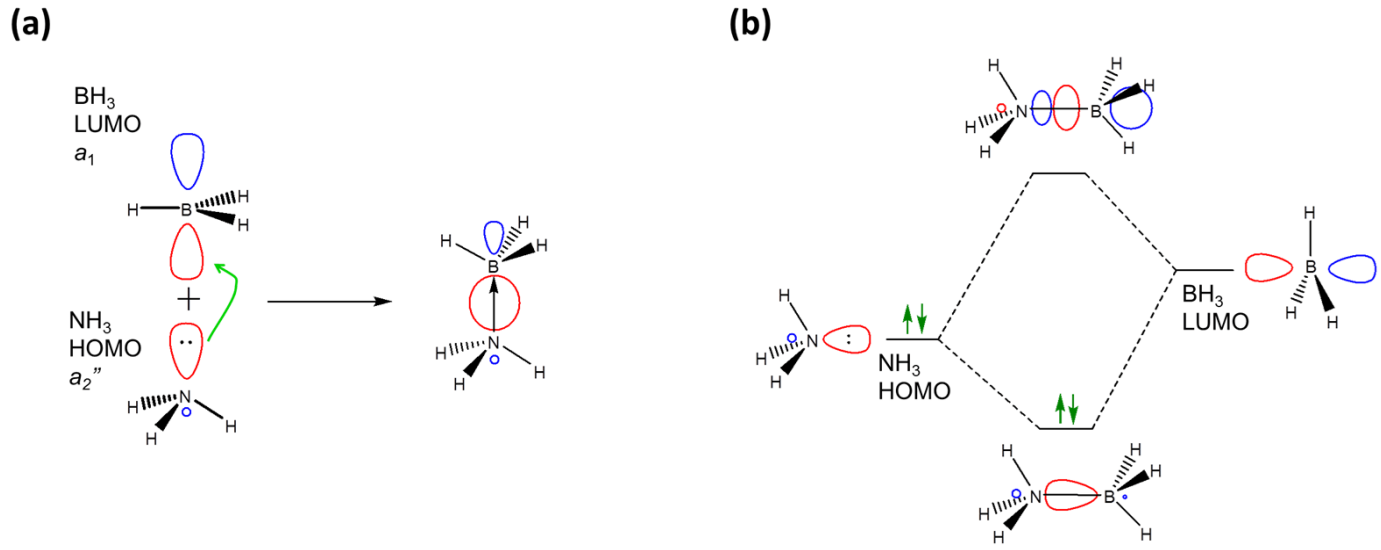


Figure 6.4.1.1. Frontier orbital picture of adduct formation between ammonia and borane. (a) As NH_3 and BH_3 approach one another, interaction between the NH_3 HOMO and BH_3 LUMO gives a bonding MO. (b) Partial molecular orbital diagram for $NH_3 \rightarrow BH_3$ showing the stabilization of the base (NH_3) lone pair in a sigma bonding MO 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 6.4.1.1). 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:

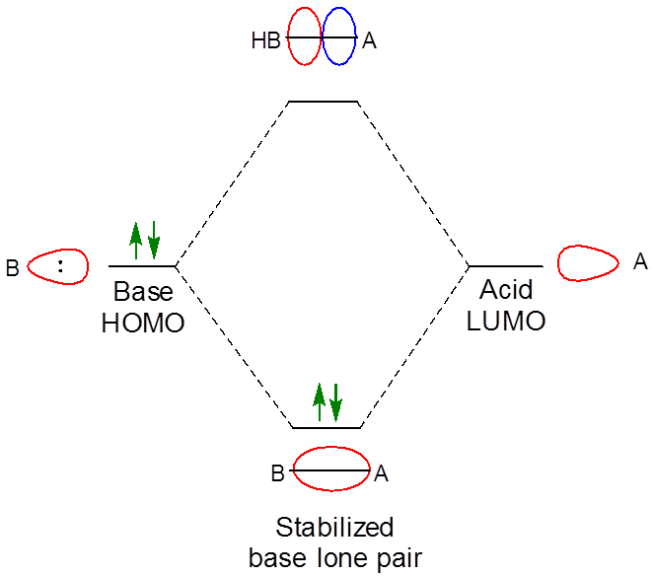
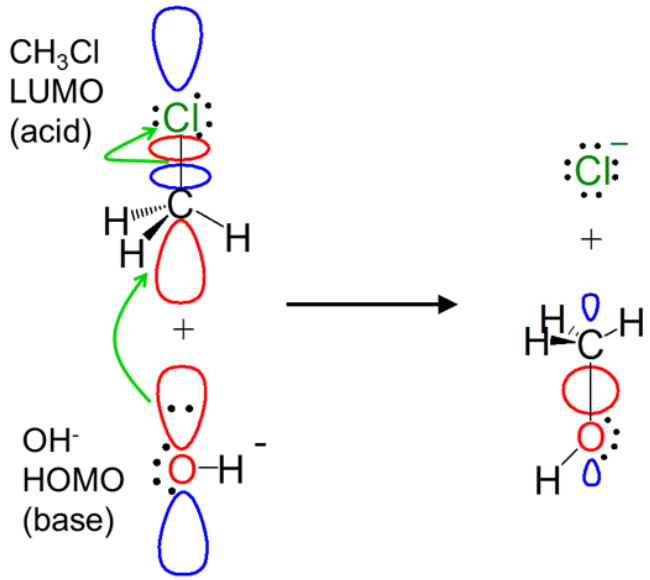


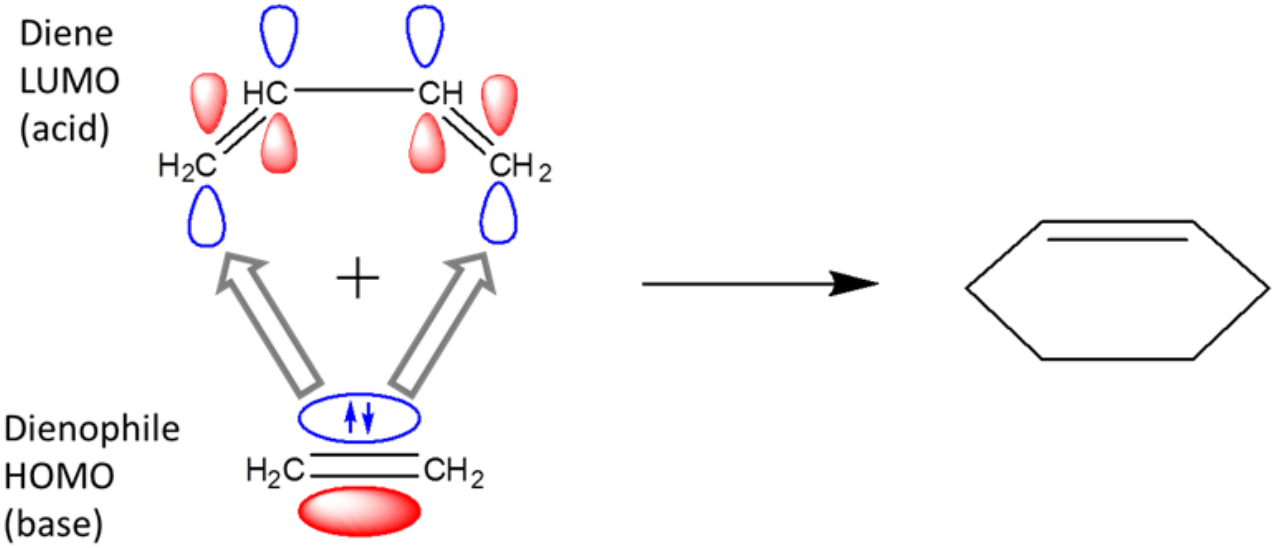
Figure 6.4.1.2. Generalized frontier orbital picture for adduct formation between a Lewis base (B) and a Lewis acid (A) involving stabilization of the lone pair of the base HOMO by formation of a bonding orbital with the acid LUMO. The relative energies of the acid LUMO and base HOMO affect the character 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:

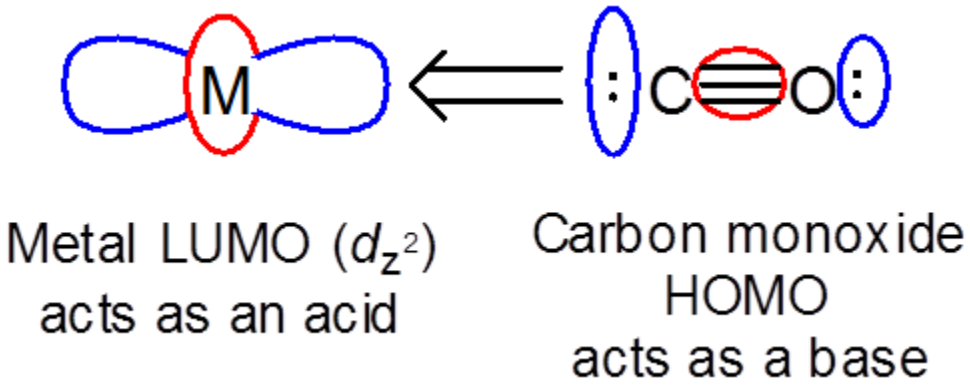


Notice how the frontier orbital approach even explains the displacement of the chloride leaving group. The donation of electrons from the hydroxide HOMO populates the antibonding CH_3Cl LUMO, breaking the C-Cl bond.

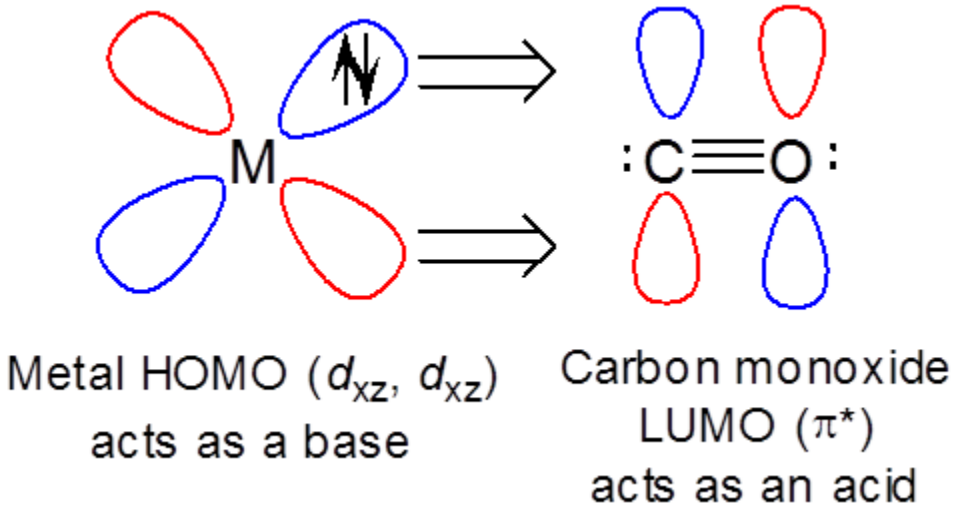
With the frontier orbital approach, it becomes apparent that pericyclic reactions are Lewis acid-base reactions. For example, in the Diels-Alder reaction, the dienophile acts as a Lewis base and the diene as a Lewis acid.



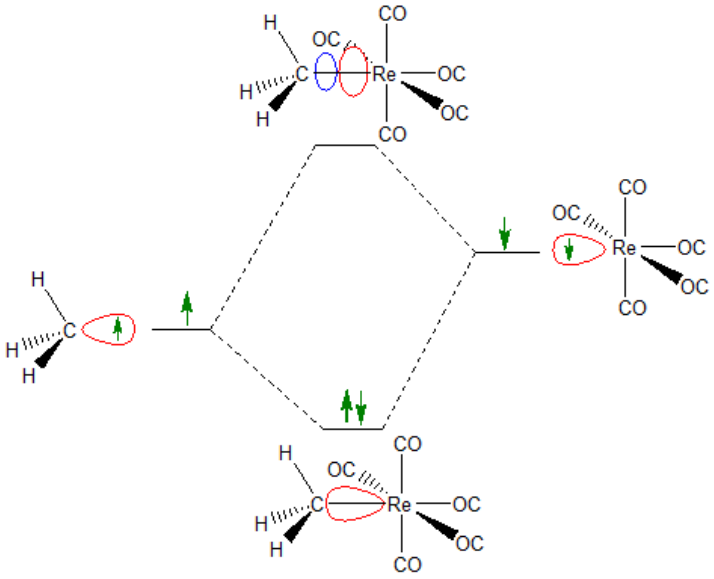
The orbital interactions involved in a given reaction can include both reactants acting as both an acid and base. In these cases the HOMO of each reactant interacts with the LUMO of the other. A good example of this involves Π-type interactions between a metal ion with occupied *d* orbitals and a pi-acceptor ligand. The ligand acts as a base and the metal as an acid to give a M-CO single bond:



However, the metal can also act as a base towards the ligand LUMO (π^*) orbitals.



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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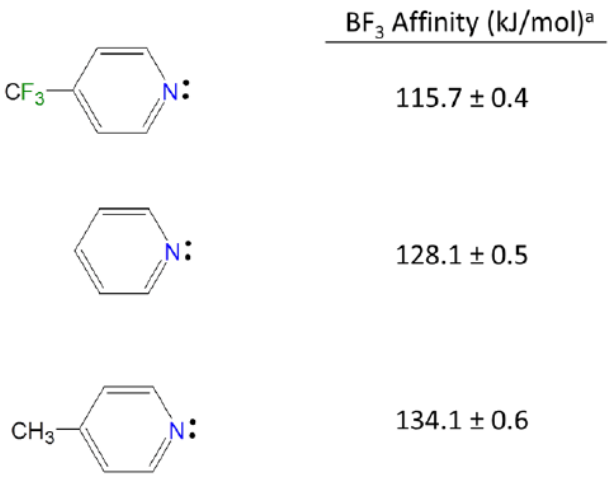
- 6.4.1: The frontier orbital approach considers Lewis acid-base reactions in terms of the donation of electrons from the base's highest occupied orbital into the acid's lowest unoccupied orbital. by Stephen M. Contakes is licensed CC BY 4.0.

6.4.2: All other things being equal, electron withdrawing groups tend to make Lewis acids stronger and bases weaker while electron donating groups tend to make Lewis bases stronger and acids weaker

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:

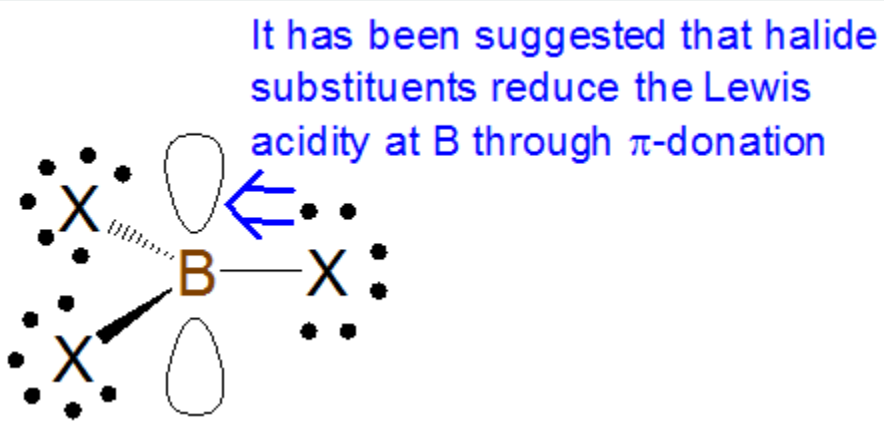
- electron withdrawing substituents tend to decrease the Lewis basicity of basic sites while electron donating substituents increase site Lewis basicity by making them more electron rich.
- electron withdrawing substituents increase the Lewis acidity of acidic sites by making those sites more electron 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 ofπ 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:

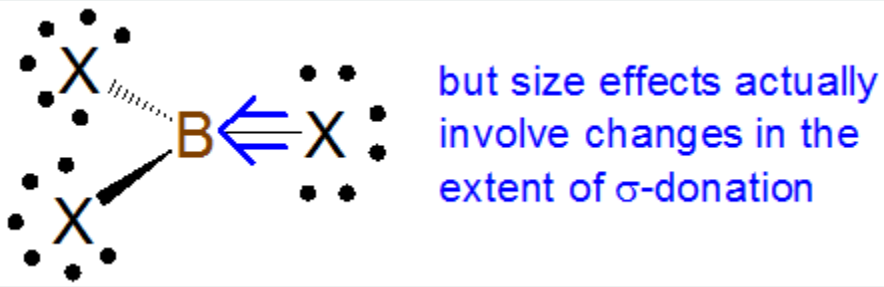


According to this explanation, the extent of this π-donation decreases down the halogen group as the boron-halogen bond distance decreases. This is consistent with the observed trend in Lewis acidity of the boron trihalides towards most bases, which runs counter to that suggested by inductive effects 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:

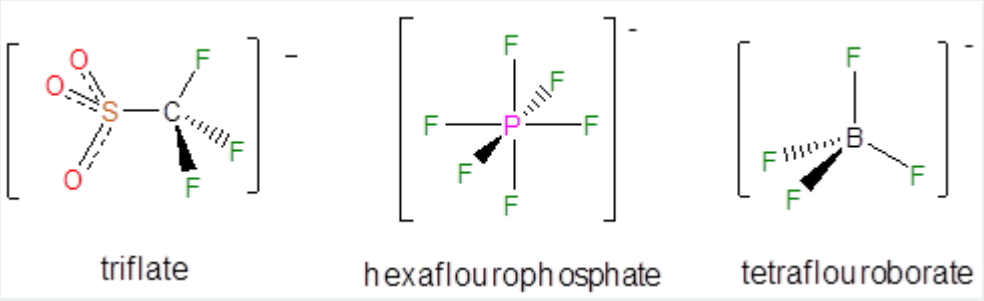
1. Plumley, J. A.; Evanseck, J. D., Periodic Trends and Index of Boron Lewis Acidity. *The Journal of Physical Chemistry A* 2009, 113 (20), 5985-5992.

2. Jupp, A. R.; Johnstone, T. C.; Stephan, D. W., Improving the Global Electrophilicity Index (GEI) as a Measure of Lewis Acidity. *Inorganic Chemistry* 2018, 57 (23), 14764-14771.

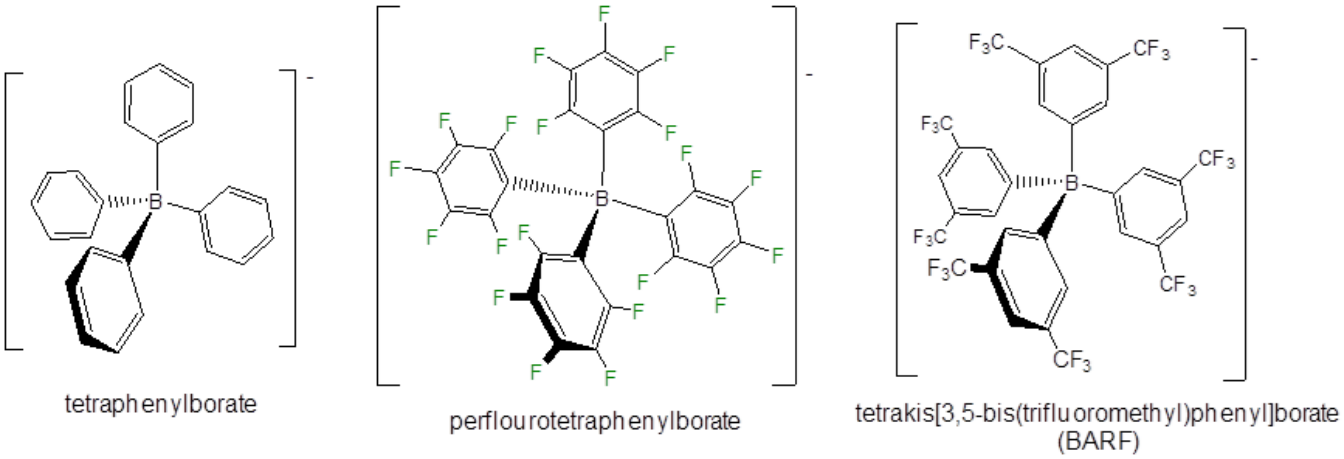
The conjugate bases of many Brønsted superacids have electron-withdrawing substituents that make them such poor Lewis bases that they are useful as noncoordinating anions.

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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6.4.3: The electronic spectra of charge transfer complexes illustrate the impact of frontier orbital interactions on the electronic structure of Lewis acid-base adducts

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 6.4.2.6.4.3.1.

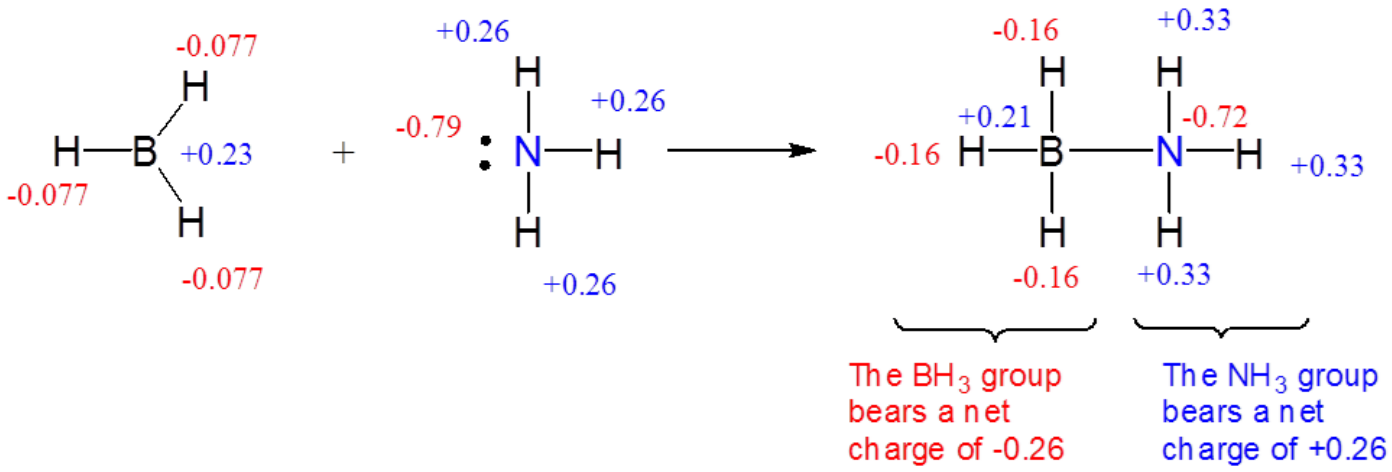


Figure 6.4.2.6.4.3.1. Calculated change in atomic charge distribution upon formation of an adduct between BH_3 and NH_3 in the gas phase. All partial charges were calculated for geometry-optimized molecules at the 6-31G** level.

Weakly bound Lewis acid-base adducts in which charge is incompletely transferred are called charge transfer complexes.

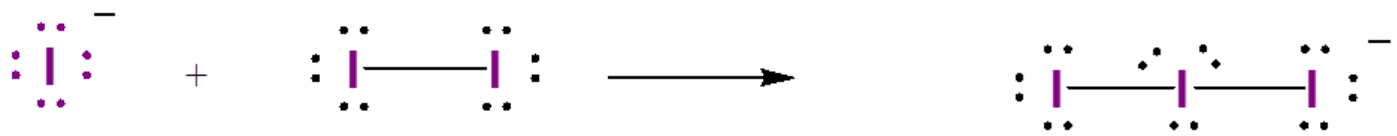
In many weakly bound Lewis acid-base complexes, the transfer of electron density and, consequently, charge from the base group to the acid group is only partial:

$$A + B \rightleftharpoons A^{\delta-}B^{\delta+}$$

Such Lewis acid-base adducts are commonly called **charge transfer complexes (CT complexes)** or **donor-acceptor complexes (DA complexes)**. In these

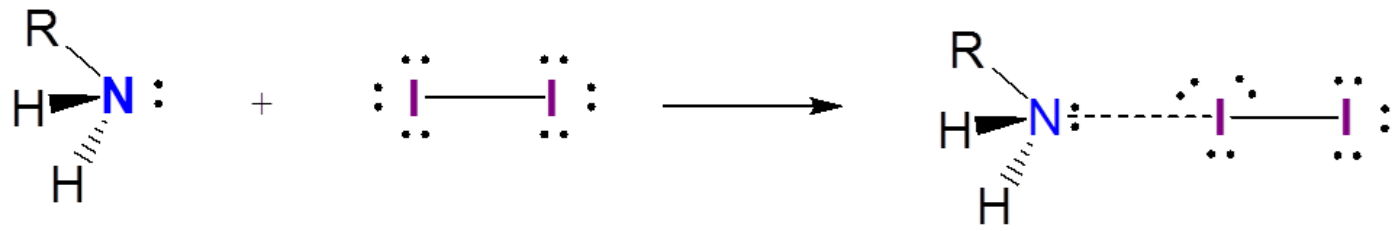
- the base is called the **donor (D)** since it is a net donor of electrons and, consequently, their negative charge
- the acid is called the **acceptor (A)** since it is a net acceptor of electrons and, consequently, their negative charge

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.

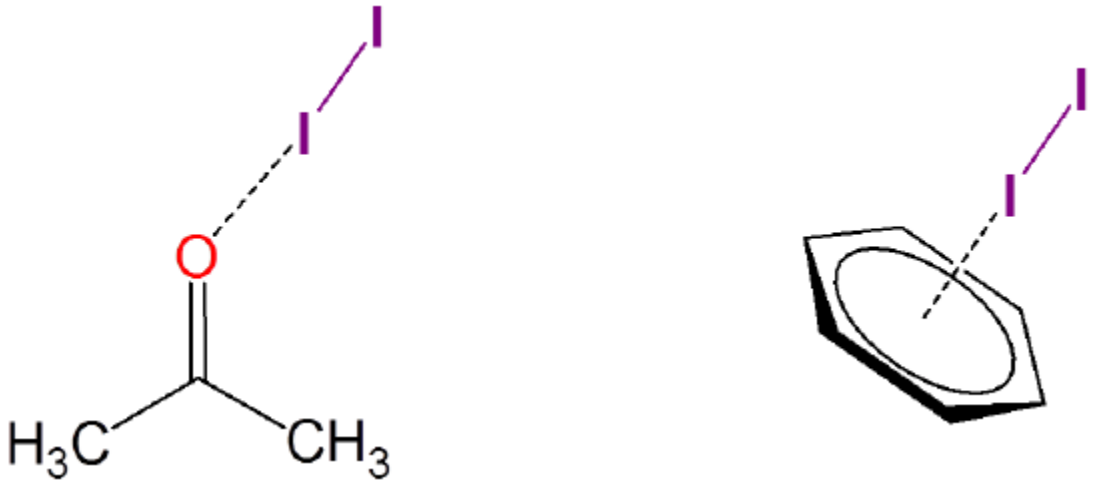


Triiodide is well-known from introductory chemistry from the bright blue color that appears when the triiodide complexes with starch to give the dark blue starch-iodide complex.

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:

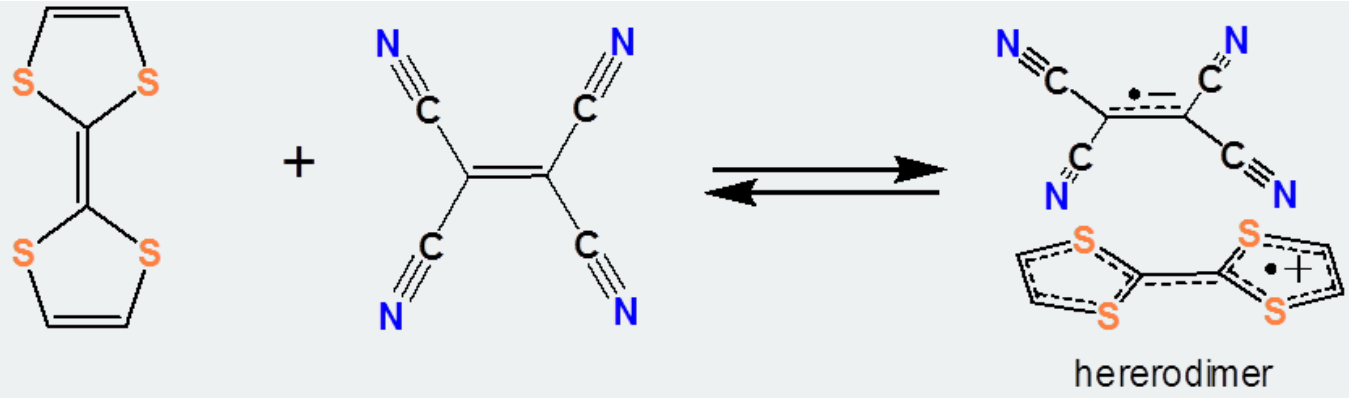


Iodine also forms weakly-associated charge transfer complexes with many solvents. For instance, iodine can weakly associate with both acetone and benzene:

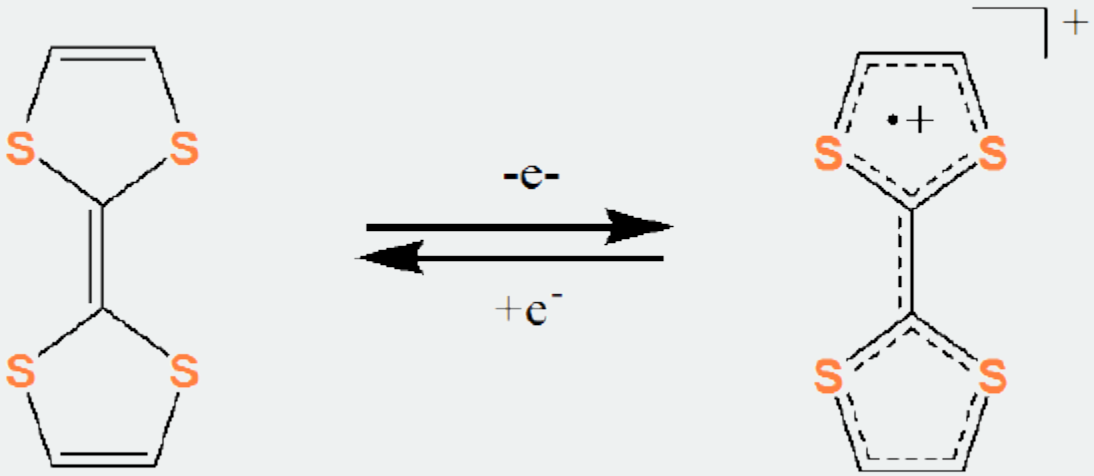


Organic Charge Transfer Complexes

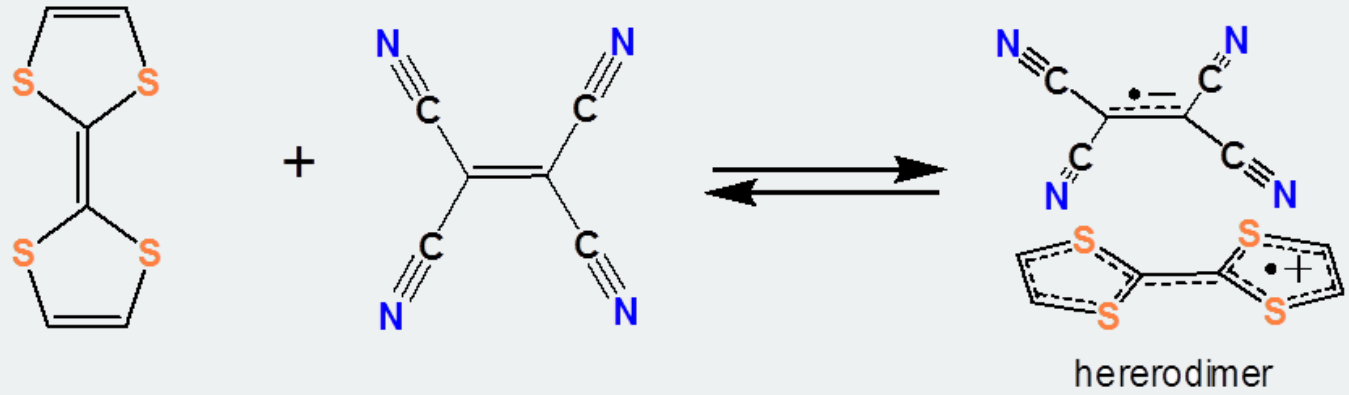
It is worth noting in passing that several organic charge transfer complex systems have been developed in which organic electron donors and acceptors weakly associate with each other. These are of considerable interest for use in molecular electronics applications, and as a result, a large variety of 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.

$$D^{\delta+} - A^{\delta-} \overset{h\nu_{CT}}{\longrightarrow} D^{+} - A^{-}$$

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.

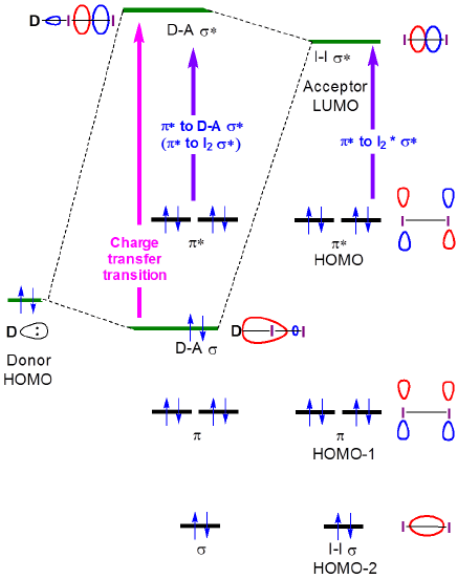


Figure 6.4.2.6.4.3.2. Frontier orbital interactions that give rise to changes in the absorption spectra of iodine when it forms a charge transfer complex with a Lewis base donor.

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.

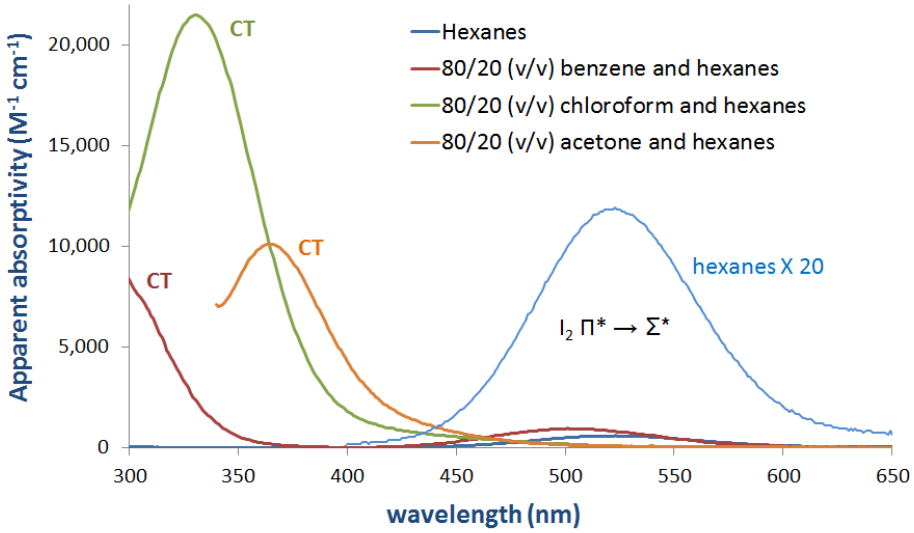


Figure 6.4.3.3. Absorption spectrum of molecular iodine (I_2) in various solvents showing the appearance of a CT band in donor solvents.*

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.

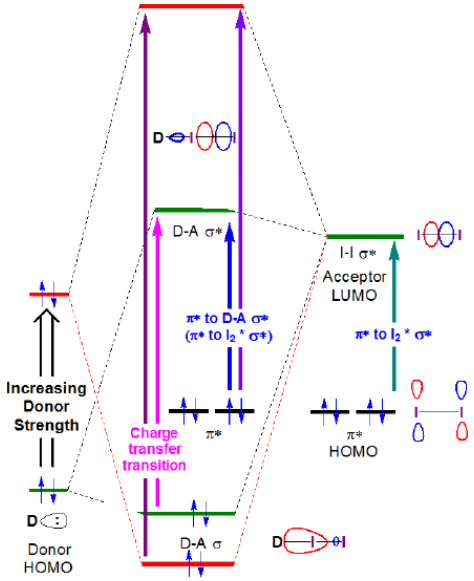


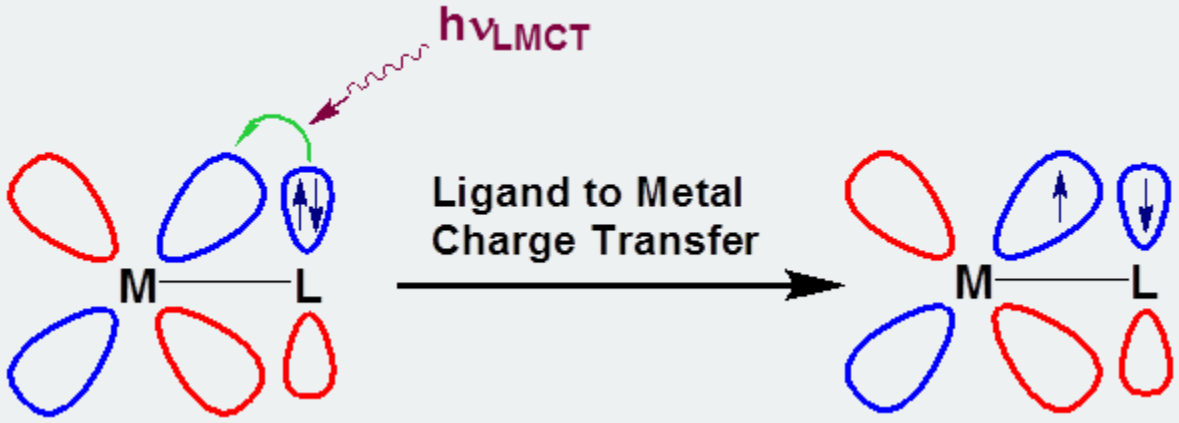
Figure 6.4.3.4. Expected change in the frontier orbital energies associated with I_2 donor acceptor complex formation when the HOMO energy of the donor is increased.

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).**

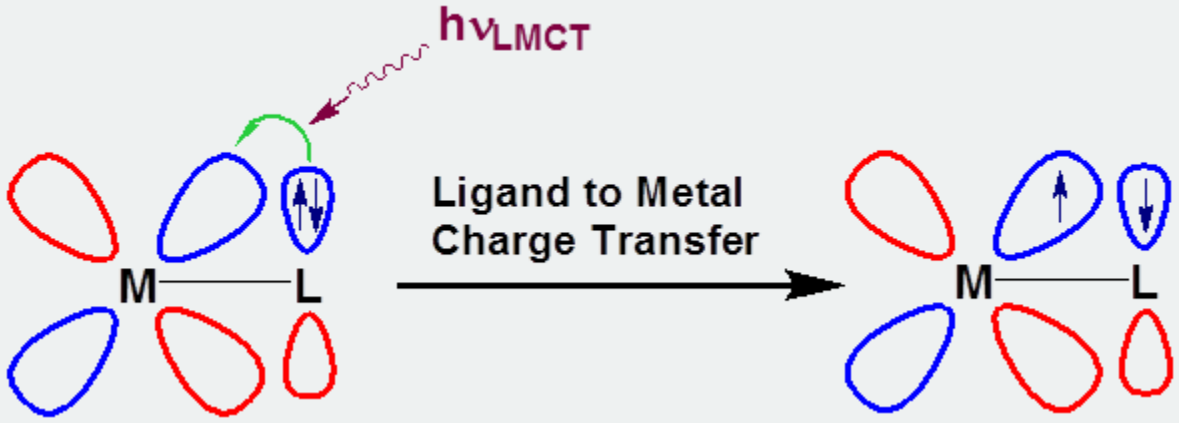
Charge Transfer Bands in Transition Metal Chemistry

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.

References

1. Meyerstein, D.; Treinin, A., Charge-transfer complexes of iodine and inorganic anions in solution. Transactions of the Faraday Society 1963, 59 (0), 1114-1120.
2. Baskar, A. J. A.; Rajpurohit, A. S.; Panneerselvam, M.; Jaccobb, M.; RoopSingh, D.; Kannappan, V., Experimental and theoretical analysis of substituent effect on charge transfer complexes of iodine and some alkylbenzenes in n-hexane solution at 303K. Chemical Data Collections 2017, 7-8, 80-92.

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6.4.4: Substances' solution phase Lewis basicity towards a given acid may be estimated using the enthalphy change for dissociation of its adduct with a reference acid of similar hardness.

A number of spectroscopic and thermodynamic scales have been developed to quantify the strength of Lewis acids and bases.[1,2] For the sake of simplicity only thermodynamic scales will be described. Thermodynamic scales are based on the energetics of Lewis acid-base reactions. When substances act as a Lewis base (B) they form adducts with a Lewis acid (A):

$$B: \ + \ A \ \rightleftharpoons \ B-A$$

Various thermodynamic parameters for this process may be taken as a measure of the strength of the Lewis base towards that acid. For instance, in the case of iodine charge transfer complexes, the equilibrium constant for adduct formation is sometimes used as an informal measure of Lewis base strength.

The thermodynamic parameters used to define Lewis acid and base strength are similar to those used to define Brønsted acidity and basicity. Just as Brønsted acidity and basicity were defined in terms of the free energy change for the dissociation and association of a hydrogen ion, Lewis acidities and basicities are defined in terms of the free energy change for adduct formation:

$$B: \ + \ A_{reference} \ \rightleftharpoons \ B-A \qquad -\Delta G \ = \ Lewis \ basicity \ of \ B \ towards \ A$$

$$B:_{reference} \ + \ A \ \rightleftharpoons \ B-A \qquad -\Delta G \ = \ Lewis \ acidity \ of \ A \ towards \ B$$

The physical meaning of Lewis acidities and basicities may be easier to grasp by considering that Lewis acidities and basicities correspond to the free energy for dissociation of acid-base adducts:

$$B-A \ \rightleftharpoons \ B: \ + \ A_{reference} \qquad \Delta G \ = \ Lewis \ basicity \ of \ B \ towards \ A$$

$$B-A \ \rightleftharpoons \ B:_{reference} \ + \ A \qquad \Delta G \ = \ Lewis \ acidity \ of \ A \ towards \ B$$

Since in practice it is much easier to measure the reaction enthalpies for these processes, many scales use the enthalpy change instead of the free energies. To distinguish these enthalpy changes from Lewis *acidities* and *basicities,* the enthalpy changes are called Lewis acid and base *affinities*. Of these, however, Lewis acid affinities are poorly characterized at present (perhaps one of you readers will help redress this). Thus the remainder of this section will focus on Lewis base affinities.

Before discussing Lewis base affinities it is worth noting that there is no universal reference scale of Lewis base strength. That is because the thermodynamics of a given Lewis acid-base interaction is contingent on a number of factors, including:

- The relative hardness of the acid and base according to Pearson's hard-soft acid base principle. Roughly, Lewis acids tend to associate more strongly with Lewis bases with similar charge densities and polarizabilities. This means that the affinity of a given base for Lewis acids is not a static parameter. Rather it differs markedly with the acid's hardness.
- Steric effects. Sterically hindered Lewis acid-base interactions will be weaker than sterically accessible ones.
- Solvent effects. In solutions, the adduct and the free acid and base pair will in general be differentially stabilized. To avoid solvent effects, some scales quantify Lewis acid and base strength in terms of gas phase adduct formation. However, it is not always possible or desirable to quantify a Lewis acid or base's strength in the gas phase, since gas phase affinities do not always allow for adequate prediction of the strength of a Lewis acid-base interaction in solution.

Because Lewis base affinity depends on hardness, steric effects, and solvent effects care should be taken when acid-base parameters are used to predict the strength of a given interaction. In particular, steric effects should be considered separately, and if predictions are made using scales that employ reference acids or bases that differ markedly in hardness from the interaction to be predicted or which correspond to unrealistic solvent conditions, they should always be taken as tentative.

References

1. Laurence, C.; Graton, J.; Gal, J.-F., An Overview of Lewis Basicity and Affinity Scales. Journal of Chemical Education 2011, 88 (12), 1651-1657.
2. Laurence, C.; Gal, J.-F. o., Lewis basicity and affinity scales: data and measurement. John Wiley: Chichester, West Sussex, U.K., 2010.

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6.4.5: In the boron trifluoride affinity scale, the enthalphy change on formation of an adduct between the base and boron trifluoride is taken as a measure of Lewis basicity.

The physical meaning of Lewis acid and base affinities are defined as the negative of the enthalphy for formation of an adduct with a reference base and acid, respectively:

$$B + A_{reference} \rightleftharpoons B-A \qquad -\Delta H = \text{Lewis basicity of B towards A}$$

$$B_{reference} + A \rightleftharpoons B-A \qquad -\Delta H = \text{Lewis acidity of A towards B}$$

Two common scales of Lewis base affinity involve the use of $SbCl_5$ and BF_3 as the reference base. Specifically,

- In the **Guttman donor-acceptor scale,** Lewis bases' **donor numbers** are equal to the negative enthalpy change for formation of the base's $SBCl_5$ adduct in dilute 1,2-dichloroethane (EDC*):

$$Base(EDC\ solution) + SbCl_5(EDC\ solution) \rightarrow Base-SbCl_5(EDC\ solution) \qquad -\Delta H = \text{Guttman Donor Number}$$

- The **BF_3 affinity scale** has largely supplanted the Guttman scale owing to the ease with which its results may be correlated with computational data (it is easier to calculate energies for adducts of BF_3 than of SbF_5). In the BF_3 affinity scale, Lewis bases' **BF_3 affinities** are equal to the negative enthalpy change for formation of a solution phase adduct between the base and gaseous BF_3. The reaction is:

$$Base(solution) + BF_3(g) \rightarrow Base-BF_3(solution) \qquad -\Delta H = BF_3 \text{ Affinity}$$

BF_3 affinity values for a wide range of organic bases were compiled by Laurence, Graton, and Gal in reference 2 and salient trends in this data will be discussed in subsequent sections.

References

1. Laurence, C.; Graton, J.; Gal, J.-F., An Overview of Lewis Basicity and Affinity Scales. Journal of Chemical Education 2011, 88 (12), 1651-1657.
2. Laurence, C.; Gal, J.-F. o., Lewis basicity and affinity scales: data and measurement. John Wiley: Chichester, West Sussex, U.K., 2010.

Notes

* EDC stands for ethylene dichloride, the common name of 1,2-dichloroethane.

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6.4.6: Lewis base strength may also be estimated by measuring structural or energy changes upon formation of a Lewis acid-base complex, as illustrated by efforts to spectroscopically assess the strengths of halogen bonds

When a Lewis acid and base form an adduct, it shifts the bond lengths, and strengths in the acid and base also shift.

According to the frontier orbital description of Lewis acid-base interactions, adduct formation results in a net transfer of electron density from the base HOMO to the acid LUMO. This transfer

- increases the electron density between the acid (A) and base (D)
- alters the strength of the bonding within the base as the base LUMO becomes partially populated.

These changes result in structural and spectroscopic shifts on adduct formation that can be taken as a measure of the strength of the Lewis acid-base interaction. Since these shifts depend on the nature of the bonding in the acid and base, in practice structural and spectroscopic measurements of Lewis basicity are applied to a few classes of Lewis acid-base interactions, most notably hydrogen bonding and halogen bonding. Since hydrogen bonds will be discussed in section 6.5.1. the remainder of this subsection will focus on halogen bonds.

Halogen bonds are coordinate covalent bonds formed between a Lewis base and an organohalogen.

The halogens in compounds containing a singly-bonded halogen can engage in a special type of intermolecular interaction called halogen bonding, since the bonded halogens are electrophilic on the opposite side of the bond. This electrophilicity is apparent from the charge distribution in CF_5I shown in Figure 4.5.1, in which the charge is distributed on the I such that the I is Lewis basic perpendicular to the C-I bond and Lewis acidic opposite to it. This region of diminished electron density on the halogen opposite the existing sigma bond is called a σ-hole.*

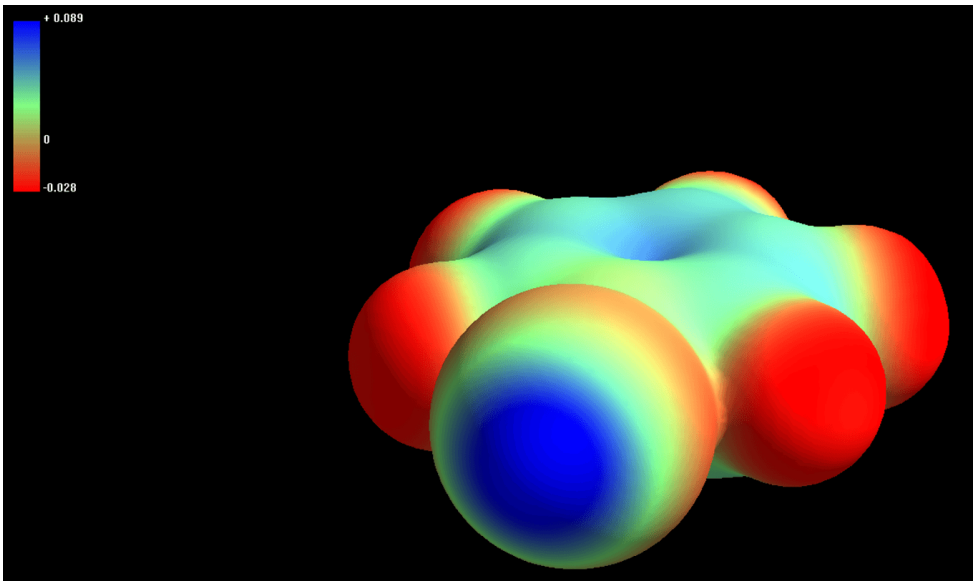
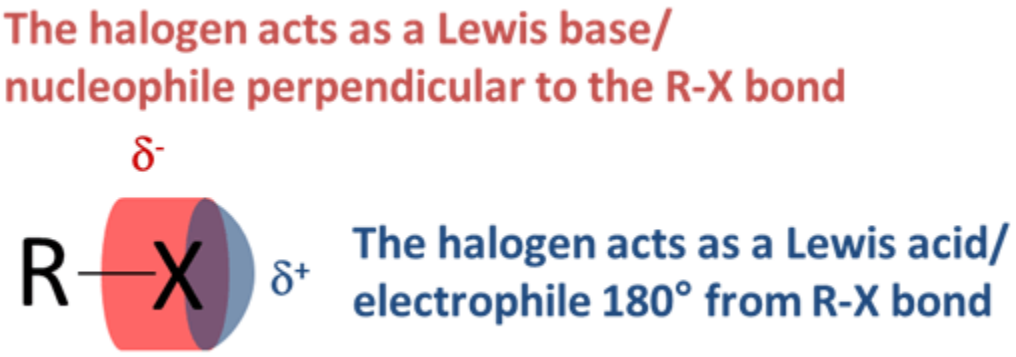
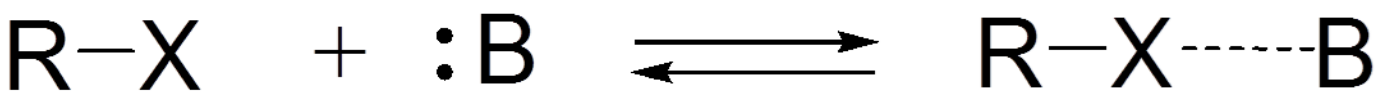


Figure 6.4.6.1. Electrostatic surface calculated for CF_5I at the STO-3-21G level oriented so that the C-I bond is facing toward the viewer. The sigma hole shown is the region of positive electron density on the I atom at the front of the image. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Schematically,



Since the halogen can act as a Lewis acid in the direction opposite the R-X bond it can form adducts with Lewis bases in that direction.



The bonds holding these adducts together are called **halogen bonds**, often abbreviated XB.

The halogen is said to act as a halogen bond donor when it forms a halogen bond with a base along that direction, with the base acting as the halogen bond acceptor. Consequently, the two previous schemes may also be given as:



The ability of singly-bonded halogen atoms to form halogen bonds forms the basis of many efforts to engineer structures in which halogen-containing compounds are held together into chains, sheets, or 3D structures using halogen bonds. One easy-to-see example involves 1D chains formed between *p*-diiodotetrafluorobenzene and *p*-bis(dimethylamino)benzene.[3]

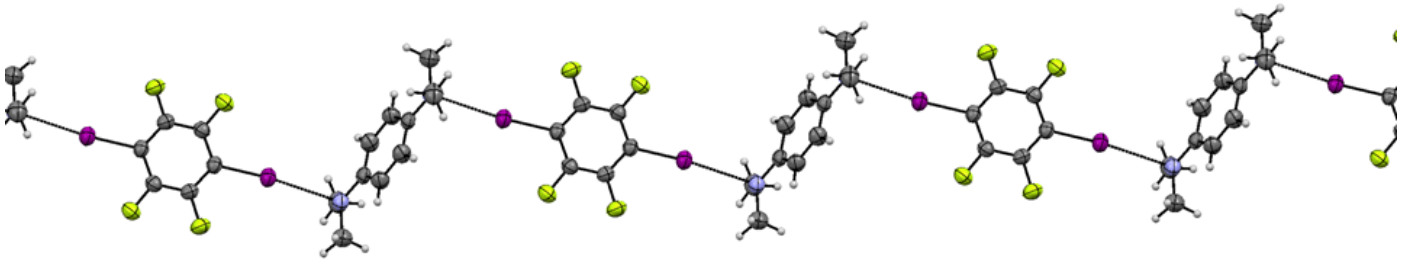
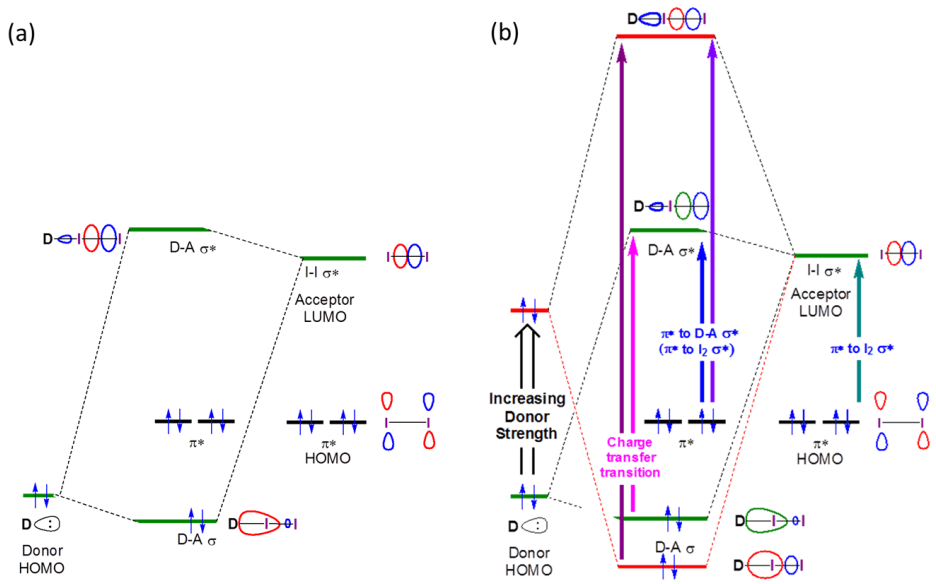


Figure 6.4.6.2. 1D chains of *p*-tetrafluorodiiodobenzene and *p*-bis(dimethylamino)benzene molecules in which I is shown in purple, N in blue, F in yellow, and C in grey. The chains are held together by C-I---N halogen bonds with a contact angle of 174 degrees. The figure was produced using Mercury 3.5.1 based on Cambridge crystallographic database entry 172272. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Trends in halogen bond strength in a closely-related series of compounds may be assessed by examining how the vibrational stretching frequency of I_2 and the I_2 π^* to σ^* transition energy change upon formation of the adduct.

From the description of halogen bonding above it should be apparent that the iodine charge transfer complexes described in section 6.4.2 are held together by halogen bonds. This means that the description of the bonding in I_2 charge transfer complexes given in that section illustrate how vibrational and electronic transitions shift when a halogen-bonded adduct is formed between a halogen bond donor and acceptor.

The orbital interactions involved in halogen bond formation are shown in Figure 6.4.5.3. As can be seen from that figure, the formation of an adduct between I_2 and a Lewis base is expected to result in weakening of the I-I bond and a shift in the I_2 $\pi^* \rightarrow \sigma^*$ transition energy to higher energy/shorter wavelengths (*i.e.,* a blueshift). Further, both the weakening of the I-I bond and the I_2 $\pi^* \rightarrow \sigma^*$ blueshift are expected to increase with the HOMO energy of the Lewis base.



Figures 6.4.2.2 and 6.4.2.4. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Because the I-I bond strength and $I_2\ \pi^* \rightarrow \sigma^*$ blueshift increase with the Lewis basicity of the donor, the blueshift and the I-I vibrational stretching frequency are sometimes used as measures of donor's halogen bond affinity. However, the data obtained from such spectroscopic measurements should be interpreted with a degree of caution. As seen in Table 6.4.5.1, the extent to which the I-I bond is weakened (indicated by $\Delta\nu_{I-I}$) and the $I_2's\ \pi^* \rightarrow \sigma^*$ band is blue shifted are imperfectly correlated overall. However, a careful comparison of the data in 6.4.5.1. reveals that the I-I bond weakening and $I_2's\ \pi^* \rightarrow \sigma^*$ blue shift correlate well for Lewis bases of a given type. Consequently, shifts in the I-I stretching frequency and $I_2\ \pi^* \rightarrow \sigma^*$ absorption band are not useful as an absolute measure of Lewis basicity but can be used to rank the halogen bond affinity of a closely-related set of donors.**

Table 6.4.6.1. *Spectroscopic measures of Lewis basicity for* I_2 *adducts of selected bases arranged in order of extent of blue shift. The data are excerpted from the extensive compilation given in reference 4.*

Base (type)	$\Delta\nu_{I-I}\ cm^{-1}$	Blue shift of $I_2's\ \pi* \rightarrow \sigma*$
4-methylpyridine (pyridines)	29.1	4730
pyridine (pyridines)	27.4	4560
tetrahydrothiophene (thioethers)	44.5	3640
tetrahydrofuran, THF (ethers)	6.4	2280
diethyl ether (ethers)	5.5	1950
acetone (ketone)	5.0	1850
acetophenone (ketone)	4.6	1650
acetonitrile (nitrile)	4.1	1610
hexamethylbenzene (aromatic)	10.4	1070
benzene (aromatic)	4.3	450

References and Further Reading

1. Cavallo, G.; Metrangolo, P.; Milani, R.; Pilati, T.; Priimagi, A.; Resnati, G.; Terraneo, G., The Halogen Bond. *Chemical Reviews* 2016, *116 (4)*, 2478-2601.
2. Politzer, P.; Murray, J.S. σ-Hole Interactions: Perspectives and Misconceptions. *Crystals* **2017**, *7*, 212.
3. R.Liantonio, S.Luzzati, P.Metrangolo, T.Pilati, G.Resnati, *Tetrahedron*, 2002, 58, 4023, DOI: 10.1016/S0040-4020(02)00264-8

4. Laurence, C.; Gal, J.-F. o., *Lewis Basicity and Affinity scales: Data and Measurement*. John Wiley: Chichester, West Sussex, U.K., 2010.

Notes

* Other compounds also exhibit σ-holes (and π-holes) that can be used in crystal engineering. For details see reference 2.

** for more details consult reference 4, pp. 286-309.

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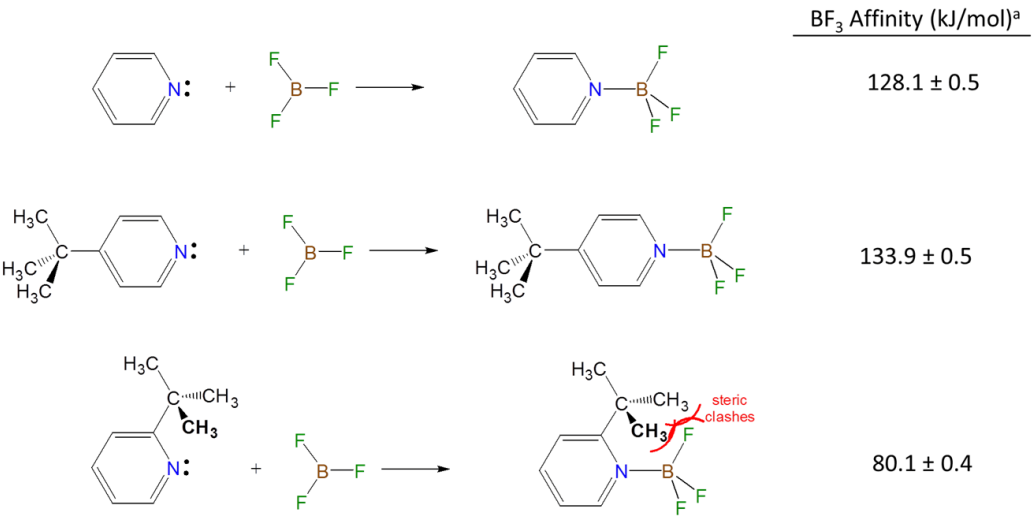
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6.4.7: Bulky groups weaken the strength of Lewis acids and bases because they introduce steric strain into the resulting acid-base adduct.

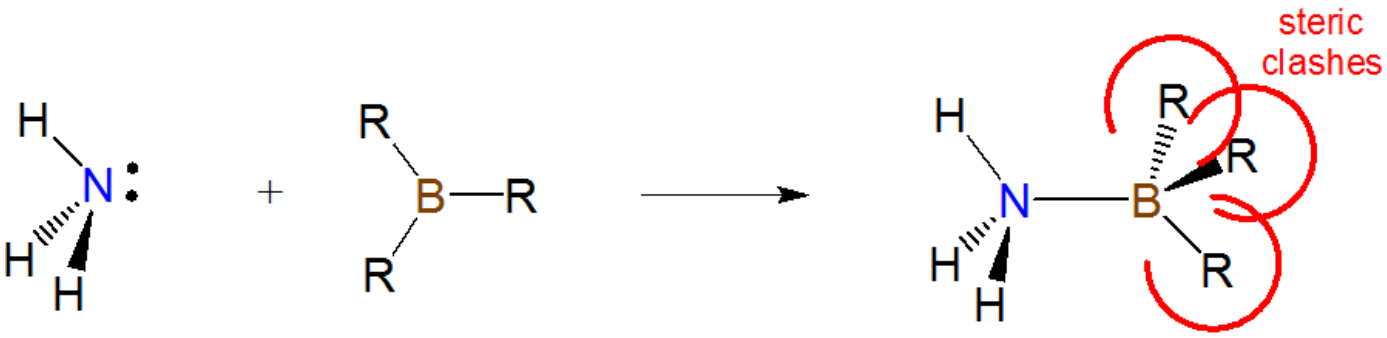
Steric effects can influence the ability of a Lewis acid or base to form adducts by introducing:

- **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

1. Alder, R. W., Strain effects on amine basicities. *Chemical Reviews* 1989, 89 (5), 1215-1223.

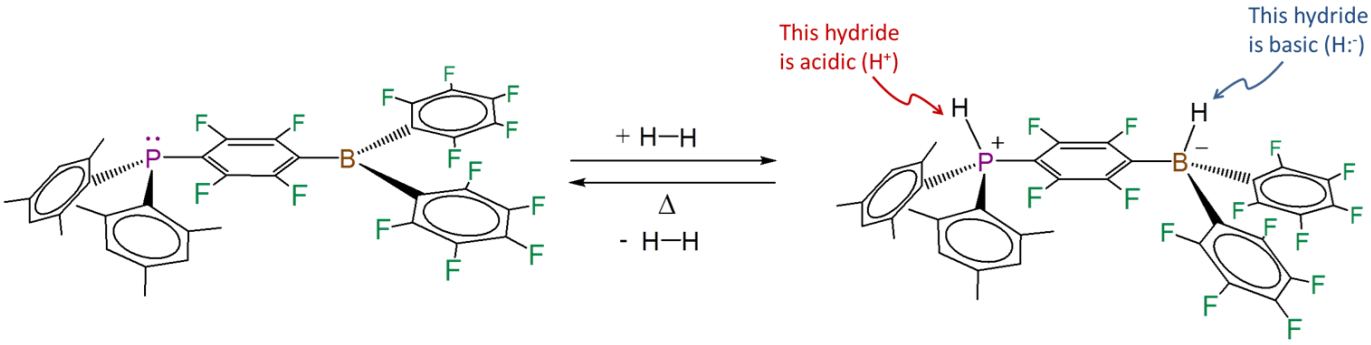
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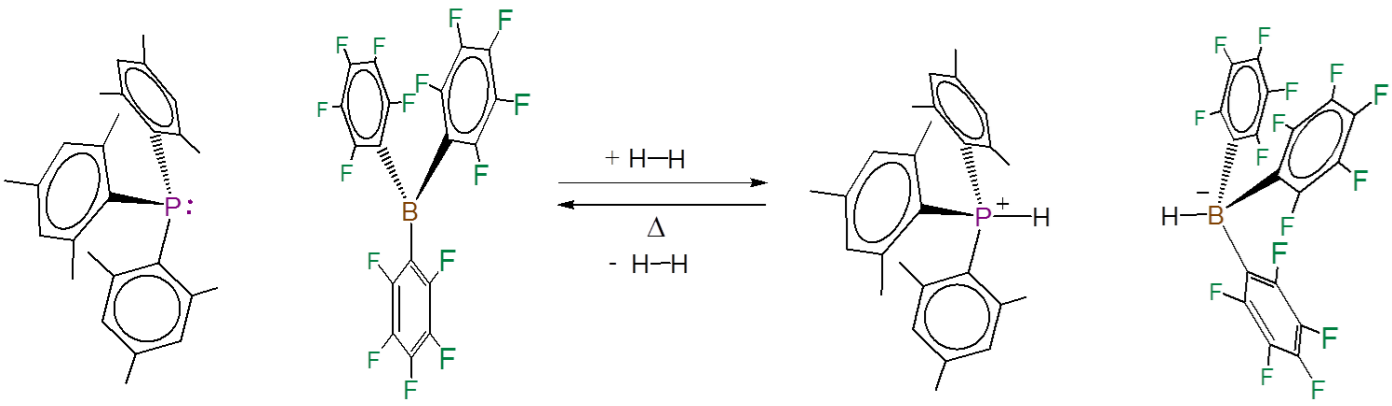
6.4.8: Frustrated Lewis pair chemistry uses Lewis acid and base sites within a molecule that are sterically restricted from forming an adduct with each other.

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**.

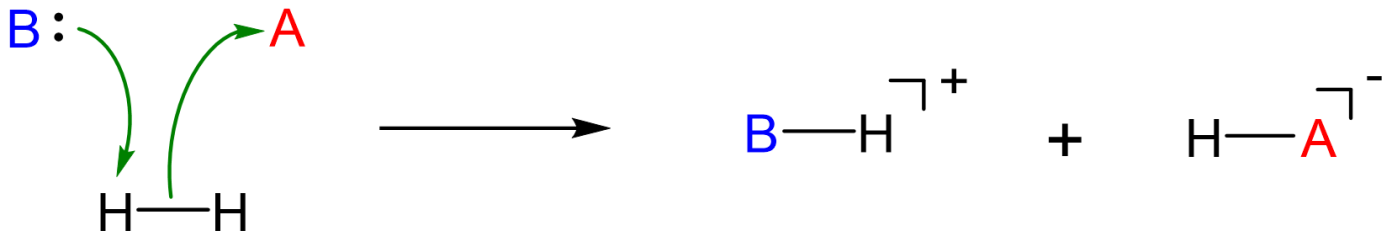
The **Stephan's phosphinoborane** illustrates how FLP chemistry works. It reversibly cleaves dihydrogen to give a zwitterionic species containing both acidic and basic element hydride bonds.



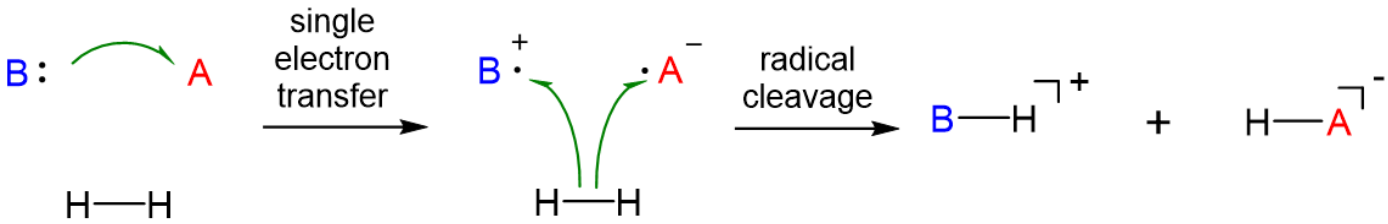
Note that the Lewis acid and base do not need to be part of the same molecule. Hydrogen is also heterolytically cleaved by mixtures of sterically encumbered triarylphosphines and triarylboranes. This time the reaction gives phosphonium and hydroborate ions:



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

1. Stephan, D. W., Frustrated Lewis Pairs: From Concept to Catalysis. *Accounts of Chemical Research* 2015, 48 (2), 306-316.
2. Fontaine, F.-G.; Stephan D. W., On the concept of frustrated Lewis pairs. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 2017, 375 (2101), 20170004.
3. Jupp, A. R.; Stephan, D. W., New Directions for Frustrated Lewis Pair Chemistry. *Trends in Chemistry* 2019, 1 (1), 35-48.

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6.5: Intermolecular Forces

As suggested by the Lewis acid-base concept's ability to describe halogen bonding in terms of the interaction between electrophilic and nucleophilic centers, the Lewis concept can be applied to the understanding of a variety of intermolecular interactions. In the next two sections the utility of Lewis Theory for understanding hydrogen bond and $\pi - \pi$ stacking interactions will be examined.

Contributors and Attributions

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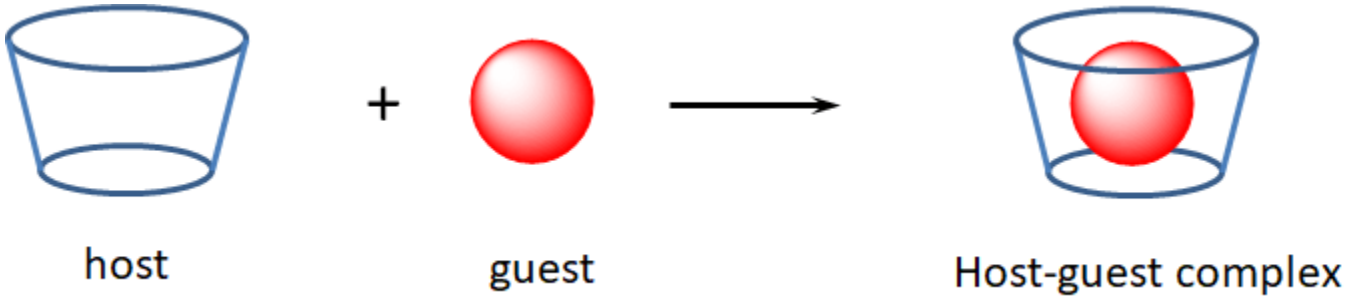
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6.5.1: Host-Guest Chemistry and π-π Stacking Interactions

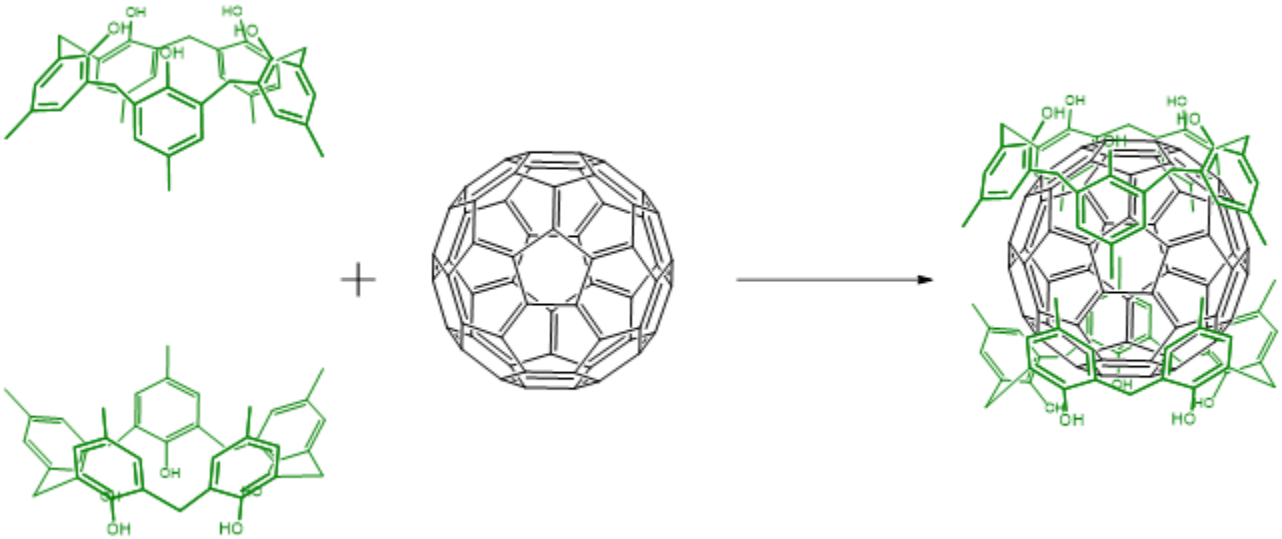
This section sidesteps the discussion of topics related to acid-base chemistry and indulges in a brief aside about one type of intermolecular interaction that is used in host-guest chemistry. This section will first describe the concept of host-guest chemistry, then outline the types of interactions and design principles that can be used to promote host-guest interactions, and finally conclude with a discussion of $\pi - \pi$ interactions.

In Host-Guest Chemistry a large molecule or network material noncovalently binds a smaller molecule in a binding pocket.

In host-guest chemistry, a large molecule or network host uses noncovalent interactions to bind a smaller molecule guest in a binding pocket. Schematically this interaction is often represented as:



Host-guest binding is analogous to the way many biomolecule-substrate interactions occur - *e.g.,* to how antibodies bind antigens and many enzymes bind their substrates. In this way many biomolecular systems can be said to form host-guest complexes, although that terminology is not often used in the biochemistry field. Usually when someone refers to a host-guest complex in inorganic or organic chemistry they are referring to organic or metal-organic cages that bind small organics. A simple example involves the binding of buckminsterfullerene, C_{60}, by calix-[5]-arenes.



In principle any type of intermolecular interaction can hold a host-guest complex together, but whichever one you choose, it helps to pay attention to a few design principles.

The types of interactions that are used to effect host-guest binding are diverse. In the fullerene-calixarene example above, the interactions will primarily involve π stacking interactions between the aromatic rings of the calixarenes and those in the fullerene. Other host-guest systems use some combination of:

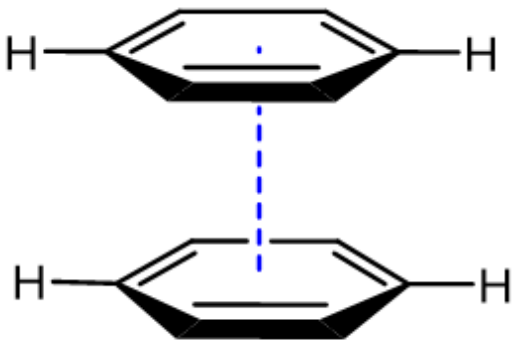
- hydrogen bonds
- halogen bonds
- ionic interactions whereby charged groups from the host attract oppositely charged groups of the guest
- ion-dipole interactions whereby charged groups on one component interact with the appropriate end of a polar group on the other.
- dipole-dipole interactions
- cation-π, X-H-π, and similar interactions in which full or partial positive charges induce a complementary dipole in a π system.
- $\pi - \pi$ interactions
- dispersion forces

Many effective host-guest systems employ a few design principles to favor host-guest binding. These principles include:

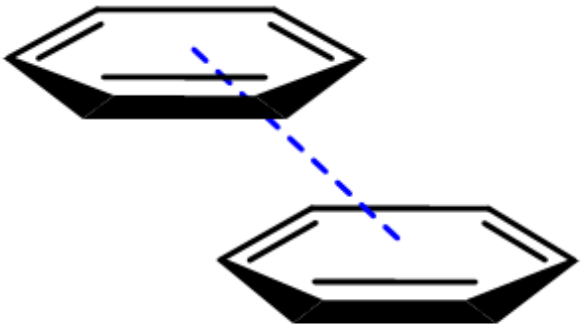
- **host preorganization** - when conformationally flexible (-*i.e.,* floppy) hosts bind a guest, the host will conform to the shape of the guest and so become more rigid. In other words, when a floppy host binds to a guest, a lot of conformational entropy is lost. This will make the ΔS term for the binding free energy more negative and tends to disfavor host-guest binding. To avoid this, effective hosts minimize the loss of conformational entropy on binding. This is usually done by limiting the conformational entropy of the host to begin with by fusing multiple binding sites into a macrocyclic ring, cage, or cluster. The more rigid these are the better.
- **host-guest size and shape complementarity** - this simply means that complexes form when the binding pocket or cavity of the host is complementary to that of the guest. Specifically, its size and shape both fit the guest and allow for tight interactions (*i.e.,* the guest doesn't rattle around inside). Moreover, any charged, polar, or any-directional binding sites on the host are arranged in such a way that they interact favorably with complementary sites on the guest.
- **preferencing of guest desolvation via preferential solvent-solvent interactions*** - $\pi - \pi$ interactions like those which hold the calixarene-fullerene complex together are weak compared to stronger interactions like hydrogen bonds or even water-π bonding (a type of X-H π bonding. However, water-water hydrogen bonds and other interactions between H-bond-capable and polar systems are stronger still. This means that favorable water-water interactions must be broken when a nonpolar host or guest is dissolved in a very polar or ionic solution. Every dipole-induced dipole or X-H π interaction that takes place is a lost opportunity for solute molecules to engage in hydrogen bonding interactions. Thus, when an aqueous solution of a nonpolar host and guest are mixed, the nonpolar parts of these molecules will tend to stick together, freeing water or other polar molecules to interact with one another as they do so.**

$\pi - \pi$ interactions occur when aromatic π systems bind face to face with one another and involve a combination of dispersion and dipole-induced dipole interactions.

Since the electron distribution in aromatic systems is relatively easily distorted, they can engage in atypically strong dispersion and dipole-induced dipole interactions called $\pi - \pi$ **stacking interactions**. These interactions are so named because they occur when the planes of aromatic rings are stacked parallel to one another. This parallel stacking can occur in either a sandwich or a displaced stacking arrangement.

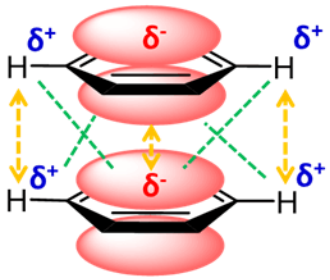


Sandwich
or eclipse stacked

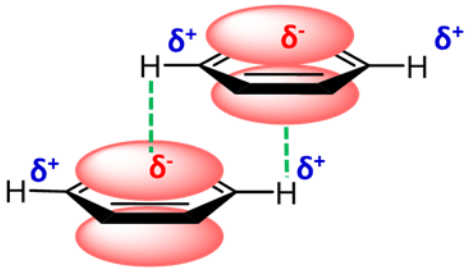


DIsplaced stacked

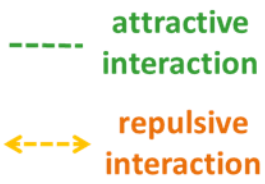
In either case the rings can be attracted to one another by a combination of dispersion and electrostatic interactions. The latter depend on the specific bonding parameters of the system and can be attractive or repulsive. The eclipsed arrangement of the benzene dimer is electrostatically disfavored, while attractions between the positive hydrogen substituents and the π system of an adjacent ring are attractive in the eclipsed arrangement.



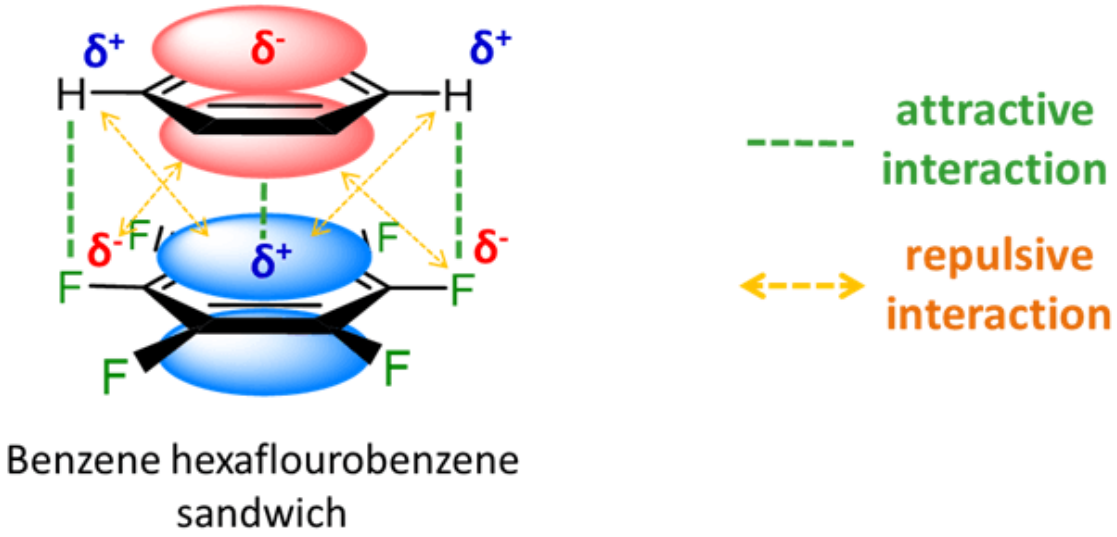
Benzenes sandwich
or eclipse stacked



Benzenes displaced stacked



With electronegative substituents, the polarity of the ring system is reversed so that there are favorable electrostatic interactions in an eclipsed heterodimer of benzene and hexafluorobenzene.



Benzene hexaflourobenzene sandwich

In the heterodimer of benzene and hexafluorobenzene, at last we have an example of a π stacking system that can more readily be described as involving a Lewis acid-base interaction. Specifically, the relatively electron-rich benzene π system acts as a Lewis base in donating "electron pairs" to the electron-poor hexafluorobenzene π system.

Notes

* The most prominent example of desolvation as a driving force is the hydrophobic effect. The hydrophobic effect governs the structure of soaps, micelles, biomolecules, and other amphiphilic or nonpolar systems in water. In the hydrophobic effect, the preference of an aqueous solution of a hydrophobic solute to maximize water-water interactions means that hydrophobic groups tend to stick together in solution.

** A good analogy for this effect is the magnetic marble analogy. When magnetic and ordinary marbles are mixed, the magnetic marbles will tend to stick together because they will attract one another strongly, not because the interactions between the nonmagnetic marbles are somehow disfavored.

† This is not to say that the stacking arrangements lead to attraction in every instance. There are arrangements in which the parallel rings are expected to repel.

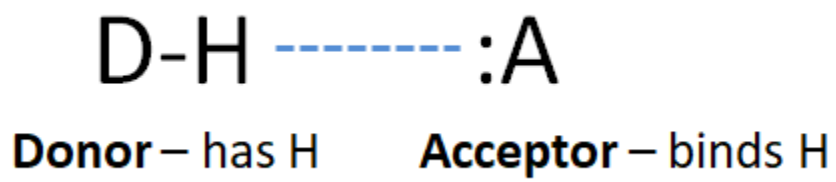
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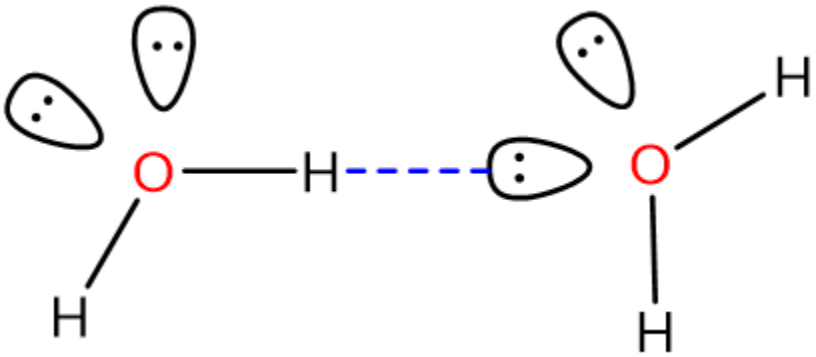
6.5.2: Hydrogen bonds may be considered as a special type of Lewis acid-base interaction in which a Lewis acid hydrogen ion is shared between Lewis bases

A hydrogen bond is a bonding interaction in which an E-H hydrogen bond donor unit acts as a Lewis acid in donating a hydrogen ion to a hydrogen bond acceptor, A.

Classically, hydrogen bonds (H-bonds) have been defined as a special type of intermolecular force between D-H and :A, where D & A = N, O, F, and occasionally S. The D-H is said to be the hydrogen bond donor while :A is the hydrogen bond acceptor.



Consider, for instance, a hydrogen bond between two water molecules:



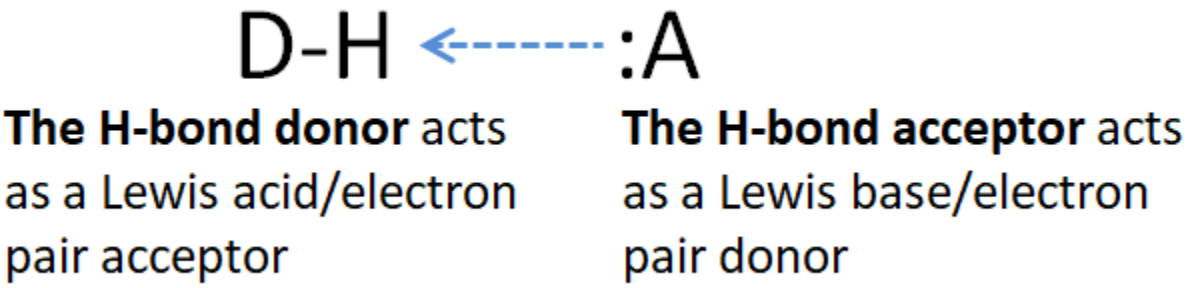
An O-H bond in the water on the left serves as the hydrogen bond donor while one of the lone pairs on the oxygen of the water on the right acts as the hydrogen bond acceptor.* The strength of this classical hydrogen bonding interaction is ~12-20 kJ/mol, much greater than typical dipole-dipole interaction energies (<4 kJ/mol), and even though the hydrogen bonds in water are somewhat flexible, the O-H---O hydrogen bond axis prefers to be linear in many cases [1]. These factors suggest that hydrogen bonds are more than just a special type of dipole-dipole interaction involving hydrogen. Instead, hydrogen bonds involve a combination of factors, including:

- dipole-dipole interactions
- covalent bonding
- dispersion forces
- X-H π-interactions**

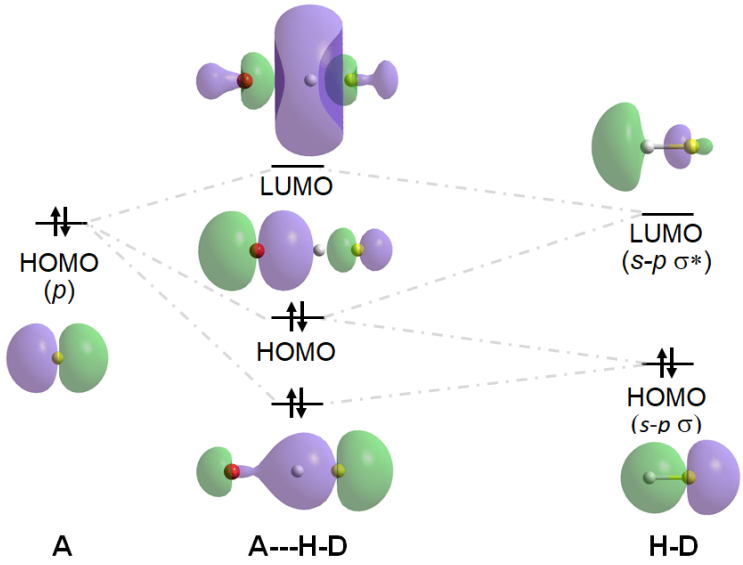
The relative importance of these interactions can differ significantly from one system to another.

In considering how to better understand hydrogen bonding, both Brønsted and Lewis acid-base concepts have been employed. In Brønsted terms, hydrogen bonding has been described as involving a partial transfer of a hydrogen ion from D to A. The

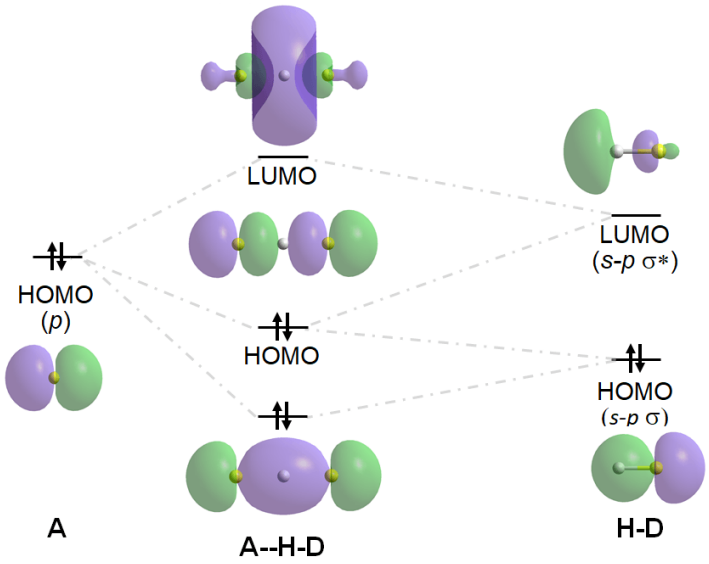
Lewis definition is often more useful for understanding the role of covalency, however, owing to the ease with which Lewis theory accommodates orbital interactions through the Frontier orbital approach to chemical bonding and reactivity. Moreover, from the classical definition of hydrogen bonding as involving donation of H by a D-H unit and its acceptance by a lone pair on A, it is apparent that in some sense D-H is acting as a Lewis acid in donating an electron-deficient H to A while A is acting as a Lewis base in using its lone pair to accept it. In this respect, the hydrogen bond is perhaps better thought of as involving Lewis acid-base adduct formation between a D-H bond and A.



This more expansive definition of a hydrogen bond as involving a Lewis acid-base interaction accommodates the much wider variety of hydrogen bonding interactions that have been recognized since the 1990s. While the classical definition of hydrogen bonding accounts for much of the hydrogen bonding that occurs in water, organic, and biomolecular systems, the large number of multicenter H-bonds[†] and the ability of C-H, P-H, and Au-H to function as hydrogen bond donors and for π systems to function as hydrogen bond acceptors is excluded by the classical definition of a hydrogen bond. In contrast, the Lewis-based definition allows for the understanding of covalent contributions to hydrogen bonding in such systems in terms of the overlap of frontier orbitals on D, H, and A. Consider, for example, the frontier orbital interactions involved in a typical hydrogen bond between D-H and A:[††]



Hydrogen bonds like the one above are called asymmetric hydrogen bonds since the D-H bond is shorter and more stabilized than the A-H bond. When D and A are of equal or similar energy, however, the D-H and A-H interactions are of similar energy, and the H will be centered in between D and A, making it difficult to identify which atom is the donor and which is the acceptor. Such H-bonds are called symmetric H-bonds. An example is the H-bond in $[F{---}H{----}F]^-$, for which the stabilizing and destabilizing frontier orbital interactions are



In general, symmetric hydrogen bonds are stronger and more stable than asymmetric ones. In fact, one approach to predicting the strength of classical hydrogen bonds called Gili's **pKa Slide Rule**‡ considers the pKa of the protonated form of both the neutral donor (D-H) and the neutral acceptor (A, which is then protonated to H-A^+). In this approach the H-bond is considered to involve transfer of a hydronium ion between the donor and acceptor, and the pK_a values of the donor and acceptor serve as proxies for D^- and A's ability to draw the hydrogen ion in the H-bond to itself. When the

- donor is more basic (*i.e.,* its pK_a is higher) relatively little transfer occurs, and the hydrogen bond is better represented as D-H----A
- acceptor is more basic (i.e., its pK_a is higher) the hydrogen ion is transferred from D to A, giving a hydrogen bond better represented as D----H-A
- donor and acceptor are about equally basic (have similar pK_a values) the hydrogen ion is roughly shared equally between D and A in a symmetric H-bond, D--H--A

Specifically, Gili proposed the following criteria for predicting the strength of these ordinary hydrogen bonds:

Hydrogen Bond type	ΔpK_a
Strong (11.5-15.8 kcal/mol)	0-3
Medium Strong (6.8-11.5 kcal/mol)	3-11
Medium (4.1-6.8) kcal/mol	11-21
Medium Weak (2.5-4.1 kcal/mol)	21-31
Weak (1.1-2.5 kcal/mol)	>31

Experimentally, the existence of hydrogen bonds and their approximate strength is inferred from crystallographic bond distances and angles, changes in the D-H vibrational frequency, and shifts in ^{1}H NMR peak positions, although all such measures should be interpreted with caution.

If hydrogen bonds involve full or partial coordinate covalent bond formation between a D-H bond and an acceptor site, then the resulting adduct should exhibit evidence of bond formation. In practice such evidence is sought from three main sources:

1. *Crystallographic bond distances and angles.* In the structure of crystalline solids, hydrogen bonds can be distinguished from

Van der Waals contacts in that

- the D----A distance is closer than that expected from the Van der Waals surfaces of D and A.
- when the H can be located, the D-H distance is longer than non-hydrogen-bonded D-H bonds in similar systems.
- for two-centered hydrogen bonds unconstrained by external factors, the D-H---A angle will approach linearity, as VSEPR theory would predict for a D:H:A unit.

2. *D-H vibrational frequencies.* Since hydrogen bonding involves weakening of the D-H bond and the formation of an H-A bond, in theory both the D-H and A-H vibrational modes will be found in the IR spectrum of a hydrogen-bonded system, albeit redshifted to lower wavenumbers than the unweakened D-H and A-H bonds. In practice, the shift in the D-H vibrational band to lower wavenumbers (along with a broadening and intensifying of the band) is taken as evidence for hydrogen bonding (Figure 6.5.1.1).

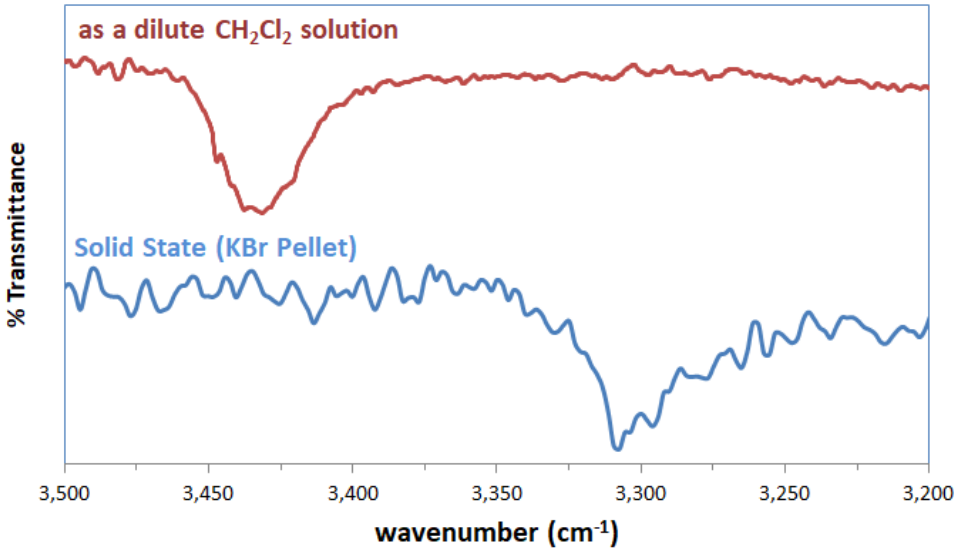
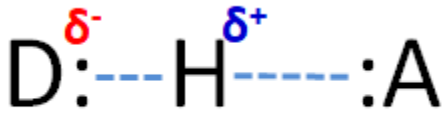


Figure 6.5.1.1. N-H vibrational bands in the IR spectrum of *N*-ferrocenylisonicotinamide. In dilute solution the N-H stretch of isolated molecules occurs at 3430 cm^{-1} but in the solid it shifts to 3307 cm^{-1} as the molecules form a network of H-bonded chains.

3. Shifts in the ^1H NMR peak position of the donor hydrogen. As the hydrogen is partially transferred from D to A it becomes deshielded and so is shifted downfield, sometimes by as much as several ppm.



Care should be taken in applying these criteria since:

- The criteria work best for classical hydrogen bonded systems. Other aspects of the bonding in a given system can influence apparent bond strengths and NMR chemical shifts, particularly for intramolecular H-bonds and in nonclassical hydrogen bonding systems.
- Stronger hydrogen bonds are more likely to adhere to these criteria than weaker ones. Moreover, stronger hydrogen bonds generally exhibit greater linearity, shorter distances relative to those expected from Van der Waals radii, larger stretching frequency lowering for D-H, and greater downfield shifts in their NMR spectra.

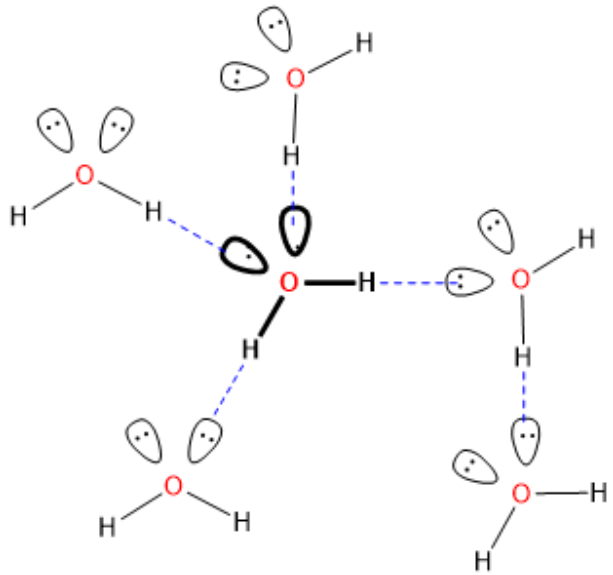
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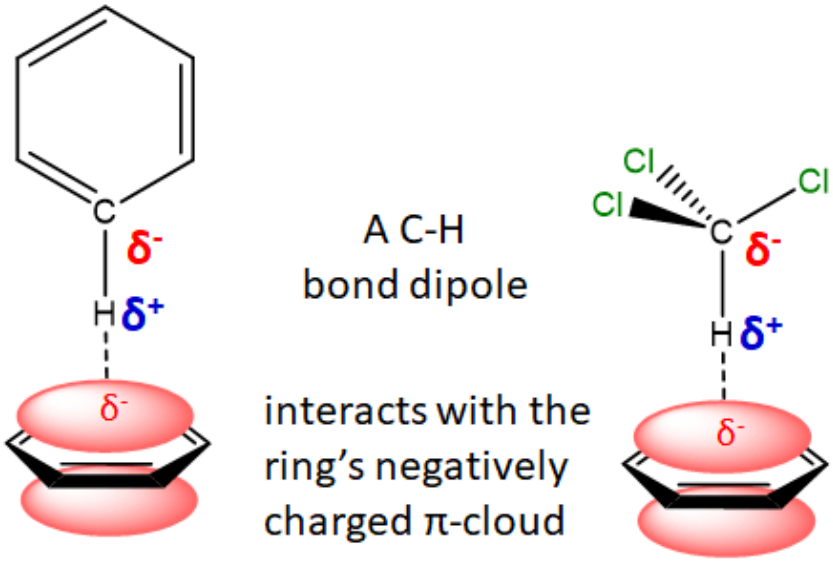
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Notes

* Of course in solutions where there are many hydrogen bonding interactions many of the water molecules might simultaneously act as a hydrogen bond donor and acceptor.



** X-H π interactions are interactions between the partial positive charge on the H end of a polar X-H bond and a negatively-charged π-bond. These are particularly for understanding hydrogen bonded systems in which as π-system serves as the hydrogen bond acceptor,. Examples of X-H interactions in which benzene is the acceptor are illustrated below.



† In a multicenter H-bond the D-H is donated to multiple acceptors simultaneously.

†† The MOs shown in the diagrams were calculated by performing *ab initio* calculations at the 6-31G** level. Those for the symmetric H-bond correspond to FHF^- and the assymetric H bond to OHF^-.

‡ So called because it involves a sliding bar chart with common classes of H-bond donors and acceptors that may be slid along the rule in a manner similar to the operation of a pre-late 20th Century device for performing mathematical computations called a slide rule.

‡‡ for example, intramolecular hydrogen bonds are sometimes constrained to by the overall geometry of the interacting groups.

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6.6: Hard and Soft Acids and Bases

Origin of the Hard-Soft Acid-Base Principle

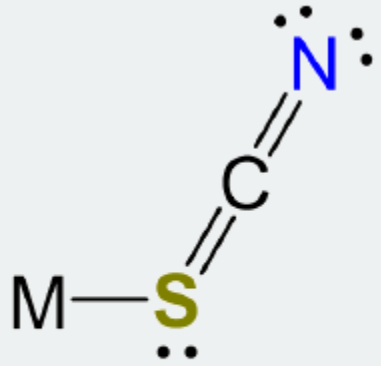
One of the strengths of the Lewis acid-base concept is the readiness with which it illuminates the role that covalent and electrostatic interactions in acid base behavior, specifically through its ability to explain chemical interactions in terms of frontier orbitals and the interactions between charged 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:

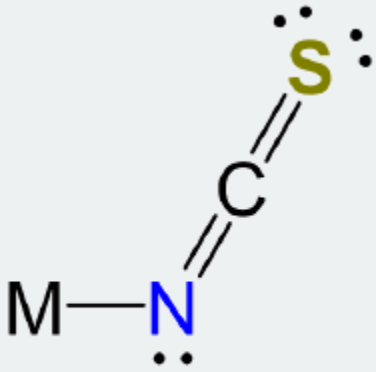
- Some metals are commonly found in nature as salts of chloride or as oxide ores while others are found in combination with sulfur. Geochemists even use the Goldschmidtt classification scheme to classify the halide and oxide formers as lithophiles and the sulfide formers as chalcophiles.
- In living 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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6.6.1: Quantitative Measures of Hardness, Softness, and Acid-Base Interactions from a Hard Soft Acid-Base Principle Perspective Involve Orbital Energies and/or Apportioning Acid-Base Bonding in Terms of Electrostatic and Covalent Factors

Pearson Absolute Hardness is a useful metric of hardness based on orbital energies

The recognition that hard acids and bases possess a large HOMO-LUMO gap suggests that the gap size itself might serve as a useful index of hardness. The basis for this idea may be found by considering Pearson's definition of absolute hardness, η.[1] **Pearson's absolute hardness, η**, is half the second derivative of a species' energy with respect to changes in total number of electrons, N_{e^-}.

$$\text{Pearson's absolute hardness} = \eta = \frac{1}{2}\frac{d^2E}{dN_{e^-}^2}$$

$$(in \;\; eV)$$

and, since acids' and bases' hardness and softness are inversely related, Pearson's absolute softness, σ, is just the inverse of hardness.

$$\text{Pearson's softness} = \frac{1}{\eta}$$

Of these, Pearson's absolute hardness is related to the **Mulliken definition of electronegativity** as the first derivative of a species' energy with respect to changes in total number of electrons.

$$\text{Mulliken electronegativity} = \chi = \frac{dE}{dN_{e^-}}$$

$$(in \;\; eV)$$

Operationally, both the Pearson hardness and Mulliken electronegativity are approximated in terms of the energies associated with unit changes in the number of electrons – *i.e.,* in terms of ionization energies and electronegativities. Specifically,

$$\text{Pearson's absolute hardness} = \eta \approx \frac{IE–EA}{2}$$

$$\text{Mulliken electronegativity} = \chi \approx \frac{IE + EA}{2}$$

where IE and EA are in eV.

The connection between Pearson's absolute hardness/softness and the HOMO-LUMO gap then follows from Koopman's theorem, in which the ionization energy (IE) is just the opposite of the HOMO energy.

$$IE = -E_{HOMO}$$

Similarly, the electron affinity (EA), defined as the opposite of the energy released on absorption of an electron, may be taken as an approximation of the LUMO energy.

$$E_{LUMO} \approx -EA$$

So Pearson's absolute hardness is just half the HOMO-LUMO gap (band gap) size in electron volts:

$$\text{Pearson's absolute hardness} = \eta \approx \frac{E_{LUMO} - E_{HOMO}}{2}$$

where all values are given in eV,

and the Mulliken electronegativity is just the average of the HOMO and LUMO energies (~Fermi energy):

$$Mulliken\ electronegativity, \chi \approx -\frac{E_{LUMO} + E_{HOMO}}{2}$$

$$where\ all\ values\ are\ given\ in\ eV$$

The relationships between the Pearson absolute hardness, Mulliken electronegativity, and HOMO and LUMO energies are depicted schematically for the group 1A monocations in Figure 6.6.1.1.

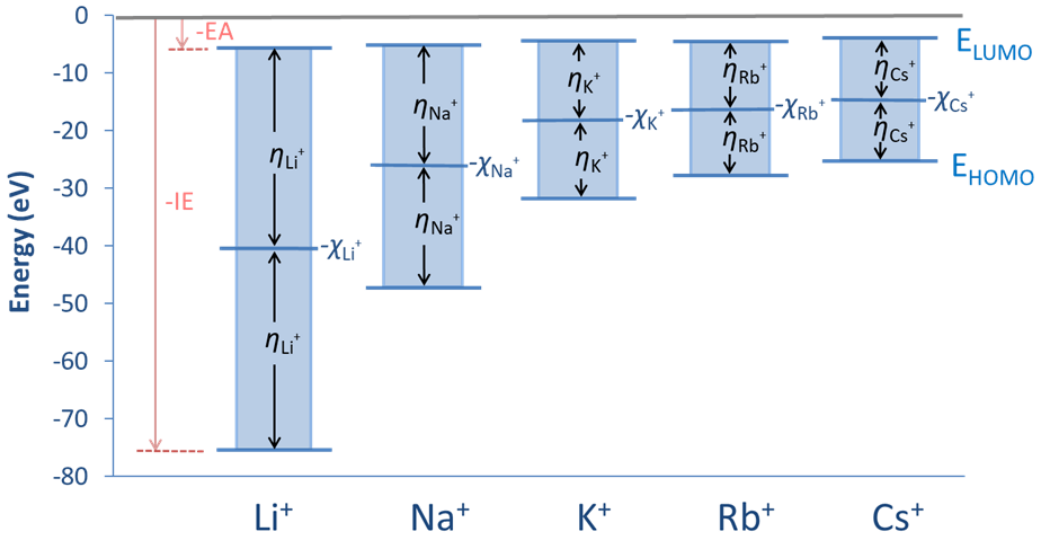


Figure 6.6.1.1. Relationships between Pearson absolute hardness, Mulliken electronegativity, and HOMO and LUMO energies for the group 1A monocations.

Values of the Pearson hardness and Mulliken electronegativity for several acids and bases are given in Table 6.6.1.1. The values in the table confirm the expected trends, showing an increase in hardness with size (down a group), with increasing charge, and as substituent electronegativity increases for a series of isolobal ions.

Table 6.6.1.1: Pearson Absolute Hardness and Related Parameters for Selected Acids and Bases.[2] *Taken from Pearson, R. G., Absolute electronegativity and hardness: application to inorganic chemistry. Inorganic Chemistry 1988, 27 (4), 734-740.*

Species	Ionization Energy, IE or I (eV)	Electron Affinity, EA or A (eV)	Mulliken Electronegativity, χ (eV)	Pearson Absolute Hardness, η (eV)
Selected Acids				
Group 1A monocations				
Li^+	75.64	5.39	40.52	35.12
Na^+	47.29	5.14	26.21	21.08
K^+	31.63	4.34	17.99	13.64
Rb^+	27.28	4.18	15.77	11.55
Cs^+	25.1	3.89	14.5	10.6

Species	Ionization Energy, IE or I (eV)	Electron Affinity, EA or A (eV)	Mulliken Electronegativity, χ (eV)	Pearson Absolute Hardness, η (eV)
Group 11 monocations				
Cu^+	20.29	7.73	14.01	6.28
Ag^+	21.49	7.58	14.53	6.96
Au^+	20.5	9.23	14.9	5.6
Isoelectronic Row 3 Metal Cations				
Na^+	47.29	5.14	26.21	21.08
Mg^{2+}	80.14	15.04	47.59	32.55
Al^{3+}	119.99	28.45	74.22	45.77
Changes with Transition Metal Ion Charge				
Fe^{2+}	30.65	16.18	23.42	7.24
Fe^{3+}	54.8	30.65	42.73	12.08
Co^{2+}	33.50	17.06	25.28	8.22
Co^{3+}	51.3	22.5	42.4	8.9
Boron trihalides				
BF_3	15.81	-3.5	6.2	9.7
BCl_3	11.60	0.33	5.97	5.64
BBr_3	10.51	0.82	5.67	4.85
CO_2	13.8	-3.8	5.0	8.8
CS_2	10.08	0.62	5.35	5.56
Selected Bases				
Group 17 monoanions (taken to be identical to the free atom values; for arguments as to why this is reasonable see Pearson, R. G., Inorg. Chem. 1988, 27 (4), 734-740.)				
F^-	17.42	3.40	10.41	7.01
Cl^-	13.01	3.62	8.31	4.70
Br^-	11.84	3.36	7.60	4.24
I^-	10.45	3.06	6.76	3.70
Group 15 hydrides				
NH_3	10.7	-5.6	2.6	8.2
PH_3	10.0	-1.9	4.1	6.0
Trimethylpnictides				
NMe_3	7.8	-4.8	1.5	6.3
PMe_3	8.6	-3.1	2.8	5.9
$AsMe_3$	8.7	-2.7	3.0	5.7
Group 16 hydrides				

Species	Ionization Energy, IE or I (eV)	Electron Affinity, EA or A (eV)	Mulliken Electronegativity, χ (eV)	Pearson Absolute Hardness, η (eV)
H_2O	12.6	-6.4	3.1	9.5
H_2S	10.5	-2.1	4.2	6.2
Phosphorous trihalides				
PF_3	12.3	-1.0	5.7	6.7
PCl_3	10.2	0.8	5.5	4.7
PBr_3	9.9	1.6	5.6	4.2

Drago-Wayland Acid-Base Parameters allow for estimation of the electrostatic and covalent contributions to the enthalpy of formation of a Lewis acid-base adduct.

Although Pearson hardness values are a useful metric of acids' and bases' hardness, they cannot easily be used to estimate the Lewis acid-base interaction energy. This is not the case for the EC model developed by Drago and Wayland.[3] In the **Drago and Wayland's EC Model,** the enthalpy of formation of an acid-base adduct, AB,

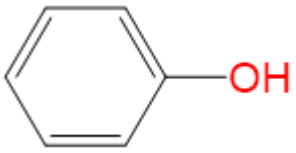
$$A + B \rightleftharpoons AB \qquad \Delta H_{AB\ adduct}$$

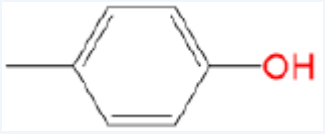
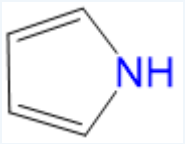
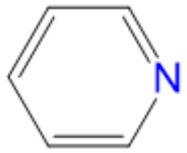
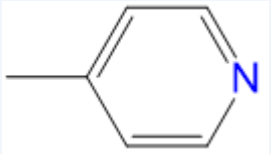
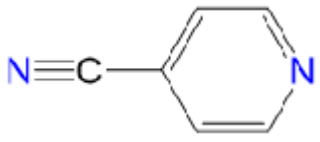
from the acid (A) and base (B) can be calculated as the sum of products of electrostatic (E) and covalent (C) factors that reflect the propensity of the acid and base to engage in strong electrostatic and covalent interactions with one another:

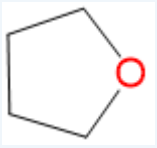
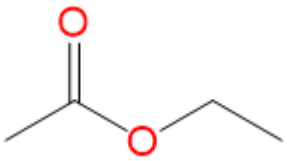
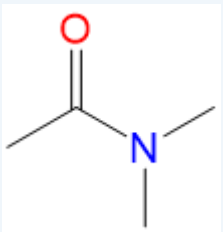
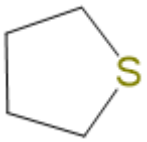
$$-\Delta H_{AB\ adduct} = E_A E_B + C_A C_B$$

where E_A and C_A are the electrostatic and covalent parameters for the acid and E_B and C_B the electrostatic and covalent parameters for the base given in units of kcal^{½} mol$^{-½}$. E and C parameters for selected acids and bases are given in Table 6.6.1.2 .

Table 6.6.1.2: E and C Parameters for selected Lewis acids and bases according to the ECW model.[4,5] Taken from Vogel, G. C.; Drago, R. S., The ECW Model. Journal of Chemical Education 1996, 73 (8), 701 and Drago, R. S. A modern approach to acid-base chemistry. Journal of Chemical Education 1974, 51 (5), 300 (for BF_3).

Species	E (kcal^{½} mol$^{-½}$)	C (kcal^{½} mol$^{-½}$)	W (kcal mol^{-1})	C/E
Acids				
I_2	0.5†	2†	0	4
ICl	2.92	1.66	0	0.57
H_2O	1.31	0.78	0	0.59
SO_2	0.51	1.56	0	3.1
$HCCl_3$ (chloroform)	1.56	0.44	0	0.28
$(CH_3)_3COH$	1.07	0.69	0	0.65
$(CF_3)_3COH$	3.06	1.88	-0.87	0.61
	2.27	1.07	0	0.47

Species	E (kcal^{½} mol$^{-½}$)	C (kcal^{½} mol$^{-½}$)	W (kcal mol^{-1})	C/E
	2.23	1.03	0	0.46
	2.30	1.11	0	0.48
	1.38	0.68	0	0.49
BF_3	1.62	9.88		6.10
$B(CH_3)_3$	2.90	3.60	0	1.2
$Al(CH_3)_3$	8.66	3.68	0	0.43
$Ga(C_2H_5)_3$	6.95	1.48	0	0.21
$In(CH_3)_3$	6.60	2.15	0	0.33
$Zn[N(Si(CH_3)_3)]_2$	2.75	2.32	0	0.84
$Cd[N(Si(CH_3)_3)]_2$	2.50	1.83	0	0.73
Bases				
NH_3	2.31	2.04		0.88
CH_3NH_2	2.16	3.13		1.4
$(CH_3)_2NH$	1.80	4.21		2.3
$(CH_3)_3N$	1.21	5.61		4.6
	1.78	3.54		2.0
	1.81	3.73		2.0
	1.53	2.94		1.9
CH_3CN	1.64	0.71		0.43
$ClCH_2CN$	1.67	0.33		0.20
$CH_3C(O)CH_3$	1.74	1.26		0.72

Species	E (kcal^{½} mol$^{-½}$)	C (kcal^{½} mol$^{-½}$)	W (kcal mol^{-1})	C/E
$(C_2H_5)_2O$	1.80	1.63		0.91
	1.64	2.18		1.3
 (EtOAc)	1.63	0.95		0.58
	2.35†	1.31		0.56
$(CH_3)_2S$	0.25	3.75		15
$(CH_3CH_2)_2S$	0.24	3.92†		15
	0.26	4.07		16
$(CH_3)_2Se$	0.05	4.24		83
$(CH_3)_2SO$	2.4	1.47		0.61
$(CH_3)_3P$	0.25	5.81		24
$(CH_3O)_3P$	0.13	4.83		37
$(C_6H_5)_3PO$	2.59	1.67		0.64
$(C_6H_5)_3PS$	0.35	3.65		10
C_6H_6	0.70	0.45		0.64

† These values were fixed to parameterize the rest of the E and C parameters.

Trends in the relative values of C and E for the acids and bases in Table 6.6.1.2 are very roughly consistent with the trends in hardness and softness outlined earlier. However, the parameters suggest that some trends in hardness reflect changes in species' ability to engage in ionic interactions while others reflect changes in species' ability to engage in strong covalent interactions. For example, C_B for the dimethylchalcogenides increases steadily from 1.5 to 4.25 kcal^{½} mol$^{-½}$ on going from Me_2O to Me_2Se while E_B decreases from 1.68 to 0.05 kcal^{½} mol$^{-½}$, suggesting that electrostatic and covalent factors are both involved in a decrease in base hardness down group 16. However, in the case of phosphines and amines it appears that electrostatic factors are primarily responsible for the decrease in hardness down group 15. On going from Me_3N to Me_3P, C_B only increases slightly from 5.61 to 5.81 kcal^{½} mol$^{-½}$ while E_B decreases from 1.21 to 0.25 kcal^{½} mol$^{-½}$ - *i.e.*, to 20% of the Me_3N value.

However, some species tend to have very high values for both E and C, reflecting their ability to engage in strong electrostatic

and covalent interactions, while others have small values for both, reflecting their relative stability as free species in solution.

As can be seen by comparing the acids and bases listed in the absolute hardness table (Table 6.6.1.1) and the EC parameters table (Table 6.6.1.2). The EC model has primarily been applied to organic and main group organometallic acids and bases. However, a variety of extensions have been proposed that enable its wider applicability.

The simple EC model only includes electrostatic and covalent considerations and thus ignores steric, lattice energy, and other contributions to the interaction energy. Thus it is only useful for analyzing the interaction energies of sterically unhindered adducts in which solvation energy and other contributions to the overall interaction energy are insignificant. However, additional refinements of the model attempt to extend its usefulness by accomodating various factors, such as

- *Steric strain*. Specifically, Hancock and Martell[6] introduced a D parameter to account for any additional steric strain introduced upon adduct formation,* giving

$$-\Delta H_{AB\ adduct} = E_A E_B + C_A C_B - D_A D_B$$

- *Charge transfer upon adduct formation*. As discussed in section 6.4.2, the formation of a Lewis acid-base complex results in a net transfer of electron density from the electron donor (base) to the acceptor (acid). Drago and Wong[7] extended the EC model to include that charge transfer by adding what they called receptance factors that account for the acid's ability to receive electron density (R_A) and transference factors that account for the base's ability to donate electron density (T_B), giving

$$-\Delta H_{AB\ adduct} = E_A E_B + C_A C_B + R_A T_B$$

  This extension of the EC model is called the **electrostatic-covalent-transfer or ECT model**. Notably, it has been applied successfully to adducts involving ions, for which the R_AT_B term can account for as much as 31% of the interaction energy.

- *Any constant energy term, such as the energy needed to cleave a dimer in order to make the Lewis acid (e.g., $Al_2Cl_6 \rightarrow 2AlCl_3$).* Drago and Vogel[4] extended the EC model to accommodate these constant energy terms, which they designated W. The resulting model is called the **ECW model,** for which

$$-\Delta H_{AB\ adduct} = E_A E_B + C_A C_B + W$$

where

$$W = W_A + W_B$$

A simple application of EC and extended EC models is that they allow the enthalpy of adduct formation to be calculated. These enthalpy calculations based on the EC model are consistent with the superior interaction energy of hard-hard and soft-soft interactions compared to hard-soft ones. Consider, for example, the transfer of I_2 between BF_3 and $InMe_3$, H_3N-BF_3, and H_3N-$InMe_3$.

$$H_3N - BF_3 + InMe_3 \rightleftharpoons BF_3 + H_3N - InMe_3$$

Since H_3N is a hard base and BF_3 and $InMe_3$ are harder and softer acids, respectively, the equilibrium is expected to favor the reactant, H_3N-BF_3. Assuming the equilbrium is enthalpically driven, this qualitative analysis is consistent with the expected endothermic enthalpy of the reaction, as may be seen from the calculated enthalpies of adduct formation for both H_3N-BF_3 and H_3N-$InMe_3$.

For H_3N-BF_3:

$$-\Delta H_{H_3N-BF_3} = E_{BF_3}E_{NH_3} + C_{BF_3}C_{NH_3}$$

$$-\Delta H_{H_3N-BF_3} = (1.62)(2.31) + (9.88)(2.04)$$

$$-\Delta H_{H_3N-BF_3} = 3.74\ kcal/mol + 20.1\ kcal/mol = 23.8\ kcal/mol$$

$$\Delta H_{H_3N-BF_3} = -23.8\ kcal/mol$$

For H_3N-$InMe_3$:

$$-\Delta H_{H_3N-InMe_3} = E_{InMe_3}E_{NH_3} + C_{InMe_3}C_{NH_3}$$

$$-\Delta H_{H_3N-InMe_3} = (6.6)(2.31) + (2.15)(2.04)$$

$$-\Delta H_{H_3N-InMe_3} = 15.25\ kcal/mol + 4.39\ kcal/mol = 19.63\ kcal/mol$$

$$\Delta H_{H_3N-InMe_3} = -19.63\ kcal/mol$$

So H_3N-BF_3 is enthalpically favored by -4.2 kcal/mol [=-23.8 kcal/mol - (-19.63 kcal/mol) according to Hess' Law].

In addition to their utility for estimating enthalpies of Lewis acid-base complex formation, EC and related models serve as a useful tool for estimating the relative importance of ionic, covalent, and steric factors in complex formation. Specifically,

- The relative contributions of ionic and covalent factors can be calculated directly, as from the E and C terms. This can provide insight into why some complexes are more stable than others. Such calculations reveal that the hard-hard adduct H_3N-BF_3 is favored over the hard-soft adduct H_3N-$InMe_3$ because of the strong covalent interaction holding together H_3N-BF_3. The covalent term accounts for 84% of the energy of the H_3N-BF_3 interaction and is largely lost upon formation of H_3N-$InMe_3$, for which it contributes only 22% of the interaction energy. When the electrostatic term is accounted for, it can be seen that the formation of H_3N-$InMe_3$ from H_3N-BF_3 is disfavored, since it would result in a loss of 15.7 kcal/mol of covalent stabilization that would be incompletely compensated for by a gain of 11.5 kcal/mol of electrostatic stabilization.
- The role of other contributions to the bonding in a Lewis acid-base complex may be estimated from the discrepancy between the experimental and EC model calculated stabilization energies. This is because the EC parameters assume sigma bonding and so any deviation between the calculated and experimental enthalpies of complex formation can be attributed to non-sigma contributions.
  - This is done explicitly in extensions of the EC model. For instance, in the case of the Hancock and Martell, ECT, and ECW extensions of the EC model, the contributions of the steric, charge transfer, and constant energy factors (like dimer dissociation) are directly computed in the model.
  - Comparisons of the difference between the energies calculated using ordinary EC parameters and the observed enthalpies has also been used as an estimate of the
    - steric strain energy in strained adducts, which exhibit a less exothermic heat of adduct formation than expected
    - π-backbonding energy in adducts which are capable of such interactions and exhibit a more exothermic heat of formation than expected.[8-10]
  - For examples see (a) Drago, R. S., The interpretation of reactivity in chemical and biological systems with the E and C model. Coordination Chemistry Reviews 1980, 33 (3), 251-277; (b) Drago, R. S.; Bilgrien, C. J., Inductive transfer and coordination of ligands in metal—metal bonded systems. Polyhedron 1988, 7 (16), 1453-1468; (c) Drago, R. S., The question of a synergistic metal-metal interaction leading to .pi.-back-bond stabilization in dirhodium tetrabutyrate adducts. Inorganic Chemistry 1982, 21 (4), 1697-1698.
- The role of electrostatic, covalent, and other contributions to the spectroscopic behavior of Lewis acid-base complexes can be assessed similarly using specialized versions of the ECW or ECT model that allow for calculation of changes in spectroscopic parameters upon adduct formation - *e.g.,* OH stretching frequencies. Details are beyond the scope of this text but may be found in the original literature,[11] for example, Drago, R. S.; Vogel, G. C. *JACS* 1992, 114 (24), 9527-9532; Vogel, G. C.; Drago, R. S., *J. Chem. Educ.* 1996, 73 (8), 701; Drago, R. S.; Wong, N. M., *J. Chem. Educ.* 1996, 73 (2), 123.).

Pearson Softness Parameters have been proposed as a means of calculating the equilibrium constant for formation of a Lewis acid-base adduct, although they are more commonly used to estimate metal toxicity

Pearson also proposed a softness parameter that can be used to estimate the thermodynamics of Lewis acid-base complex formation, this time in the form of the equilibrium constant for

$$A + B \overset{K}{\rightleftharpoons} AB$$

for which Pearson proposed

$$logK = S_A S_B + \sigma_A \sigma_B$$

where S_A and S_B are acid and base parameters related to the strength of the acid-base interaction and σ_A and σ_B are acid and base parameters related to softness. This approach hasn't found as wide an acceptance in studies of chemical reactivity as the Drago-Wayland and absolute hardness parameters. However, because the toxicity of metal ions sometimes depends on their propensity to bind soft Lewis bases in living systems, the softness parameters which Pearson and Mawby subsequently proposed based on the relative energies of metal fluorine and metal iodine bonds[12] have been widely used as a tool for predicting metal ion toxicity.[13]

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Notes

* More precisely, the D parameters account for the difference in steric strain in the adduct relative to a water adduct of the Lewis acid.

This page titled 6.6.1: Quantitative Measures of Hardness, Softness, and Acid-Base Interactions from a Hard Soft Acid-Base Principle Perspective Involve Orbital Energies and/or Apportioning Acid-Base Bonding in Terms of Electrostatic and Covalent Factors is shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Stephen M. Contakes.

- 6.6.1: Quantitative Measures of Hardness, Softness, and Acid-Base Interactions from a Hard Soft Acid-Base Principle Perspective Involve Orbital Energies and/or Apportioning Acid-Base Bonding in Terms of Electrostatic and Covalent Factors by Stephen M. Contakes is licensed CC BY 4.0.

6.6.2: Hard-Hard and Soft-Soft preferences may be explained and quantified in terms of electrostatic and covalent and electronic stabilization on the stability of Lewis acid-base adducts

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 6.6.2.1). Pearson terms acids and bases which are relatively polarizable **soft** and those which are difficult to polarize **hard.**

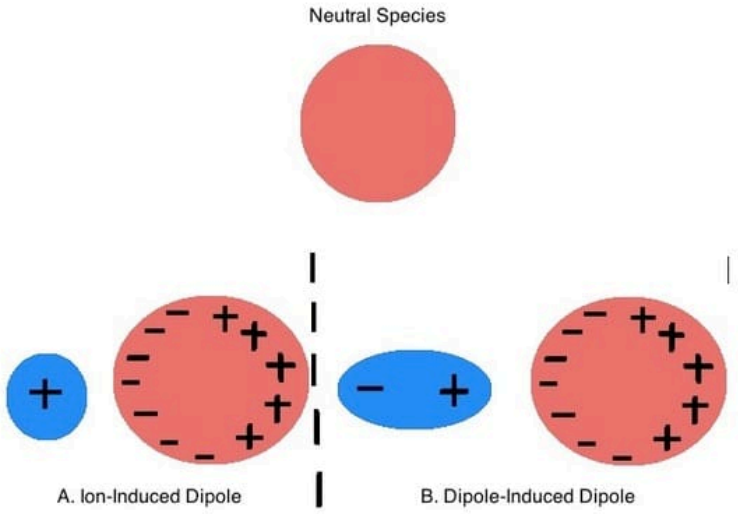


Figure 6.6.2.1: Polarizability refers to the ease with which a substance's electron cloud may be distorted under the action of an electric field. A fragment's polarizability determines the degree to which its electron cloud is distorted by A.) an Ion and B.) a polar molecule to induce a dipole moment. The figure is taken from (and the caption expanded from) Cox, Kelly and Dana Reusser "Polarizability"

Recognizing Hard and Soft Acids and Bases

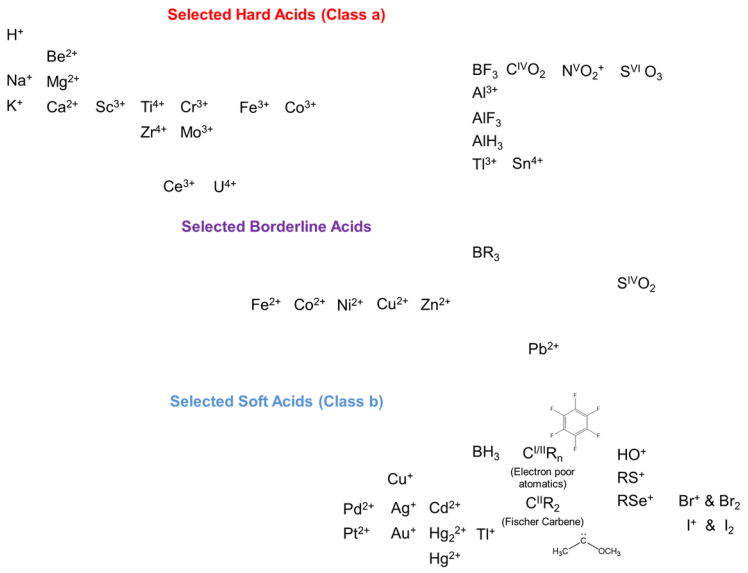
Hard acids and bases come in two varieties:

1. hard acid and base sites that possess few valence electrons and for which polarization therefore involves distorting core electrons, which are difficult to distort because they are close to the nucleus and experience a high nuclear charge. The most common examples of such substances are Lewis acid hard acids towards the left of the periodic table.
2. hard acid and base sites with a high charge density (highly charged relative to size) and/or which are electron deficient. In these cases polarization involves distorting electrons that already experience strong unshielded electrostatic interactions.

Soft acids and bases also come in two varieties

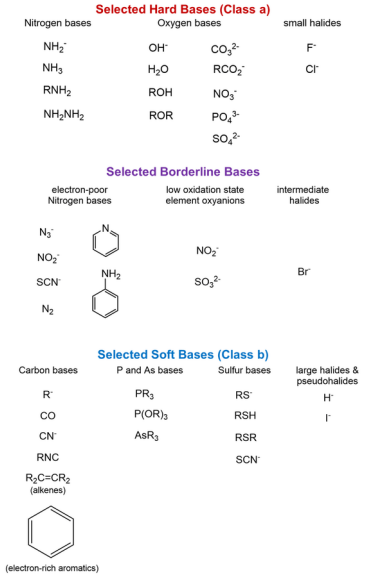
1. soft acids and bases which posses many valence electrons and so are more readily polarized. In consequence, all other things being equal, soft acids and bases are more likely to be found towards the middle or right of the periodic table.
2. soft acids and bases with little charge density and/or which are relatively electron rich.

Note that the hard-soft classification should not be thought of as if all hard acids and bases are equally hard and all soft acids and bases equally soft. There is a graduation in hardness and softness and a number of intermediate acids and bases which do not fit neatly in either category. With this caveat in mind, representative **hard, soft, and borderline acids** are given below. Notice how they illustrate the trends just outlined.



As expected, hard acids tend to be found towards the left side of the periodic table and involve higher oxidation states and/or electron donating substituents while soft acids are more common to the right of the periodic table and involve lower oxidation states and/or electron donating substituents.

Illustrative hard, soft, and borderline bases are given below. Again, notice how these substances illustrate the general trends.



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

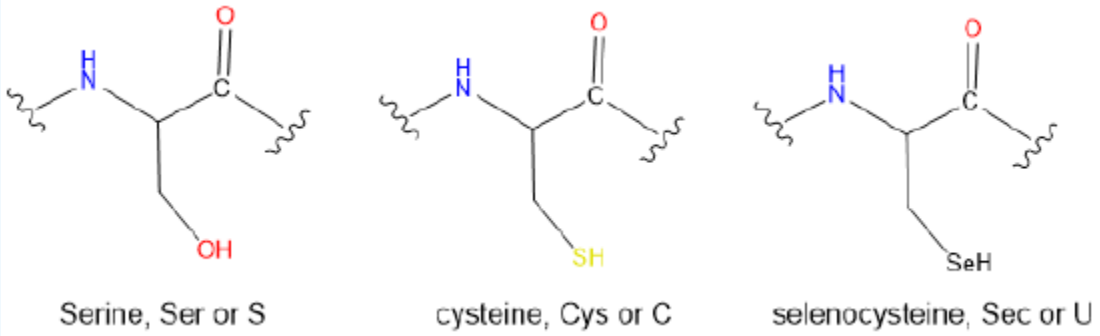
In contrast to hard acids and bases, **soft acids are relatively electron-rich and soft bases larger and more electron poor** since they have comparatively

- 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 6.6.2.1

Rank the acids or bases in each set in increasing order of expected hardness.

a. Cr^{2+} and Cr^{3+}
b. H^+, Cs^+, and Tl^+
c. SCN^- (acting as a base at N) and SCN^- (acting as a base at S)
d. AlF_3, AlH_3, $AlMe_3$
e. The side chains of the following proteinogenic amino acids



Answer available at the end of this section.

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

$$\mathrm{A_1 : B_1 + A_2 : B_2 \overset{k_1,\ K_{eq}}{\rightleftharpoons} A_1 : B_2 + A_2 : B_1}$$

For example, the equilibrium position of the metathesis reaction between TlF and $\mathrm{K_2S}$ favors the products:

$$\mathrm{2\,TlF + H_2S \rightleftharpoons Tl_2S + 2\,KF}$$

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

$$\mathrm{HI + HgSCH_3^+ \rightleftharpoons CH_3SHgI + H^+}$$

involves displacement of an iodide from HI to give $\mathrm{CH_3HgI}$. The position of the equilibrium favors $\mathrm{CH_3HgI}$ since both $\mathrm{CH_3Hg^+}$ and $\mathrm{I^-}$ are soft, while $\mathrm{H^+}$ is a hard acid.



Exercise 6.6.2.2

Predict the position of equilibrium for the following reaction.

$$\mathrm{Fe_2O_3 + 3\,Ag_2S \rightleftharpoons Fe_2S_3 + 3\,Ag_2O}$$

Answer available at the end of this section.

Exercise 6.6.2.3

Predict whether K for the following equilibria will be <<1, ~1, or >>1.

a. $\mathrm{2\,HF + (CH_3Hg)_2S \rightleftharpoons 2\,CH_3HgF + H_2S}$
b. $\mathrm{Ag(NH_3)_2^+ + 2\,PH_3 \rightleftharpoons Ag(PH_3)_2^+ + 2\,NH_3}$

c. $Ag(PH_3)_2^+ + 2\,H_3B{-}SH_2 \rightleftharpoons 2\,H_3B{-}PH_3 + Ag(SH_2)_2^+$
d. $H_3B{-}NH_3 + F_3B{-}SH_2 \rightleftharpoons H_3B{-}SH_2 + F_3B{-}NH_3$

Answer available at the end of this section.

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.[†]

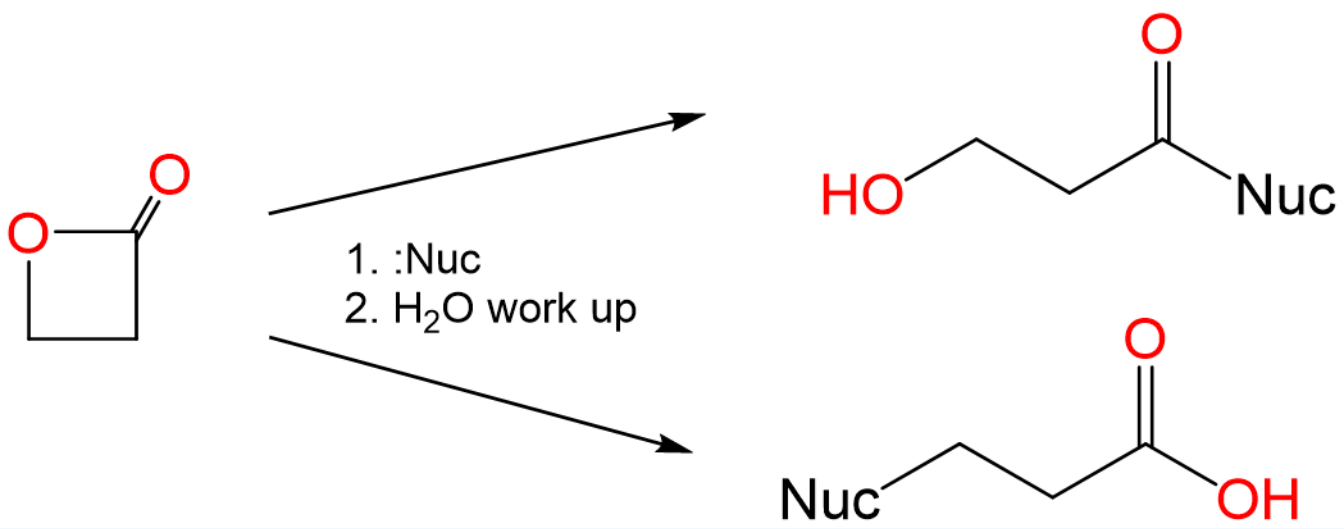
Exercise 6.6.2.4

Which acid will form the most stable complex with CO: BH_3, BF_3, or BMe_3?

Answer available at the end of this section.

Exercise 6.6.2.5

When lactones react with nucleophiles, they can undergo ring opening reactions to give either an alcohol or a carboxylic acid, as shown for propiolactone below:



In the reaction above, sterically unhindered alkoxides give one product and sterically unhindered thioalkoxides the other. Explain why this is the case and predict the products of the reaction between propiolactone and the sodium salts of ethoxide and thioethoxide.

Answer available at the end of this section.

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.

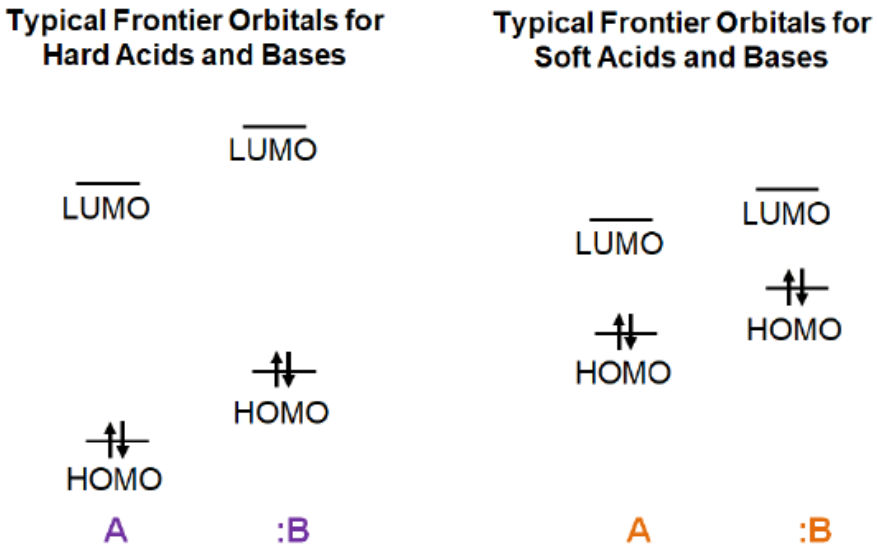
- The lone pair of a hard or soft base is comparatively weakly stabilized by an acid opposite to it in hardness or softness since the overall electrostatic and covalent stabilization of the adduct is comparatively weak.

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:

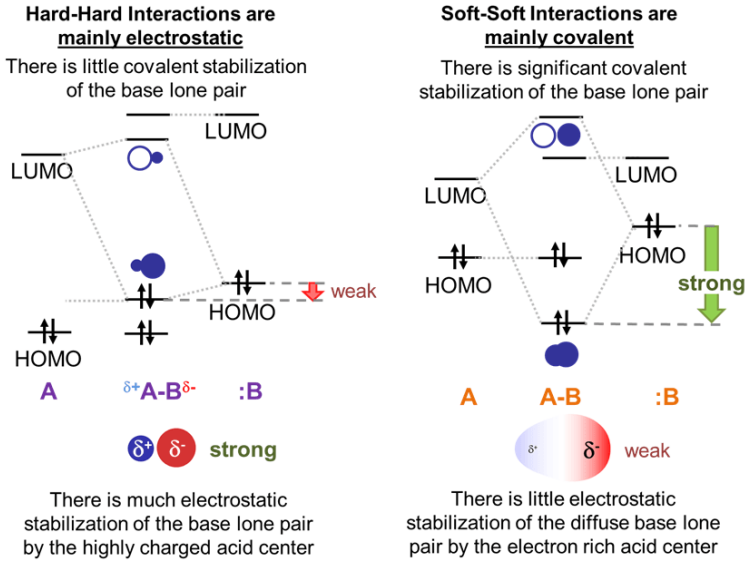
Interaction Energy = Electrostatic attractions and repulsions of partial atomic charges (Ionic term) + Interactions between filled orbitals on one fragment and unfilled orbitals on the other (Covalent term) + Electrostatic repulsions between filled orbitals on the two fragments (Steric term)

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.



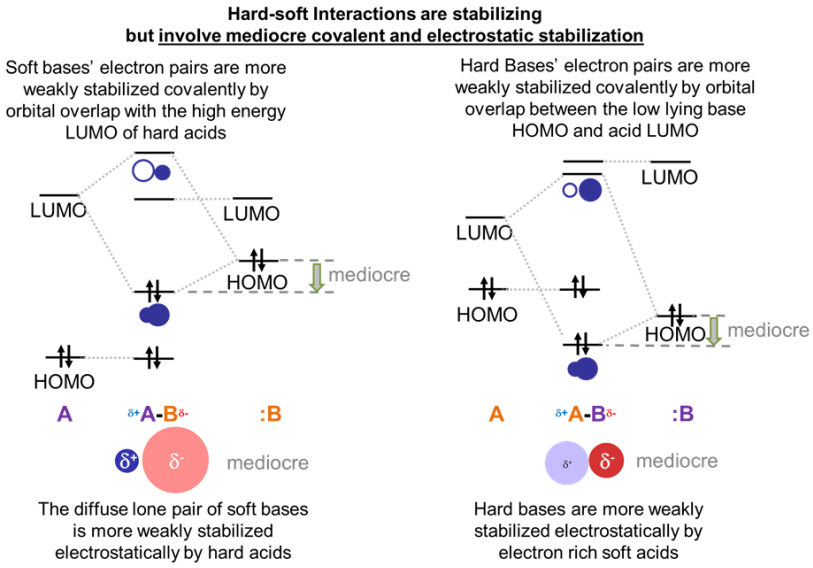
Given this, consider the frontier orbital interactions involved in the formation of an acid-base complex for the possible cases, as illustrated schematically below.



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.

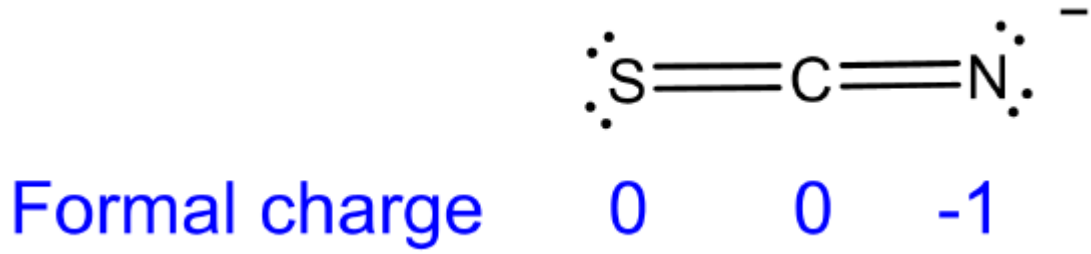
Answers

Exercise 6.6.2.1

(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.

Exercise 6.6.2.2

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 6.6.2.3

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.

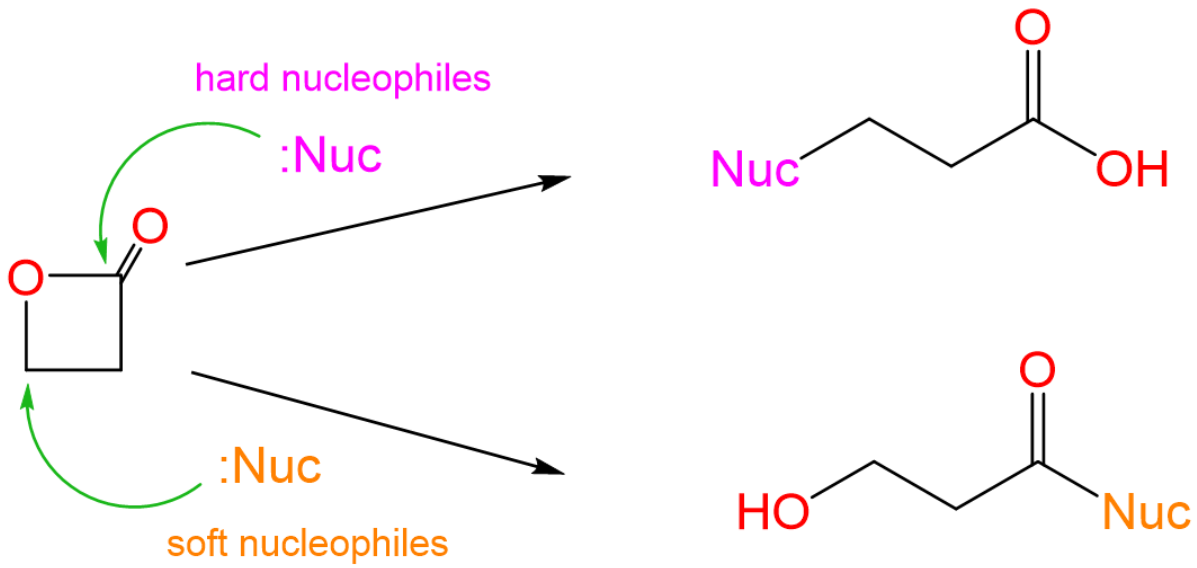
d. K>>1 since BH_3 is a softer acid than BF_3, so it will form a stronger complex with the softer base H_2S while the harder BF_3 forms a stronger complex with the harder base NH_3.

Exercise 6.6.2.4

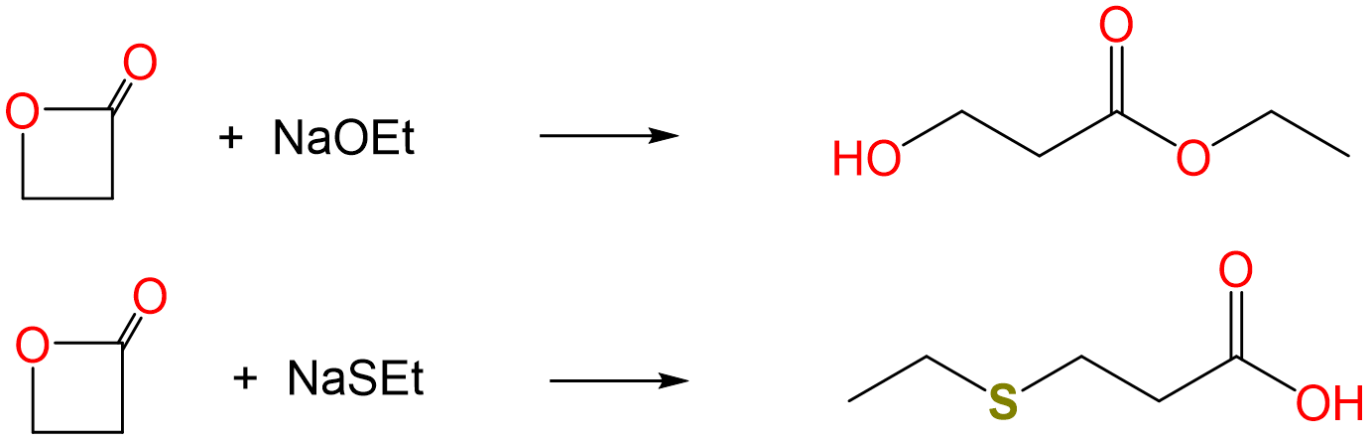
BH_3. Since CO forms complexes primarily through its carbon lone pair, it is a soft base and so will form the strongest complex with the softest Lewis acid.

Exercise 6.6.2.5

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.



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7: THE CRYSTALLINE SOLID STATE

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7.1.2: Metal-Insulator Transitions

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7.1: MOLECULAR ORBITALS AND BAND STRUCTURE

Learning Objectives

- Explain the physical basis of the Hubbard and Mott models of metal-insulator transitions.
- Understand why good superconductors derive from bad metals.
- Know the structures and the periodic trends in band gaps and colors of semiconductors.
- Obtain the band gap of an intrinsic semiconductor from the temperature dependence of the conductivity.
- Predict the doping type when impurities or defects are introduced into a semiconductor.
- Correlate the band picture and Fermi level with n- or p-type doping.
- Understand the physical principles of operation of diodes, LEDs, solar cells, and FETs.
- Explain the differences in structures and electronic properties of crystalline and amorphous semiconductors.

The band model (like MO theory) is based on a *one-electron* model. This was an approximation we made at the very beginning of our discussion of MO theory: we used hydrogen-like (one-electron) solutions to the 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***.

7.1.1: Prelude to Electronic Properties of Materials - Superconductors and Semiconductors

7.1.2: Metal-Insulator Transitions

7.1.3: Periodic Trends- Metals, Semiconductors, and Insulators

7.1.4: Semiconductors- Band Gaps, Colors, Conductivity and Doping

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7.1.8: Discussion Questions

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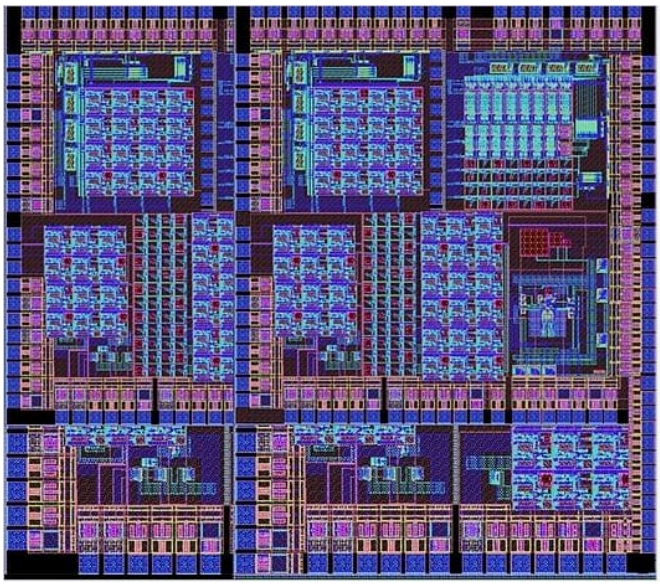
7.1.10: References

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7.1.1: 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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7.1.2: Metal-Insulator Transitions

In Chapter 6 we learned that metals and insulators not only have different electrical properties but also have very different crystal structures. Metals tend to have high coordination numbers (typically 8 or 12) whereas insulators have low coordination numbers that can be rationalized as "octet" bonding arrangements. For example, in crystalline Si or Ge (diamond structure), each atom has four nearest neighbors. There are two electrons per bond, and thus each atom has eight electrons in its valence shell. Sn, the element below Ge, exists in two different forms, one (gray tin) with the diamond structure that is a brittle narrow-gap semiconductor, and the other (white tin) with a body-centered tetragonal structure that is a malleable metal. These two forms are very close in energy, and in fact metallic white tin transforms to the brittle semiconducting gray form at low temperature. Extremely cold weather in 18th century Europe caused many tin organ pipes to break and eventually turn to dust. This transformation has been called tin blight, tin disease, tin pest or tin leprosy. The dust is actually grey tin, which lacks the malleability of its metallic cousin white tin.

Under experimentally accessible temperatures and pressures, Si and Ge are always semiconducting (i.e., insulating), and Pb is always metallic. Why is Sn different? The reason has to do with orbital overlap. Theory tells us in fact that any (and all) insulators should become metallic at high enough pressure, or more to the point, at high enough density. For most insulators, however, the pressures required are far beyond those that we can achieve in the laboratory.

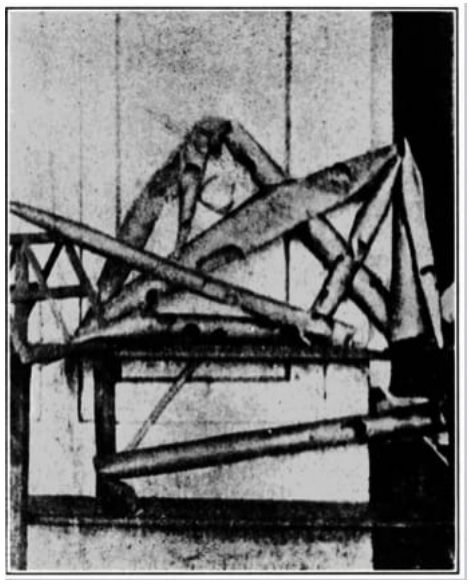
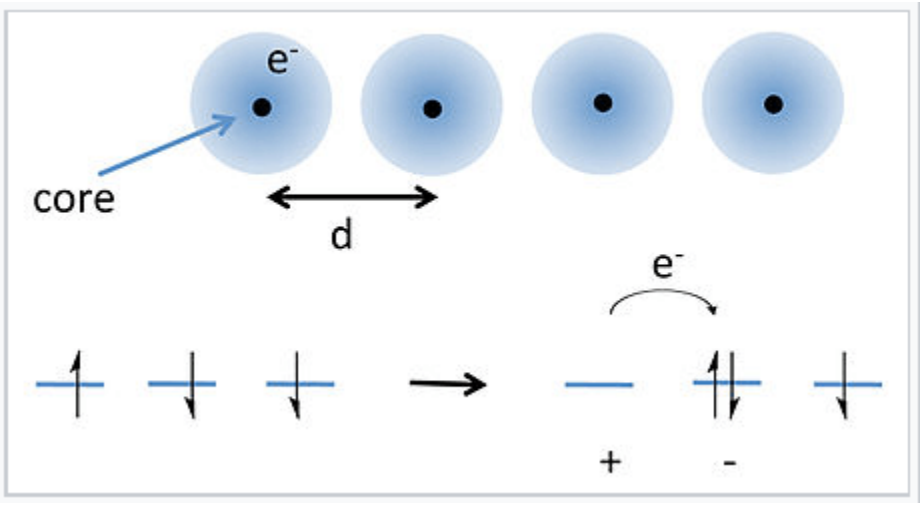


Figure 7.1.2.1: Organ pipes destroyed by "tin blight"

How can we rationalize the transition of insulators to the metallic state? Indeed, how can we understand the existence of insulators at all?

The Hubbard Model

Let's consider a chain of a large number (N) of atoms as we did in Chapter 6. For convenience, we can say that these are atoms such as H, Na, or Cs that have one valence electron. The simple band model we developed earlier suggests that the chain should be metallic, because N atoms combine to make N orbitals, and the N valence electrons only fill the band of orbitals halfway. But this conclusion doesn't depend on the density, which creates a paradox. If atoms in the chain are very far apart, we suspect that the electrons should localize on the atoms.

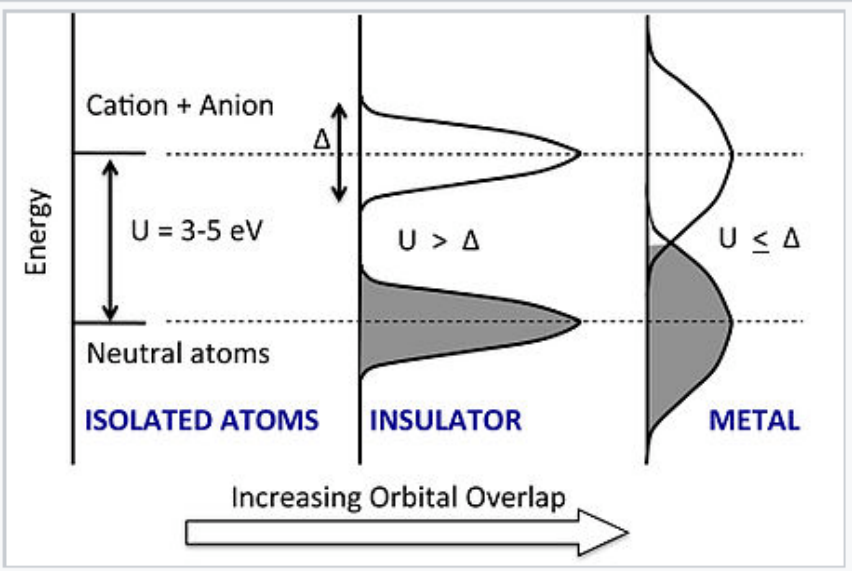


Electron hopping in a 1-D chain of atoms.

A solution to this problem was proposed by J. Hubbard in 1963.[1] Hubbard considered the energy required to transfer an electron from an atom to its nearest neighbor, as shown in the picture at the right. Because each atom already has one electron (with random spin), moving an electron over by one atom requires overcoming the energy of electron-electron repulsion to make a cation-anion pair. For well-separated atoms this energy (U) is given by:

$$U = IP - Ea - \frac{e^2}{4\pi\varepsilon_0 d} \tag{7.1.2.1}$$

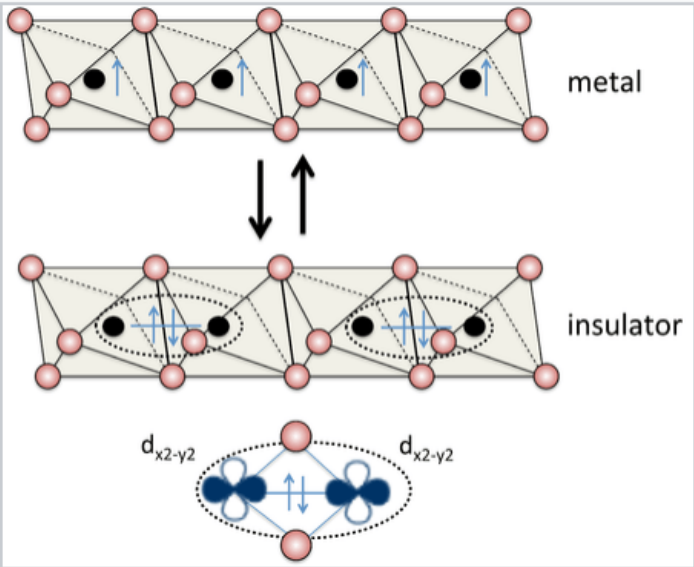
where IP and EA are the ionization energy and electron affinity, ε_0 is the permittivity of free space, and the last term in the equation represents the coulombic attraction between the cation and the anion. For atoms such as alkali metals, U is on the order of 3–5 eV, which is much larger than the thermal energy kT. Thus we expect there to be very few anion-cation pairs at room temperature, and the chain of atoms should be insulating.



Energy vs. DOS for the chain of atoms as the density and degree of orbital overlap between atoms increases. Increasing overlap broadens the neutral atom and anion-cation states into bands, each of which has a bandwidth Δ. A transition to the metallic state occurs abruptly when Δ exceeds the Hubbard gap U.

What happens when we squeeze the atoms together? In the Hubbard model, as the distance between atoms decreases, the energies of both the neutral atom states and the anion-cation states broaden into bands, each of which has a band width Δ. The lower band can accommodate exactly *N* electrons (not *2N* as in the MO picture we developed earlier) because each orbital can only take one electron without spin-pairing. Thus for small Δ the lower band is full and the upper band is empty. However, as we continue to compress the chain, the orbital overlap becomes so strong that Δ ≈ U. At this point, the bands overlap and some of the electrons fill the anion-cation states. The chain then becomes conducting and the material is metallic.

Some materials, such as Sn and VO_2, happen to have just the right degree of orbital overlap to make the Hubbard transition occur by changing the temperature or pressure. Such materials can be very useful for electrical switching, as illustrated at the right for rutile structure VO_2. Most materials are far away from the transition, either on the metallic or insulating side. An interesting periodic trend that illustrates this concept can be seen among the transition metal monoxides, MO (M = Ti, V, Cr, Mn, Fe, Co, Ni), all of which have the NaCl structure. TiO and VO are metallic, because the 3d orbitals have significant overlap in the structure. However, CrO, MnO, FeO, CoO, and NiO are all insulators, because the 3d orbitals contract (and therefore Δ < U) going across the transition metal series. In contrast, the analogous sulfides (TiS, VS,....NiS) are all metallic. The sulfides have the NiAs structure, in which all the metal atoms are eclipsed along the stacking axis (the hexagonal c-axis). The short metal-metal distances along that axis result in strong orbital overlap, making Δ > U.



Vanadium dioxide has the rutile structure, and in its undistorted form it is metallic, with one valence electron per V atom. Distortion of the lattice makes pairs of V atoms, resulting in an electronically insulating state. The metal-insulator transition can be driven reversibly by changing the temperature, pressure, or orbital occupancy. Electrical switching of this transition in VO_2 is being studied for applications in high performance thin film transistors[2]

The Mott Model

A simpler, less atomistic model of the metal-insulator transition was formulated by Neville Mott.[3] The Mott model considers the behavior of an electron in a material as a function of the density of all the other valence electrons. We know for a one-electron hydrogen-like atom (H, Na, Cs, etc.) the Schrödinger equation contains a potential energy term:

$$V(r) = -(\frac{e^2}{4\pi\varepsilon_0 r}) \tag{7.1.2.2}$$

This potential energy function gives rise to familiar ladder of allowed energy levels in the hydrogen atom. However, in a metal, this Coulomb potential must be modified to include the screening of nuclear charge by the other electrons in the solid. In this case there is a **screened Coulomb potential**:

$$V(r) = -(\frac{e^2}{4\pi\varepsilon_0 r})exp(-qr) \tag{7.1.2.3}$$

where q, which is the inverse of the **screening length**, is given by:

$$q^2 = 4m_e^2(\frac{3n}{\pi})^{\frac{1}{3}}(\frac{2\pi}{h}) \tag{7.1.2.4}$$

Here n is the density of atoms (or valence electrons), m_e is the electron mass, and h is Planck's constant. At distances much larger than the screening length q^{-1}, the electron no longer "feels" the charge on the nucleus. Mott showed that there is a critical density of electrons n_c above which the valence electrons are no longer bound by individual nuclei and are free to roam the crystal. This critical density marks the transition to the metallic state, and is given by the Mott criterion:

$$\mathbf{n_c^{\frac{1}{3}} a_H \approx 0.26} \tag{7.1.2.5}$$

In this equation, a_H is an effective Bohr radius for the valence electrons in the low-density limit, e.g. the average orbital radius of electrons in the 6s shell of a Cs atom when computing the value for Cs metal.



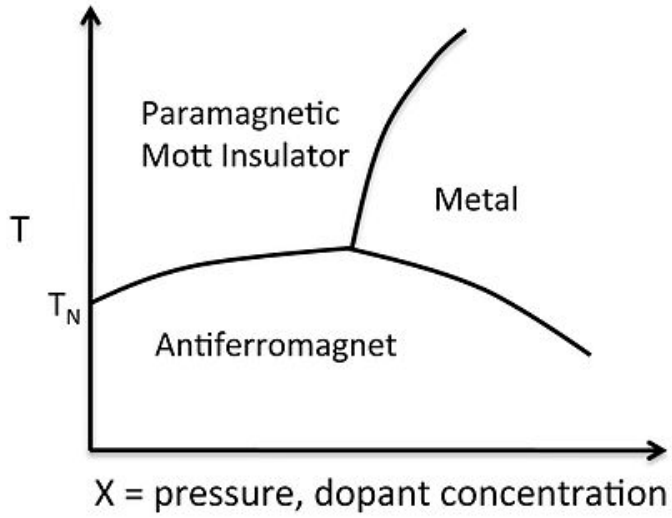
Solutions of lithium metal in liquid ammonia at low (top, ionic conductor) and higher (bottom, metal) Li concentration. From a video by Joshua Judkins

The important concept from the Mott model is that the metal-insulator transition depends very strongly on the **density of valence electrons.** This is consistent with the orbital overlap model of Hubbard, but also more general in the sense that it does not depend on a periodic structure of atoms. The Mott model is thus applicable to such diverse systems as metal atoms dissolved in liquid ammonia, metal atoms trapped in frozen gas matrices, and dopants in semiconductors.[4] In some systems, it is possible to continuously tune the density of valence electrons with rather striking results. For example, dissolving alkali metal (Li, Na, ...) in liquid ammonia (bp -33 ^{o}C) produces a blue liquid. The solvated alkali cations and negatively charged electrons impart ionic conductivity (as in a salt solution) but not electronic conductivity to the blue liquid ammonia solution. But as the concentration of electrons increases, a reflective, bronze-colored liquid phase forms that floats over the blue phase. This bronze phase is metallic and highly conducting. Eventually, with enough alkali metal added, the entire liquid is converted to the electronically conducting bronze phase.

The electrical switching of VO_2 between insulating and metallic phases (see above) can also be rationalized in terms of the Mott transition. Adding more electron density (by chemical or electric field doping) increases the concentration of valence electrons, driving the phase transition to the metallic state.

Thermodynamics and phase transitions

Thermodynamically, the metal-insulator transition is a **first-order phase transition**. In such a transition, the structure and properties change abruptly (think of the breakfast-to-lunch transition at McDonalds - there is just no way to get pancakes after, or hamburgers before 10:30 AM![5]). Thus in the case of Sn metal, the changes in structure (from four- to eight-coordination) and in electronic conductivity (insulator to metal) occur simultaneously. As in other first order phase transitions such as ice to water to steam, there is a latent heat associated with the transition and a discontinuity in derivative properties such as the heat capacity.



A typical phase diagram for a metal-insulator transition is shown at the right for V_2O_3. The octahedrally coordinated V^{3+} ion has a d^2 electron count, so there are two unpaired spins per atom, and at low temperature the spins in the lattice order antiferromagnetically. As we learned in Chapter 8, above the Néel temperature an antiferromagnet becomes a paramagnet, which is also a Mott insulator. Increasing the pressure, or doping with electrons (e.g., by substituting some d^3 Cr^{3+} for V^{3+}) pushes the electron density over the Mott transition, the spins pair, and the solid becomes metallic.

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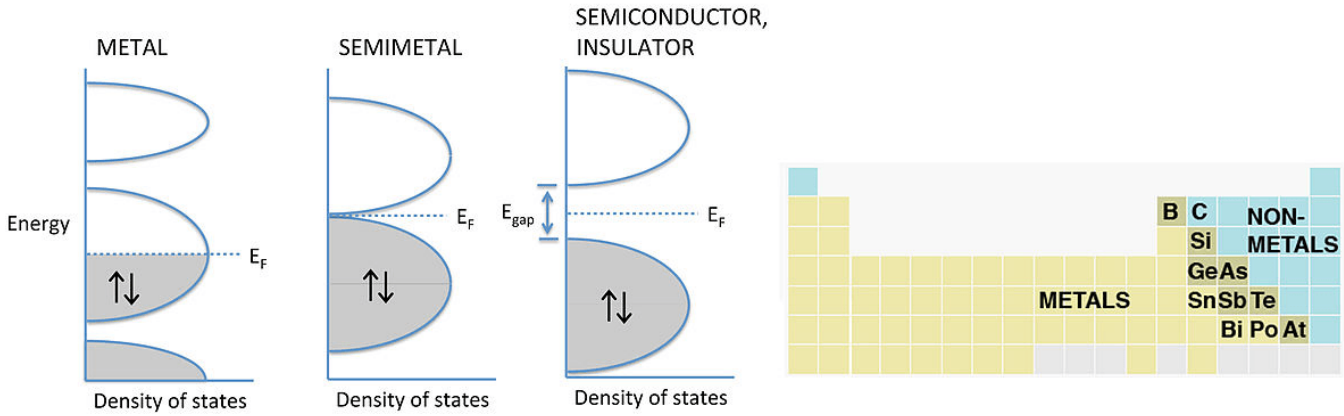
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7.1.3: Periodic Trends- Metals, Semiconductors, and Insulators

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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7.1.4: Semiconductors- Band Gaps, Colors, Conductivity and Doping

Semiconductors, as we noted above, are somewhat arbitrarily defined as insulators with **band gap energy ≤ 3.0 eV** (~290 kJ/mol). This cutoff is chosen because, as we will see, the conductivity of undoped semiconductors drops off exponentially with the band gap energy and at 3.0 eV it is very low. Also, materials with wider band gaps (e.g. $SrTiO_3$, E_{gap} = 3.2 eV) do not absorb light in the visible part of the spectrum

There are a number of places where we find semiconductors in the periodic table:

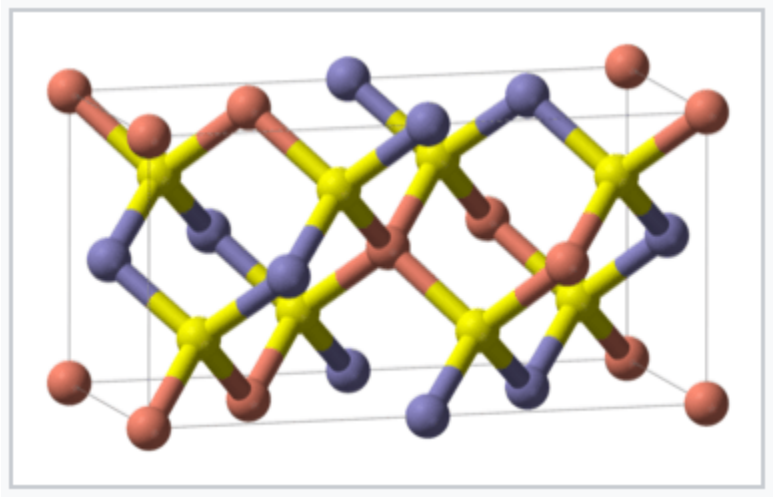
- Early transition metal oxides and nitrides, especially those with d^0 electron counts such as TiO_2, TaON, and WO_3
- Oxides of later 3d elements such as Fe_2O_3, NiO, and Cu_2O
- Layered transition metal chalcogenides with d^0, d^2 and d^6 electron counts including TiS_2, ZrS_2, MoS_2, WSe_2, and PtS_2
- d^{10} copper and sliver halides, e.g., CuI, AgBr, and AgI
- Zincblende- and wurtzite-structure compounds of the p-block elements, especially those that are isoelectronic with Si or Ge, such as GaAs and CdTe. While these are most common, there are other p-block semiconductors that are not isoelectronic and have different structures, including GaS, PbS, and Se.



A 2" wafer cut from a GaAs single crystal. GaAs, like many p-block semiconductors, has the zincblende structure.

The **p-block octet semiconductors** are by far the most studied and important for technological applications, and are the ones that we will discuss in detail.

Zincblende- and wurtzite-structure semiconductors have 8 valence electrons per 2 atoms. These combinations include 4-4 (Si, Ge, SiC,...), 3-5 (GaAs, AlSb, InP,...), 2-6 (CdSe, HgTe, ZnO,...), and 1-7 (AgCl, CuBr,...) semiconductors. Other variations that add up to an octet configuration are also possible, such as $Cu^{I}In^{III}Se_2$, which has the **chalcopyrite** structure, shown at the right.



The **chalcopyrite structure** is adopted by ABX_2 octet semiconductors such as $Cu^{I}In^{III}Se_2$ and $Cd^{II}Sn^{IV}P_2$. The unit cell is doubled relative to the parent **zincblende structure** because of the ordered arrangement of cations. Each anion (yellow) is coordinated by two cations of each type (blue and red).

How does the **band gap energy** vary with **composition**? There are two important trends

(1) Going **down a group** in the periodic table, the gap **decreases**:

C (diamond) > Si > Ge > α-Sn

E_{gap} (eV): 5.4 1.1 0.7 0.0

This trend can be understood by recalling that E_{gap} is related to the **energy splitting between bonding and antibonding orbitals**. This difference decreases (and bonds become weaker) as the principal quantum number increases.

(2) For isoelectronic compounds, **increasing ionicity** results in a **larger band gap**.

Ge < GaAs < ZnSe

0.7 1.4 2.8 eV

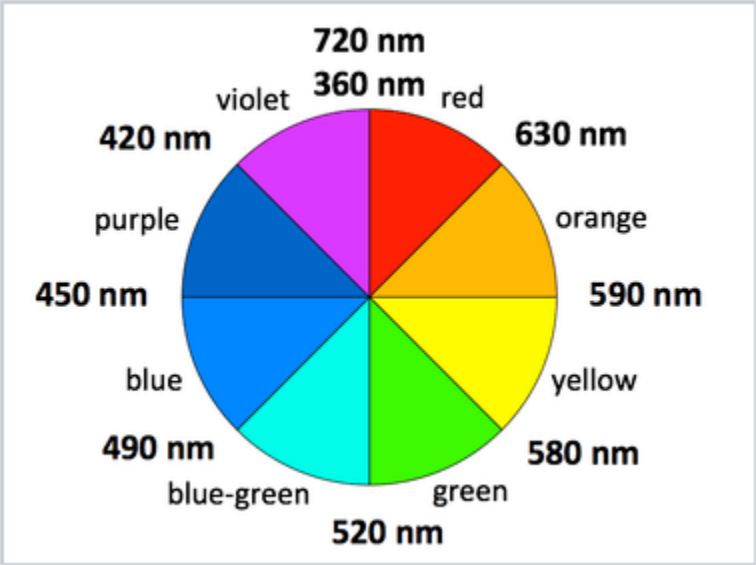
Sn < InSb < CdTe < AgI

0.0 0.2 1.6 2.8 eV

This trend can also be understood from a simple MO picture, as we discussed in Ch. 2. As the electronegativity difference $\Delta\chi$ increases, so does the energy difference between bonding and antibonding orbitals.

The band gap is a very important property of a semiconductor because it determines its color and conductivity. Many of the applications of semiconductors are related to band gaps:

- Narrow gap materials ($Hg_xCd_{1-x}Te$, VO_2, InSb, Bi_2Te_3) are used as infrared photodetectors and thermoelectrics (which convert heat to electricity).
- Wider gap materials (Si, GaAs, GaP, GaN, CdTe, $CuIn_xGa_{1-x}Se_2$) are used in electronics, light-emitting diodes, and solar cells.



Color wheel showing the colors and wavelengths of emitted light.

Semiconductor solid solutions such as $GaAs_{1-x}P_x$ have band gaps that are intermediate between the end member compounds, in this case GaAs and GaP (both zincblende structure). Often, there is a linear relation between composition and band gap, which is referred to as **Vegard's Law**. This "law" is often violated in real materials, but nevertheless offers useful guidance for designing materials with specific band gaps. For example, red and orange light-emitting diodes (LED's) are made from solid solutions with compositions of $GaP_{0.40}As_{0.60}$ and $GaP_{0.65}As_{0.35}$, respectively. Increasing the mole fraction of the lighter element (P) results in a larger band gap, and thus a higher energy of emitted photons.

Colors of semiconductors

The color of absorbed and emitted light both depend on the band gap of the semiconductor. Visible light covers the range of approximately 390-700 nm, or 1.8-3.1 eV. The **color of emitted light** from an LED or semiconductor laser corresponds to the band gap energy and can be read off the color wheel shown at the right.



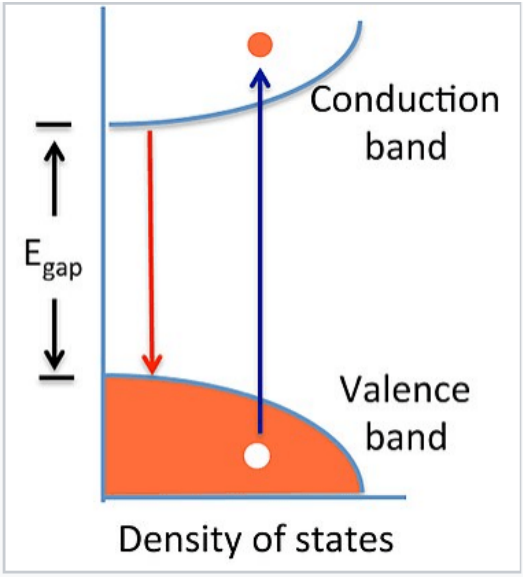
Fe_2O_3 powder is reddish orange because of its 2.2 eV band gap

The color of **absorbed light** includes the band gap energy, but also all colors of higher energy (shorter wavelength), because electrons can be excited from the valence band to a range of energies in the conduction band. Thus semiconductors with band gaps in the infrared (e.g., Si, 1.1 eV and GaAs, 1.4 eV) appear black because they absorb all colors of visible light. Wide band gap semiconductors such as TiO_2 (3.0 eV) are white because they absorb only in the UV. Fe_2O_3 has a band gap of 2.2 eV and thus absorbs light with $\lambda < 560$ nm. It thus appears reddish-orange (the colors of light reflected from Fe_2O_3) because it absorbs green, blue, and violet light. Similarly, CdS (E_{gap} = 2.6 eV) is yellow because it absorbs blue and violet light.

Electrons and holes in semiconductors

Pure (undoped) semiconductors can conduct electricity when electrons are promoted, either by heat or light, from the valence band to the conduction band. The promotion of an **electron** (e^-) leaves behind a **hole** (h^+) in the valence band. The hole, which is the absence of an electron in a bonding orbital, is also a mobile charge carrier, but with a positive charge. The motion of holes in the lattice can be pictured as analogous to the movement of an empty seat in a crowded theater. An empty seat in the middle of a row can move to the end of the row (to accommodate a person arriving late to the movie) if everyone moves over by one seat. Because the movement of the hole is in the opposite direction of electron movement, it acts as a positive charge carrier in an electric field.

The opposite process of excitation, which creates an electron-hole pair, is their recombination. When a conduction band electron drops down to recombine with a valence band hole, both are annihilated and energy is released. This release of energy is responsible for the emission of light in LEDs.



An electron-hole pair is created by adding heat or light energy E ≥ 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:

$$n \times p = n_i^2 = e^{(\frac{\Delta S^o}{R})} e^{(\frac{-\Delta H^o}{RT})} \tag{7.1.4.1}$$

The entropy change for creating electron hole pairs is given by:

$$\Delta S^o = Rln(N_V) + Rln(N_V) = Rln(N_C N_V) \tag{7.1.4.2}$$

where N_V and N_C are the effective density of states in the valence and conduction bands, respectively.

and thus we obtain

$$n_i^2 = N_C N_V e^{(-\Delta H^o RT)} \tag{7.1.4.3}$$

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

$$n_i^2 = N_C N_V e^{(\frac{-E_{gap}}{kT})} \tag{7.1.4.4}$$

and finally

$$\mathbf{n = p = n_i = (N_C N_V)^{\frac{1}{2}} e^{(\frac{-E_{gap}}{2kT})}} \tag{7.1.4.5}$$

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:

$$\sigma = ne\mu_e + pe\mu_h \tag{7.1.4.6}$$

For either type of charge carrier, we recall from Ch. 6 that the mobility μ is given by:

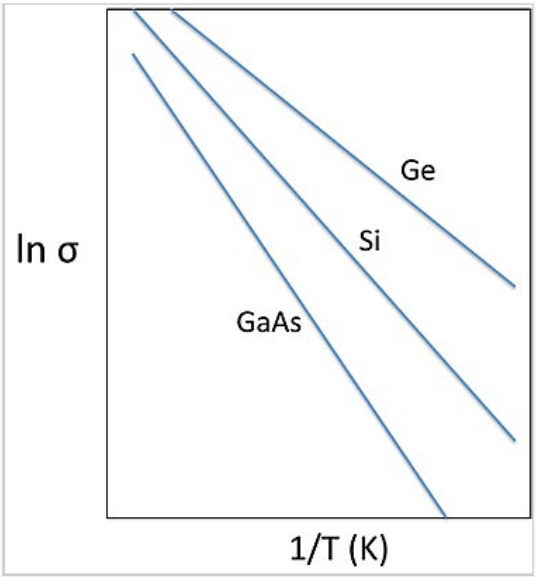
$$\mu = \frac{v_{drift}}{E} = \frac{e\tau}{m} \tag{7.1.4.7}$$

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

$$\sigma = \sigma_o e^{(\frac{-E_{gap}}{2kT})},\ where\ \sigma_o = 2(N_C N_V)^{\frac{1}{2}} e\mu \tag{7.1.4.8}$$

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.



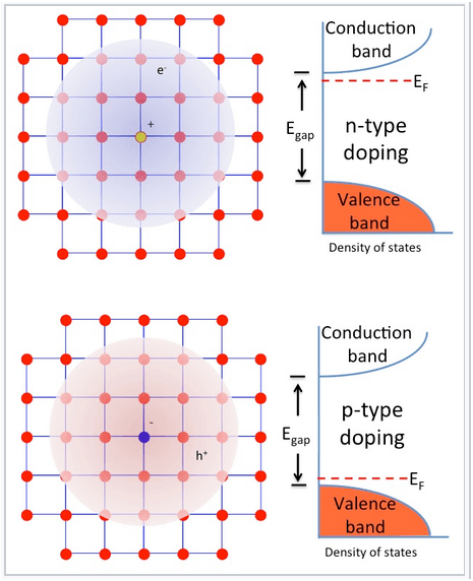
Plots of ln(σ) vs. inverse temperature for intrinsic semiconductors Ge (E_{gap} = 0.7 eV), Si (1.1 eV) and GaAs (1.4 eV). The slope of the line is -E_{gap}/2k.

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:

$$n \times p = n_i^2 = 10^{20} cm^{-6} \; at \; 300K \tag{7.1.4.9}$$

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.

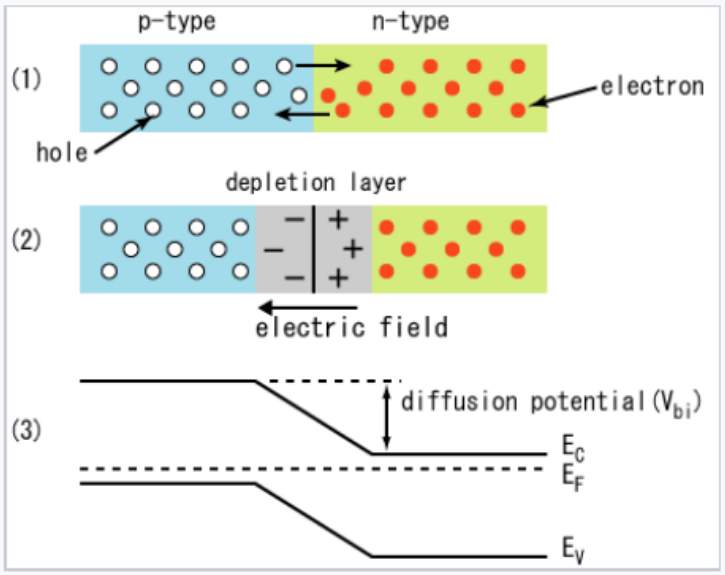
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7.1.5: Semiconductor p-n Junctions

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.

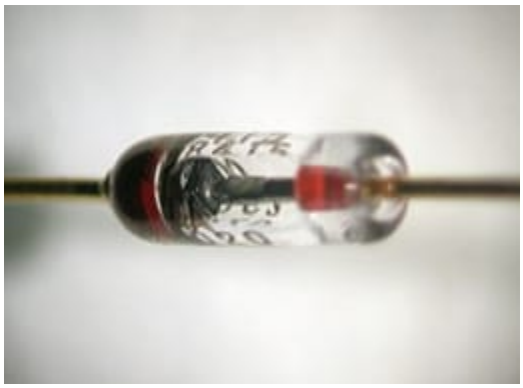
In the middle of p-n junction, the Fermi level energy, E_F, is halfway between the valence band, VB, and the conduction band, CB, and the semiconductor is intrinsic ($n = p = n_i$)

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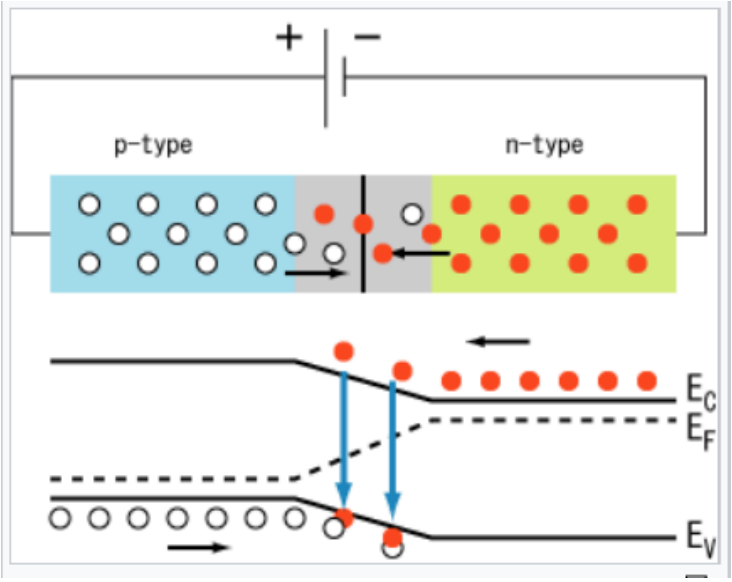
7.1.6: Diodes, LEDs and Solar Cells

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.



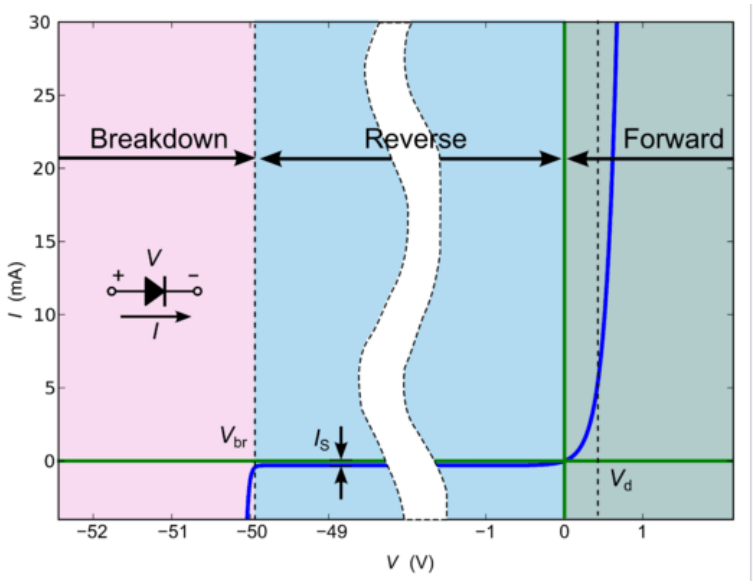
Closeup of a diode, showing the square-shaped semiconductor crystal *(black object on left)* (John Maushammer, Wikipedia, CC-BY-SA)

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."



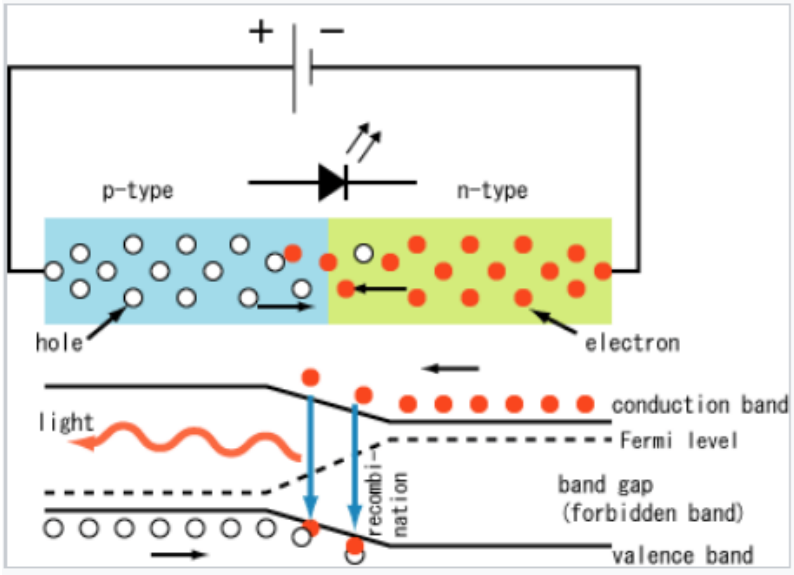
Electrons (red) and holes (white) in a forward-biased diode. (S-kei. Wikipedia, CC-BY-SA)

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)

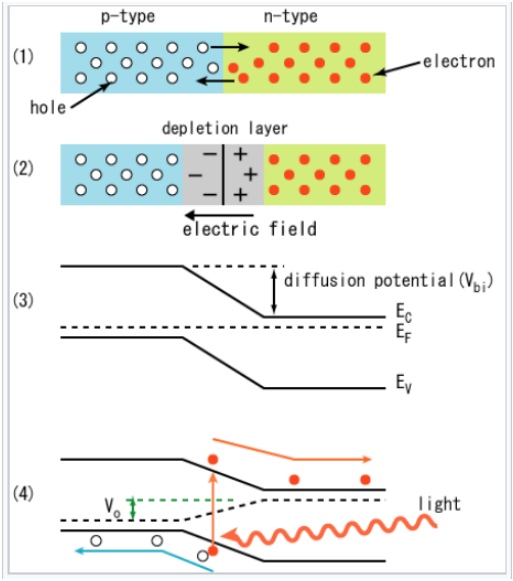
Direct-gap semiconductors such as GaAs and GaP have efficient luminescence and are also good light absorbers. In direct gap semiconductors, there is no momentum change involved in electron-hole creation or recombination. That is, the electrons and holes originate at the same value of the momentum wavevector **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.

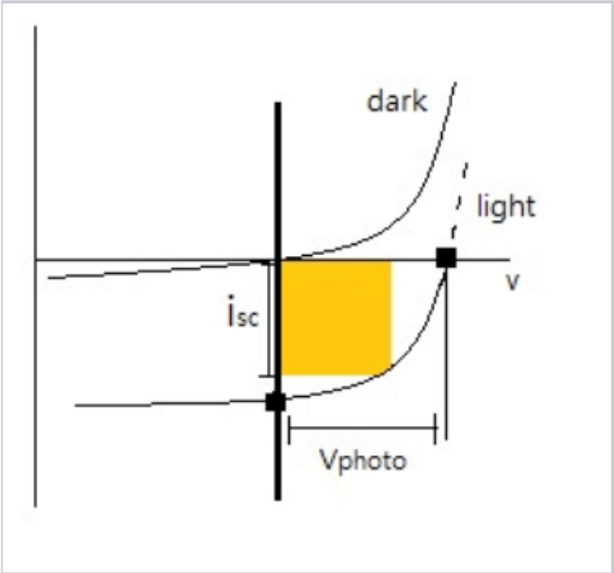
While red, orange, yellow, and green LEDs can be fabricated relatively easily from AlP-GaAs solid solutions, it was initially very difficult to fabricate blue LEDs because the best direct gap semiconductor with a bandgap in the right energy range is a nitride, GaN, which is difficult to make and to dope 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.

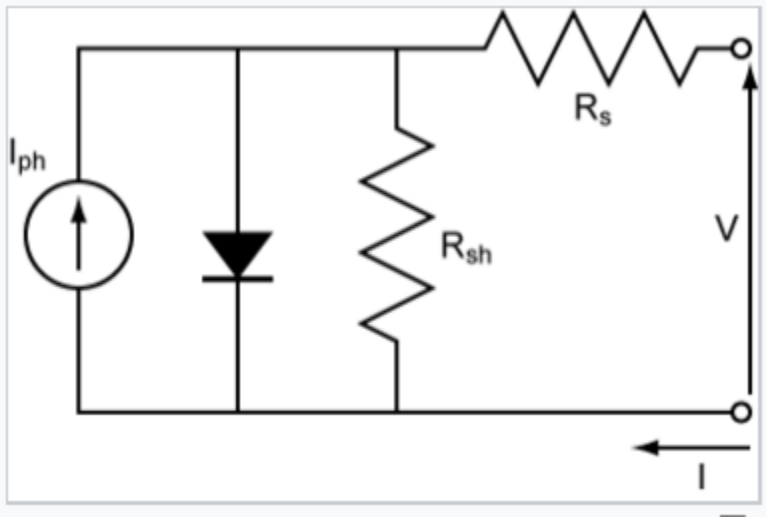


Current-voltage characteristic of a solar cell in the dark and under illumination with band gap light. The short-circuit photocurrent is indicated as i_{sc}, and the open-circuit photovoltage is V_{photo}. The maximum power generated by the solar cell is determined by the area of the orange box.

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 hν > 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.

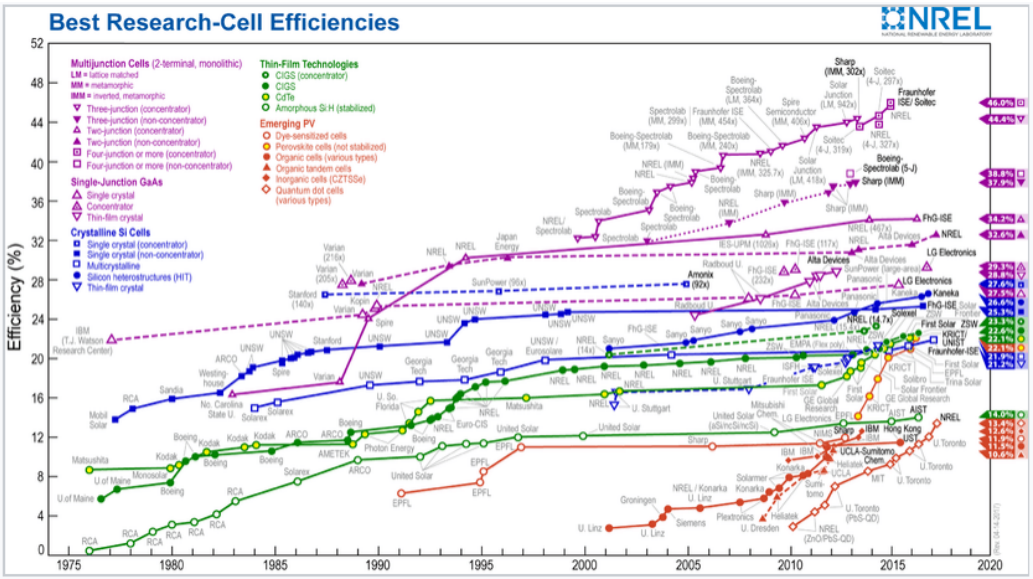
In the photodiode i-V curve above, V_{photo} is typically only about 70% of the bandgap energy E_{gap}. The photocurrent is limited by the photon flux, the recombination rate, and the re-emission of absorbed light.[6] The area of the orange rectangle indicates the power generated by the solar cell, which 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.

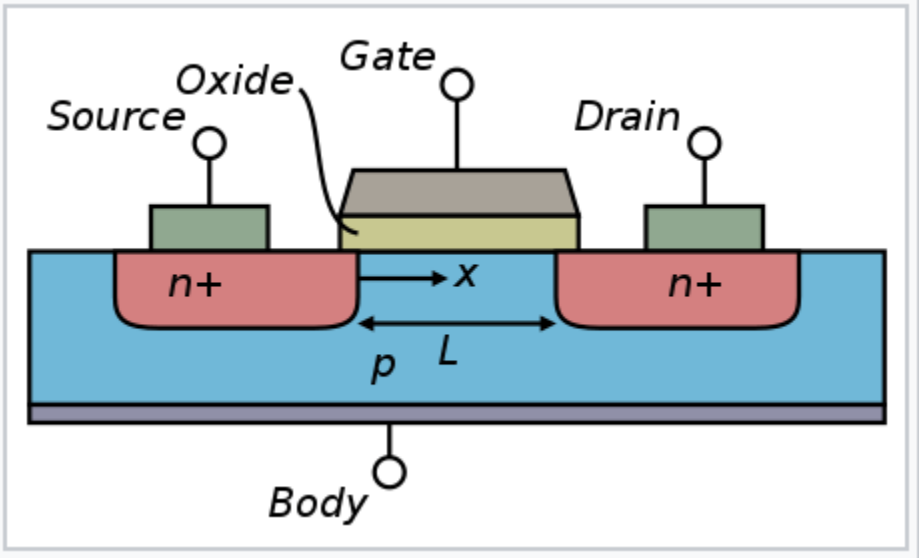
The cost of installed photovoltaics (calculated on a per-watt basis) has dropped over the past decade at a rate of about 13% per year, and has already reached grid parity in Germany and a number of other countries.[7] Photovoltaic grid parity is anticipated in U.S. power markets in the 2020 timeframe.[8] 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)

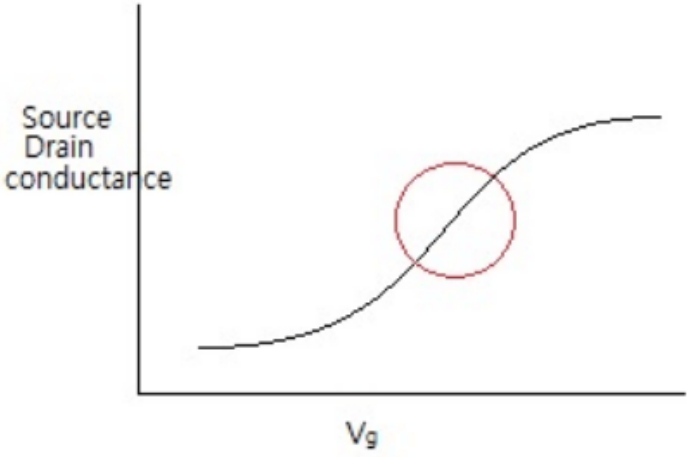
A **field effect transistor (FET)** is a transistor that uses an electric field to control the width of a conducting channel and thus the current in a semiconductor material. It is classified as unipolar transistor, in contrast to bipolar transistors.

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

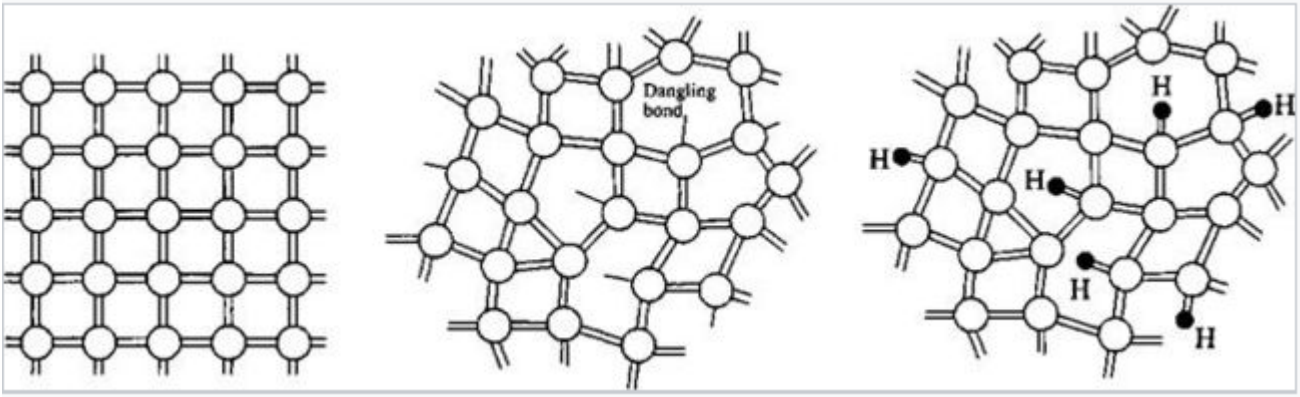
a very high gate capacitance, which requires a thin insulating oxide, but also to have a small leakage current, which requires a thick oxide. A current challenge in the semiconductor industry is to continue to scale FETs to even smaller nanoscale dimensions while maintaining acceptable values of these 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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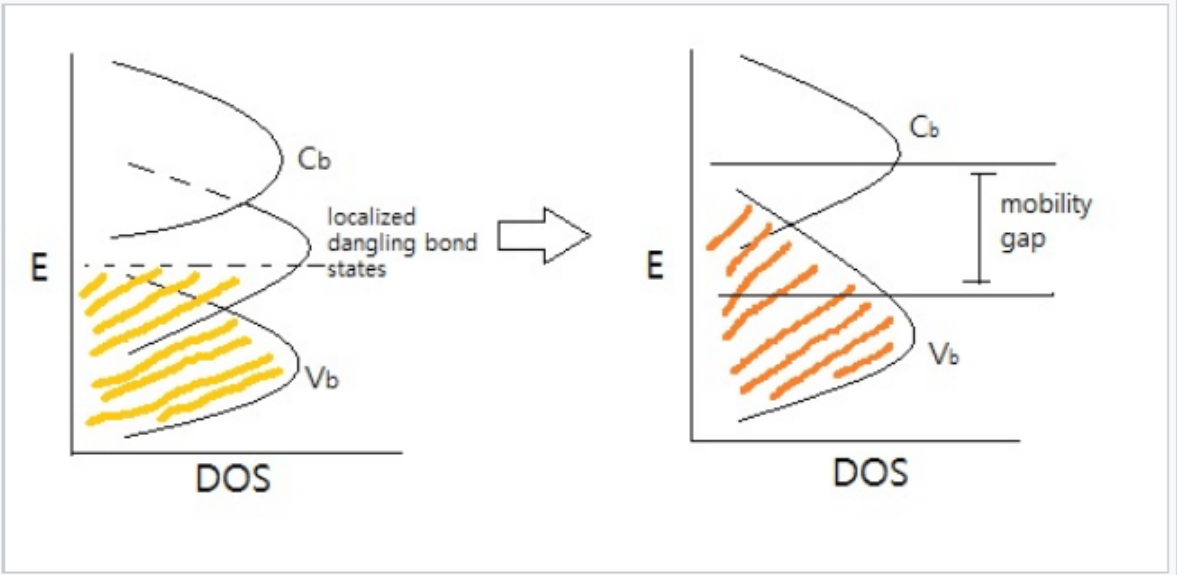
7.1.7: Amorphous Semiconductors

Amorphous semiconductors are disordered or glassy forms of crystalline semiconductor materials. Like non-conducting glasses, they are network structures with primarily covalent bonding. Crystalline silicon, which has the diamond structure, is an ordered arrangement of fused six-membered silicon rings, all in the "chair" conformation, as we saw in Ch. 8. The local bonding environment of the silicon atoms is tetrahedral. The silicon atoms in amorphous silicon (a-Si) are also predominantly tetrahedrally coordinated, but there is no long-range order in the structure. In addition to six-membered rings, there are five- and seven-membered rings, as well as some "dangling bond" sites in which Si atoms have only three nearest neighbors.



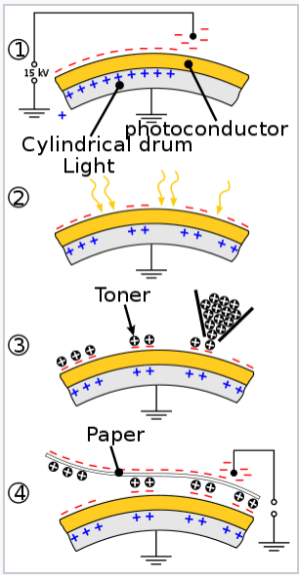
Schematic illustration of the structures of crystalline silicon (left), amorphous silicon (middle), and amorphous hydrogenated silicon (right)

Two of the most widely studied amorphous semiconductors are a-Si and amorphous selenium, a-Se. Si and Se can both be made in glassy form, usually by sputtering or evaporation at relatively low temperature. In a-Se, as in a-Si, locally, most of the atoms have their "normal" valence, but there are many defects and irregularities in the structure. Dangling bonds in amorphous semiconductors have orbital energies in the middle of gap, and electrons in these states are effectively non-bonding. Because these dangling bond sites are far apart from each other, there is little orbital overlap between them, and they also exist over a range of energies. Electrons in these mid-gap states are therefore **localized**, a phenomenon known as Anderson localizaton. Amorphous Si is insulating because electrons the Fermi level (in the middle of the gap) are not mobile in the lattice. These localized states create a mobility gap, and only electrons in states that are strongly bonding or antibonding are delocalized. Therefore, unmodified a-Si is not very useful as a semiconductor. However, by hydrogenating the material as it is formed (typically in a plasma of H atoms), the under-coordinated Si atoms are bonded to hydrogen atoms. This generates filled bonding and empty antibonding orbitals, the energies of which are outside the mobility gap. Hydrogenation thus lowers the density of states in the mobility gap. Hydrogenated amorphous silicon (a-Si:H) is insulating in the dark, but is a good photoconductor because light absorption creates electrons and holes in mobile states that are outside the mobility gap.



Energy vs. DOS for an amorphous semiconductor. Disorder and dangling bonds result in localized mid-gap states.

The photoconductivity of **amorphous Se** is exploited in xerography. A conductive drum coated with a-Se, which is insulating, is charged with static electricity by corona discharge from a wire. When the drum is exposed to a pattern of light and dark (the image to be duplicated), the illuminated a-Se areas become conductive and the static charge is dissipated from those parts of the drum. Carbon-containing toner particles then adhere via static charge to the areas that were not exposed to light, and are transferred and bonded to paper to make the copy. The speed of the process and the high resolution of pattern transfer depend on the very low conductivity of a-Se in the dark and its high conductivity under illumination.



Charging of amorphous Se and pattern transfer in the xerographic cycle.

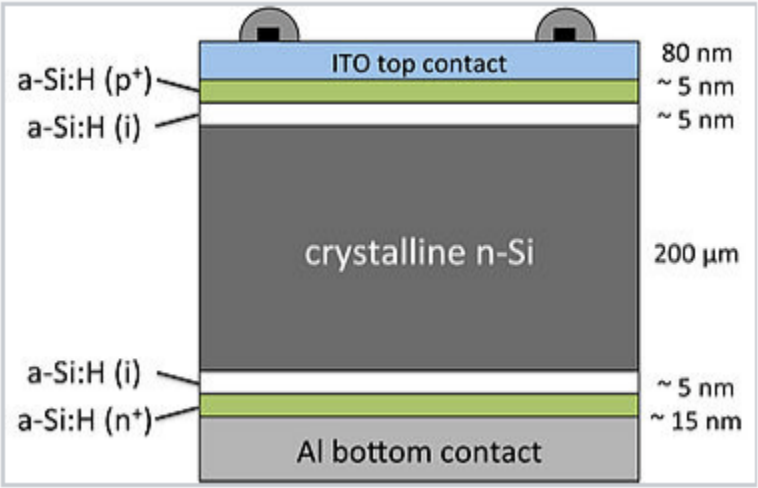
Amorphous hydrogenated Si is used in inexpensive thin film solar cells. The mobility gap is about 1.7 eV, which is larger than the bandgap crystalline of Si (1.1 eV). a-Si:H is a direct-gap material, and therefore thin films are good light absorbers. a-Si:H solar

cells can be vapor-deposited in large-area sheets. p^+Si-a-Si:H-n^+Si cells have around 10% power conversion efficiency. However amorphous Si solar cells gradually lose efficiency as they are exposed to light. The mechanism of this efficiency loss, called the Staebler-Wronski effect,[9], involves photogenerated electron-hole pairs which have sufficient energy to cause chemical changes in the material. While the exact mechanism is still unclear, it has been proposed that the energy of electron-hole recombination breaks a weak Si-Si bond, and that one of the resulting dangling bonds abstracts a H atom, leaving a passivated Si-H center and a permanent dangling bond. The effect is minimized by hydrogenating a-Si and can be partially reversed by annealing.



A calculator that runs on solar and battery power

Thin layers of amorphous silicon are used in conjunction with crystalline silicon in heterojunction intrinsic thin-layer (HIT) solar cells.[10] Because the mobility gap of a-Si is wider than the bandgap of c-Si, there is a potential energy barrier at the amorphous-crystalline interface that reflects electrons and holes away from that interface. At the p^+ contact, only holes can tunnel through the barrier, whereas only electrons can tunnel through the barrier to the n^+ contact. The passivation of surface defects that are sites of electron-hole recombination prevents a major loss mechanism in solar cells, increasing both the photovoltage and the photocurrent relative to conventional c-Si p-n junction cells. Panasonic and Sanyo have announced the production of HIT cells with power conversion efficiencies as high as 23%.



Layered structure of a HIT solar cell. The layers are not drawn to scale. A thick crystalline n-silicon layer is the light absorber, and photogenerated holes, which are the minority carriers, are reflected away from the aluminum back contact by the thin intrinsic a-Si layer there.

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7.1.8: Discussion Questions

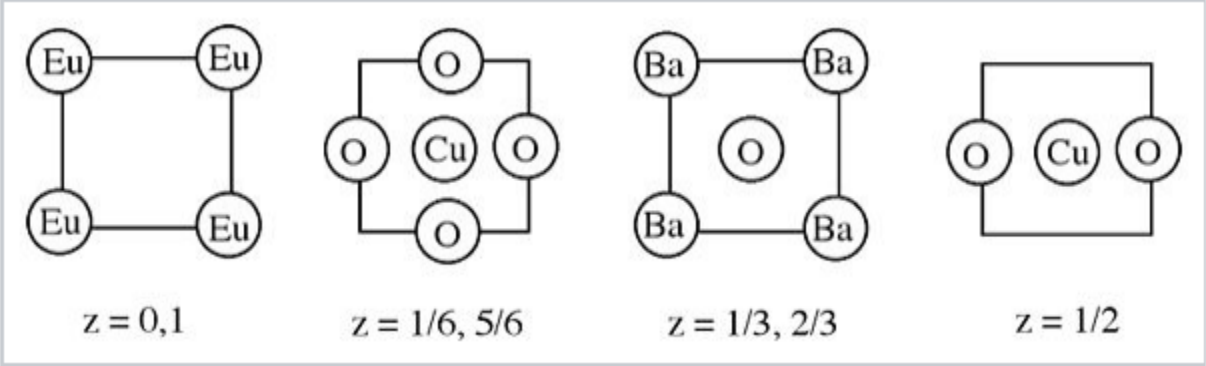
- How is magnetic ordering in the 3d transition metals (Fe, Co, Ni) and the absence of magnetism in the elements just below them (Ru, Ir, Pd) related to the metal-insulator transition?
- Why are good metals bad superconductors and vice-versa?
- Discuss why semiconducting oxides of early transition metals such as TiO_2 and Nb_2O_5 can be doped n-type but not p-type. Conversely, semiconducting late transition metal oxides such as NiO and Cu_2O can be doped p-type but not n-type.

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7.1.9: Problems

1. The structure of a high temperature superconductor containing barium, europium, copper, and oxygen is shown below. What are the coordination environments of Cu in this compound? This structure is actually closely related to perovskite, ABO_3. Explain the relationship between this structure and the ideal perovskite structure.



2. VO_2 can exist in insulating or metallic form, depending on temperature and pressure. Which form would be stabilized by increasing the temperature? Explain your answer.

3. Explain briefly how and why the bandgaps for octet p-block semiconductors vary (1) with the average principal quantum number, and (2) with the electronegativity difference between anion and cation.

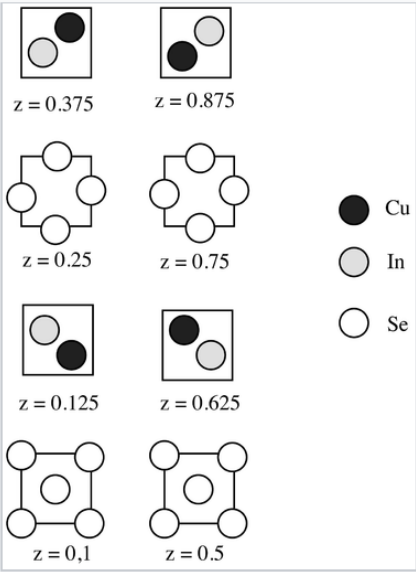
4. Indicate the type of conduction (n or p) in the following: (a) Se-doped GaAs, (b) $InAs_{1-x}$, where x << 1, (c) $Li_{0.05}Ni_{0.95}O$, (d) Li_xWO_3, where x << 1.

5. The structure of copper indium selenide, a semiconductor used in thin film solar cells, is shown below in sections.

(a) What is the stoichiometry of the compound?

(b) What kind of doping (n or p) will occur if a small amount of iodine is substituted for selenium?

(c) What kind of doping (n or p) will occur if a small fraction of the indium sites are occupied by copper atoms?

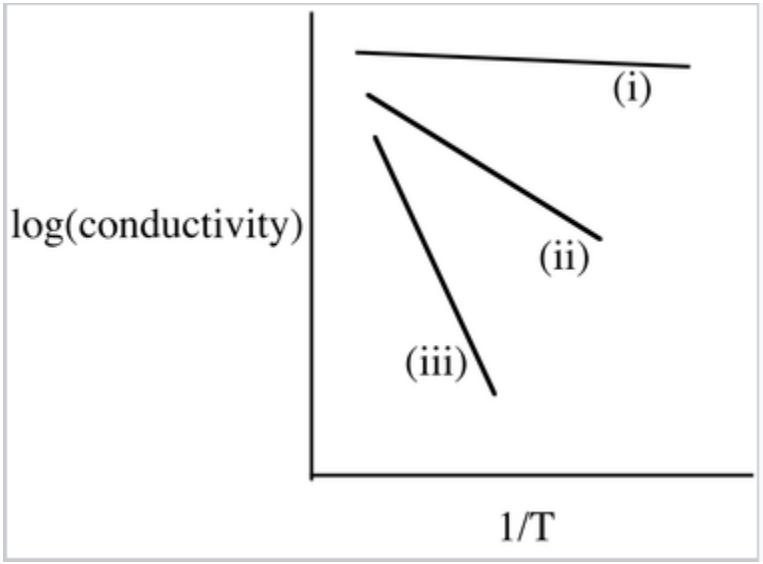


6. Using 1 eV = 1240 nm, predict the colors of anatase TiO_2 (Eg = 3.1 eV), SiC (2.0 eV), $ZnSnP_2$ (1.7 eV), $ZnGeP_2$ (1.9 eV), and InP (1.27 eV).

7. The conductivity of a certain intrinsic (undoped) semiconductor increases by a factor of two when the temperature is raised from 300 to 330 K. What is the bandgap (in eV)? R = 8.314 J/mol-K, 1 eV/atom = 96.52 kJ/mole.

8. Pure Ge is much more conductive than pure Si. Given their bandgaps (0.74 and 1.15 eV, respectively), estimate the ratio of their conductivities at room temperature.

9. The figure below illustrates the trends in conductivity vs. inverse temperature for Si, Ge, and As-doped Ge. Identify lines (i), (ii), and (iii) with the appropriate materials. Explain why the slope of line (i) is close to zero.



10. Sketch a silicon p-n junction, showing the depletion region, band bending, and the Fermi level in the absence of light or applied potential. In the dark, the p-n junction acts as a rectifier. (a) Which way do electrons and holes flow most easily in the dark? (b) Does the built in electric field increase or decrease under forward bias? (c) In the light, the junction acts as a photodiode. In this case, under short circuit conditions, do electrons flow in the same direction or in the opposite direction as in (a)? Explain.

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7.2: Formulas and Structures of Solids

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7.2.1: The Solid State of Matter

Learning Objectives

- Define and describe the bonding and properties of ionic, molecular, metallic, and covalent network crystalline solids
- Describe the main types of crystalline solids: ionic solids, metallic solids, covalent network solids, and molecular solids
- Explain the ways in which crystal defects can occur in a solid

When most liquids are cooled, they eventually freeze and form crystalline solids, solids in which the atoms, ions, or molecules are arranged in a definite repeating pattern. It is also possible for a liquid to freeze before its molecules become arranged in an orderly pattern. The resulting materials are called amorphous solids or noncrystalline solids (or, sometimes, glasses). The particles of such solids lack an ordered internal structure and are randomly arranged (Figure 7.2.1.1).

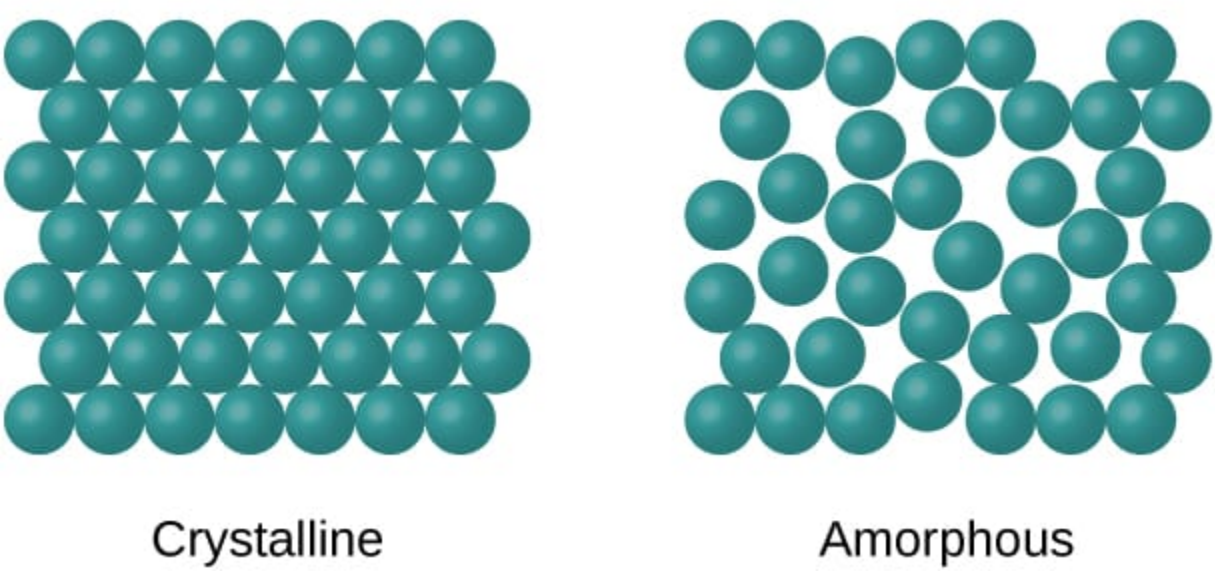


Figure 7.2.1.1: The entities of a solid phase may be arranged in a regular, repeating pattern (crystalline solids) or randomly (amorphous).

The crystalline arrangement shows many circles drawn in rows and stacked together tightly. The amorphous arrangement shows many circles spread slightly apart and in no organized pattern.

Metals and ionic compounds typically form ordered, crystalline solids. Substances that consist of large molecules, or a mixture of molecules whose movements are more restricted, often form amorphous solids. For examples, candle waxes are amorphous solids composed of large hydrocarbon molecules. Some substances, such as boron oxide (Figure 7.2.1.2), can form either crystalline or amorphous solids, depending on the conditions under which it is produced. Also, amorphous solids may undergo a transition to the crystalline state under appropriate conditions.

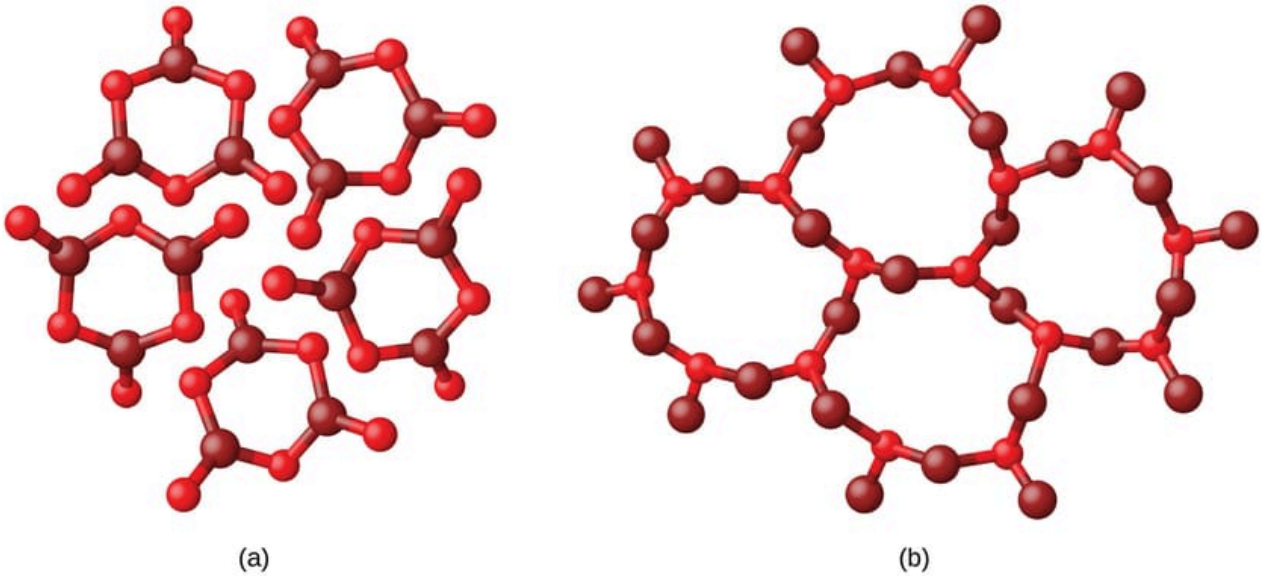


Figure 7.2.1.2: (a) Diboron trioxide, B_2O_3, is normally found as a white, amorphous solid (a glass), which has a high degree of disorder in its structure. (b) By careful, extended heating, it can be converted into a crystalline form of B_2O_3, which has a very ordered arrangement.

The first structure of diboron trioxide shows five identical and separated hexagonal rings. The second structure of diboron trioxide shows a more interconnected structure with four large rings forming a more stable structure.

Crystalline solids are generally classified according the nature of the forces that hold its particles together. These forces are primarily responsible for the physical properties exhibited by the bulk solids. The following sections provide descriptions of the major types of crystalline solids: ionic, metallic, covalent network, and molecular.

Ionic Solids

Ionic solids, such as sodium chloride and nickel oxide, are composed of positive and negative ions that are held together by electrostatic attractions, which can be quite strong (Figure 7.2.1.3). Many ionic crystals also have high melting points. This is due to the very strong attractions between the ions—in ionic compounds, the attractions between full charges are (much) larger than those between the partial charges in polar molecular compounds. This will be looked at in more detail in a later discussion of lattice energies. Although they are hard, they also tend to be brittle, and they shatter rather than bend. Ionic solids do not conduct electricity; however, they do conduct when molten or dissolved because their ions are free to move. Many simple compounds formed by the reaction of a metallic element with a nonmetallic element are ionic.

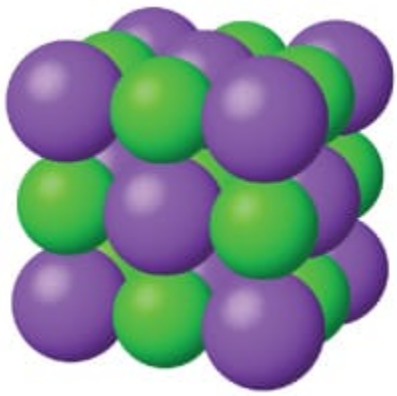


Figure 7.2.1.3: Sodium chloride is an ionic solid.

A cube composed of purple and green spheres is shown. The cube has dimensions of three by three spheres. The purple spheres are slightly larger than the green spheres.

Metallic Solids

Metallic solids such as crystals of copper, aluminum, and iron are formed by metal atoms Figure 7.2.1.4. The structure of metallic crystals is often described as a uniform distribution of atomic nuclei within a “sea” of delocalized electrons. The atoms within such a metallic solid are held together by a unique force known as *metallic bonding* that gives rise to many useful and varied bulk properties. All exhibit high thermal and electrical conductivity, metallic luster, and malleability. Many are very hard and quite strong. Because of their malleability (the ability to deform under pressure or hammering), they do not shatter and, therefore, make useful construction materials. The melting points of the metals vary widely. Mercury is a liquid at room temperature, and the alkali metals melt below 200 °C. Several post-transition metals also have low melting points, whereas the transition metals melt at temperatures above 1000 °C. These differences reflect differences in strengths of metallic bonding among the metals.

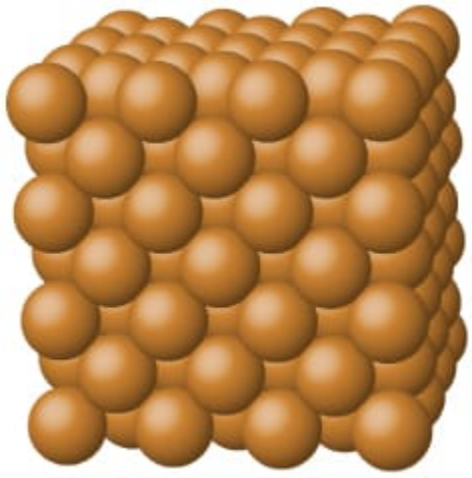


Figure 7.2.1.4: Copper is a metallic solid.

Covalent Network Solids

Covalent network solids include crystals of diamond, silicon, some other nonmetals, and some covalent compounds such as silicon dioxide (sand) and silicon carbide (carborundum, the abrasive on sandpaper). Many minerals have networks of covalent bonds. The atoms in these solids are held together by a network of covalent bonds, as shown in Figure 7.2.1.5. To break or to melt a covalent network solid, covalent bonds must be broken. Because covalent bonds are relatively strong, covalent network solids are typically characterized by hardness, strength, and high melting points. For example, diamond is one of the hardest substances known and melts above 3500 °C.

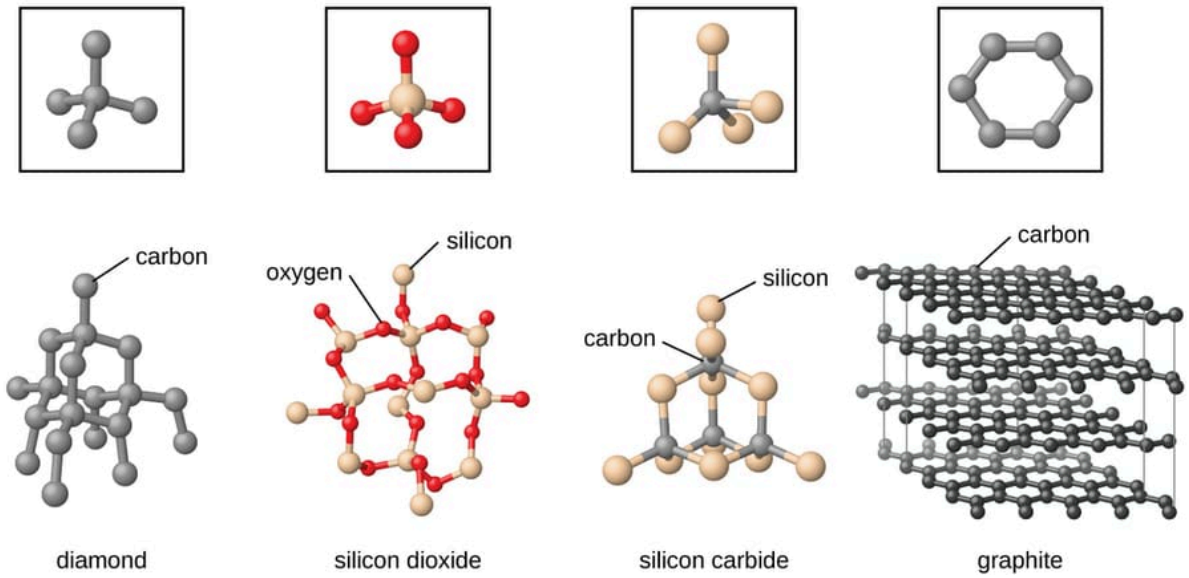


Figure 7.2.1.5. A covalent crystal contains a three-dimensional network of covalent bonds, as illustrated by the structures of diamond, silicon dioxide, silicon carbide, and graphite. Graphite is an exceptional example, composed of planar sheets of covalent crystals that are held together in layers by noncovalent forces. Unlike typical covalent solids, graphite is very soft and electrically conductive.

The complex three dimensional structure of diamond, silicon dioxide, silicon carbide and graphite is shown along with a a smaller repeating unit of the structure shown above each structure.

Molecular Solids

Molecular solids, such as ice, sucrose (table sugar), and iodine, as shown in Figure 7.2.1.6, are composed of neutral molecules. The strengths of the attractive forces between the units present in different crystals vary widely, as indicated by the melting points of the crystals. Small symmetrical molecules (nonpolar molecules), such as H_2, N_2, O_2, and F_2, have weak attractive forces and form molecular solids with very low melting points (below –200 °C). Substances consisting of larger, nonpolar molecules have larger attractive forces and melt at higher temperatures. Molecular solids composed of molecules with permanent dipole moments (polar molecules) melt at still higher temperatures. Examples include ice (melting point, 0 °C) and table sugar (melting point, 185 °C).

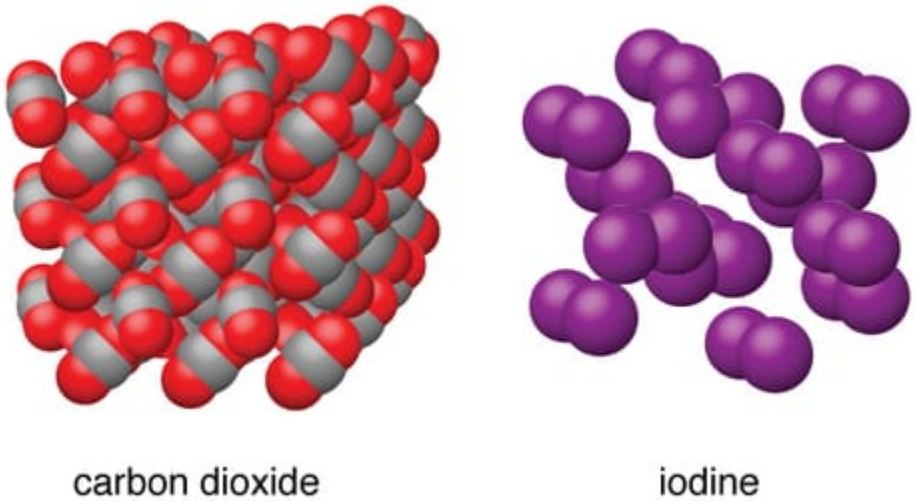


Figure 7.2.1.6: Carbon dioxide (CO_2) consists of small, nonpolar molecules and forms a molecular solid with a melting point of –78 °C. Iodine (I_2) consists of larger, nonpolar molecules and forms a molecular solid that melts at 114 °C.

On the left, many red and grey molecules are densely stacked in a 3-D drawing to represent carbon dioxide. On the right, purple molecules are scattered randomly to represent iodine.

Properties of Solids

A crystalline solid, like those listed in Table 7.2.1.1 has a precise melting temperature because each atom or molecule of the same type is held in place with the same forces or energy. Thus, the attractions between the units that make up the crystal all have the same strength and all require the same amount of energy to be broken. The gradual softening of an amorphous material differs dramatically from the distinct melting of a crystalline solid. This results from the structural nonequivalence of the molecules in the amorphous solid. Some forces are weaker than others, and when an amorphous material is heated, the weakest intermolecular attractions break first. As the temperature is increased further, the stronger attractions are broken. Thus amorphous materials soften over a range of temperatures.

Table 7.2.1.1: Types of Crystalline Solids and Their Properties

Type of Solid	Type of Particles	Type of Attractions	Properties	Examples
ionic	ions	ionic bonds	hard, brittle, conducts electricity as a liquid but not as a solid, high to very high melting points	NaCl, Al_2O_3
metallic	atoms of electropositive elements	metallic bonds	shiny, malleable, ductile, conducts heat and electricity well, variable hardness and melting temperature	Cu, Fe, Ti, Pb, U
covalent network	atoms of electronegative elements	covalent bonds	very hard, not conductive, very high melting points	C (diamond), SiO_2, SiC
molecular	molecules (or atoms)	IMFs	variable hardness, variable brittleness, not conductive, low melting points	H_2O, CO_2, I_2, $C_{12}H_{22}O_{11}$

Graphene: Material of the Future

Carbon is an essential element in our world. The unique properties of carbon atoms allow the existence of carbon-based life forms such as ourselves. Carbon forms a huge variety of substances that we use on a daily basis, including those shown in Figure 7.2.1.7. You may be familiar with diamond and graphite, the two most common *allotropes* of carbon. (Allotropes are different structural forms of the same element.) Diamond is one of the hardest-known substances, whereas graphite is soft enough to be used as pencil lead. These very different properties stem from the different arrangements of the carbon atoms in the different allotropes.

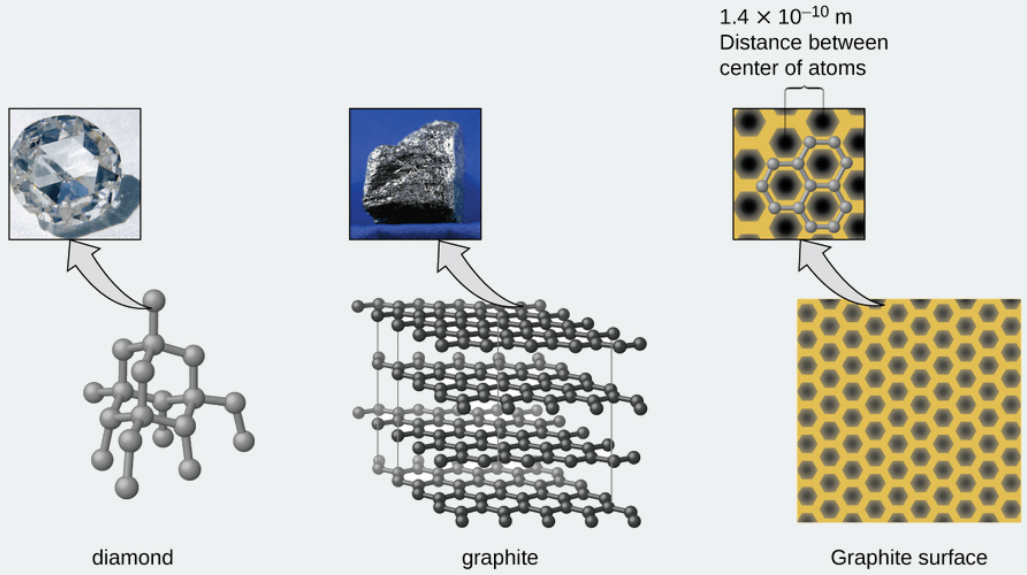


Figure 7.2.1.7: Diamond is extremely hard because of the strong bonding between carbon atoms in all directions. Graphite (in pencil lead) rubs off onto paper due to the weak attractions between the carbon layers. An image of a graphite surface shows the distance between the centers of adjacent carbon atoms. (credit left photo: modification of work by Steve Jurvetson; credit middle photo: modification of work by United States Geological Survey)

A close up of a piece of diamond shows a three dimensional sturcture of a complex network of well bonded carbon atoms. A close up of a graphite shows several layers of carbon sheets. Each sheet is composed of a repeated and connected hexagonal structure of carbon atoms. The third diagram shows that the distance between the center of atoms is 1.4 times 10 to the power of negative 10 meters.

You may be less familiar with a recently discovered form of carbon: graphene. Graphene was first isolated in 2004 by using tape to peel off thinner and thinner layers from graphite. It is essentially a single sheet (one atom thick) of graphite. Graphene, illustrated in Figure 7.2.1.8, is not only strong and lightweight, but it is also an excellent conductor of electricity and heat. These properties may prove very useful in a wide range of applications, such as vastly improved computer chips and circuits, better batteries and solar cells, and stronger and lighter structural materials. The 2010 Nobel Prize in Physics was awarded to Andre Geim and Konstantin Novoselov for their pioneering work with graphene.

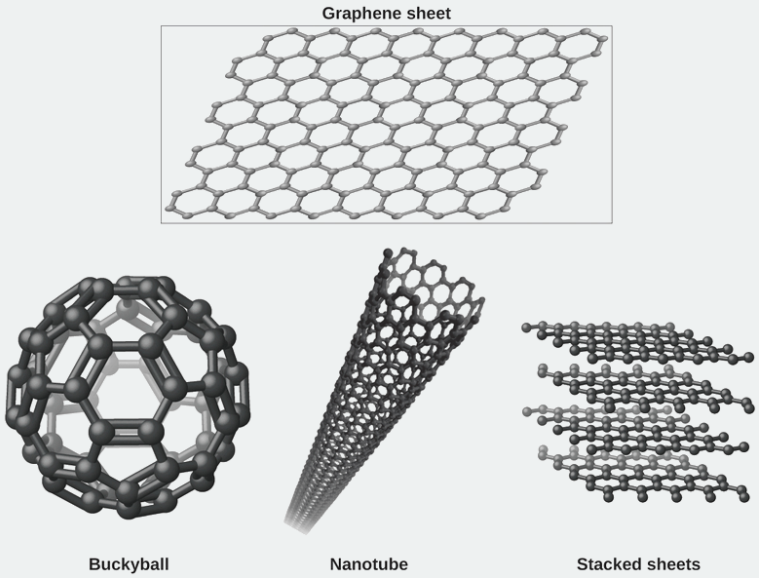


Figure 7.2.1.8: Graphene sheets can be formed into buckyballs, nanotubes, and stacked layers.

A sheet of interconnected hexagonal rings is shown at the top. Below it, a bukcyball is shown which is a sphere is composed of hexagonal rings. In the lower middle image, a nanotube is shown that is made by rolling a graphene sheet into a tube. In the lower right image, stacked sheets made up of four horizontal sheets composed of joined, hexagonal rings is shown.

Crystal Defects

In a crystalline solid, the atoms, ions, or molecules are arranged in a definite repeating pattern, but occasional defects may occur in the pattern. Several types of defects are known, as illustrated in Figure 7.2.1.9. Vacancies are defects that occur when positions that should contain atoms or ions are vacant. Less commonly, some atoms or ions in a crystal may occupy positions, called interstitial sites, located between the regular positions for atoms. Other distortions are found in impure crystals, as, for example, when the cations, anions, or molecules of the impurity are too large to fit into the regular positions without distorting the structure. Trace amounts of impurities are sometimes added to a crystal (a process known as *doping)* in order to create defects in the structure that yield desirable changes in its properties. For example, silicon crystals are doped with varying amounts of different elements to yield suitable electrical properties for their use in the manufacture of semiconductors and computer chips.

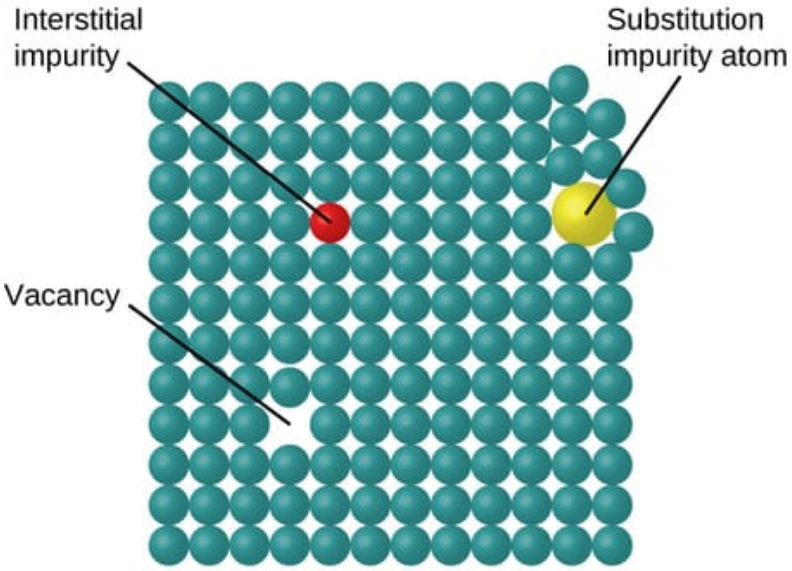


Figure 7.2.1.9: Types of crystal defects include vacancies, interstitial atoms, and substitutions impurities.

Summary

Some substances form crystalline solids consisting of particles in a very organized structure; others form amorphous (noncrystalline) solids with an internal structure that is not ordered. The main types of crystalline solids are ionic solids, metallic solids, covalent network solids, and molecular solids. The properties of the different kinds of crystalline solids are due to the types of particles of which they consist, the arrangements of the particles, and the strengths of the attractions between them. Because their particles experience identical attractions, crystalline solids have distinct melting temperatures; the particles in amorphous solids experience a range of interactions, so they soften gradually and melt over a range of temperatures. Some crystalline solids have defects in the definite repeating pattern of their particles. These defects (which include vacancies, atoms or ions not in the regular positions, and impurities) change physical properties such as electrical conductivity, which is exploited in the silicon crystals used to manufacture computer chips.

Glossary

amorphous solid
: (also, noncrystalline solid) solid in which the particles lack an ordered internal structure

covalent network solid
: solid whose particles are held together by covalent bonds

crystalline solid
: solid in which the particles are arranged in a definite repeating pattern

interstitial sites
: spaces between the regular particle positions in any array of atoms or ions

ionic solid
: solid composed of positive and negative ions held together by strong electrostatic attractions

metallic solid
: solid composed of metal atoms

molecular solid
: solid composed of neutral molecules held together by intermolecular forces of attraction

vacancy
: defect that occurs when a position that should contain an atom or ion is vacant

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7.2.2: Lattice Structures in Crystalline Solids

Learning Objectives

- Describe the arrangement of atoms and ions in crystalline structures
- Compute ionic radii using unit cell dimensions
- Explain the use of X-ray diffraction measurements in determining crystalline structures

Over 90% of naturally occurring and man-made solids are crystalline. Most solids form with a regular arrangement of their particles because the overall attractive interactions between particles are maximized, and the total intermolecular energy is minimized, when the particles pack in the most efficient manner. The regular arrangement at an atomic level is often reflected at a macroscopic level. In this module, we will explore some of the details about the structures of metallic and ionic crystalline solids, and learn how these structures are determined experimentally.

The Structures of Metals

We will begin our discussion of crystalline solids by considering elemental metals, which are relatively simple because each contains only one type of atom. A pure metal is a crystalline solid with metal atoms packed closely together in a repeating pattern. Some of the properties of metals in general, such as their malleability and ductility, are largely due to having identical atoms arranged in a regular pattern. The different properties of one metal compared to another partially depend on the sizes of their atoms and the specifics of their spatial arrangements. We will explore the similarities and differences of four of the most common metal crystal geometries in the sections that follow.

Unit Cells of Metals

The structure of a crystalline solid, whether a metal or not, is best described by considering its simplest repeating unit, which is referred to as its unit cell. The unit cell consists of lattice points that represent the locations of atoms or ions. The entire structure then consists of this unit cell repeating in three dimensions, as illustrated in Figure 7.2.2.1.

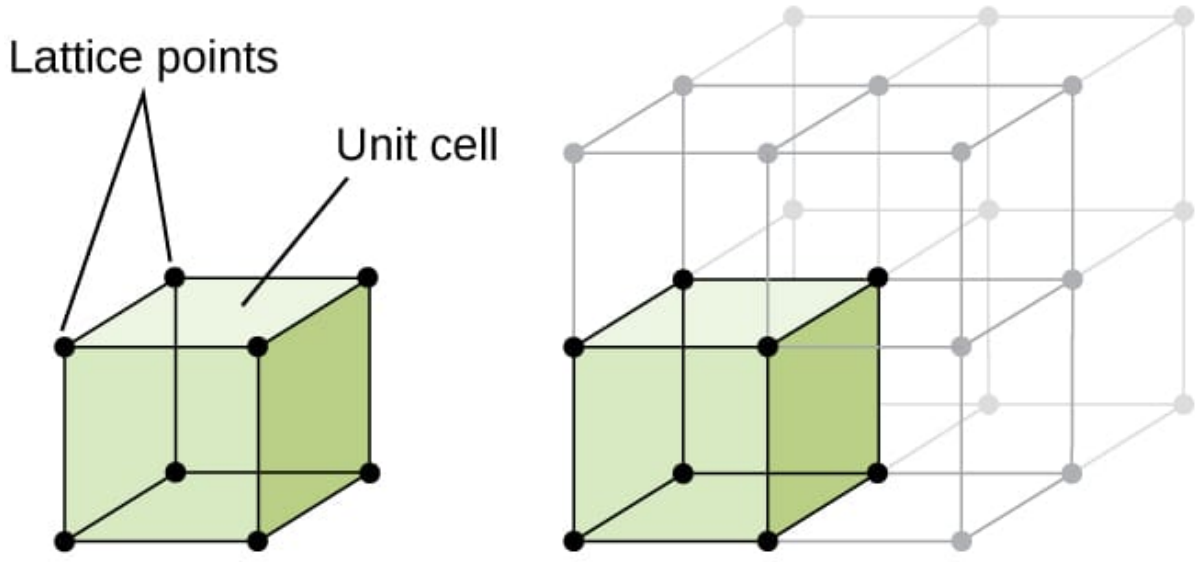


Figure 7.2.2.1: A unit cell shows the locations of lattice points repeating in all directions.

A diagram of two images is shown. In the first image, a cube with a sphere at each corner is shown. The cube is labeled “Unit cell” and the spheres at the corners are labeled “Lattice points.” The second image shows the same cube, but this time it is one cube amongst eight that make up a larger cube. The original cube is shaded a color while the other cubes are not.

Let us begin our investigation of crystal lattice structure and unit cells with the most straightforward structure and the most basic unit cell. To visualize this, imagine taking a large number of identical spheres, such as tennis balls, and arranging them uniformly in a container. The simplest way to do this would be to make layers in which the spheres in one layer are directly above those in the layer below, as illustrated in Figure 7.2.2.2. This arrangement is called simple cubic structure, and the unit cell is called the simple cubic unit cell or primitive cubic unit cell.

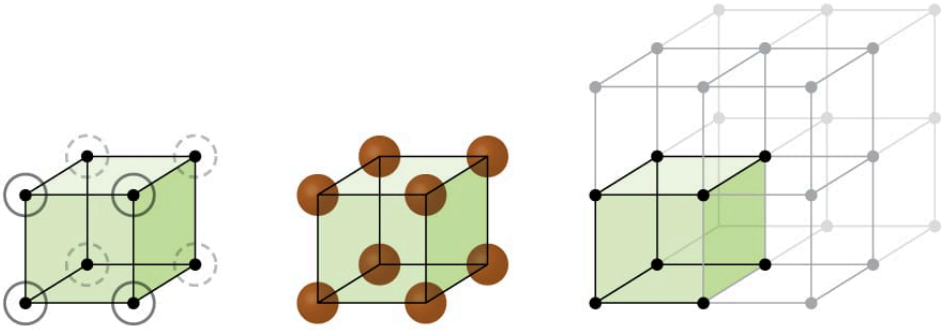


Figure 7.2.2.2: .When metal atoms are arranged with spheres in one layer directly above or below spheres in another layer, the lattice structure is called simple cubic. Note that the spheres are in contact.

A diagram of three images is shown. In the first image, a cube with a sphere at each corner is shown. The spheres at the corners are circled. The second image shows the same cube, but this time the spheres at the corners are larger and shaded in. In the third image, the cube is one cube amongst eight that make up a larger cube. The original cube is shaded a color while the other cubes are not.

In a simple cubic structure, the spheres are not packed as closely as they could be, and they only "fill" about 52% of the volume of the container. This is a relatively inefficient arrangement, and only one metal (polonium, Po) crystallizes in a simple cubic structure. As shown in Figure 7.2.2.3, a solid with this type of arrangement consists of planes (or layers) in which each atom contacts only the four nearest neighbors in its layer; one atom directly above it in the layer above; and one atom directly below it in the layer below. The number of other particles that each particle in a crystalline solid contacts is known as its coordination number. For a polonium atom in a simple cubic array, the coordination number is, therefore, six.

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Figure 7.2.2.3: An atom in a simple cubic lattice structure contacts six other atoms, so it has a coordination number of six.

In a simple cubic lattice, the unit cell that repeats in all directions is a cube defined by the centers of eight atoms, as shown in Figure 7.2.2.4. Atoms at adjacent corners of this unit cell contact each other, so the edge length of this cell is equal to two atomic radii, or one atomic diameter. A cubic unit cell contains only the parts of these atoms that are within it. Since an atom at a corner of a simple cubic unit cell is contained by a total of eight unit cells, only one-eighth of that atom is within a specific unit cell. And since each simple cubic unit cell has one atom at each of its eight "corners," there is $8 \times \frac{1}{8} = 1$ atom within one simple cubic unit cell.

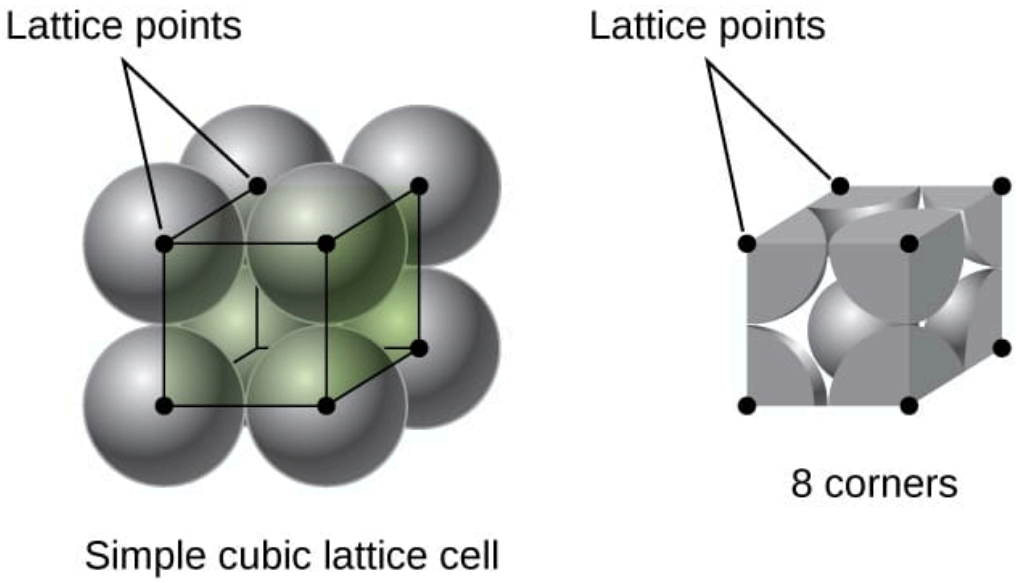


Figure 7.2.2.4: A simple cubic lattice unit cell contains one-eighth of an atom at each of its eight corners, so it contains one atom total.

A diagram of two images is shown. In the first image, eight spheres are stacked together to form a cube and dots at the center of each sphere are connected to form a cube shape. The dots are labeled “Lattice points” while a label under the image reads “Simple cubic lattice cell.” The second image shows the portion of each sphere that lie inside the cube. The corners of the cube are shown with small circles labeled “Lattice points” and the phrase “8 corners” is written below the image.

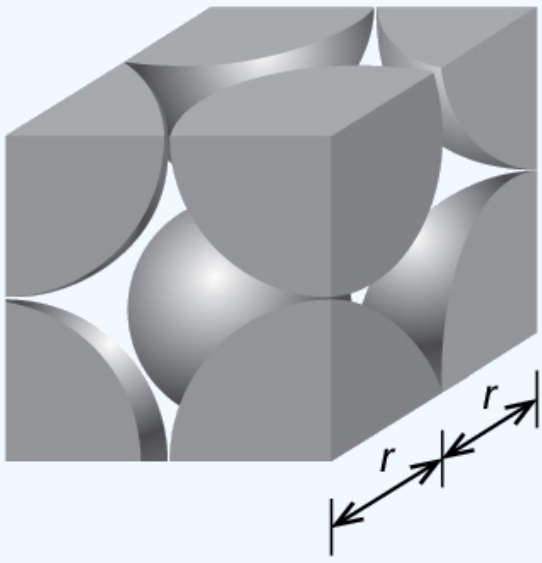
Example 7.2.2.1: Calculating Atomic Radius and Density for Metals (Part 1)

The edge length of the unit cell of alpha polonium is 336 pm.

a. Determine the radius of a polonium atom.
b. Determine the density of alpha polonium.

Solution

Alpha polonium crystallizes in a simple cubic unit cell:



(a) Two adjacent Po atoms contact each other, so the edge length of this cell is equal to two Po atomic radii: $l = 2r$. Therefore, the radius of Po is

$$r = \frac{l}{2} = \frac{336\ \text{pm}}{2} = 168\ \text{pm}$$

(b) Density is given by

$$\text{density} = \frac{\text{mass}}{\text{volume}}.$$

The density of polonium can be found by determining the density of its unit cell (the mass contained within a unit cell divided by the volume of the unit cell). Since a Po unit cell contains one-eighth of a Po atom at each of its eight corners, a unit cell contains one Po atom.

The mass of a Po unit cell can be found by:

$$1\ \text{Po unit cell} \times \frac{1\ \text{Po atom}}{1\ \text{Po unit cell}} \times \frac{1\ \text{mol Po}}{6.022 \times 10^{23}\ \text{Po atoms}} \times \frac{208.998\ \text{g}}{1\ \text{mol Po}} = 3.47 \times 10^{-22}\ \text{g}$$

The volume of a Po unit cell can be found by:

$$V = l^3 = (336 \times 10^{-10}\ \text{cm})^3 = 3.79 \times 10^{-23}\ \text{cm}^3$$

(Note that the edge length was converted from pm to cm to get the usual volume units for density.)

Therefore, the density of

$$\text{Po} = \frac{3.471 \times 10^{-22}\ \text{g}}{3.79 \times 10^{-23}\ \text{cm}^3} = 9.16\ \text{g/cm}^3$$

Exercise 7.2.2.1

The edge length of the unit cell for nickel is 0.3524 nm. The density of Ni is 8.90 g/cm^3. Does nickel crystallize in a simple cubic structure? Explain.

Answer available at the end of this section.

Most metal crystals are one of the four major types of unit cells. For now, we will focus on the three cubic unit cells: simple cubic (which we have already seen), body-centered cubic unit cell, and face-centered cubic unit cell—all of which are illustrated in Figure 7.2.2.5. (Note that there are actually seven different lattice systems, some of which have more than one type of lattice, for a total of 14 different types of unit cells. We leave the more complicated geometries for later in this module.)

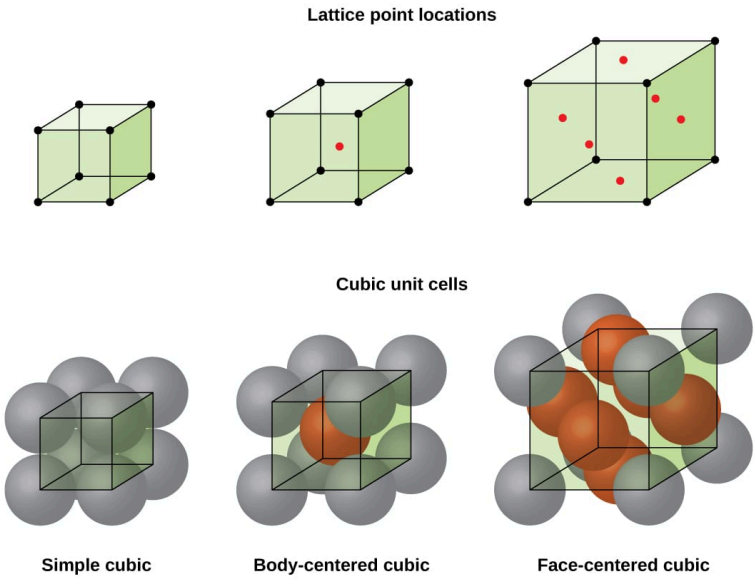


Figure 7.2.2.5: Cubic unit cells of metals show (in the upper figures) the locations of lattice points and (in the lower figures) metal atoms located in the unit cell.

Three pairs of images are shown. The first three images are in a row and are labeled “Lattice point locations” while the second three images are in a row labeled “Cubic unit cells.” The first image in the top row shows a cube with black dots at each corner while the first image in the second row is composed of eight spheres that are stacked together to form a cube and dots at the center of each sphere are connected to form a cube shape. The name under this image reads “Simple cubic.” The second image in the top row shows a cube with black dots at each corner and a red dot in the center while the second image in the second row is composed of eight spheres that are stacked together to form a cube with one sphere in the center of the cube and dots at the center of each corner sphere connected to form a cube shape. The name under this image reads “Body-centered cubic.” The third image in the top row shows a cube with black dots at each corner and red dots in the center of each face while the third image in the second row is composed of eight spheres that are stacked together to form a cube with six more spheres located in the center of each face of the cube. Dots at the center of each corner sphere are connected to form a cube shape. The name under this image reads “Face-centered cubic.”

Some metals crystallize in an arrangement that has a cubic unit cell with atoms at all of the corners and an atom in the center, as shown in Figure 7.2.2.6. This is called a body-centered cubic (BCC) solid. Atoms in the corners of a BCC unit cell do not contact each other but contact the atom in the center. A BCC unit cell contains two atoms: one-eighth of an atom at each of the eight corners ($8 \times \frac{1}{8} = 1$ atom from the corners) plus one atom from the center. Any atom in this structure touches four atoms in the layer above it and four atoms in the layer below it. Thus, an atom in a BCC structure has a coordination number of eight.

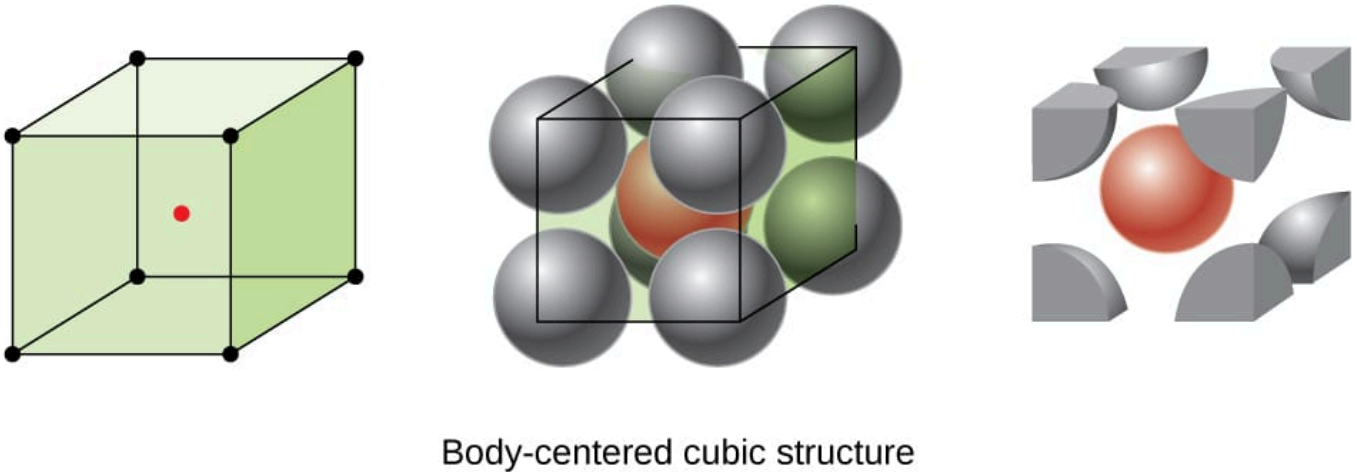


Figure 7.2.2.6: In a body-centered cubic structure, atoms in a specific layer do not touch each other. Each atom touches four atoms in the layer above it and four atoms in the layer below it.

Three images are shown. The first image shows a cube with black dots at each corner and a red dot in the center while the second image is composed of eight spheres that are stacked together to form a cube with one sphere in the center of the cube and dots at the center of each corner sphere connected to form a cube shape. The name under this image reads “Body-centered cubic structure.” The third image is the same as the second, but only shows the portions of the spheres that lie inside the cube shape.

Atoms in BCC arrangements are much more efficiently packed than in a simple cubic structure, occupying about 68% of the total volume. Isomorphous metals with a BCC structure include K, Ba, Cr, Mo, W, and Fe at room temperature. (Elements or compounds that crystallize with the same structure are said to be isomorphous.)

Many other metals, such as aluminum, copper, and lead, crystallize in an arrangement that has a cubic unit cell with atoms at all of the corners and at the centers of each face, as illustrated in Figure 7.2.2.7. This arrangement is called a face-centered cubic (FCC) solid. A FCC unit cell contains four atoms: one-eighth of an atom at each of the eight corners ($8 \times \frac{1}{8} = 1$ atom from the corners) and one-half of an atom on each of the six faces ($6 \times \frac{1}{2} = 3$ atoms from the faces). The atoms at the corners touch the atoms in the centers of the adjacent faces along the face diagonals of the cube. Because the atoms are on identical lattice points, they have identical environments.

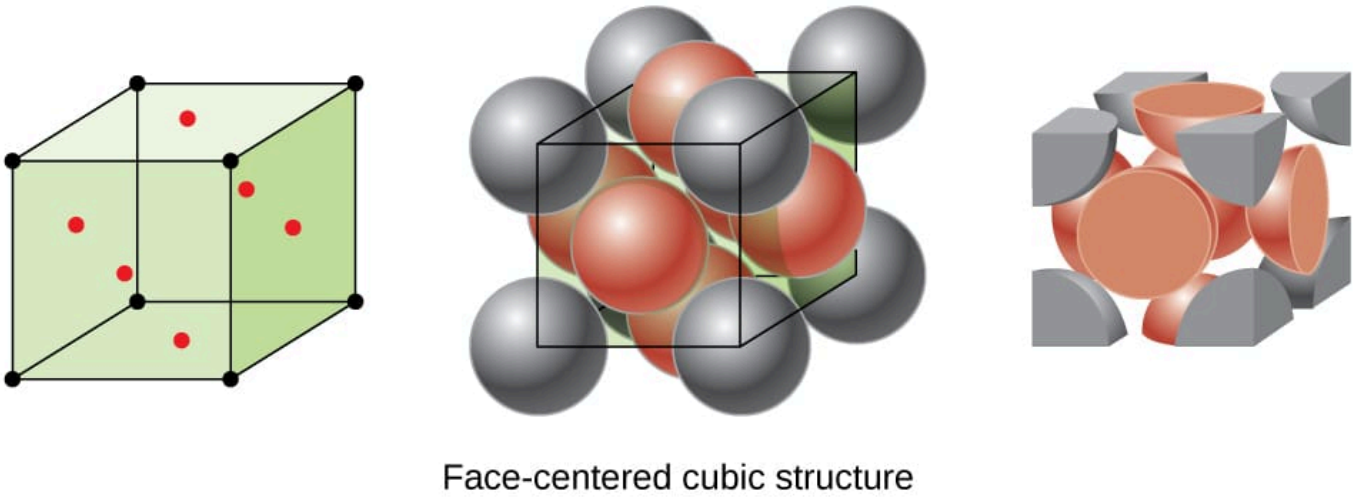


Figure 7.2.2.7:A face-centered cubic solid has atoms at the corners and, as the name implies, at the centers of the faces of its unit cells.

Three images are shown. The first image shows a cube with black dots at each corner and red dots in the center of each face of the cube while the second image is composed of eight spheres that are stacked together to form a cube with six more spheres, one located on each face of the structure. Dots at the center of each corner sphere are connected to form a cube shape. The name under this image reads “Face-centered cubic structure.” The third image is the same as the second, but only shows the portions of the spheres that lie inside the cube shape.

Atoms in an FCC arrangement are packed as closely together as possible, with atoms occupying 74% of the volume. This structure

is also called cubic closest packing (CCP). In CCP, there are three repeating layers of hexagonally arranged atoms. Each atom contacts six atoms in its own layer, three in the layer above, and three in the layer below. In this arrangement, each atom touches 12 near neighbors, and therefore has a coordination number of 12. The fact that FCC and CCP arrangements are equivalent may not be immediately obvious, but why they are actually the same structure is illustrated in Figure 7.2.2.8.

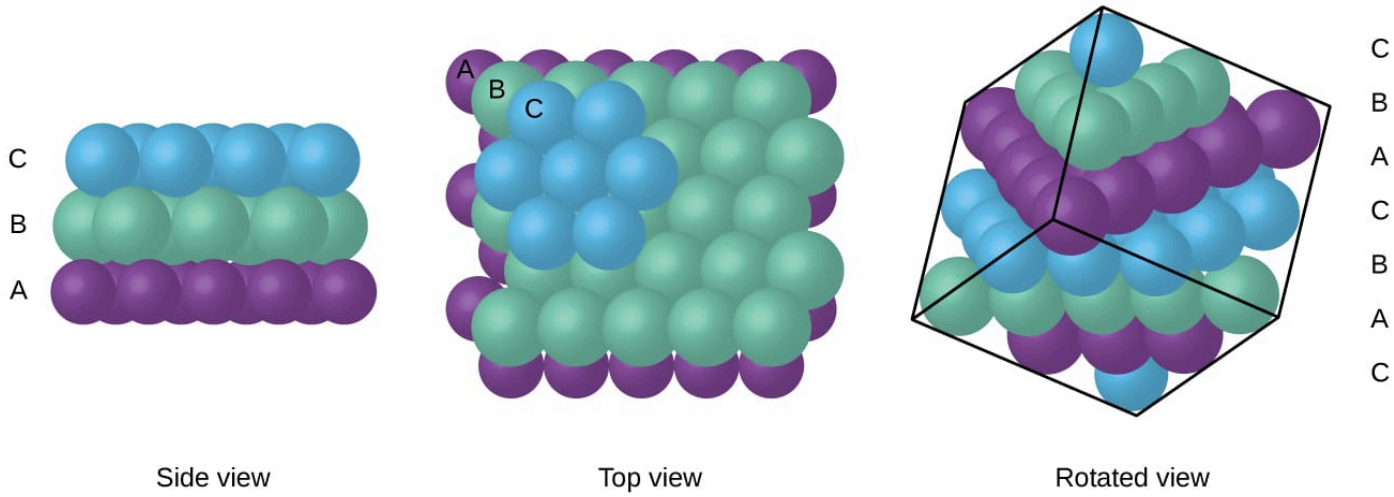


Figure 7.2.2.8: A CCP arrangement consists of three repeating layers (ABCABC...) of hexagonally arranged atoms. Atoms in a CCP structure have a coordination number of 12 because they contact six atoms in their layer, plus three atoms in the layer above and three atoms in the layer below. By rotating our perspective, we can see that a CCP structure has a unit cell with a face containing an atom from layer A at one corner, atoms from layer B across a diagonal (at two corners and in the middle of the face), and an atom from layer C at the remaining corner. This is the same as a face-centered cubic arrangement.

Three images are shown. In the first image, a side view shows a layer of blue spheres, labeled “C” stacked on top of, and sitting in between the gaps in a second layer that is composed of green spheres, labeled “B,” which are sitting atop a purple layer of spheres labeled “A.” A label below this image reads “Side view.” The second image shows a top view of the same layers of spheres, where the top layer is “C,” the second layer is “B” and the lowest layer is “C.” This image is labeled “Top view” and written under this is the phrase “Cubic closest packed structure.” The third image shows an upper view of the side of a cube composed of two sets of the repeating layers shown in the other images. The layers are arranged “C, B, A, C, B, A, C” and the phrase written under this image reads “Rotated view.”

Because closer packing maximizes the overall attractions between atoms and minimizes the total intermolecular energy, the atoms in most metals pack in this manner. We find two types of closest packing in simple metallic crystalline structures: CCP, which we have already encountered, and hexagonal closest packing (HCP) shown in Figure 7.2.2.9. Both consist of repeating layers of hexagonally arranged atoms. In both types, a second layer (B) is placed on the first layer (A) so that each atom in the second layer is in contact with three atoms in the first layer. The third layer is positioned in one of two ways. In HCP, atoms in the third layer are directly above atoms in the first layer (i.e., the third layer is also type A), and the stacking consists of alternating type A and type B close-packed layers (i.e., ABABAB⋯). In CCP, atoms in the third layer are not above atoms in either of the first two layers (i.e., the third layer is type C), and the stacking consists of alternating type A, type B, and type C close-packed layers (i.e., ABCABCABC⋯). About two–thirds of all metals crystallize in closest-packed arrays with coordination numbers of 12. Metals that crystallize in an HCP structure include Cd, Co, Li, Mg, Na, and Zn, and metals that crystallize in a CCP structure include Ag, Al, Ca, Cu, Ni, Pb, and Pt.

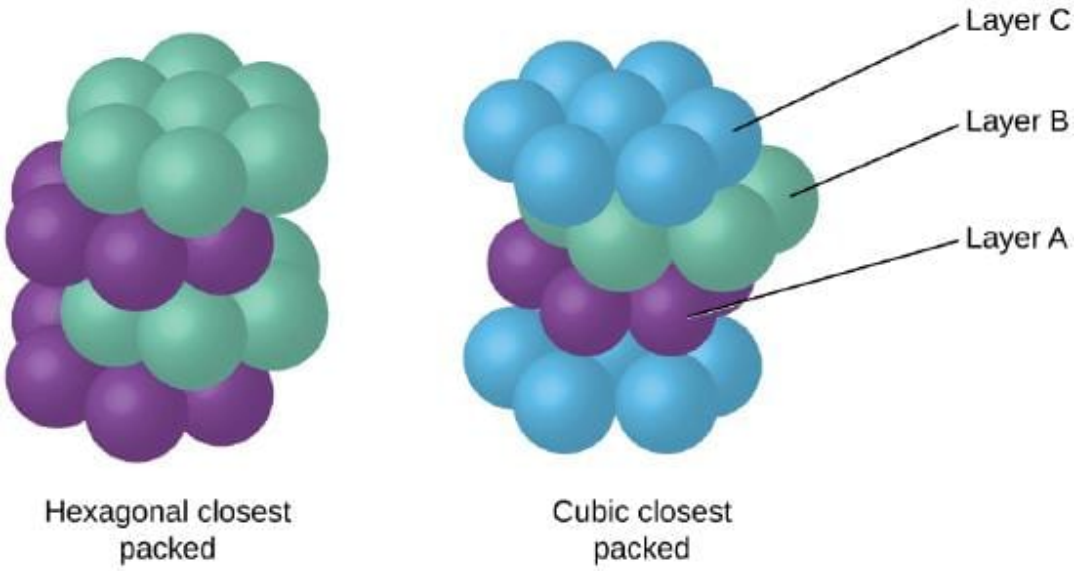


Figure 7.2.2.9: In both types of closest packing, atoms are packed as compactly as possible. Hexagonal closest packing consists of two alternating layers (ABABAB...). Cubic closest packing consists of three alternating layers (ABCABCABC...).

Two images are shown. The first image, labeled “Hexagonal closest packed,” shows seven green spheres arranged in a circular sheet lying atop another sheet that is the same except the spheres are purple. The second sheet is offset just a bit so that the spheres of the top sheet lie in the grooves of the second sheet. Two more alternating green and purple layers of spheres lie below the first pair. The second image shows seven blue spheres, labeled “Layer C,” arranged in a circular sheet laying atop another sheet, labeled “Layer B” that is the same except the spheres are green. The second sheet is offset just a bit so that the spheres of the top sheet lie in the grooves of the second sheet. Two more alternating purple and then blue layers of spheres lie below the first pair. The purple layer is labeled “Layer A” and the phrase written below this image reads “Cubic closest packed.”

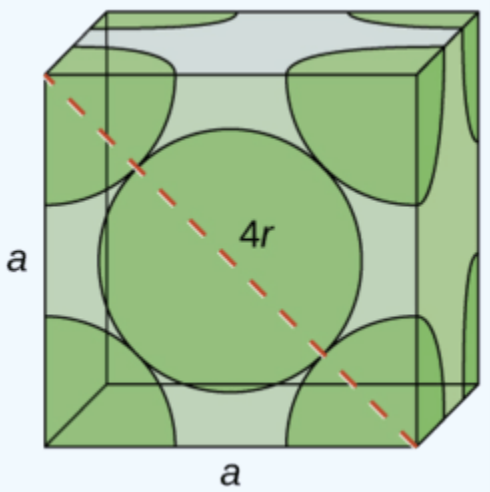
Example 7.2.2.2: Calculating Atomic Radius and Density for Metals (Part 2)

Calcium crystallizes in a face-centered cubic structure. The edge length of its unit cell is 558.8 pm.

a. What is the atomic radius of Ca in this structure?
b. Calculate the density of Ca.

Solution

(a) In an FCC structure, Ca atoms contact each other across the diagonal of the face, so the length of the diagonal is equal to four Ca atomic radii (d = 4*r*).



Two adjacent edges and the diagonal of the face form a right triangle, with the length of each side equal to 558.8 pm and the length of the hypotenuse equal to four Ca atomic radii:

$$a^2 + a^2 = d^2$$
$$(558.8\text{ pm})^2 + (558.5\text{ pm})^2 = (4r)^2$$

Solving this gives

$$r = \sqrt{\frac{(558.8\text{ pm})^2 + (558.5\text{ pm})^2}{16}} = 197.6\text{ pmg for a Ca radius.}$$

(b) Density is given by $\text{density} = \frac{\text{mass}}{\text{volume}}$. The density of calcium can be found by determining the density of its unit cell: for example, the mass contained within a unit cell divided by the volume of the unit cell. A face-centered Ca unit cell has one-eighth of an atom at each of the eight corners ($8 \times \frac{1}{8} = 1$atom) and one-half of an atom on each of the six faces $6 \times \frac{1}{2} = 3$ atoms), for a total of four atoms in the unit cell.

The mass of the unit cell can be found by:

$$1\text{ Ca unit cell} \times \frac{4\text{ Ca atoms}}{1\text{ Ca unit cell}} \times \frac{1\text{ mol Ca}}{6.022 \times 10^{23}\text{ Ca atoms}} \times \frac{40.078\text{ g}}{1\text{ mol Ca}} = 2.662 \times 10^{-22}\text{ g}$$

The volume of a Ca unit cell can be found by:

$$V = a^3 = (558.8 \times 10^{-10}\text{ cm})^3 = 1.745 \times 10^{-22}\text{ cm}^3$$

(Note that the edge length was converted from pm to cm to get the usual volume units for density.)

Then, the density of polonium:

$$\text{Po} = \frac{2.662 \times 10^{-22}\text{ g}}{1.745 \times 10^{-22}\text{ cm}^3} = 1.53\text{ g/cm}^3$$

Exercise 7.2.2.2

Silver crystallizes in an FCC structure. The edge length of its unit cell is 409 pm.

a. What is the atomic radius of Ag in this structure?
b. Calculate the density of Ag.

Answer a available at the end of this section.

In general, a unit cell is defined by the lengths of three axes (*a*, *b*, and *c*) and the angles (*α*, *β*, and *γ*) between them, as illustrated in Figure 7.2.2.10. The axes are defined as being the lengths between points in the space lattice. Consequently, unit cell axes join points with identical environments.

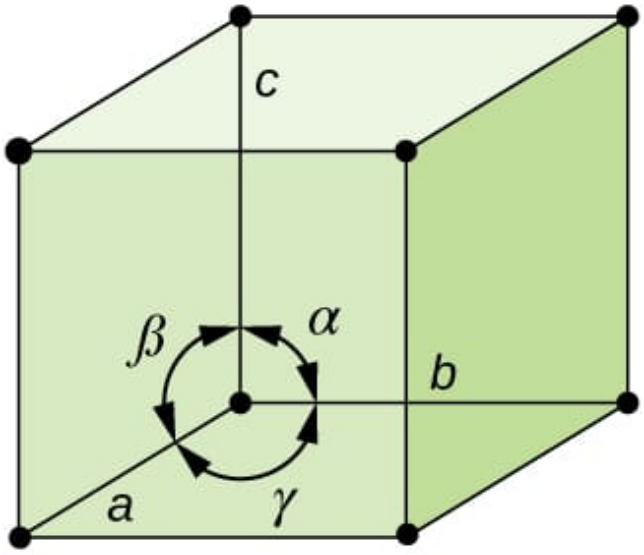


Figure 7.2.2.10: A unit cell is defined by the lengths of its three axes (a, b, and c) and the angles (α, β, and γ) between the axes.

A cube is shown where each corner has a black dot drawn on it. A circle in the bottom of the cube is composed of three double-ended arrows. The left top of this circle is labeled “alpha,” the top right is labeled “beta” and the bottom is labeled “gamma.” The bottom left corner of the cube is labeled “a” while the bottom of the back face is labeled “b” and the top, back, left corner is labeled “c.”

There are seven different lattice systems, some of which have more than one type of lattice, for a total of fourteen different unit cells, which have the shapes shown in Figure 7.2.2.11.

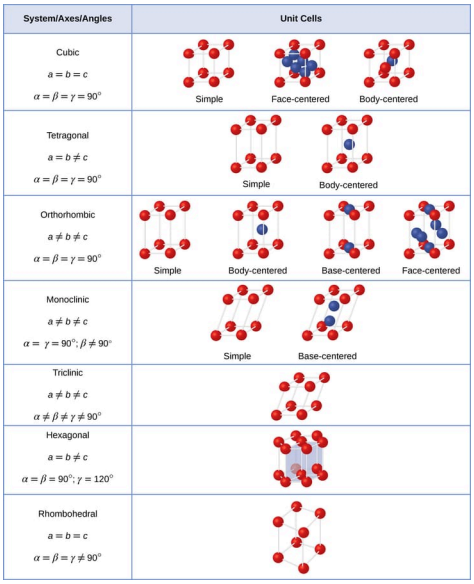


Figure 7.2.2.11:There are seven different lattice systems and 14 different unit cells.

A table is composed of two columns and eight rows. The header row reads “System / Axes / Angles” and “Unit Cells .” The first column reads “Cubic, a equals b equals c, alpha equals beta equals gamma equals 90 degrees,” “Tetragonal, a equals b does not equal c, alpha equals beta equals gamma equals 90 degrees,” “Orthorhombic, a does not equal b does not equal c, alpha equals beta equals gamma equals 90 degrees,” “Monoclinic, a does not equal b does not equal c, alpha equals gamma equals 90 degrees, beta does not equal 90 degrees,” “Triclinic, a does not equal b does not equal c, alpha does not equal beta does not equal gamma does not equal 90 degrees,” “Hexagonal, a equals b does not equal c, alpha equals beta equals 90 degrees, gamma equals 120 degrees,” “Rhombohedral, a equals b equals c, alpha equals beta equals gamma does not equal 90 degrees.” The second column is composed of diagrams. The first set of diagrams in the first cell show a cube with spheres at each corner labeled “Simple,” a cube with spheres in each corner and on each face labeled “Face-centered” and a cube with spheres in each corner and one in the center labeled “Body-centered.” The second set of diagrams in the second cell show a vertical rectangle with spheres at each corner labeled “Simple” and a vertical rectangle with spheres in each corner and one in the center labeled “Body-centered.” The third set of diagrams in the third cell show a vertical rectangle with spheres at each corner labeled “Simple,” a vertical rectangle with spheres in each corner and one in the center labeled “Body-centered,” a vertical rectangle with spheres in each corner and one on the top and bottom faces labeled “Base-centered,” and a vertical rectangle with spheres in each corner and one on each face labeled “Face-centered.” The fourth set of diagrams in the fourth cell show a vertical rectangle with spheres at each corner that is slanted to one side labeled “Simple” and a vertical rectangle with spheres in each corner that is slanted to one side and has two spheres in the center is labeled “Body-centered.” The fifth diagrams in the fifth cell show a cube that is slanted with spheres at each corner while the sixth diagram in the sixth cell shows a pair of hexagonal rings that are connected together to form a six-sided shape with spheres at each corner. The seventh diagram in the seventh cell shows a rectangle that is slanted with spheres at each corner.

The Structures of Ionic Crystals

Ionic crystals consist of two or more different kinds of ions that usually have different sizes. The packing of these ions into a crystal structure is more complex than the packing of metal atoms that are the same size. Most monatomic ions behave as charged spheres, and their attraction for ions of opposite charge is the same in every direction. Consequently, stable structures for ionic compounds result (1) when ions of one charge are surrounded by as many ions as possible of the opposite charge and (2) when the cations and anions are in contact with each other. Structures are determined by two principal factors: the relative sizes of the ions and the ratio of the numbers of positive and negative ions in the compound.

In simple ionic structures, we usually find the anions, which are normally larger than the cations, arranged in a closest-packed array. (As seen previously, additional electrons attracted to the same nucleus make anions larger and fewer electrons attracted to the same nucleus make cations smaller when compared to the atoms from which they are formed.) The smaller cations commonly occupy one of two types of holes (or interstices) remaining between the anions. The smaller of the holes is found between three anions in one plane and one anion in an adjacent plane. The four anions surrounding this hole are arranged at the corners of a tetrahedron, so the hole is called a tetrahedral hole. The larger type of hole is found at the center of six anions (three in one layer and three in an adjacent layer) located at the corners of an octahedron; this is called an octahedral hole. Figure 7.2.2.12 illustrates both of these types of holes.

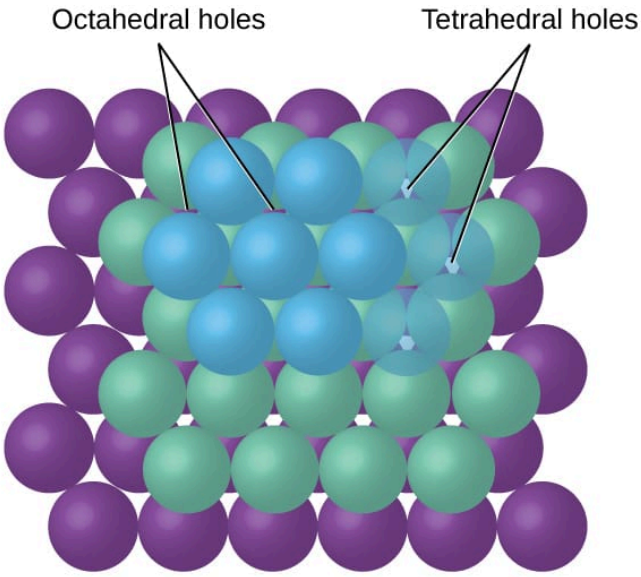


Figure 7.2.2.12: Cations may occupy two types of holes between anions: octahedral holes or tetrahedral holes.

An image shows a top-view of a layer of blue spheres arranged in a sheet lying atop another sheet that is the same except the spheres are green. The second sheet is offset just a bit so that the spheres of the top sheet lie in the grooves of the second sheet. A third sheet composed of purple spheres lies at the bottom. The spaces created between the spheres in each layer are labeled “Octahedral holes” and “Tetrahedral holes.”

Depending on the relative sizes of the cations and anions, the cations of an ionic compound may occupy tetrahedral or octahedral holes, as illustrated in Figure 7.2.2.13. Relatively small cations occupy tetrahedral holes, and larger cations occupy octahedral holes. If the cations are too large to fit into the octahedral holes, the anions may adopt a more open structure, such as a simple cubic array. The larger cations can then occupy the larger cubic holes made possible by the more open spacing.

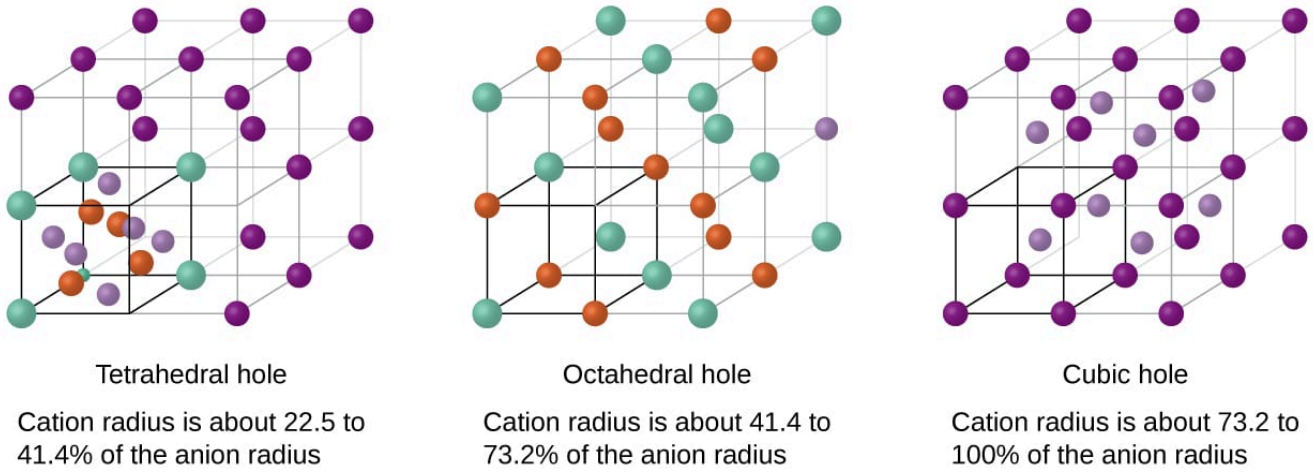


Figure 7.2.2.13:A cation’s size and the shape of the hole occupied by the compound are directly related.

A diagram of three images is shown. In the first image, eight stacked cubes, with purple spheres at each corner, that make up one large cube are shown. The bottom left cube is different. It has green spheres at each corner and has four orange and six light purple spheres located on the faces of the cube. Labels below this structure read “Tetrahedral hole” and “Cation radius is about 22.5 to 41.4 percent of the anion radius. In the second image, eight stacked cubes, with alternating orange and green spheres at each corner, make up one large cube that is shown. The bottom left cube has darker lines that connect the spheres together. Labels below this structure read “Octahedral hole” and “Cation radius is about 41.4 to 73.2 percent of the anion radius. In the third image, eight stacked cubes, with purple spheres at each corner and light purple spheres on their interior faces, make up one large cube that is shown. Labels below this structure read “Cubic hole” and “Cation radius is about 73.2 to 100 percent of the anion radius.”

There are two tetrahedral holes for each anion in either an HCP or CCP array of anions. A compound that crystallizes in a closest-packed array of anions with cations in the tetrahedral holes can have a maximum cation:anion ratio of 2:1; all of the tetrahedral holes are filled at this ratio. Examples include Li_2O, Na_2O, Li_2S, and Na_2S. Compounds with a ratio of less than 2:1 may also crystallize in a closest-packed array of anions with cations in the tetrahedral holes, if the ionic sizes fit. In these compounds,

however, some of the tetrahedral holes remain vacant.

Example 7.2.2.3: Occupancy of Tetrahedral Holes

Zinc sulfide is an important industrial source of zinc and is also used as a white pigment in paint. Zinc sulfide crystallizes with zinc ions occupying one-half of the tetrahedral holes in a closest-packed array of sulfide ions. What is the formula of zinc sulfide?

Solution

Because there are two tetrahedral holes per anion (sulfide ion) and one-half of these holes are occupied by zinc ions, there must be $\frac{1}{2} \times 2$, or 1, zinc ion per sulfide ion. Thus, the formula is ZnS.

Exercise 7.2.2.3: Lithium selenide

Lithium selenide can be described as a closest-packed array of selenide ions with lithium ions in all of the tetrahedral holes. What it the formula of lithium selenide?

Answer available at the end of this section.

The ratio of octahedral holes to anions in either an HCP or CCP structure is 1:1. Thus, compounds with cations in octahedral holes in a closest-packed array of anions can have a maximum cation:anion ratio of 1:1. In NiO, MnS, NaCl, and KH, for example, all of the octahedral holes are filled. Ratios of less than 1:1 are observed when some of the octahedral holes remain empty.

Example 7.2.2.4: Stoichiometry of Ionic Compounds Sapphire

Aluminum oxide crystallizes with aluminum ions in two-thirds of the octahedral holes in a closest-packed array of oxide ions. What is the formula of aluminum oxide?

Solution

Because there is one octahedral hole per anion (oxide ion) and only two-thirds of these holes are occupied, the ratio of aluminum to oxygen must be $\frac{2}{3}$:1, which would give $\mathrm{Al}_{2/3}\mathrm{O}$. The simplest whole number ratio is 2:3, so the formula is Al_2O_3.

Exercise 7.2.2.4

The white pigment titanium oxide crystallizes with titanium ions in one-half of the octahedral holes in a closest-packed array of oxide ions. What is the formula of titanium oxide?

Answer available at the end of this section.

In a simple cubic array of anions, there is one cubic hole that can be occupied by a cation for each anion in the array. In CsCl, and in other compounds with the same structure, all of the cubic holes are occupied. Half of the cubic holes are occupied in SrH_2, UO_2, $SrCl_2$, and CaF_2.

Different types of ionic compounds often crystallize in the same structure when the relative sizes of their ions and their stoichiometries (the two principal features that determine structure) are similar.

Unit Cells of Ionic Compounds

Many ionic compounds crystallize with cubic unit cells, and we will use these compounds to describe the general features of ionic

structures. When an ionic compound is composed of cations and anions of similar size in a 1:1 ratio, it typically forms a simple cubic structure. Cesium chloride, CsCl, (Figure 7.2.2.14) is an example of this, with Cs^+ and Cl^- having radii of 174 pm and 181 pm, respectively. We can think of this as chloride ions forming a simple cubic unit cell, with a cesium ion in the center; or as cesium ions forming a unit cell with a chloride ion in the center; or as simple cubic unit cells formed by Cs^+ ions overlapping unit cells formed by Cl^- ions. Cesium ions and chloride ions touch along the body diagonals of the unit cells. One cesium ion and one chloride ion are present per unit cell, giving the l:l stoichiometry required by the formula for cesium chloride. Note that there is no lattice point in the center of the cell, and CsCl is not a BCC structure because a cesium ion is not identical to a chloride ion.

Figure 7.2.2.14: Ionic compounds with similar-sized cations and anions, such as CsCl, usually form a simple cubic structure. They can be described by unit cells with either cations at the corners or anions at the corners.

Three images are shown. The first image shows a cube with black dots at each corner and a red dot in the center. This cube is stacked with seven others that are not colored to form a larger cube. The second image is composed of eight spheres that are grouped together to form a cube with one smaller sphere in the center. The name under this image reads “Body-centered simple cubic structure.” The third image shows five horizontal layers of purple spheres with layers of smaller green spheres in between.

We have said that the location of lattice points is arbitrary. This is illustrated by an alternate description of the CsCl structure in which the lattice points are located in the centers of the cesium ions. In this description, the cesium ions are located on the lattice points at the corners of the cell, and the chloride ion is located at the center of the cell. The two unit cells are different, but they describe identical structures.

When an ionic compound is composed of a 1:1 ratio of cations and anions that differ significantly in size, it typically crystallizes with an FCC unit cell, like that shown in Figure 7.2.2.15. Sodium chloride, NaCl, is an example of this, with Na^+ and Cl^- having radii of 102 pm and 181 pm, respectively. We can think of this as chloride ions forming an FCC cell, with sodium ions located in the octahedral holes in the middle of the cell edges and in the center of the cell. The sodium and chloride ions touch each other along the cell edges. The unit cell contains four sodium ions and four chloride ions, giving the 1:1 stoichiometry required by the formula, NaCl.

Figure 7.2.2.15: Ionic compounds with anions that are much larger than cations, such as NaCl, usually form an FCC structure. They can be described by FCC unit cells with cations in the octahedral holes.

Three images are shown. The first image shows a cube with black dots at each corner and a red dot in the center. This cube is stacked with seven others that are not colored to form a larger cube. The second image is composed of eight spheres that are grouped together to form a cube with one much larger sphere in the center. The name under this image reads “Body-centered simple cubic structure.” The third image shows seven horizontal layers of alternating purple and green spheres that are slightly offset with one another and form a large cube.

The cubic form of zinc sulfide, zinc blende, also crystallizes in an FCC unit cell, as illustrated in Figure 7.2.2.16. This structure contains sulfide ions on the lattice points of an FCC lattice. (The arrangement of sulfide ions is identical to the arrangement of chloride ions in sodium chloride.) The radius of a zinc ion is only about 40% of the radius of a sulfide ion, so these small Zn^{2+} ions are located in alternating tetrahedral holes, that is, in one half of the tetrahedral holes. There are four zinc ions and four sulfide ions in the unit cell, giving the empirical formula ZnS.

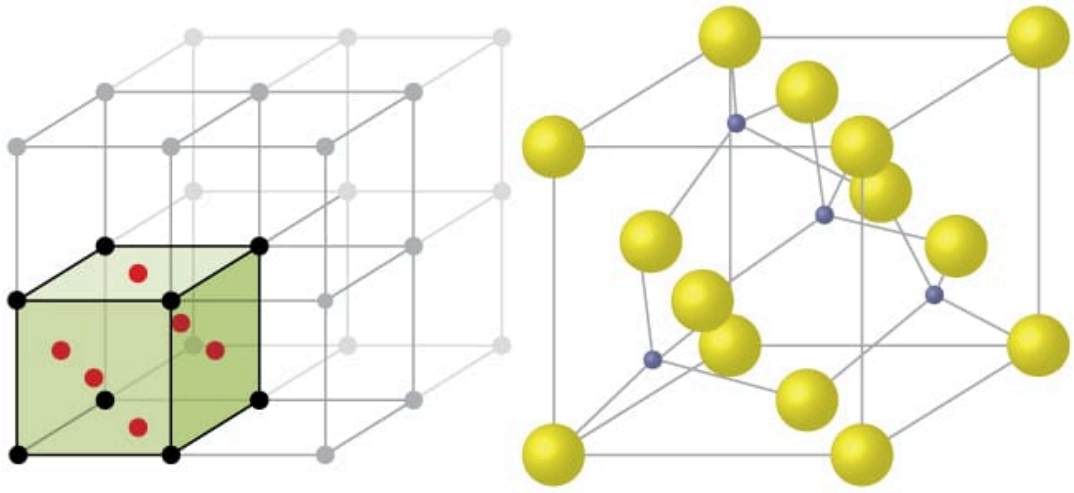


Figure 7.2.2.16: ZnS, zinc sulfide (or zinc blende) forms an FCC unit cell with sulfide ions at the lattice points and much smaller zinc ions occupying half of the tetrahedral holes in the structure.

Two images are shown. The first image shows a cube with black dots at each corner and a red dot in the center of each face of the cube. This cube is stacked with seven others that are not colored to form a larger cube. The second image is composed of eight spheres that form the corners of a cube with six other spheres located in the face of the cube. The spheres are connected to one another by lines. The name under this image reads “Z n S, face-centered unit cell.”

A calcium fluoride unit cell, like that shown in Figure 7.2.2.17, is also an FCC unit cell, but in this case, the cations are located on the lattice points; equivalent calcium ions are located on the lattice points of an FCC lattice. All of the tetrahedral sites in the FCC array of calcium ions are occupied by fluoride ions. There are four calcium ions and eight fluoride ions in a unit cell, giving a calcium:fluorine ratio of 1:2, as required by the chemical formula, CaF_2. Close examination of Figure 7.2.2.17 will reveal a simple cubic array of fluoride ions with calcium ions in one half of the cubic holes. The structure cannot be described in terms of a space lattice of points on the fluoride ions because the fluoride ions do not all have identical environments. The orientation of the four calcium ions about the fluoride ions differs.

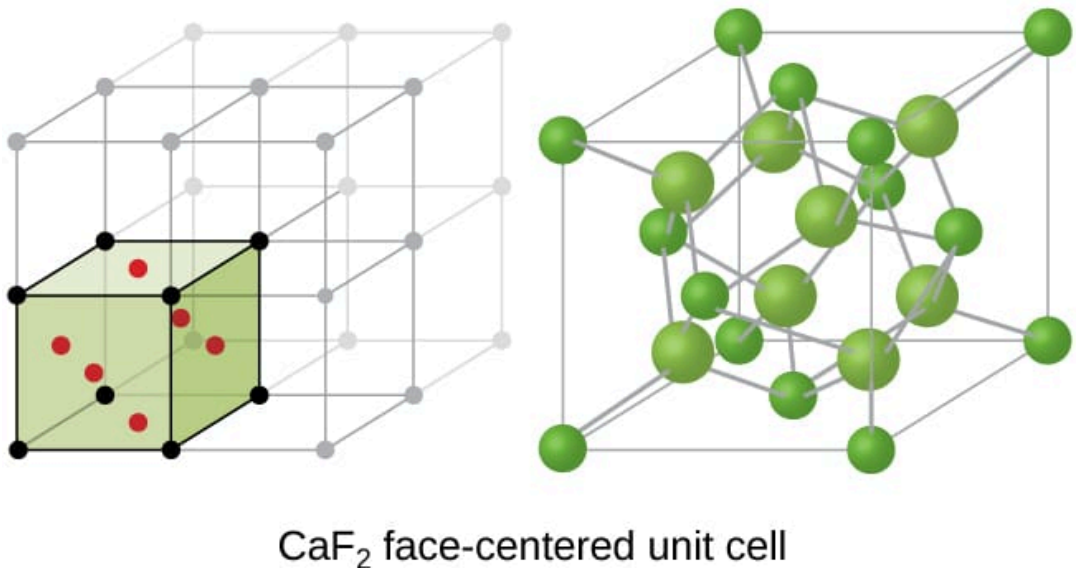


Figure 7.2.2.17: Calcium fluoride, CaF_2, forms an FCC unit cell with calcium ions (green) at the lattice points and fluoride ions (red) occupying all of the tetrahedral sites between them.

Two images are shown. The first image shows a cube with black dots at each corner and a red dot in the center of each face of the cube. This cube is stacked with seven others that are not colored to form a larger cube. The second image is composed of eight small green spheres that form the corners of a cube with six other small green spheres located in the faces of the cube. Eight larger green spheres are spaced inside the cube and all of the spheres are connect to one another by lines. The name under this image reads “C a F, subscript 2, face-centered unit cell.”

Calculation of Ionic Radii

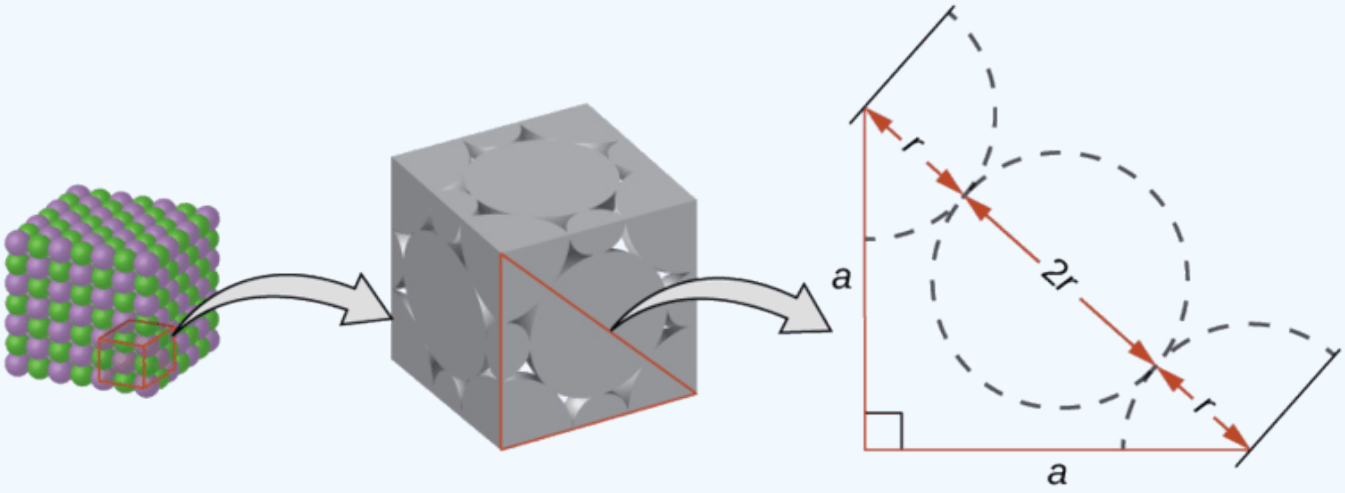
If we know the edge length of a unit cell of an ionic compound and the position of the ions in the cell, we can calculate ionic radii for the ions in the compound if we make assumptions about individual ionic shapes and contacts.

Example 7.2.2.5: Calculation of Ionic Radii

The edge length of the unit cell of LiCl (NaCl-like structure, FCC) is 0.514 nm or 5.14 Å. Assuming that the lithium ion is small enough so that the chloride ions are in contact, calculate the ionic radius for the chloride ion. Note: The length unit angstrom, Å, is often used to represent atomic-scale dimensions and is equivalent to 10^{-10} m.

Solution

On the face of a LiCl unit cell, chloride ions contact each other across the diagonal of the face:



Drawing a right triangle on the face of the unit cell, we see that the length of the diagonal is equal to four chloride radii (one radius from each corner chloride and one diameter—which equals two radii—from the chloride ion in the center of the face), so $d = 4r$. From the Pythagorean theorem, we have:

$$a^2 + a^2 = d^2$$

which yields:

$$(0.514\ \text{nm})^2 + (0.514\ \text{nm})^2 = (4r)^2 = 16r^2$$

Solving this gives:

$$r = \sqrt{\frac{(0.514\ \text{nm})^2 + (0.514\ \text{nm})^2}{16}} = 0.182\ \text{nm}\ (1.82\ \text{Å})\ \text{for a}\ \text{Cl}^-\ \text{radius.}$$

Exercise 7.2.2.6

The edge length of the unit cell of KCl (NaCl-like structure, FCC) is 6.28 Å. Assuming anion-cation contact along the cell edge, calculate the radius of the potassium ion. The radius of the chloride ion is 1.82 Å.

Answer available at the end of this section.

It is important to realize that values for ionic radii calculated from the edge lengths of unit cells depend on numerous assumptions, such as a perfect spherical shape for ions, which are approximations at best. Hence, such calculated values are themselves approximate and comparisons cannot be pushed too far. Nevertheless, this method has proved useful for calculating ionic radii from experimental measurements such as X-ray crystallographic determinations.

X-Ray Crystallography

The size of the unit cell and the arrangement of atoms in a crystal may be determined from measurements of the *diffraction* of X-rays by the crystal, termed X-ray crystallography. Diffraction is the change in the direction of travel experienced by an electromagnetic wave when it encounters a physical barrier whose dimensions are comparable to those of the wavelength of the light. X-rays are electromagnetic radiation with wavelengths about as long as the distance between neighboring atoms in crystals (on the order of a few Å).

When a beam of monochromatic X-rays strikes a crystal, its rays are scattered in all directions by the atoms within the crystal. When scattered waves traveling in the same direction encounter one another, they undergo *interference*, a process by which the waves combine to yield either an increase or a decrease in amplitude (intensity) depending upon the extent to which the

combining waves' maxima are separated (Figure 7.2.2.18).

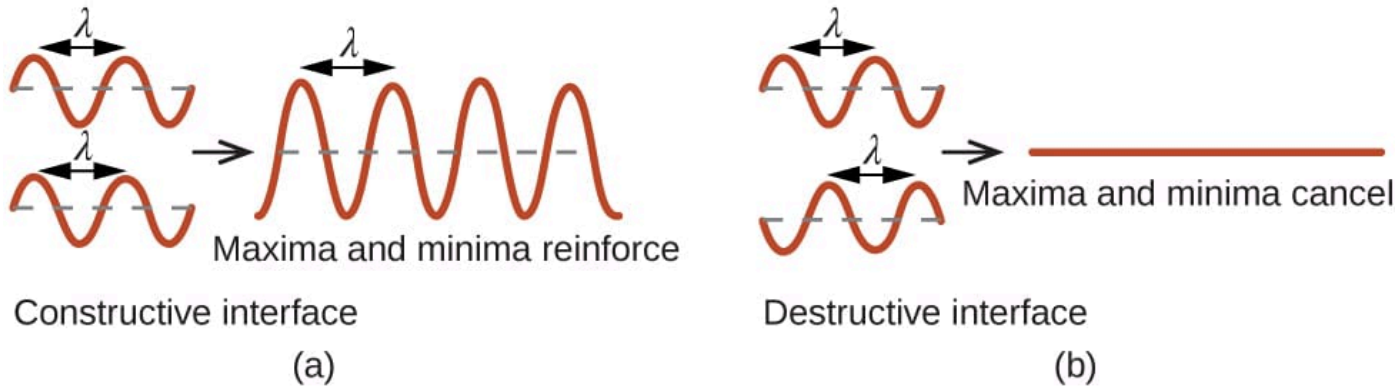


Figure 7.2.2.18: Light waves occupying the same space experience interference, combining to yield waves of greater (a) or lesser (b) intensity, depending upon the separation of their maxima and minima.

A pair of images is shown that has four sections. In the first section, two sinusoidal waves are shown, one drawn above the other, and a section from the top of one curve to the top of the next curve is labeled "lambda." The curves align with one another. The phrase below this reads "Constructive interference." A right facing arrow leads from the first section to the second, which shows one larger sinusoidal curve that has higher and lower peaks and troughs. A section from the top of one curve to the top of the next curve is labeled "lambda" and the phrase below this reads "Maxima and minima reinforce." In the second section, two sinusoidal waves are shown, one drawn above the other, and a section from the top of one curve to the top of the next curve is labeled "lambda." The curves do not align with one another. The phrase below this reads "Destructive interference." A right facing arrow leads from the first section to the second, which shows one flat line. The phrase below this reads "Maxima and minima cancel."

When X-rays of a certain wavelength, λ, are scattered by atoms in adjacent crystal planes separated by a distance, d, they may undergo constructive interference when the difference between the distances traveled by the two waves prior to their combination is an integer factor, n, of the wavelength. This condition is satisfied when the angle of the diffracted beam, θ, is related to the wavelength and interatomic distance by the equation:

$$n\lambda = 2d\sin\theta \tag{7.2.2.1}$$

This relation is known as the Bragg equation in honor of W. H. Bragg, the English physicist who first explained this phenomenon. Figure 7.2.2.18 illustrates two examples of diffracted waves from the same two crystal planes. The figure on the left depicts waves diffracted at the Bragg angle, resulting in constructive interference, while that on the right shows diffraction and a different angle that does not satisfy the Bragg condition, resulting in destructive interference.

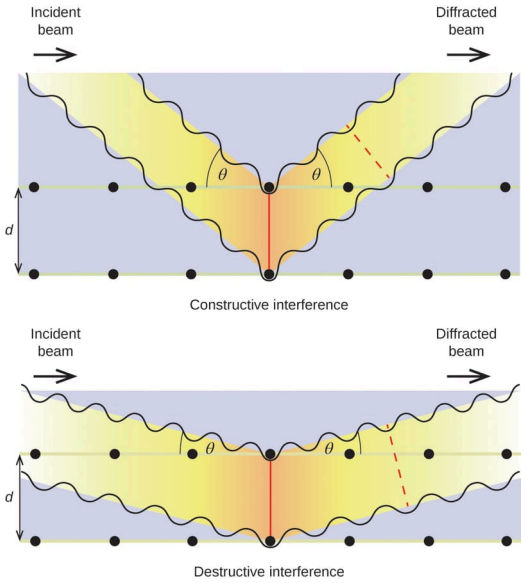


Figure 7.2.2.19: The diffraction of X-rays scattered by the atoms within a crystal permits the determination of the distance between the atoms. The top image depicts constructive interference between two scattered waves and a resultant diffracted wave of high intensity. The bottom image depicts destructive interference and a low intensity diffracted wave.

Two similar figures are shown. The first figure, labeled “Constructive Interference,” shows two horizontal rows of seven black dots with a line passing through them. The fourth dots of each row have a vertical line connecting them. The distance between these rows is labeled “d.” A beam labeled “Incident beam” descends at an angle labeled “theta” until it hits the line connecting the fourth dots, after which a diffracted beam ascends at the same angle “theta.” A dotted line is drawn across the diffracted beam. The second figure, labeled “Destructive interference,” is very similar, except that the angles “theta” are far more acute, making the slopes of the beams more shallow.

An X-ray diffractometer, such as the one illustrated in Figure 7.2.2.20, may be used to measure the angles at which X-rays are diffracted when interacting with a crystal as described earlier. From such measurements, the Bragg equation may be used to compute distances between atoms as demonstrated in the following example exercise.

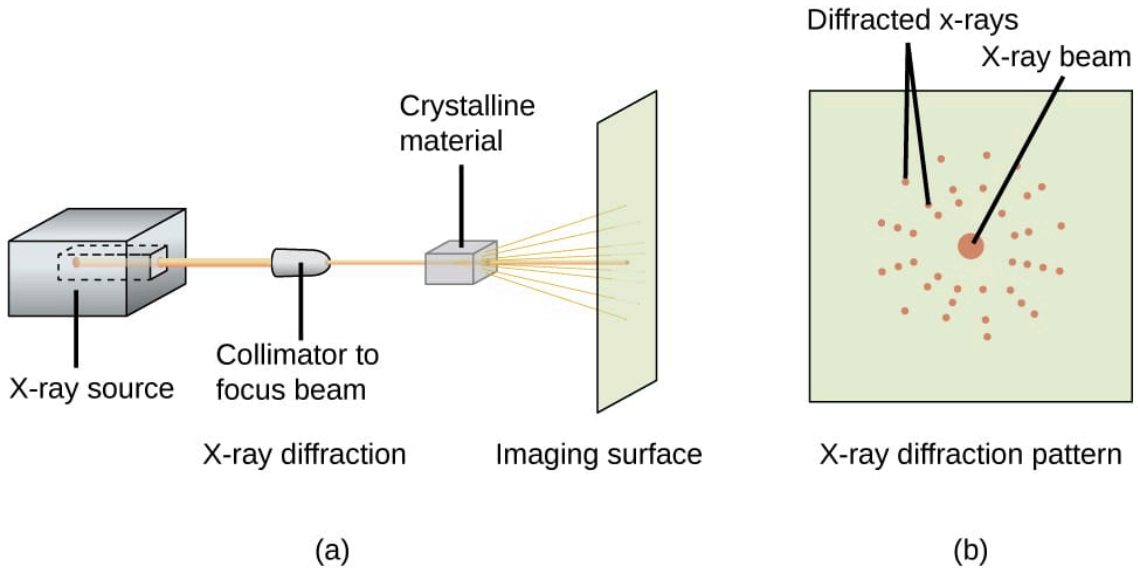


Figure 7.2.2.20: (a) In a diffractometer, a beam of X-rays strikes a crystalline material, producing (b) an X-ray diffraction pattern that can be analyzed to determine the crystal structure.

A diagram, labeled “a” shows a cube on the left with a channel bored into its right side labeled “X dash ray source.” A beam is leaving from this channel and traveling in a horizontal line toward an oval-shaped, short tube, labeled “Collimator to focus beam” and “X dash ray diffraction,” where it passes through a cube labeled “Crystalline material” and scatters onto a vertical sheet labeled “Imaging surface.” A second diagram, labeled “b,” shows a square sheet with a large dot in the center labeled “X dash ray beam,” that is surrounded by smaller dots arranged in rings and labeled “Diffracted X dash rays.”

Example 7.2.2.6: Using the Bragg Equation

In a diffractometer, X-rays with a wavelength of 0.1315 nm were used to produce a diffraction pattern for copper. The first order diffraction (n = 1) occurred at an angle θ = 25.25°. Determine the spacing between the diffracting planes in copper.

Solution

The distance between the planes is found by solving the Bragg equation (Equation 7.2.2.1) for d.

This gives

$$d = \frac{n\lambda}{2\sin\theta} = \frac{1(0.1315\text{ nm})}{2\sin(25.25°)} = 0.154\text{ nm}$$

Exercise 7.2.2.6

A crystal with spacing between planes equal to 0.394 nm diffracts X-rays with a wavelength of 0.147 nm. What is the angle for the first order diffraction?

Answer available at the end of this section.

X-ray Crystallographer Rosalind Franklin

The discovery of the structure of DNA in 1953 by Francis Crick and James Watson is one of the great achievements in the history of science. They were awarded the 1962 Nobel Prize in Physiology or Medicine, along with Maurice Wilkins, who provided experimental proof of DNA's structure. British chemist Rosalind Franklin made invaluable contributions to this monumental achievement through her work in measuring X-ray diffraction images of DNA. Early in her career, Franklin's research on the structure of coals proved helpful to the British war effort. After shifting her focus to biological systems in the early 1950s, Franklin and doctoral student Raymond Gosling discovered that DNA consists of two forms: a long, thin fiber formed when wet (type "B") and a short, wide fiber formed when dried (type "A"). Her X-ray diffraction images of DNA provided the crucial information that allowed Watson and Crick to confirm that DNA forms a double helix, and to determine details of its size and structure. Franklin also conducted pioneering research on viruses and the RNA that contains their genetic information, uncovering new information that radically changed the body of knowledge in the field. After developing ovarian cancer, Franklin continued to work until her death in 1958 at age 37. Among many posthumous recognitions of her work, the Chicago Medical School of Finch University of Health Sciences changed its name to the Rosalind Franklin University of Medicine and Science in 2004, and adopted an image of her famous X-ray diffraction image of DNA as its official university logo.

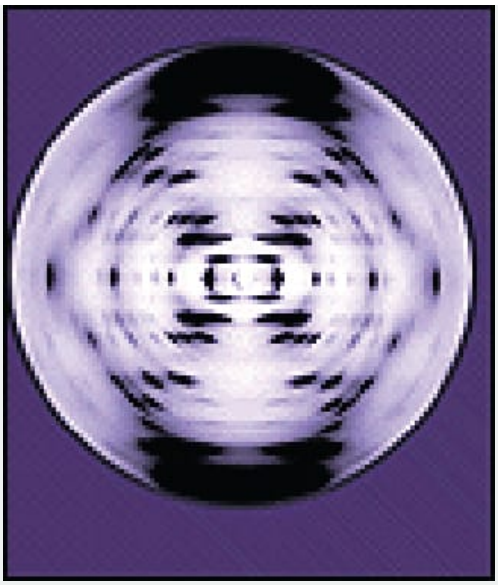


Figure 7.2.2.7.This illustration shows an X-ray diffraction image similar to the one Franklin found in her research. (credit: National Institutes of Health)

Key Concepts and Summary

The structures of crystalline metals and simple ionic compounds can be described in terms of packing of spheres. Metal atoms can pack in hexagonal closest-packed structures, cubic closest-packed structures, body-centered structures, and simple cubic structures. The anions in simple ionic structures commonly adopt one of these structures, and the cations occupy the spaces remaining between the anions. Small cations usually occupy tetrahedral holes in a closest-packed array of anions. Larger cations usually occupy octahedral holes. Still larger cations can occupy cubic holes in a simple cubic array of anions. The structure of a solid can be described by indicating the size and shape of a unit cell and the contents of the cell. The type of structure and dimensions of the unit cell can be determined by X-ray diffraction measurements.

Glossary

body-centered cubic (BCC) solid
: crystalline structure that has a cubic unit cell with lattice points at the corners and in the center of the cell

body-centered cubic unit cell
: simplest repeating unit of a body-centered cubic crystal; it is a cube containing lattice points at each corner and in the center of the cube

Bragg equation
: equation that relates the angles at which X-rays are diffracted by the atoms within a crystal

coordination number
: number of atoms closest to any given atom in a crystal or to the central metal atom in a complex

cubic closest packing (CCP)
: crystalline structure in which planes of closely packed atoms or ions are stacked as a series of three alternating layers of different relative orientations (ABC)

diffraction
: redirection of electromagnetic radiation that occurs when it encounters a physical barrier of appropriate dimensions

face-centered cubic (FCC) solid
: crystalline structure consisting of a cubic unit cell with lattice points on the corners and in the center of each face

face-centered cubic unit cell
: simplest repeating unit of a face-centered cubic crystal; it is a cube containing lattice points at each corner and in the center of each face

hexagonal closest packing (HCP)
: crystalline structure in which close packed layers of atoms or ions are stacked as a series of two alternating layers of different relative orientations (AB)

hole
: (also, interstice) space between atoms within a crystal

isomorphous
: possessing the same crystalline structure

octahedral hole
: open space in a crystal at the center of six particles located at the corners of an octahedron

simple cubic unit cell
: (also, primitive cubic unit cell) unit cell in the simple cubic structure

simple cubic structure
: crystalline structure with a cubic unit cell with lattice points only at the corners

space lattice
: all points within a crystal that have identical environments

tetrahedral hole
: tetrahedral space formed by four atoms or ions in a crystal

unit cell
: smallest portion of a space lattice that is repeated in three dimensions to form the entire lattice

X-ray crystallography
: experimental technique for determining distances between atoms in a crystal by measuring the angles at which X-rays are diffracted when passing through the crystal

Paul Flowers (University of North Carolina - Pembroke), Klaus Theopold (University of Delaware) and Richard Langley (Stephen F. Austin State University) with contributing authors. Textbook content produced by OpenStax College is licensed under a Creative Commons Attribution License 4.0 license. Download for free at http://cnx.org/contents/85abf193-2bd...a7ac8df6@9.110).

Answers

Exercise 7.2.2.1

No. If Ni were simple cubic, its density would be given by:

$$1\ \text{Ni atom} \times \frac{1\ \text{mol Ni}}{6.022 \times 10^{23}\ \text{Ni atoms}} \times \frac{58.693\ \text{g}}{1\ \text{mol Ni}} = 9.746 \times 10^{-23}\ \text{g}$$

$$V = l^3 = (3.524 \times 10^{-8}\ \text{cm})^3 = 4.376 \times 10^{-23}\ \text{cm}^3$$

Then the density of Ni would be

$$(= \frac{9.746 \times 10^{-23}\ \text{g}}{4.376 \times 10^{-23}\ \text{cm}^3} = 2.23\ \text{g/cm}^3$$

Since the actual density of Ni is not close to this, Ni does not form a simple cubic structure.

Exercise 7.2.2.2

144 pm

10.5 g/cm^3

Exercise 7.2.2.3**: Lithium selenide**

Li_2Se

Exercise 7.2.2.4

TiO_2

Exercise 7.2.2.6

The radius of the potassium ion is 1.33 Å.

Exercise 7.2.2.6

21.9°

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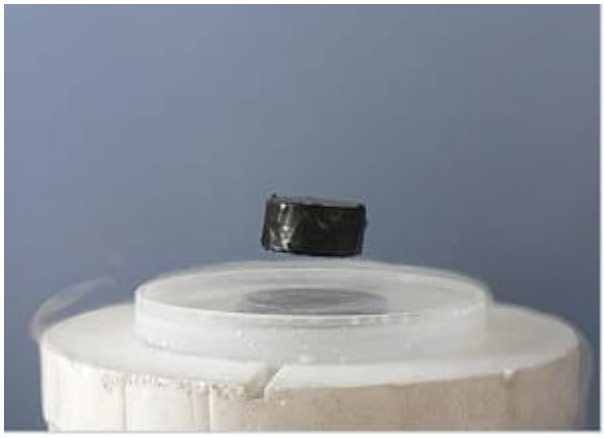
7.3: Superconductivity

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7.3.1: 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.

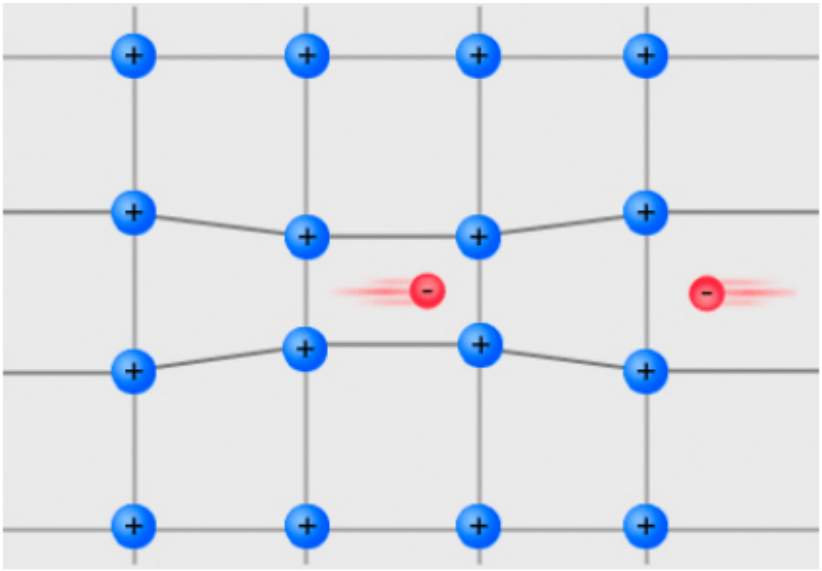


A magnet levitating above a high-temperature superconductor, cooled with liquid nitrogen. Persistent electric current flows on the surface of the superconductor, excluding the magnetic field of the magnet. This current effectively forms an electromagnet that repels the magnet.

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.

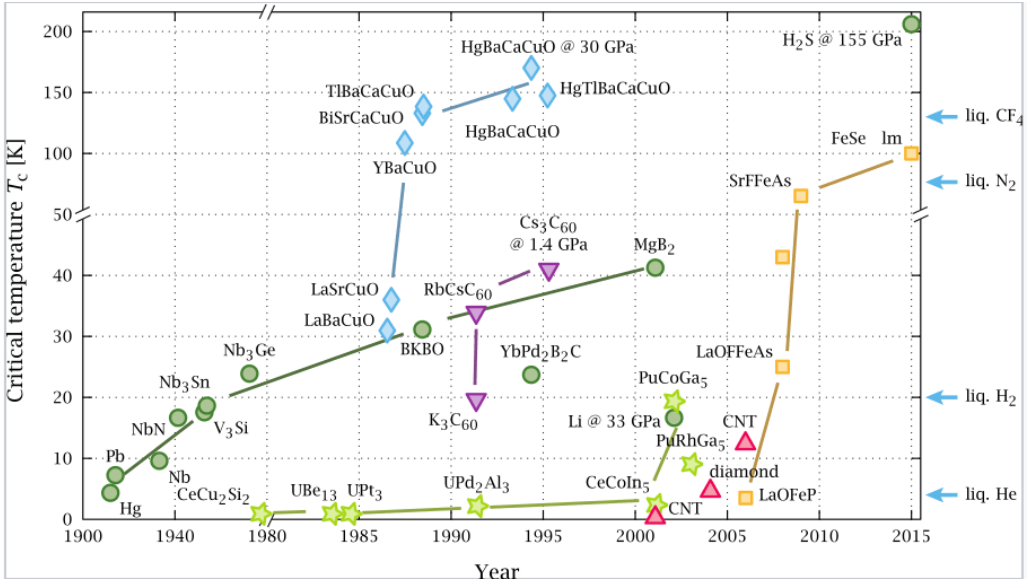
Superconductivity occurs when electrons spin pair into so-called Cooper pairs, which can travel through the lattice together. The electrons in a Cooper pair, although spin-paired, have a long-distance relationship: the spatial extent of a Cooper pair is a few nanometers in cuprate superconductors, and 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.

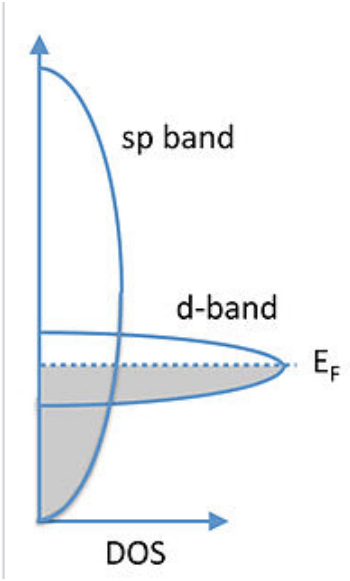
Bad metals make good superconductors. All superconductors are "normal" metals - with finite electrical resistance - above their critical transition temperature, T_c. If you ask where in the periodic table one might look for superconductors, the answer is surprising. The most conductive metals (Ag, Au, 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.



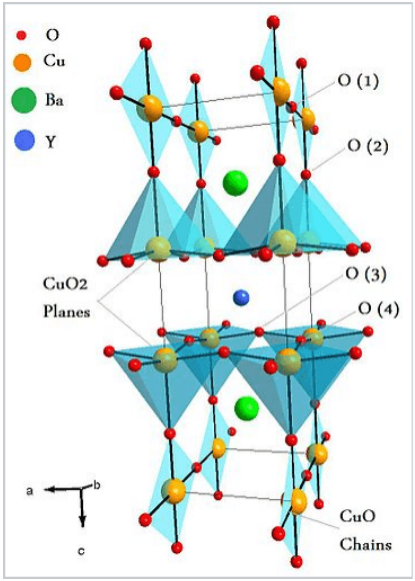
Generic E vs. DOS for a bad metal.

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

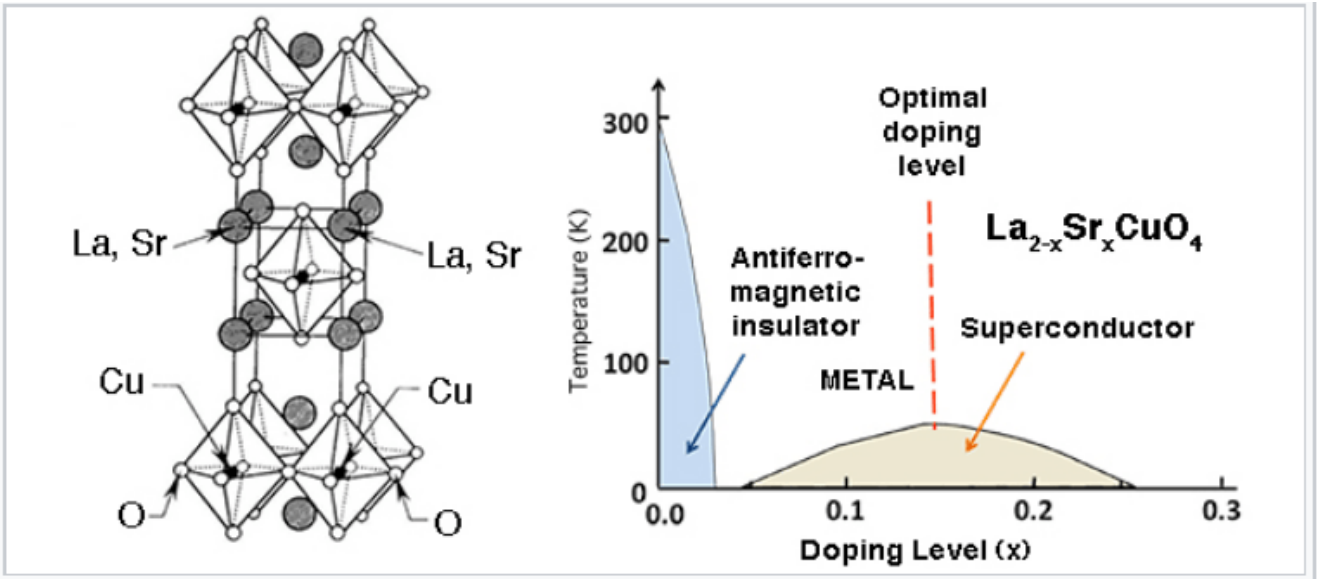
In addition to having weak orbital overlap in the metallic state - which results in a high DOS at E_F - high temperature superconductors also typically contain elements in mixed oxidation states (for example, $Cu^{2+/3+}$ or $Bi^{3+/5+}$) that are close in energy to the O^{2-}/O^- couple in the lattice. 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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7.4: Bonding in Ionic Crystals

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7.5: Imperfections in Solids

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7.5.1: Imperfections

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7.6: Silicates

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7.6.1: Silicon

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7.7: THERMODYNAMICS OF IONIC CRYSTAL FORMATION

Lattice enthalpy is a measure of the strength of the forces between the ions in an ionic solid. The greater the lattice enthalpy, the stronger the forces. Those forces are only completely broken when the ions are present as gaseous ions, scattered so far apart that there is negligible attraction between them.

7.7.1: Lattice Energy

7.7.2: Lattice Energy - The Born-Haber cycle

7.7.3: Lattice Enthalpies and Born Haber Cycles

7.7.4: The Born-Lande' equation

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7.7.1: Lattice Energy

Discussion Questions

- How is lattice energy estimated using Born-Haber cycle?
- How is lattice energy related to crystal structure?

The Lattice energy, U, is the amount of energy required to separate a mole of the solid (s) into a gas (g) of its ions.

$$\mathrm{M}_a\ \mathrm{L}_b\,(\mathrm{s}) \ \rightarrow a\,\mathrm{M}^{b+}\,(\mathrm{g}) + b\,\mathrm{X}^{a-}\,(\mathrm{g}) \tag{7.7.1.1}$$

This quantity cannot be experimentally determined directly, but it can be estimated using a Hess Law approach in the form of *Born-Haber cycle*. It can also be calculated from the electrostatic consideration of its crystal structure. As defined in Equation 7.7.1.1, the lattice energy is positive, because energy is always required to separate the ions. For the reverse process of Equation 7.7.1.1:

$$a\,\mathrm{M}^{b+}\,(\mathrm{g}) + b\,\mathrm{X}^{a-}\,(\mathrm{g}) \ \rightarrow \mathrm{M}_a\mathrm{L}_b\,(\mathrm{s})$$

the energy released is called **energy of crystallization** (E_{cryst}). Therefore,

$$U_{lattice} = -E_{cryst}$$

Values of lattice energies for various solids have been given in literature, especially for some common solids. Some are given here.

Table 7.7.1.1*: Comparison of Lattice Energies (U in kJ/mol) of Some Salts*

Solid	*U*	Solid	*U*	Solid	*U*	Solid	*U*
LiF	1036	LiCl	853	LiBr	807	LiI	757
NaF	923	NaCl	786	NaBr	747	NaI	704
KF	821	KCl	715	KBr	682	KI	649
MgF_2	2957	$MgCl_2$	2526	$MgBr_2$	2440	MgI_2	2327

The following trends are obvious at a glance of the data in Table 7.7.1.1:

- As the ionic radii of either the cation or anion increase, the lattice energies decrease.
- The solids consists of divalent ions have much larger lattice energies than solids with monovalent ions.

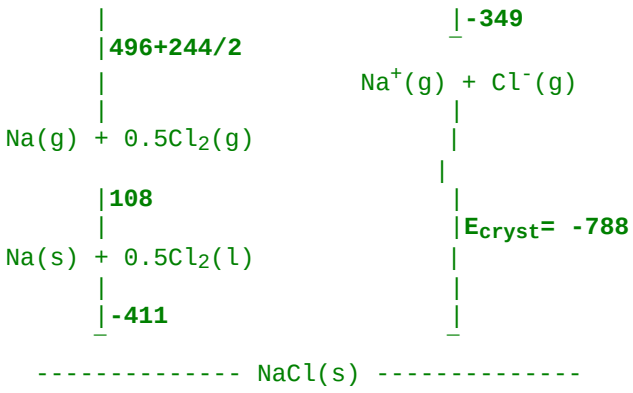
How is lattice energy estimated using Born-Haber cycle?

Estimating lattice energy using the Born-Haber cycle has been discussed in Ionic Solids. For a quick review, the following is an example that illustrate the estimate of the energy of crystallization of NaCl.

Hsub of Na = 108 kJ/mol (Heat of sublimation)
D of Cl2 = 244 (Bond dissociation energy)
IP of Na(g) = 496 (Ionization potential or energy)
EA of Cl(g) = -349 (Electron affinity of Cl)
Hf of NaCl = -411 (Enthalpy of formation)

The Born-Haber cycle to evaluate $E_{lattice}$ is shown below:

```
----------Na+ + Cl(g)--------
                            |
```



E_{cryst} = -411-(108+496+244/2)-(-349) kJ/mol
= -788 kJ/mol.

Discussion
The value calculated for *U* depends on the data used. Data from various sources differ slightly, and so is the result. The lattice energies for NaCl most often quoted in other texts is about 765 kJ/mol.

Compare with the method shown below

Na(s) + 0.5 Cl_2(l) ® NaCl(s)	- 411	H_f
Na(g) ® Na(s)	- 108	-H_{sub}
Na^+(g) + e ® Na(g)	- 496	-*IP*
Cl(g) ® 0.5 Cl_2(g)	- 0.5 * 244	-0.5*D
Cl^-(g) ® Cl(g) + 2 e	349	-*EA*
Add all the above equations leading to		
Na^+(g) + Cl^-(g) ® NaCl(s)	-788 kJ/mol = E_{cryst}	

Lattice Energy is Related to Crystal Structure

There are many other factors to be considered such as covalent character and electron-electron interactions in ionic solids. But for simplicity, let us consider the ionic solids as a collection of positive and negative ions. In this simple view, appropriate number of cations and anions come together to form a solid. The positive ions experience both attraction and repulson from ions of opposite charge and ions of the same charge.

As an example, let us consider the the NaCl crystal. In the following discussion, assume *r* be the distance between Na^+ and Cl^- ions. The nearest neighbors of Na^+ are 6 Cl^- ions at a distance 1*r*, 12 Na^+ ions at a distance 2*r*, 8 Cl^- at 3*r*, 6 Na^+ at 4*r*, 24 Na^+ at 5*r*, and so on. Thus, the energy due to one ion is

$$E = \frac{Z^2 e^2}{4\pi\epsilon_o r} M \tag{7.7.1.2}$$

The Madelung constant, M, is a poorly converging series of interaction energies:

$$M = \frac{6}{1} - \frac{12}{2} + \frac{8}{3} - \frac{6}{4} + \frac{24}{5} \ldots \tag{7.7.1.3}$$

with

- Z is the number of charges of the ions, (e.g., 1 for NaCl),
- e is the charge of an electron ($1.6022 \times 10^{-19}\ C$),

- $4\pi\epsilon_o$ is 1.11265x10^{-10} C^2/(J m).

The above discussion is valid only for the sodium chloride (also called rock salt) structure type. This is a geometrical factor, depending on the arrangement of ions in the solid. The Madelung constant depends on the structure type, and its values for several structural types are given in Table 6.13.1.

A is the number of anions coordinated to cation and *C* is the numbers of cations coordinated to anion.

Table 7.7.1.2: Madelung Constants

Compound	Crystal Lattice	M	A : C	Type
NaCl	NaCl	1.74756	6 : 6	Rock salt
CsCl	CsCl	1.76267	6 : 6	CsCl type
CaF_2	Cubic	2.51939	8 : 4	Fluorite
$CdCl_2$	Hexagonal	2.244		
MgF_2	Tetragonal	2.381		
ZnS (wurtzite)	Hexagonal	1.64132		
TiO_2 (rutile)	Tetragonal	2.408	6 : 3	Rutile
bSiO_2	Hexagonal	2.2197		
Al_2O_3	Rhombohedral	4.1719	6 : 4	Corundum
A is the number of anions coordinated to cation and *C* is the numbers of cations coordinated to anion.				

Madelung constants for a few more types of crystal structures are available from the Handbook Menu. There are other factors to consider for the evaluation of energy of crystallization, and the treatment by *M. Born* led to the formula for the evaluation of crystallization energy E_{cryst}, for a mole of **crystalline solid**.

$$E_{cryst} = \frac{NZ^2e^2}{4\pi\epsilon_o r}\left(1 - \frac{1}{n}\right) \tag{7.7.1.4}$$

where *N* is the Avogadro's number (6.022x10^{-23}), and *n* is a number related to the electronic configurations of the ions involved. The *n* values and the electronic configurations (e.c.) of the corresponding inert gases are given below:

n =	5	7	9	10	12
e.c.	He	Ne	Ar	Kr	Xe

The following values of *n* have been suggested for some common solids:

n =	5.9	8.0	8.7	9.1	9.5
e.c.	LiF	LiCl	LiBr	NaCl	NaBr

Example 7.7.1.1

Estimate the energy of crystallization for NaCl.

Solution

Using the values giving in the discussion above, the estimation is given by Equation 7.7.1.4:

$$E_c ryst = \frac{(6.022 \times 10^{23}/mol(1.6022 \times 10^{-19})^2(1.747558)}{4\pi\,(8.854 \times 10^{-12} C^2/m)(282 \times 10^{-12}\ m} \left(1 - \frac{1}{9.1}\right)$$
$$= -766 kJ/mol$$

Discussion

Much more should be considered in order to evaluate the lattice energy accurately, but the above calculation leads you to a good start. When methods to evaluate the energy of crystallization or lattice energy lead to reliable values, these values can be used in the Born-Haber cycle to evaluate other chemical properties, for example the electron affinity, which is really difficult to determine directly by experiment.

Exercise 7.7.1.1

Which one of the following has the largest lattice energy? LiF, NaF, CaF_2, AlF_3

Answer available at the end of this section.

Exercise 7.7.1.2

Which one of the following has the largest lattice energy? LiCl, NaCl, $CaCl_2$, Al_2O_3

Answer available at the end of this section.

Exercise 7.7.1.3

Lime, CaO, is know to have the same structure as NaCl and the edge length of the unit cell for CaO is 481 pm. Thus, Ca-O distance is 241 pm. Evaluate the energy of crystallization, E_{cryst} for CaO.

Answer available at the end of this section.

Exercise 7.7.1.4

Assume the interionic distance for $NaCl_2$ to be the same as those of NaCl (r = 282 pm), and assume the structure to be of the fluorite type (M = 2.512). Evaluate the energy of crystallization, E_{cryst} .

Answer available at the end of this section.

Contributors and Attributions

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Answers

Exercise 7.7.1.1

Skill: Explain the trend of lattice energy.

Exercise 7.7.1.2

Corrundum Al_2O_3 has some covalent character in the solid as well as the higher charge of the ions.

Exercise 7.7.1.3

Energy of crystallization is -3527 kJ/mol

Skill: Evaluate the lattice energy and know what values are needed.

Exercise 7.7.1.4

-515 kJ/mol

Discussion: This number has not been checked. If you get a different value, please let me know.

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7.7.2: Lattice Energy - The Born-Haber cycle

Ionic solids tend to be very stable compounds. The enthalpies of formation of the ionic molecules cannot alone account for this stability. These compounds have an additional stability due to the lattice energy of the solid structure. However, lattice energy cannot be directly measured. The Born-Haber cycle allows us to understand and determine the lattice energies of ionic solids.

Introduction

This module will introduce the idea of lattice energy, as well as one process that allows us to calculate it: the Born-Haber Cycle. In order to use the Born-Haber Cycle, there are several concepts that we must understand first.

Lattice Energy

Lattice Energy is a type of potential energy that may be defined in two ways. In one definition, the lattice energy is the energy required to break apart an ionic solid and convert its component atoms into gaseous ions. This definition causes the value for the lattice energy to always be positive, since this will always be an endothermic reaction. The other definition says that lattice energy is the reverse process, meaning it is the energy released when gaseous ions bind to form an ionic solid. As implied in the definition, this process will always be exothermic, and thus the value for lattice energy will be negative. Its values are usually expressed with the units kJ/mol.

Lattice Energy is used to explain the stability of ionic solids. Some might expect such an ordered structure to be less stable because the entropy of the system would be low. However, the crystalline structure allows each ion to interact with multiple oppositely charge ions, which causes a highly favorable change in the enthalpy of the system. A lot of energy is released as the oppositely charged ions interact. It is this that causes ionic solids to have such high melting and boiling points. Some require such high temperatures that they decompose before they can reach a melting and/or boiling point.

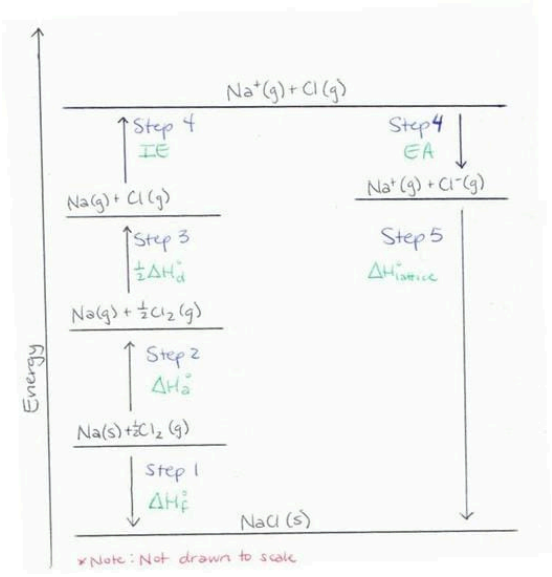
Born-Haber Cycle

There are several important concept to understand before the Born-Haber Cycle can be applied to determine the lattice energy of an ionic solid; ionization energy, electron affinity, dissociation energy, sublimation energy, heat of formation, and Hess's Law.

- **Ionization Energy** is the energy required to remove an electron from a neutral atom or an ion. This process always requires an input of energy, and thus will always have a positive value. In general, ionization energy increases across the periodic table from left to right, and decreases from top to bottom. There are some excepts, usually due to the stability of half-filled and completely filled orbitals.
- **Electron Affinity** is the energy released when an electron is added to a neutral atom or an ion. Usually, energy released would have a negative value, but due to the definition of electron affinity, it is written as a positive value in most tables. Therefore, when used in calculating the lattice energy, we must remember to subtract the electron affinity, not add it. In general, electron affinity increases from left to right across the periodic table and decreases from top to bottom.
- **Dissociation energy** is the energy required to break apart a compound. The dissociation of a compound is always an endothermic process, meaning it will always require an input of energy. Therefore, the change in energy is always positive. The magnitude of the dissociation energy depends on the electronegativity of the atoms involved.
- Sublimation energy is the energy required to cause a change of phase from solid to gas, bypassing the liquid phase. This is an input of energy, and thus has a positive value. It may also be referred to as the energy of atomization.
- **The heat of formation** is the change in energy when forming a compound from its elements. This may be positive or negative, depending on the atoms involved and how they interact.
- **Hess's Law** states that the overall change in energy of a process can be determined by breaking the process down into steps, then adding the changes in energy of each step. The Born-Haber Cycle is essentially Hess's Law applied to an ionic solid.

Using the Born-Haber Cycle

The values used in the Born-Haber Cycle are all predetermined changes in enthalpy for the processes described in the section above. Hess' Law allows us to add or subtract these values, which allows us to determine the lattice energy.



Step 1

Determine the energy of the metal and nonmetal in their elemental forms. (Elements in their natural state have an energy level of zero.) Subtract from this the heat of formation of the ionic solid that would be formed from combining these elements in the appropriate ration. This is the energy of the ionic solid, and will be used at the end of the process to determine the lattice energy.

Step 2

The Born-Haber Cycle requires that the elements involved in the reaction are in their gaseous forms. Add the changes in enthalpy to turn one of the elements into its gaseous state, and then do the same for the other element.

Step 3

Metals exist in nature as single atoms and thus no dissociation energy needs to be added for this element. However, many nonmetals will exist as polyatomic species. For example, Cl exists as Cl_2 in its elemental state. The energy required to change Cl_2 into 2Cl atoms must be added to the value obtained in Step 2.

Step 4

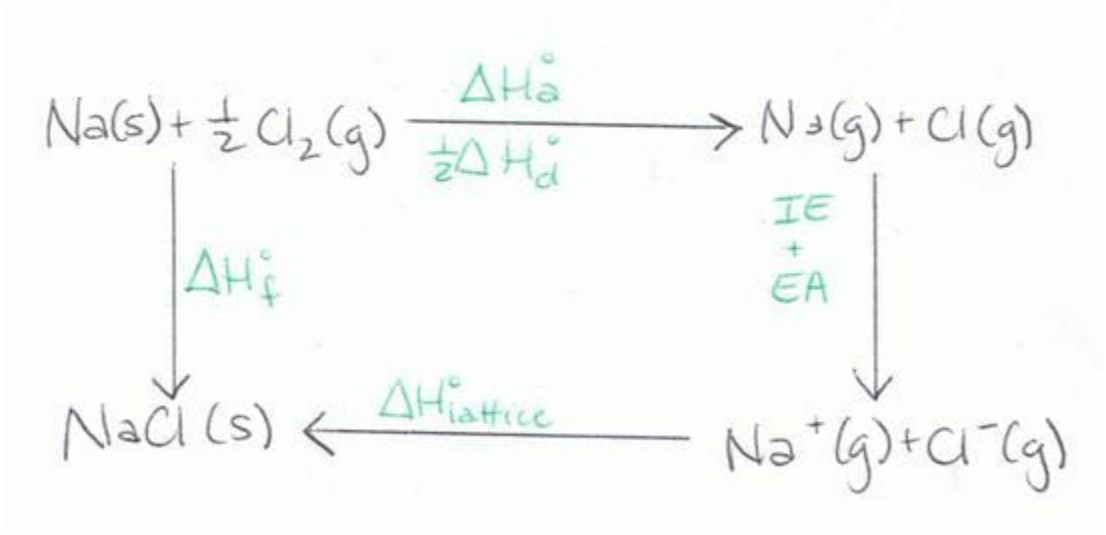
Both the metal and nonmetal now need to be changed into their ionic forms, as they would exist in the ionic solid. To do this, the ionization energy of the metal will be added to the value from Step 3. Next, the electron affinity of the nonmetal will be subtracted from the previous value. It is subtracted because it is a release of energy associated with the addition of an electron.

*This is a common error due to confusion caused by the definition of electron affinity, so be careful when doing this calculation.

Step 5

Now the metal and nonmetal will be combined to form the ionic solid. This will cause a release of energy, which is called the lattice energy. The value for the lattice energy is the difference between the value from Step 1 and the value from Step 4.

The diagram below is another representation of the Born-Haber Cycle.



Equation

The Born-Haber Cycle can be reduced to a single equation:

Heat of formation= Heat of atomization+ Dissociation energy+ (sum of Ionization energies)+ (sum of Electron affinities)+ Lattice energy

*Note: In this general equation, the electron affinity is added. However, when plugging in a value, determine whether energy is released (exothermic reaction) or absorbed (endothermic reaction) for each electron affinity. If energy is released, put a negative sign in front of the value; if energy is absorbed, the value should be positive.

Rearrangement to solve for lattice energy gives the equation:

Lattice energy= Heat of formation- Heat of atomization- Dissociation energy- (sum of Ionization energies)- (sum of Electron Affinities)

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Problems

1. Define lattice energy, ionization energy, and electron affinity.
2. What is Hess' Law?
3. Find the lattice energy of KF(s).
   Note: Values can be found in standard tables.
4. Find the lattice energy of $MgCl_2$(s).
5. Which one of the following has the greatest lattice energy?
   a. A) MgO

   b. B) NaC
   c. C) LiCl
   d. D) $MgCl_2$
6. Which one of the following has the greatest Lattice Energy?
   a. NaCl
   b. $CaCl_2$
   c. $AlCl_3$
   d. KCl

Solutions

1. Lattice energy: The difference in energy between the expected experimental value for the energy of the ionic solid and the actual value observed. More specifically, this is the energy gap between the energy of the separate gaseous ions and the energy of the ionic solid.
   Ionization energy: The energy change associated with the removal of an electron from a neutral atom or ion.
   Electron affinity: The release of energy associated with the addition of an electron to a neutral atom or ion.
2. Hess' Law states that the overall energy of a reaction may be determined by breaking down the process into several steps, then adding together the changes in energy of each step.
3. Lattice Energy= [-436.68-89-(0.5*158)-418.8-(-328)] kJ/mol= **-695.48 kJ/mol**
4. Lattice Energy= [-641.8-146-243-(737.7+1450.6)-(2*-349)] kJ/mol= **-2521.1 kJ/mol**
5. MgO. It has ions with the largest charge.
6. $AlCl_3$. According to the periodic trends, as the radius of the ion increases, lattice energy decreases.

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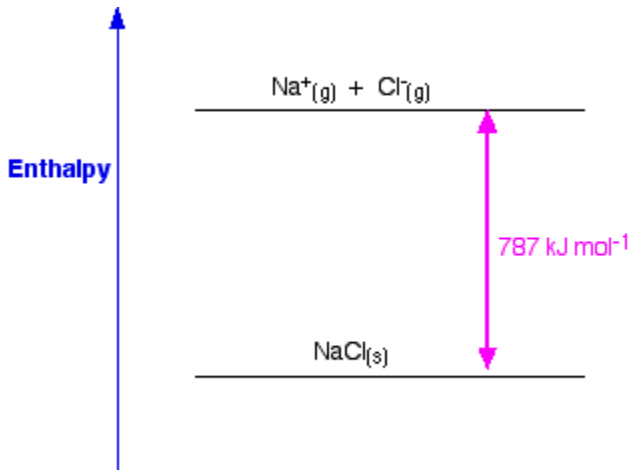
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7.7.3: Lattice Enthalpies and Born Haber Cycles

Lattice enthalpy is a measure of the strength of the forces between the ions in an ionic solid. The greater the **lattice enthalpy**, the stronger the forces. This page introduces lattice enthalpies (lattice energies) and Born-Haber cycles.

Defining Lattice Enthalpy

There are two different ways of defining lattice enthalpy which directly contradict each other, and you will find both in common use. In fact, there is a simple way of sorting this out, but many sources do not use it. Lattice enthalpy is a measure of the strength of the forces between the ions in an ionic solid. The greater the lattice enthalpy, the stronger the forces. Those forces are only completely broken when the ions are present as gaseous ions, scattered so far apart that there is negligible attraction between them. You can show this on a simple enthalpy diagram.



For sodium chloride, the solid is more stable than the gaseous ions by 787 kJ mol^{-1}, and that is a measure of the strength of the attractions between the ions in the solid. Remember that energy (in this case heat energy) is released when bonds are made, and is required to break bonds.

So lattice enthalpy could be described in either of two ways.

- It could be described as the enthalpy change when 1 mole of sodium chloride (or whatever) was formed from its scattered gaseous ions. In other words, you are looking at a downward arrow on the diagram.
- Or, it could be described as the enthalpy change when 1 mole of sodium chloride (or whatever) is broken up to form its scattered gaseous ions. In other words, you are looking at an upward arrow on the diagram.

Both refer to the same enthalpy diagram, but one looks at it from the point of view of making the lattice, and the other from the point of view of breaking it up. Unfortunately, both of these are often described as "lattice enthalpy".

Definitions

- The *lattice dissociation enthalpy* is the enthalpy change needed to convert 1 mole of solid crystal into its scattered gaseous ions. Lattice dissociation enthalpies are **always positive**.
- The *lattice formation enthalpy* is the enthalpy change when 1 mole of solid crystal is formed from its separated gaseous ions. Lattice formation enthalpies are **always negative**.

This is an absurdly confusing situation which is easily resolved by never using the term "lattice enthalpy" without qualifying it.

- You should talk about "lattice dissociation enthalpy" if you want to talk about the amount of energy needed to split up a lattice

into its scattered gaseous ions. For NaCl, the lattice dissociation enthalpy is +787 kJ mol^{-1}.
- You should talk about "lattice formation enthalpy" if you want to talk about the amount of energy released when a lattice is formed from its scattered gaseous ions. For NaCl, the lattice formation enthalpy is -787 kJ mol^{-1}.

That immediately removes any possibility of confusion.

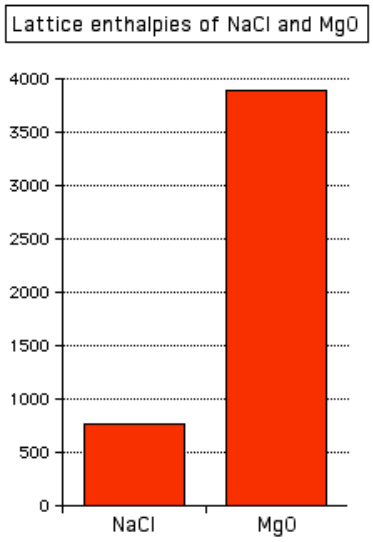
Factors affecting Lattice Enthalpy

The two main factors affecting lattice enthalpy are

- The charges on the ions and
- The ionic radii (which affects the distance between the ions).

The charges on the ions

Sodium chloride and magnesium oxide have exactly the same arrangements of ions in the crystal lattice, but the lattice enthalpies are very different.

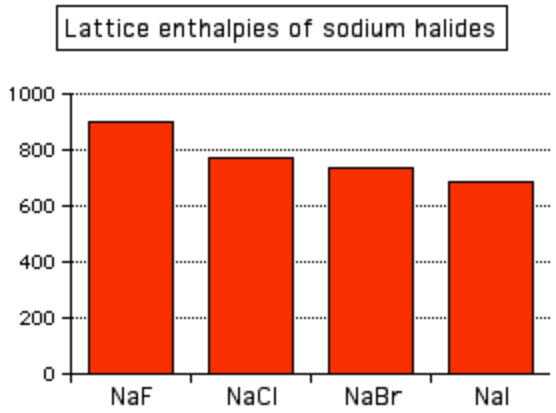


You can see that the lattice enthalpy of magnesium oxide is much greater than that of sodium chloride. That's because in magnesium oxide, 2+ ions are attracting 2- ions; in sodium chloride, the attraction is only between 1+ and 1- ions.

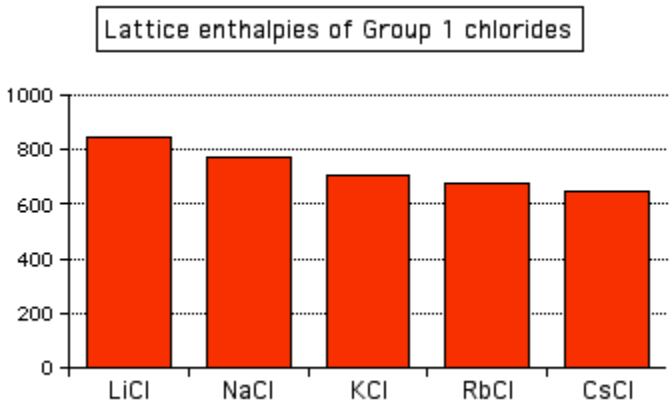
The Radius of the Ions

The lattice enthalpy of magnesium oxide is also increased relative to sodium chloride because magnesium ions are smaller than sodium ions, and oxide ions are smaller than chloride ions. That means that the ions are closer together in the lattice, and that increases the strength of the attractions.

This effect of ion size on lattice enthalpy is clearly observed as you go down a Group in the Periodic Table. For example, as you go down Group 7 of the Periodic Table from fluorine to iodine, you would expect the lattice enthalpies of their sodium salts to fall as the negative ions get bigger - and that is the case:



Attractions are governed by the distances between the centers of the oppositely charged ions, and that distance is obviously greater as the negative ion gets bigger. And you can see exactly the same effect if as you go down Group 1. The next bar chart shows the lattice enthalpies of the Group 1 chlorides.



Calculating Lattice Enthalpy

It is impossible to measure the enthalpy change starting from a solid crystal and converting it into its scattered gaseous ions. It is even more difficult to imagine how you could do the reverse - start with scattered gaseous ions and measure the enthalpy change when these convert to a solid crystal. Instead, lattice enthalpies always have to be calculated, and there are two entirely different ways in which this can be done.

1. You can can use a Hess's Law cycle (in this case called a Born-Haber cycle) involving enthalpy changes which can be measured. Lattice enthalpies calculated in this way are described as experimental values.
2. Or you can do physics-style calculations working out how much energy would be released, for example, when ions considered as point charges come together to make a lattice. These are described as theoretical values. In fact, in this case, what you are actually calculating are properly described as lattice energies.

Born-Haber Cycles

Standard Atomization Enthalpies

Before we start talking about Born-Haber cycles, we need to define the **atomization enthalpy**, ΔH_a^o. The standard atomization enthalpy is the enthalpy change when 1 mole of gaseous atoms is formed from the element in its standard state. Enthalpy change of atomization is always positive. You are always going to have to supply energy to break an element into its separate gaseous

atoms. All of the following equations represent changes involving atomization enthalpy:

$$\frac{1}{2}Cl_2(g) \rightarrow Cl(g) \quad \Delta H_a^o = +122\,kJ\,mol^{-1}$$

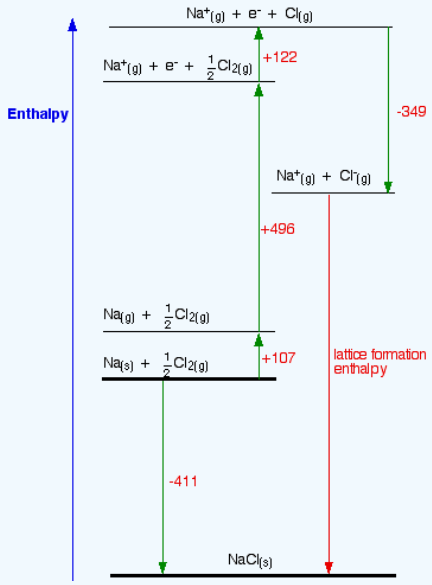
$$\frac{1}{2}Br_2(l) \rightarrow Br(g) \quad \Delta H_a^o = +122\,kJ\,mol^{-1}$$

$$Na(s) \rightarrow Na(g) \quad \Delta H_a^o = +107\,kJ\,mol^{-1}$$

Notice particularly that the "mol^{-1}" is per mole of atoms **formed** - NOT per mole of element that you start with. You will quite commonly have to write fractions into the left-hand side of the equation. Getting this wrong is a common mistake.

Example 7.7.3.1: Born-Haber Cycle for NaCl

Consider a Born-Haber cycle for sodium chloride, and then talk it through carefully afterwards. You will see that I have arbitrarily decided to draw this for lattice formation enthalpy. If you wanted to draw it for lattice dissociation enthalpy, the red arrow would be reversed - pointing upwards.



Focus to start with on the higher of the two thicker horizontal lines. We are starting here with the elements sodium and chlorine in their standard states. Notice that we only need half a mole of chlorine gas in order to end up with 1 mole of NaCl. The arrow pointing down from this to the lower thick line represents the enthalpy change of formation of sodium chloride.

The Born-Haber cycle now imagines this formation of sodium chloride as happening in a whole set of small changes, most of which we know the enthalpy changes for - except, of course, for the lattice enthalpy that we want to calculate.

- The +107 is the atomization enthalpy of sodium. We have to produce gaseous atoms so that we can use the next stage in the cycle.
- The +496 is the first ionization energy of sodium. Remember that first ionization energies go from gaseous atoms to gaseous singly charged positive ions.
- The +122 is the atomization enthalpy of chlorine. Again, we have to produce gaseous atoms so that we can use the next stage in the cycle.
- The -349 is the first electron affinity of chlorine. Remember that first electron affinities go from gaseous atoms to gaseous singly charged negative ions.
- And finally, we have the positive and negative gaseous ions that we can convert into the solid sodium chloride using the lattice formation enthalpy.

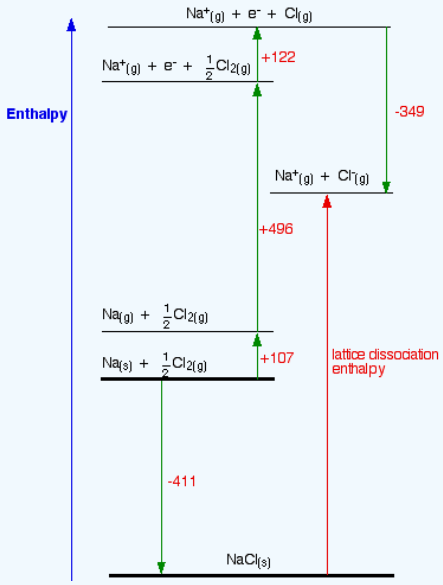
Now we can use Hess' Law and find two different routes around the diagram which we can equate. As drawn, the two routes are obvious. The diagram is set up to provide two different routes between the thick lines. So, from the cycle we get the calculations directly underneath it . . .

$$-411 = +107 + 496 + 122 - 349 + LE$$

$$LE = -411 - 107 - 496 - 122 + 349$$

$$LE = -787 \text{ kJ mol}^{-1}$$

How would this be different if you had drawn a lattice dissociation enthalpy in your diagram? Your diagram would now look like this:



The only difference in the diagram is the direction the lattice enthalpy arrow is pointing. It does, of course, mean that you have to find two new routes. You cannot use the original one, because that would go against the flow of the lattice enthalpy arrow. This time both routes would start from the elements in their standard states, and finish at the gaseous ions.

$$-411 + LE = +107 + 496 + 122 - 349$$

$$LE = +107 + 496 + 122 - 349 + 411$$

$$LE = +787 \text{ kJ mol}^{-1}$$

Once again, the cycle sorts out the sign of the lattice enthalpy.

Theoretical Estimates of Lattice Energies

Let's assume that a compound is fully ionic. Let's also assume that the ions are point charges - in other words that the charge is concentrated at the center of the ion. By doing physics-style calculations, it is possible to calculate a theoretical value for what you would expect the lattice energy to be. Calculations of this sort end up with values of *lattice energy*, and not *lattice enthalpy*. If you know how to do it, you can then fairly easily convert between the two.

There are several different equations, of various degrees of complication, for calculating lattice energy in this way. There are two possibilities:

- There is reasonable agreement between the experimental value (calculated from a Born-Haber cycle) and the theoretical value. Sodium chloride is a case like this - the theoretical and experimental values agree to within a few percent. That means

that for sodium chloride, the assumptions about the solid being ionic are fairly good.
- The experimental and theoretical values do not agree. A commonly quoted example of this is silver chloride, AgCl. Depending on where you get your data from, the theoretical value for lattice enthalpy for AgCl is anywhere from about 50 to 150 kJ mol^{-1} less than the value that comes from a Born-Haber cycle. In other words, treating the AgCl as 100% ionic underestimates its lattice enthalpy by quite a lot.

The explanation is that silver chloride actually has a significant amount of covalent bonding between the silver and the chlorine, because there is not enough electronegativity difference between the two to allow for complete transfer of an electron from the silver to the chlorine. Comparing experimental (Born-Haber cycle) and theoretical values for lattice enthalpy is a good way of judging how purely ionic a crystal is.

Example 7.7.3.2: Born-Haber Cycle for $MgCl_2$

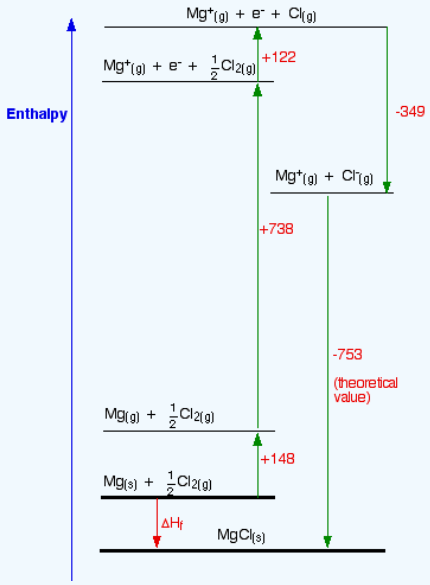
The question arises as to why, from an energetics point of view, magnesium chloride is $MgCl_2$ rather than MgCl or $MgCl_3$ (or any other formula you might like to choose). It turns out that $MgCl_2$ is the formula of the compound which has the most negative enthalpy change of formation - in other words, it is the most stable one relative to the elements magnesium and chlorine.

Let's look at this in terms of Born-Haber cycles of and contrast the enthalpy change of formation for the imaginary compounds MgCl and $MgCl_3$. That means that we will have to use theoretical values of their lattice enthalpies. We ca not use experimental ones, because these compounds obviously do not exist! I'm taking theoretical values for lattice enthalpies for these compounds that I found on the web. I can't confirm these, but all the other values used by that source were accurate. The exact values do not matter too much anyway, because the results are so dramatically clear-cut.

1. The Born-Haber cycle for MgCl

We will start with the compound MgCl, because that cycle is just like the NaCl one we have already looked at.

$$Mg\,(s) + \tfrac{1}{2}\,Cl_2\,(g) \rightarrow MgCl\,(s)$$



Find two routes around this without going against the flow of any arrows. That's easy:

$$\Delta H_f = +148 + 738 + 122 - 349 - 753$$

$$\Delta H_f = -94 \text{ kJ mol}^{-1}$$

So the compound MgCl is definitely energetically **more stable** than its elements. I have drawn this cycle very roughly to scale, but that is going to become more and more difficult as we look at the other two possible formulae. So I am going to rewrite it as a table. You can see from the diagram that the enthalpy change of formation can be found just by adding up all the other numbers in the cycle, and we can do this just as well in a table.

	kJ
atomization enthalpy of Mg	+148
1st IE of Mg	+738
atomization enthalpy of Cl	+122
electron affinity of Cl	-349
lattice enthalpy	-753
calculated ΔH_f	-94

2. The Born-Haber cycle for $MgCl_2$

The equation for the enthalpy change of formation this time is

$$Mg\,(s) + Cl_2\,(g) \rightarrow MgCl_2\,(s)$$

So how does that change the numbers in the Born-Haber cycle?

- You need to add in the second ionization energy of magnesium, because you are making a 2+ ion.
- You need to multiply the atomization enthalpy of chlorine by 2, because you need 2 moles of gaseous chlorine atoms.
- You need to multiply the electron affinity of chlorine by 2, because you are making 2 moles of chloride ions.
- You obviously need a different value for lattice enthalpy.

	kJ
atomization enthalpy of Mg	+148
1st IE of Mg	+738
2nd IE of Mg	+1451
atomization enthalpy of Cl (x 2)	+244
electron affinity of Cl (x 2)	-698
lattice enthalpy	-2526
calculated ΔH_f	-643

You can see that much more energy is released when you make $MgCl_2$ than when you make MgCl. Why is that? You need to put in more energy to ionize the magnesium to give a 2+ ion, but a lot more energy is released as lattice enthalpy. That is because there are stronger ionic attractions between 1- ions and 2+ ions than between the 1- and 1+ ions in MgCl. So what about $MgCl_3$? The lattice energy here would be even greater.

3. The Born-Haber cycle for $MgCl_3$

The equation for the enthalpy change of formation this time is

$$Mg\,(s) + \tfrac{3}{2}\,Cl_2\,(g) \rightarrow MgCl_3\,(s)$$

So how does that change the numbers in the Born-Haber cycle this time?

- You need to add in the third ionization energy of magnesium, because you are making a 3+ ion.
- You need to multiply the atomization enthalpy of chlorine by 3, because you need 3 moles of gaseous chlorine atoms.
- You need to multiply the electron affinity of chlorine by 3, because you are making 3 moles of chloride ions.

- You again need a different value for lattice enthalpy.

	kJ
atomization enthalpy of Mg	+148
1st IE of Mg	+738
2nd IE of Mg	+1451
3rd IE of Mg	+7733
atomization enthalpy of Cl (x 3)	+366
electron affinity of Cl (x 3)	-1047
lattice enthalpy	-5440
calculated ΔH_f	+3949

This time, the compound is hugely energetically unstable, both with respect to its elements, and also to other compounds that could be formed. You would need to supply nearly 4000 kJ to get 1 mole of $MgCl_3$ to form!

Look carefully at the reason for this. The lattice enthalpy is the **highest** for all these possible compounds, but it is not high enough to make up for the very large third ionization energy of magnesium.

Why is the third ionization energy so big? The first two electrons to be removed from magnesium come from the 3s level. The third one comes from the 2p. That is closer to the nucleus, and lacks a layer of screening as well - and so much more energy is needed to remove it. The 3s electrons are screened from the nucleus by the 1 level and 2 level electrons. The 2p electrons are only screened by the 1 level (plus a bit of help from the 2s electrons).

Conclusion

Magnesium chloride is $MgCl_2$ because this is the combination of magnesium and chlorine which produces the most energetically stable compound - the one with the most negative enthalpy change of formation.

Contributors and Attributions

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7.7.4: The Born-Lande' equation

The Born-Landé equation is a concept originally formulated in 1918 by the scientists Born and Landé and is used to calculate the lattice energy (measure of the strength of bonds) of a compound. This expression takes into account both the Born interactions as well as the Coulomb attractions.

Introduction

Due to its high simplicity and ease, the Born-Landé equation is commonly used by chemists when solving for lattice energy. This equation proposed by Max Born and Alfred Landé states that lattice energy can be derived from ionic lattice based on electrostatic potential and the potential energy due to repulsion. To solve for the Born-Landé equation, you must have a basic understanding of lattice energy:

- Lattice energy decreases as you go down a group (as atomic radii goes up, lattice energy goes down).
- Going across the periodic table, atomic radii decreases, therefore lattice energy increases.

The Born-Landé equation was derived from these two following equations. the first is the electrostatic potential energy:

$$\Delta U = -\frac{N_A M \left|Z^+\right| \left|Z^-\right| e^2}{4\pi\epsilon_o r} \tag{7.7.4.1}$$

with

- M_A is Avogadro's constant (6.022×10^{23})
- M is the Madelung Constant (a constant that varies for different structures)
- e is the charge of an electron (1.6022×10^{-19} C)
- Z^+ is the cation charge
- Z^- is the anion charge
- ϵ_o is the permittivity of free space

The second equation is the repulsive interaction:

$$\Delta U = \frac{N_A B}{r^n} \tag{7.7.4.2}$$

with

- B is the repulsion coefficient and
- n is the Born Exponent (typically ranges between 5-12) that is used to measure how much a solid compresses

These equations combine to form:

$$\Delta U(0K) = \frac{N_A M \left|Z^+\right| \left|Z^-\right| e^2}{4\pi\epsilon_o r_o}\left(1 - \frac{1}{n}\right) \tag{7.7.4.3}$$

with

- r_0 is the closest ion distance

Calculate Lattice Energy

Lattice energy, based on the equation from above, is dependent on multiple factors. We see that the charge of ions is proportional to the increase in lattice energy. In addition, as ions come into closer contact, lattice energy also increases.

Example 7.7.4.1

Which compound has the greatest lattice energy?

- AlF_3
- NACl
- LiF
- $CaCl_2$

Solution

This question requires basic knowledge of lattice energy. Since F_3 gives the compound a +3 positive charge and the Al gives the compound a -1 negative charge, the compound has large electrostatic attraction. The bigger the electrostatic attraction, the greater the lattice energy.

Example 7.7.4.2

What is the lattice energy of NaCl? (Hint: you must look up the values for the constants for this compound)

Solution

-756 kJ/mol (again, this value is found in a table of constants)

Example 7.7.4.3

Calculate the lattice energy of NaCl.

Solution

$$Lattice\ Energy\ of\ NaCl = -\frac{\frac{6.022\,x\,10^{23}}{mole}\left(1.6022^{-19}\right)\times 1.747}{4\pi \times 8.85\,x\,10^{-12}\frac{c^2}{m}\times 282\,x\,10^{-12}m}\left(1-\frac{1}{9}\right) \approx -756\ \frac{kJ}{mol}$$

References

1. Johnson, D. A. *Metals and Chemical Change*. Cambridge: Royal Society of Chemistry, 2002.
2. Cotton, F. Albert, and F. Albert Cotton. *Advanced Inorganic Chemistry*. New York: Wiley, 1999.

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7.P: Problems

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8: CHEMISTRY OF THE MAIN GROUP ELEMENTS

8.1: General Trends in Main Group Chemistry

8.1.1: The Periodic Table is an Organizing Concept in Main Group Chemistry

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8.1.1.2: There are qualitative differences between the chemistry of the elements in the first two rows and those in the rest of the periodic table

8.1.2: Electronegativity increases and radius decreases towards the upper left of the periodic table, with electron withdrawing substituents, and with oxidation state

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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

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8.13.1: Physical Properties of the Halogens
8.13.1.1: Atomic and Physical Properties of Halogens
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8.P: Problems

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8.1: 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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8.1.1: 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 8.1.1.1 .

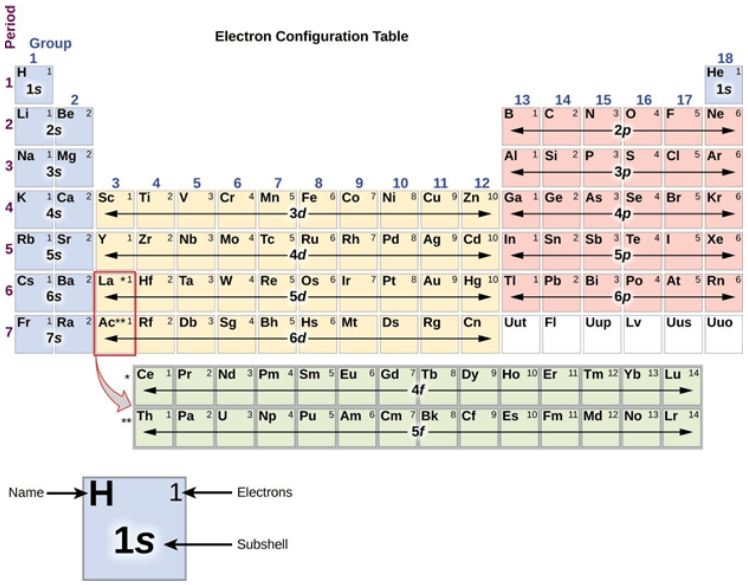


Figure 8.1.1.1. Subshells of the outermost valence electrons of the elements. The image is taken from OpenStax College. **Located at:** http://openstaxcollege.org. **License:** *CC BY: Attribution*. **License Terms:** Download for free at https://openstaxcollege.org/textbooks/chemistry/get

From Figure 8.1.1.1 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 8.1.1.2.

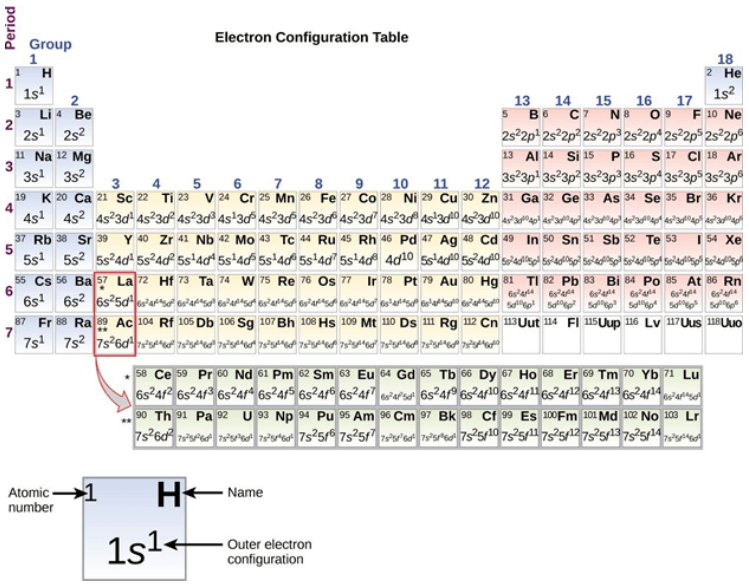


Figure 8.1.1.2. Valence electron configurations of the elements. Note that for most purposes *d* and *f* electrons in lower shells do not contribute significantly to the bonding. The image is taken from OpenStax College. **Located at:** http://openstaxcollege.org. **License:** *CC BY: Attribution*. **License Terms:** Download for free at https://openstaxcollege.org/textbooks/chemistry/get

From Figure 8.1.1.2 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 8.1.1.3.

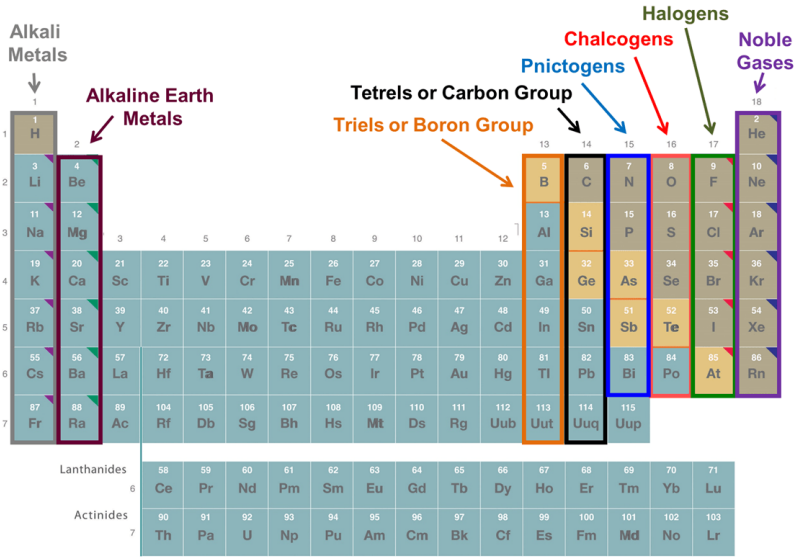


Figure 8.1.1.3. Commonly used group names. Note that hydrogen is not typically regarded as an alkali metal even though it is sometimes placed in the alkali metal goup. The image is adapted from https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/02._Atoms%2C_Molecules%2C_and_Ions/2.5%3A_The_Periodic_Table. 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 8.1.1.4.

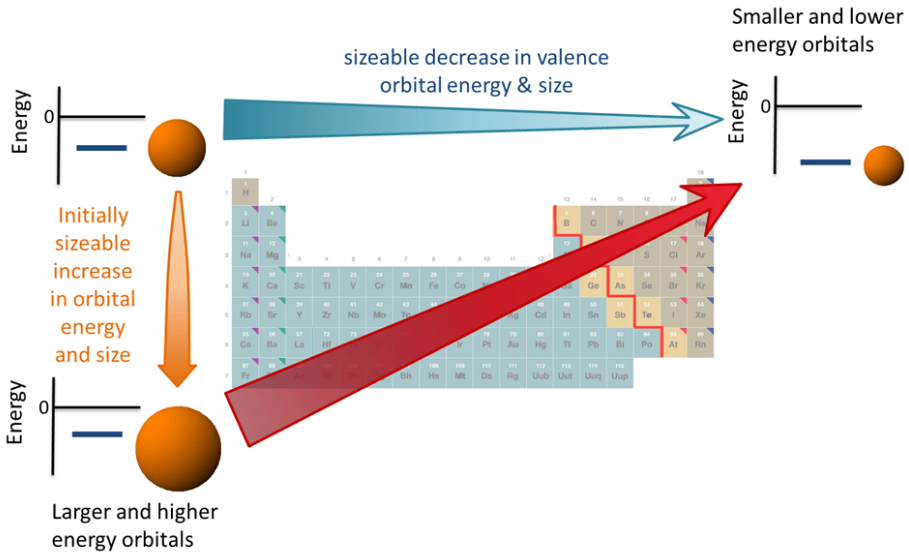


Figure 8.1.1.4. Trends in valence orbital properties. The image is adapted from https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/02._Atoms%2C_Molecules%2C_and_Ions/2.5%3A_The_Periodic_Table. Otherwise this work by Stephen Contakes is licensed 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 8.1.1.5.

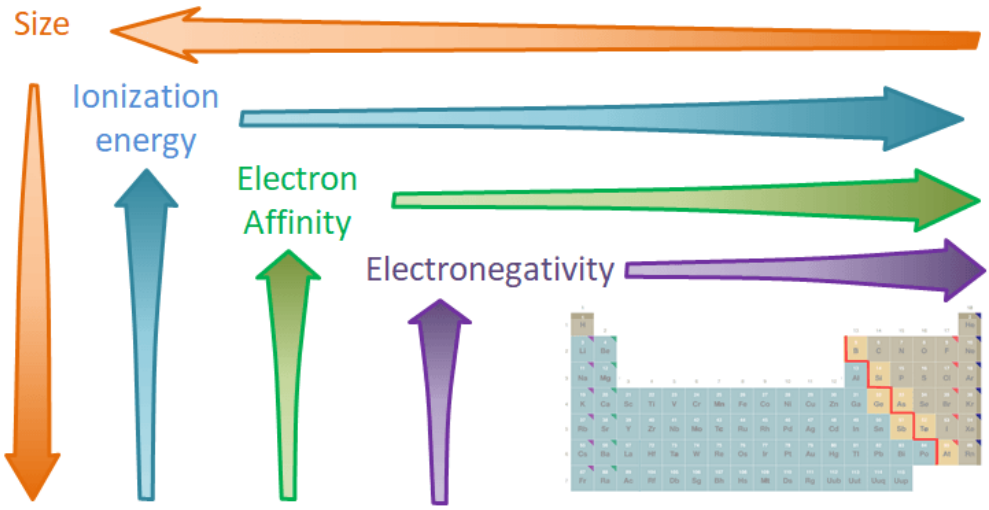


Figure 8.1.1.5. Periodic trends in atomic properties. The image is adapted from https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/02._Atoms%2C_Molecules%2C_and_Ions/2.5%3A_The_Periodic_Table. Otherwise this work by Stephen Contakes is licensed 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.

---

[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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8.1.1.1: 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 8.1.1.1.1, 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.

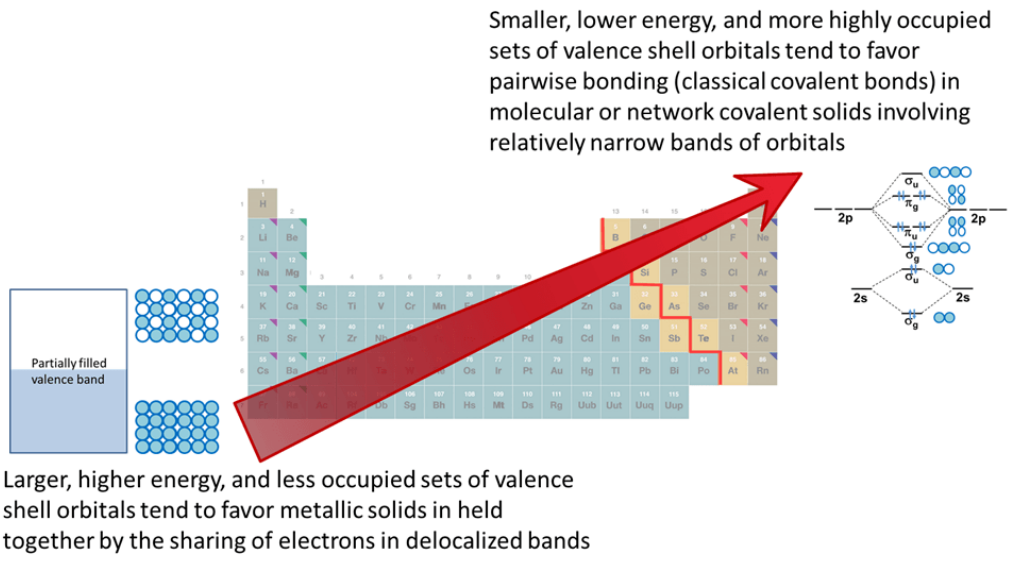


Figure 8.1.1.1.1. Trends in bonding across the periodic table. The image is adapted from https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/02._Atoms%2C_Molecules%2C_and_Ions/2.5%3A_The_Periodic_Table. Otherwise this work by Stephen Contakes 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 8.1.1.1.2. As can be seen from Figure 8.1.1.1.2, 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**.

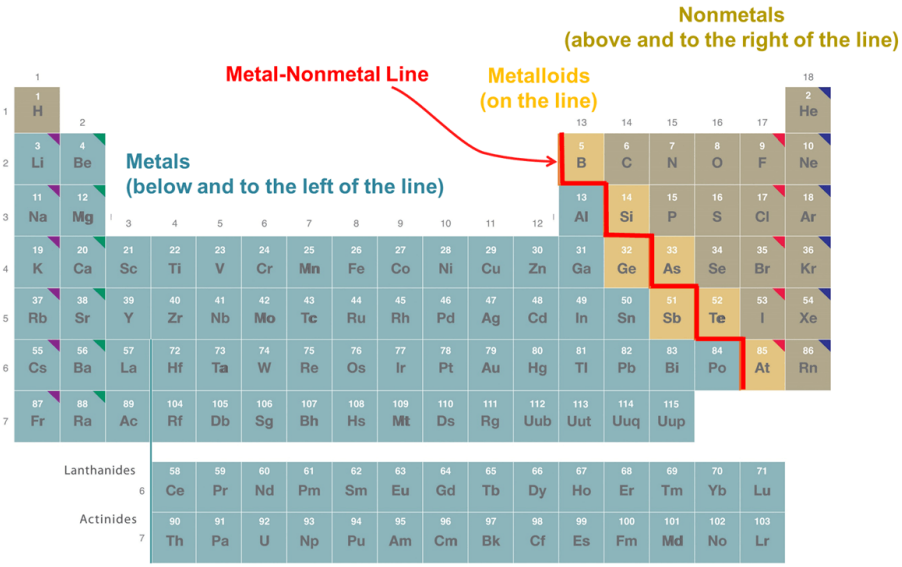


Figure 8.1.1.1.2. The metal-nonmetal-metalloid distinction and the metal-nonmetal "line". The image is adapted from https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/02._Atoms%2C_Molecules%2C_and_Ions/2.5%3A_The_Periodic_Table. Otherwise this 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 π-bonds sometimes have small or nonexistent band gaps. For example, the graphite allotrope of carbon is an outstanding electrical conductor because its π-valence band and π*-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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8.1.1.2: 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 8.1.1.2.1.

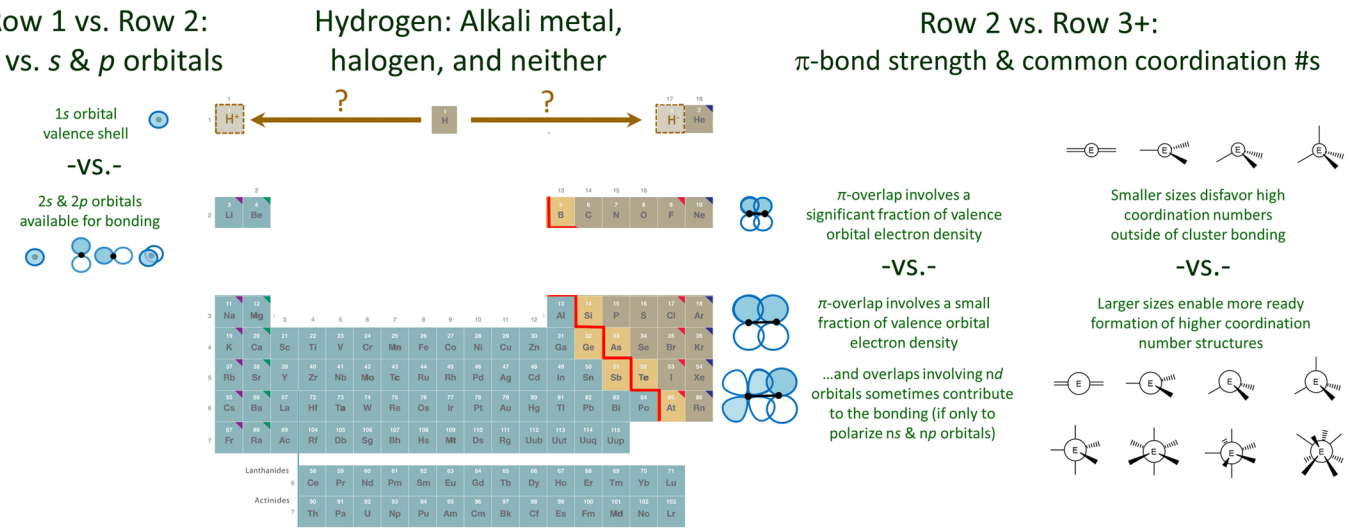


Figure 8.1.1.2.1. Factors that contribute to major differences in the chemical properties between the elements of the first two rows and between the row 2 elements and those in the rest of the periodic table. The image is adapted from https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/02._Atoms%2C_Molecules%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 1s orbital.

In the case of He the 1s 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 8.1.1.2.1, 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 8.1.1.2.2, Row 3+ elements have a greater tendency to form extended structures held together by single bonds than their Row 2 counterparts.

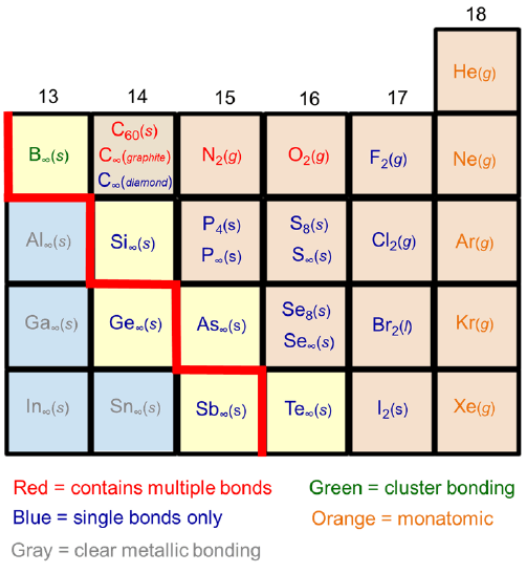


Figure 8.1.1.2.2. Characteristics of the common allotropes of selected *p* block elements. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

As shown in Figure 8.1.1.2.3, 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.

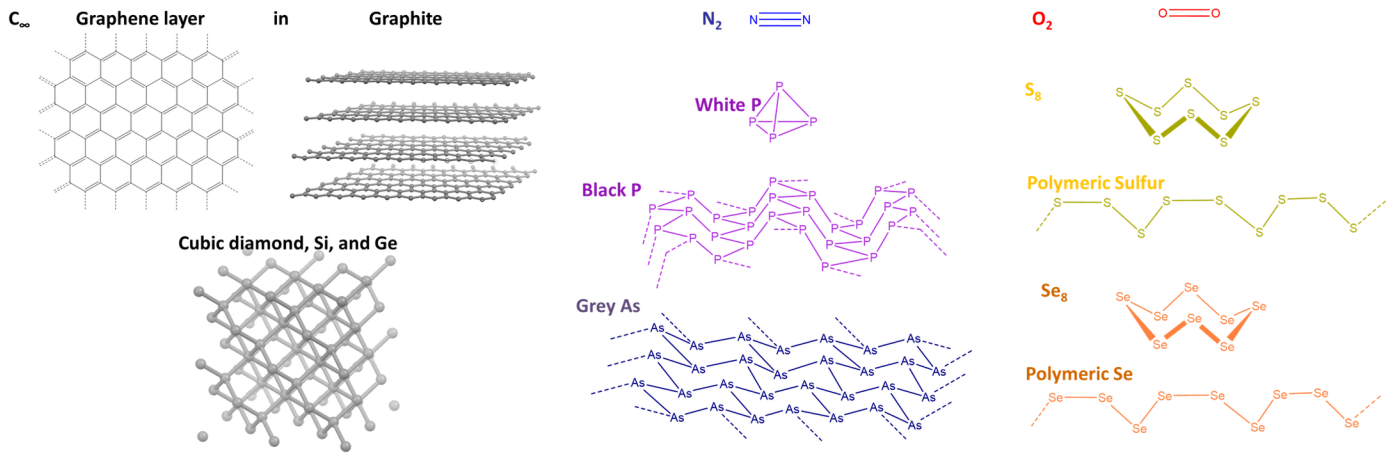


Figure 8.1.1.2.3. While row 2 elements like C, N, and O form structures held together by multiple bonds, their heavier cogeners form singly bonded clusters, rings, chains, sheets, and networks. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

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 8.1.1.2.1, **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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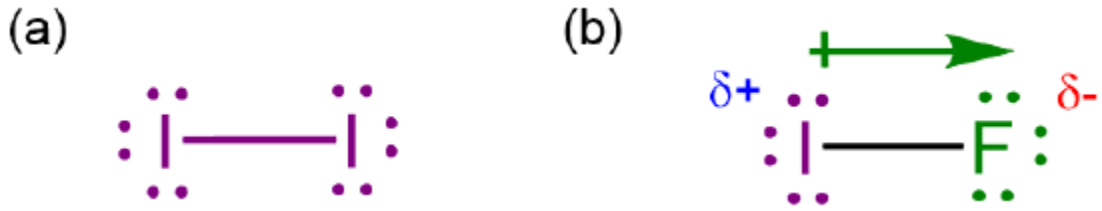
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8.1.2: Electronegativity increases and radius decreases towards the upper left of the periodic table, with electron withdrawing substituents, and with oxidation state

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 $8.1.2.I$.



Scheme $8.1.2.I$. (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.

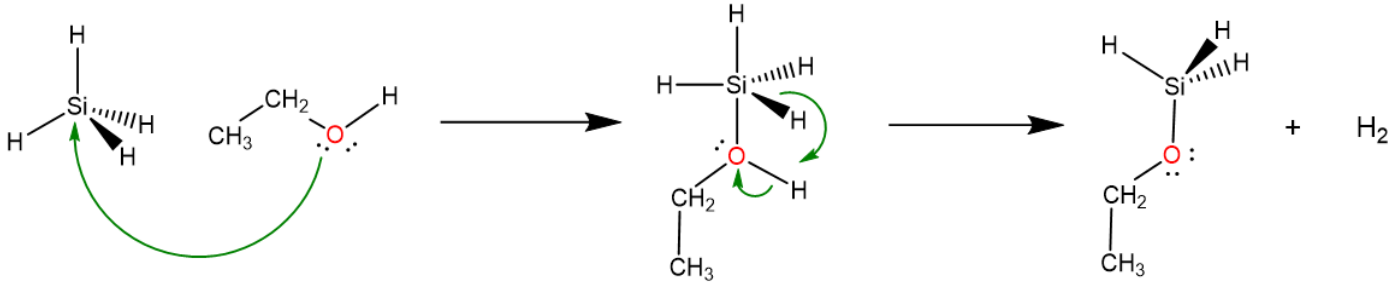
Because electronegativity determines the polarity of bonds and by extension molecules, it is one of the key determinants of the chemical and physical properties of main group compounds.

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

$$CH_4 + 4HOEt \rightarrow \text{No reaction}$$

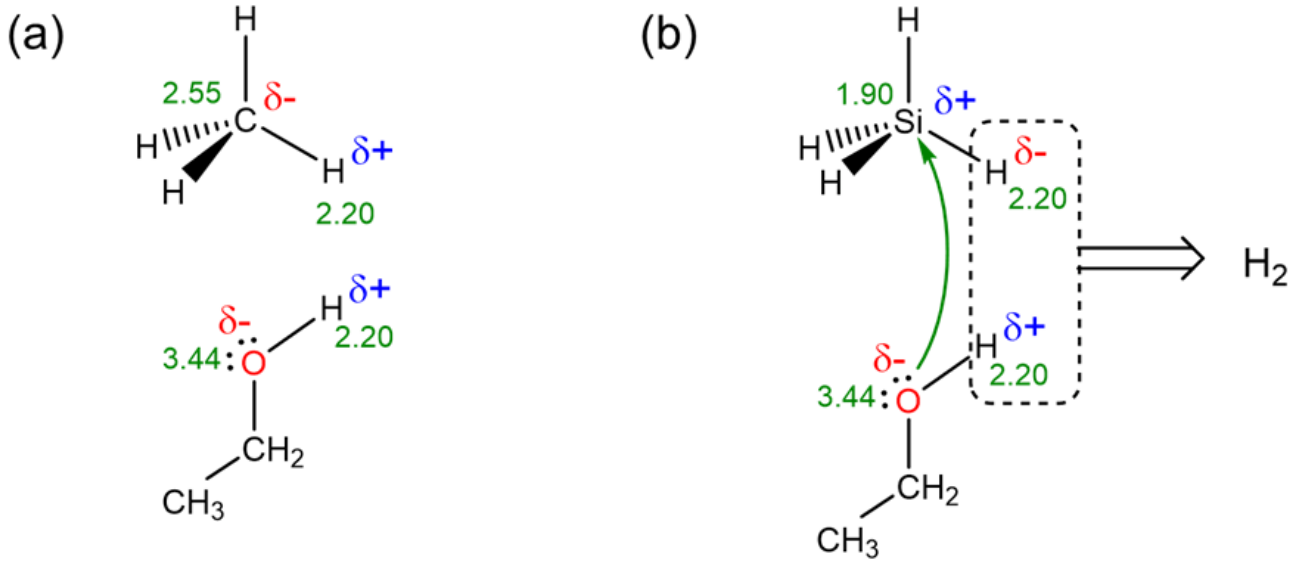
$$SiH_4 + 4HOEt \rightarrow Si(OEt)_4 + 4H_2$$

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 $8.1.2.I$. As can be seen in part a of Scheme $8.1.2.I$, 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 8.1.2.*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 8.1.2.1. 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 8.1.2.1**.** 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 8.1.2.2.

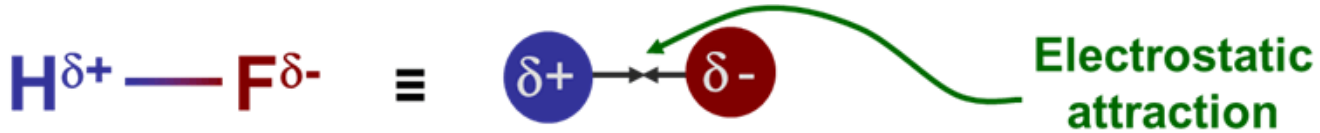


Figure 8.1.2.1. Electrostatic attraction between partial atomic charges in HF.

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 8.1.2.2:

$$\left|\chi_A - \chi_B\right| = \sqrt{E_{\text{A–B}}(\text{in eV}) - \frac{E_{\text{A–A}}(\text{in eV}) + E_{\text{B–B}}(\text{in eV})}{2}}$$

where A and B are a given pair of elements.

Equation 8.1.2.2 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 8.1.2.2.

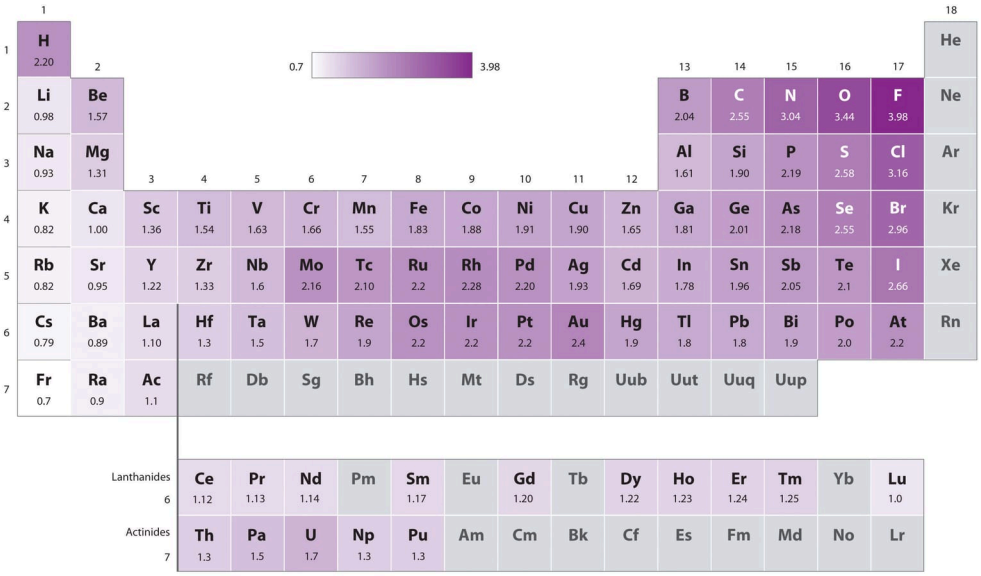


Figure 8.1.2.3. Pauling electronegativities of the elements. Taken from https://chem.libretexts.org/Courses/Mount_Royal_University/Chem_1201/Unit_2._Periodic_Properties_of_the_Elements/2.12%3A_Electronegativity

Electronegativity generally increases across a row and decreases down a group

As can be seen from the Pauling electronegativity values in Figure 8.1.2.4, 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.

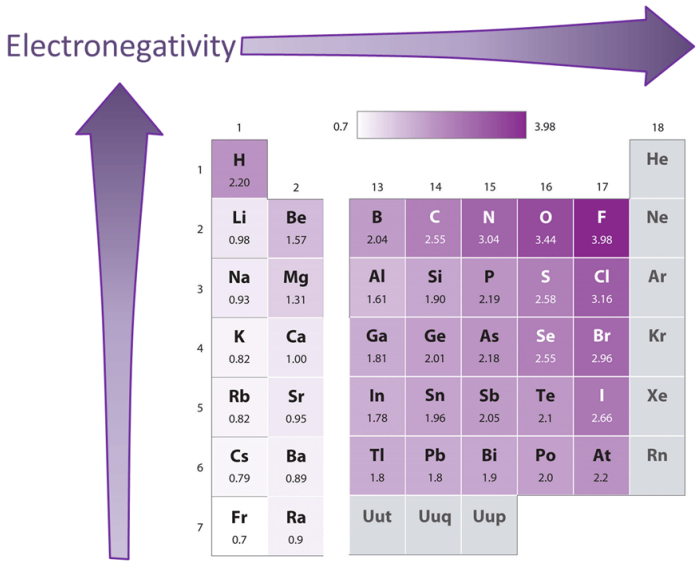


Figure 8.1.2.4. Pauling electronegativities of the main group elements. Adapted from https://chem.libretexts.org/Courses/Mount_Royal_University/Chem_1201/Unit_2._Periodic_Properties_of_the_Elements/2.12%3A_Electronegativity

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 8.1.2.5.

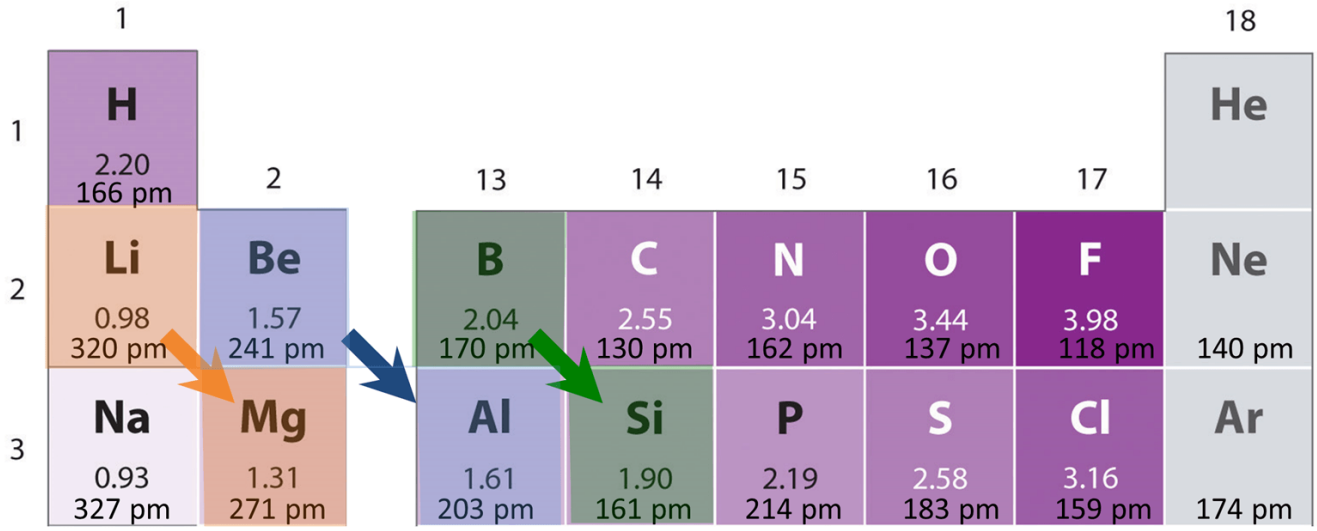


Figure 8.1.2.5. Some commonly recognized diagonal relationships among the main group elements, which are listed along with their Pauling electronegativities and calculated Van der Waals radii. The radii are taken as the radii calculated at the CCSD(T) level using an ANO-RCC basis set as reported in Mantina, 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 8.1.2.2. In contrast, the larger alkali metals form insoluble polymeric carbanion reagents, superoxides or peroxides and not oxides, and extremely unstable nitrides.

Table 8.1.2.2. 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 ($Table 8.1.2.3$). 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 8.1.2.3. Amphoteric behavior of the oxides and hydroxides of beryllium and aluminum.

Reaction	Be
Oxide hydrolysis to hydroxide	$BeO + H_2O \rightarrow Be(OH)_2$

Hydroxide as an Arrhenius and Brønsted Base	$Be(OH)_2 \rightarrow BeO(OH)^+ + OH^-$ or $Be(OH)_2 + 2H^+ \rightarrow Be^{2+} + 2H_2O$
Hydroxide as a Lewis Acid	$Be(OH)_2 + 2OH^- \rightarrow Be(OH)_4^{2-}$

- **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 8.1.2.4.

Table 8.1.2.4: 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_Properties/Electronegativity/Allred-Rochow_Electronegativity

H **2.20**																
Li **0.97**	Be **1.47**											B **2.01**	C **2.50**	N **3.07**	O **3.50**	F **4.10**
Na **1.01**	Mg **1.23**											Al **1.47**	Si **1.74**	P **2.06**	S **2.44**	Cl **2.83**
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**	Se **2.48**	Br **2.74**
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**	Te **2.01**	I **2.21**
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**	Po **1.76**	At **1.90**

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.

$$Mulliken\ electronegativity\ of\ Lewis\ acid, \chi \approx -\frac{E_{LUAO} + E_{HOAO}}{2}$$

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 8.1.2.4.

Table 8.1.2.4**.** 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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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

As with electronegativity, the ionization energy of the main group elements (Figure 8.1.3.1) decreases down a group and increases from left to right across the periodic table.

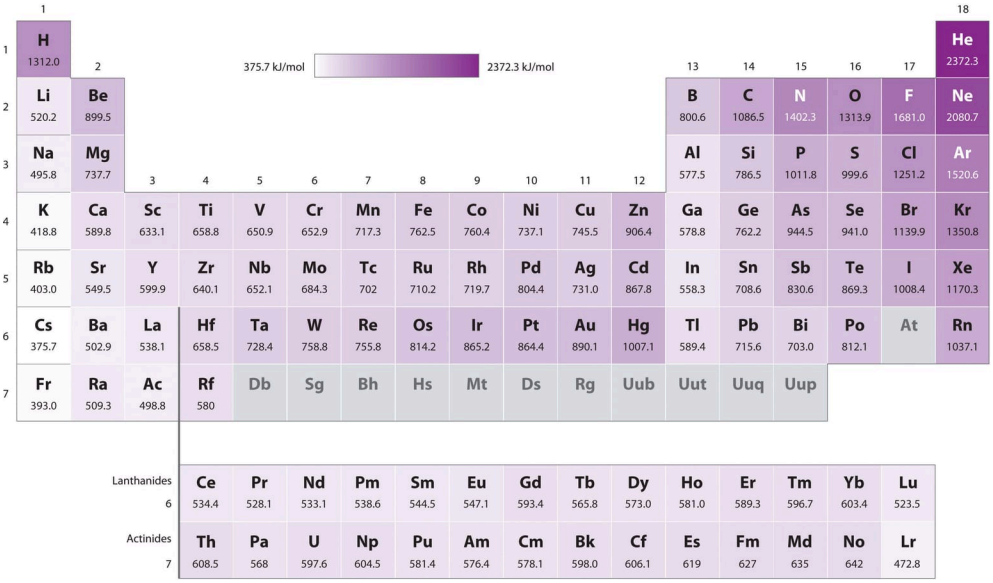


Figure 8.1.3.1. Ionization energies of the elements in kJ/mol. (CC BY-SA-NC 3.0; anonymous)

As may be seen in Figure 8.1.3.1, ionization energy does not increase steadily from left to right across a group. Instead, there are two discontinuities. These discontinuities are summarized in Figure 8.1.3.2.

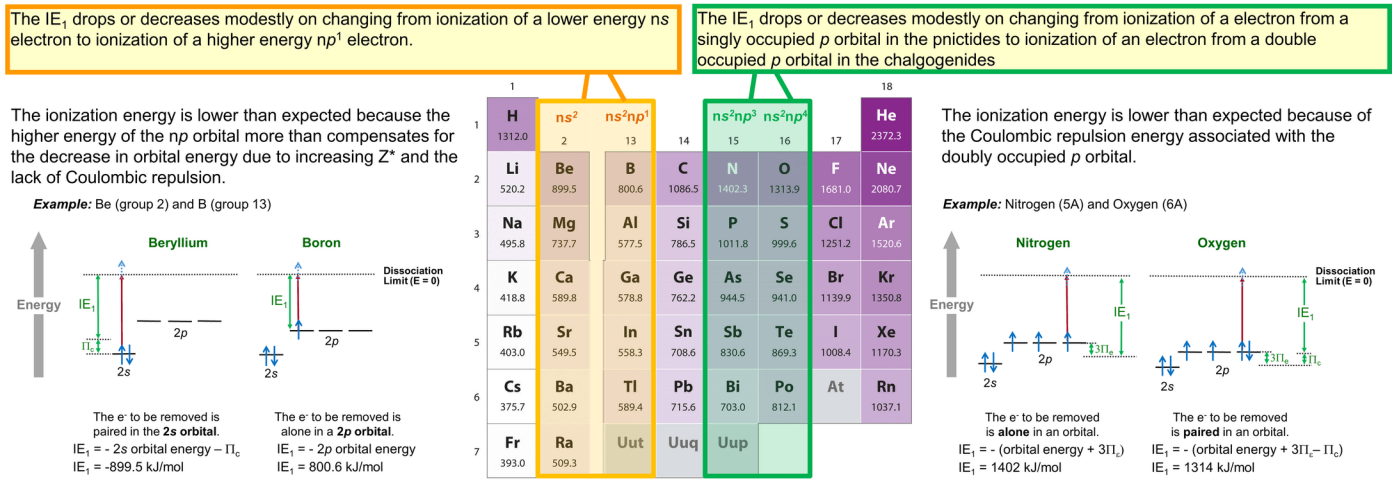


Figure 8.1.3.2. Discontinuities in the expected increase in first ionization energy (IE_1) trends among the main group elements and their explanation in terms of changing valence subshells and their occupancy. The periodic table of ionization energies in this figure is adapted from https://chem.libretexts.org/Courses/Mount_Royal_University/Chem_1201/Unit_2._Periodic_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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8.1.4: 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

$$\underset{\text{reductant}}{\text{substance}_{ox}(\text{solv})} + \text{ne}^- \rightarrow \underset{\text{oxidant}}{\text{substance}_{red}(\text{solv})}$$

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 \{{8{.}1{.}4{.}\eatSpaces{1} \endSpaces}\).

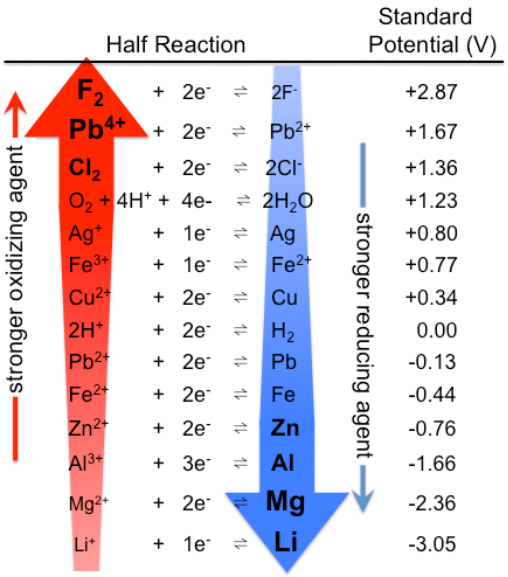


Figure 8.1.4.1. Substances with more positive reduction potentials are better oxidants while the reduction products of substances with more negative reduction potentials are better reductants. The image and redox potentials are taken from https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Supplemental_Modules_(Analytical_Chemistry)/Electrochemistry/Redox_Chemistry/Comparing_Strengths_of_Oxidants_and_Reductants

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 8.1.4.2.

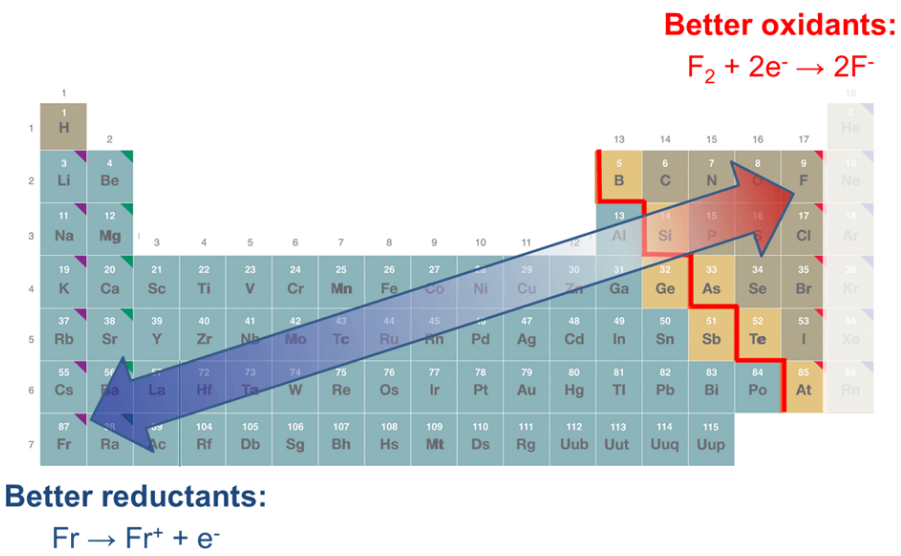


Figure 8.1.4.2. Idealized scheme showing how elements' ability to act as reductants roughly increases towards the lower left of the periodic table while, noble gases excepted, their oxidizing power increases towards the upper left.

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 8.1.4.1, 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 8.1.4.1, 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 8.1.4.1 . 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.

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This page titled 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 shared under a CC BY 4.0 license and was authored, remixed, and/or curated by Stephen Contakes.

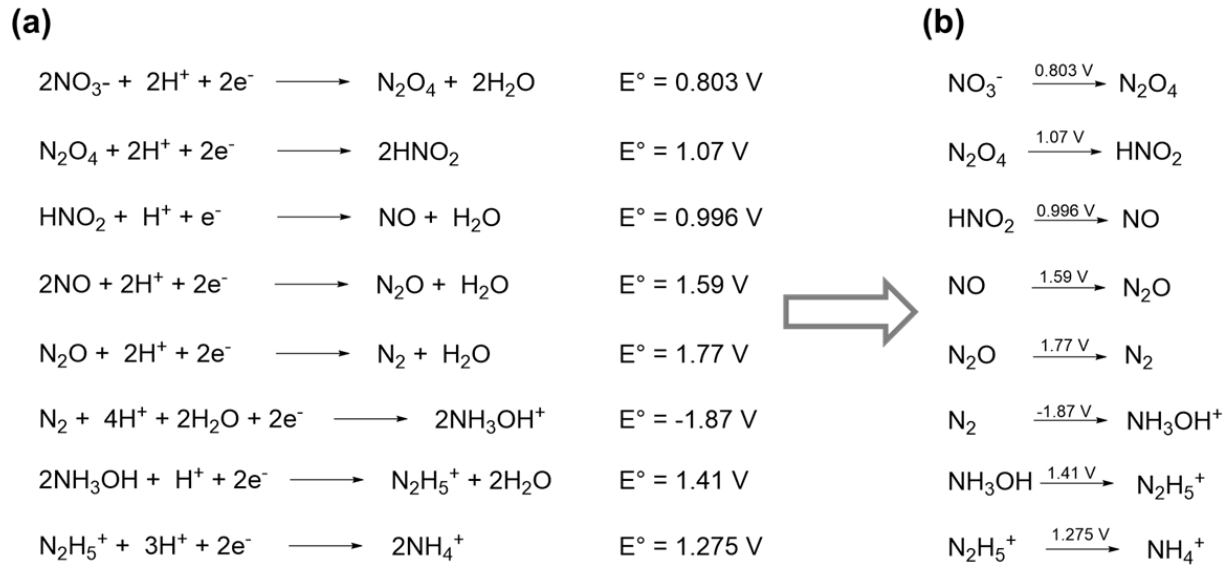
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8.1.4.1: Latimer Diagrams summarize elements' redox properties on a single line

Latimer diagrams helpfully summarize elements' redox chemistry in a compact format

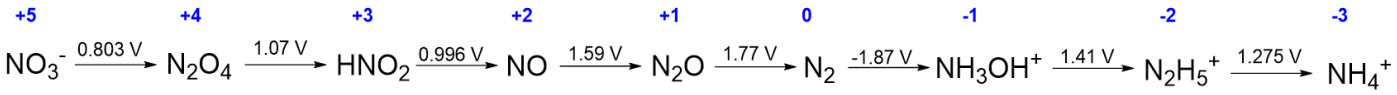
To see how Latimer diagrams work and why they are so useful, it is helpful to start with an example.

A selection of the redox reactions nitrogen is known to undergo in 1.0 *M* aqueous acid is given in Scheme $8.1.4.1.Ia$.



Scheme 8.1.4.1.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 $8.1.4.1.Ia$ 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 $8.1.4.1.Ia$ 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 $8.1.4.1.Ib$. Notice that in Scheme $8.1.4.1.Ib$, 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.

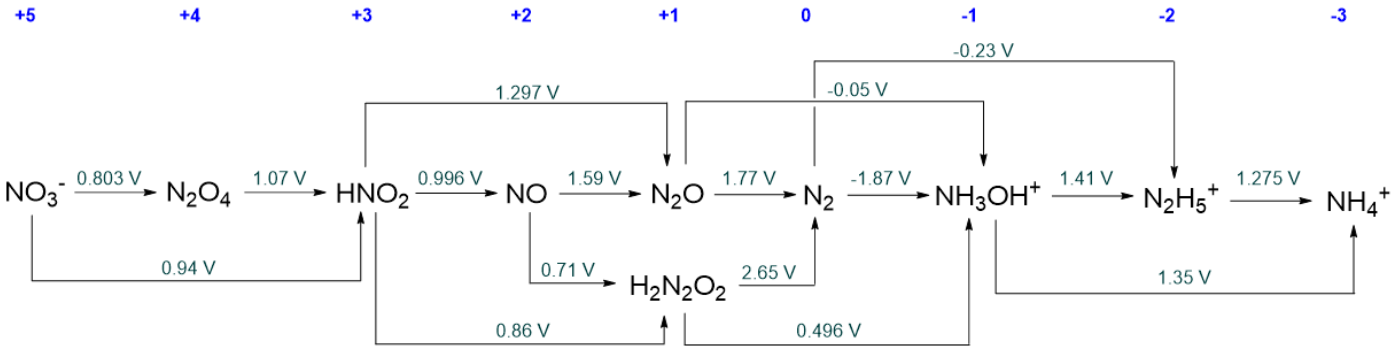


Scheme 8.1.4.1.II. Acidic Latimer diagram for nitrogen.

The type of diagram shown in Scheme 8.1.4.1.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 $8.1.4.1.II$.

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 8.1.4.1.*III*.



Scheme 8.1.4.1.III. Latimer Diagram for Nitrogen at pH 0. Redrawn from reference 1.

The diagram in Scheme 8.1.4.1.**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,

$$F_2(g) \; + \; 2H^+ \; 2e^- \; \rightarrow \; 2HF \quad E^\circ \; = \; 3.053 \text{ V} \;\; \text{in} \;\; \text{acid}$$

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 8.1.4.1.1 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:

    $$\text{Reduction} : Re^{VI}O_3 + H_2O + 2H^+ + e^- \rightarrow Re^{V}O_2 \cdot 2H_2O \qquad E^\circ = -0.446V$$

    $$\text{Oxidation} : Re^{VI}O_3 + H_2O \rightarrow Re^{VII}O_4^- + 2H^+ + e^- \qquad E^\circ = +0.889V$$

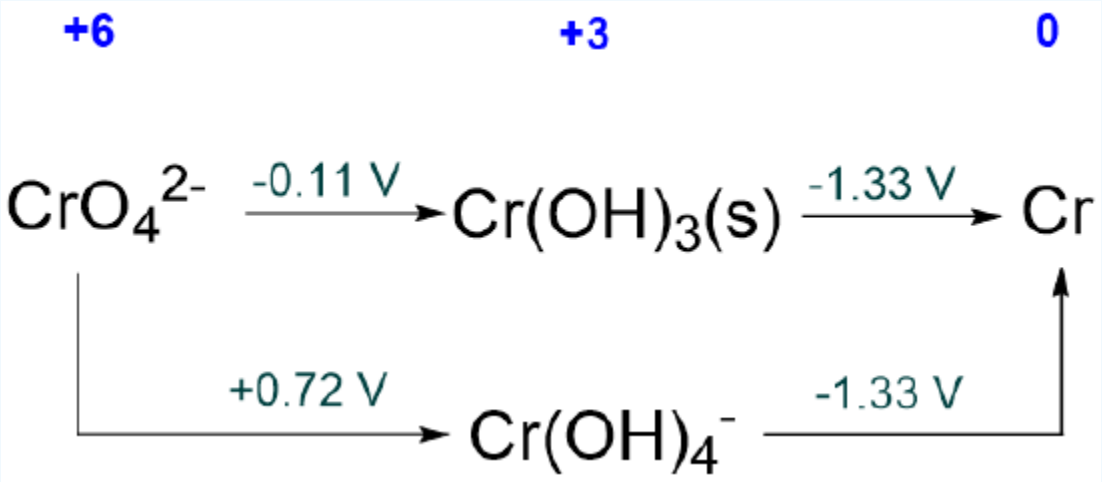
    $$\text{Sum} : 2Re^{VI}O_3 + 2H_2O \rightarrow Re^{VII}O_4^- + Re^{V}O_2 \cdot 2H_2O \qquad E^\circ = -0.446V + 0.889V = +0.443V$$

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 8.1.4.1.1

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?

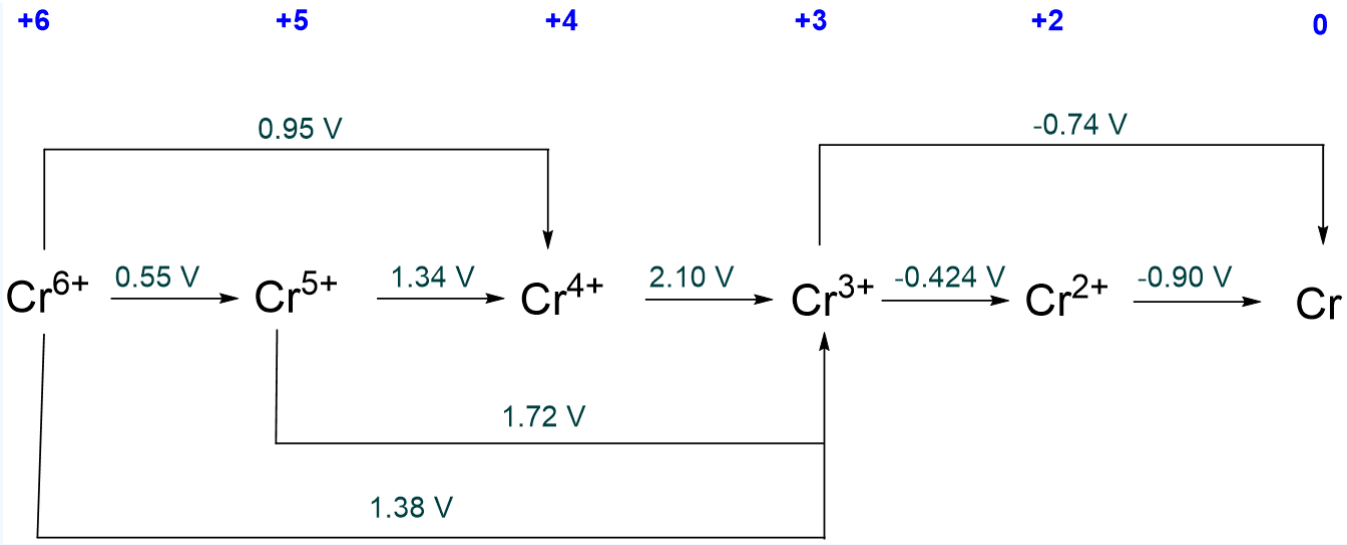


Solution

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 8.1.4.1.2

The Latimer diagram for Cr in pH 0 aqueous solution is given below. Which, if any, species are unstable with respect to disproportionation?

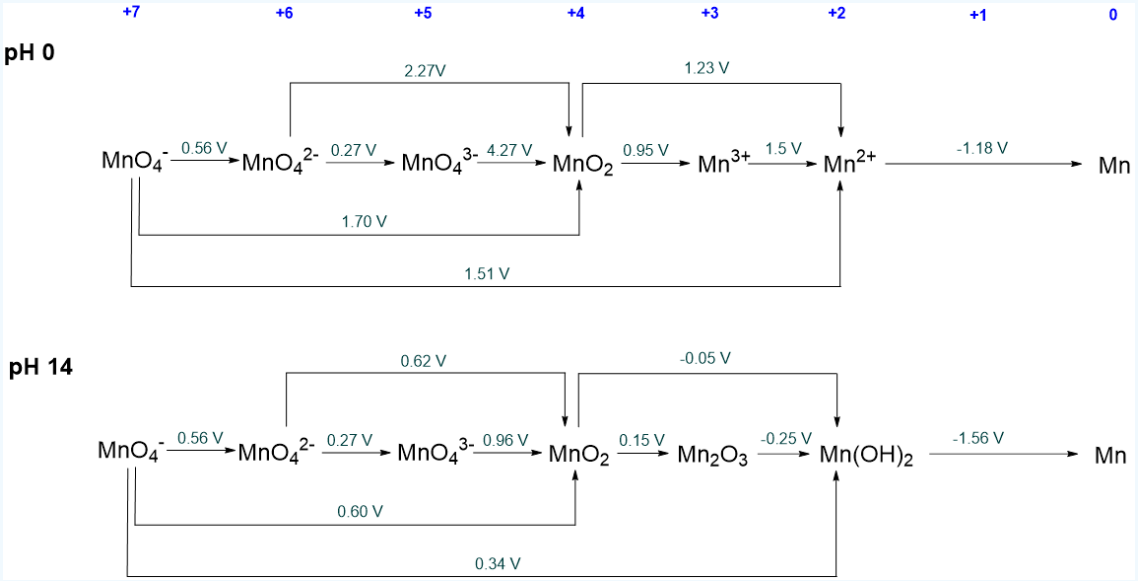


Solution

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 8.1.4.1.3

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.

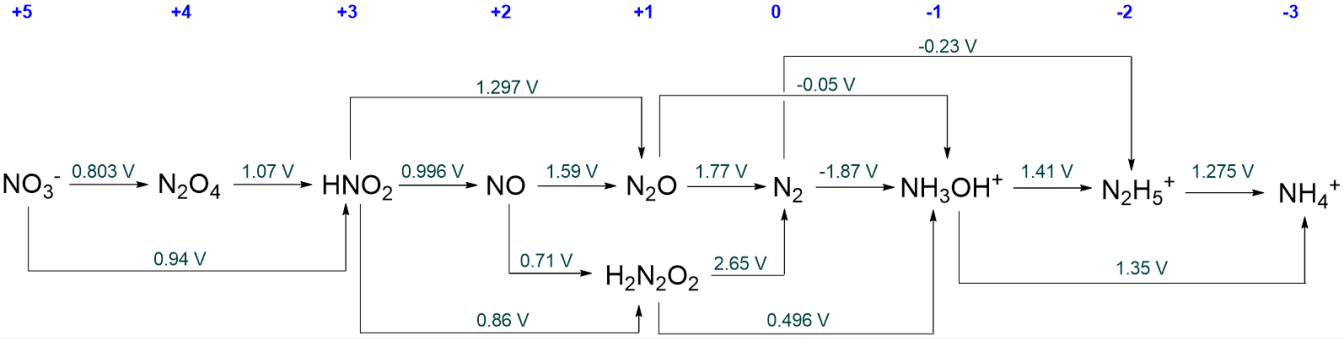
- MnO_4^{3-} is unstable with respect to MnO_4^{2-} and MnO_2. However, since MnO_4^{2-} is unstable with respect to disproportionation the ultimate products of the disproportionation will be MnO_4^- and MnO_2.
- Mn^{3+} is unstable towards disproportionation to MnO_2 and Mn^{2+}.

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 Runaway argument for \eatSpaces?



Which nitrogen species in Scheme 8.1.4.1.III, (which for convenience is reproduced above) are unstable with respect to disproportionation?

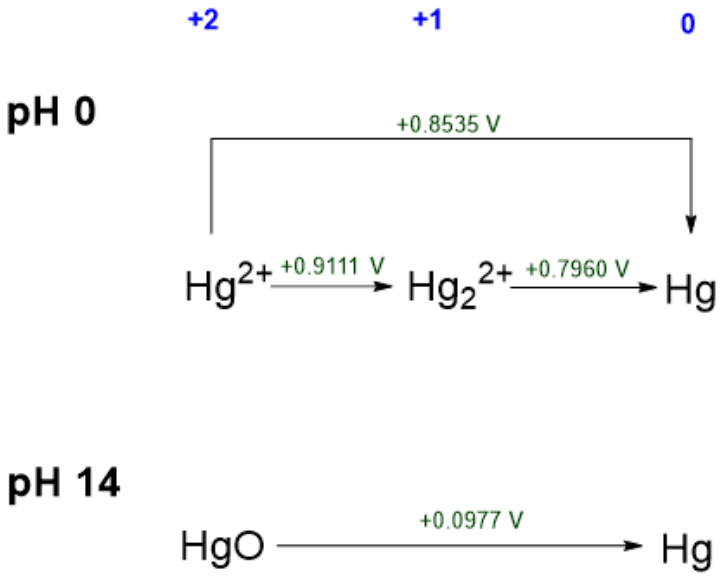
Answer available at the end of this section.

Exercise Runaway argument for \eatSpaces?

As far as you are able, determine what each metastable nitrogen species will disproportionate to at pH 0.

Answer available at the end of this section.

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 8.1.4.1.1 and 8.1.4.1.2. A simple instance involves the acidic and basic Latimer diagrams of mercury shown in Scheme 8.1.4.1.IV.

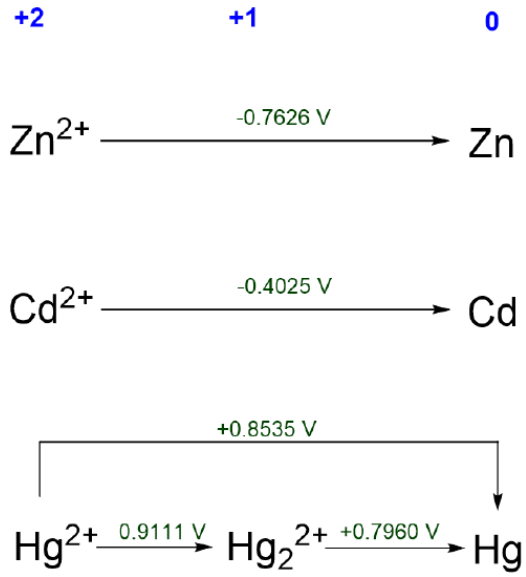


Scheme $8.1.4.1.IV$: Latimer diagrams for mercury in aqueous solution.

From Scheme $8.1.4.1.IV$, 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 $8.1.4.1.V$).



Scheme $8.1.4.1.V$. Latimer diagrams for the group 12 elements in pH 0 aqueous solution.

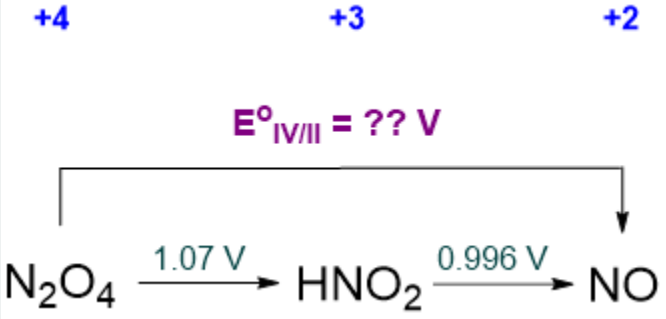
From Scheme $8.1.4.1.V$, it is clear that Zn and Cd exhibit similar redox behavior. Both should dissolve at pH 0 to give dications. In

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.

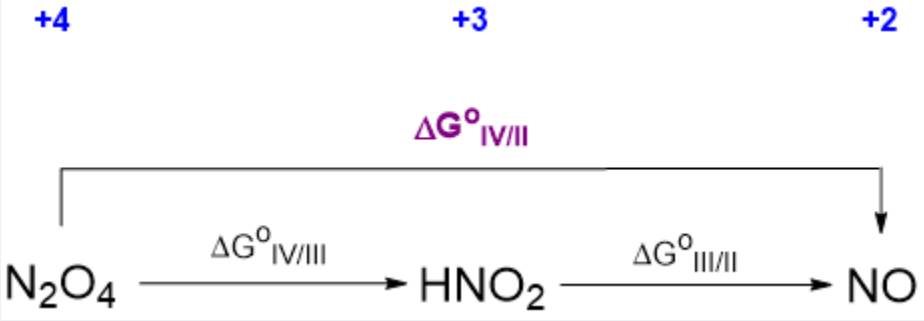
Note 8.1.4.1.1.

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 Runaway argument for \eatSpaces?. Part of that diagram is reproduced as Scheme Runaway argument for \eatSpaces? below.



Scheme Runaway argument for \eatSpaces?. 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 Runaway argument for \eatSpaces?.

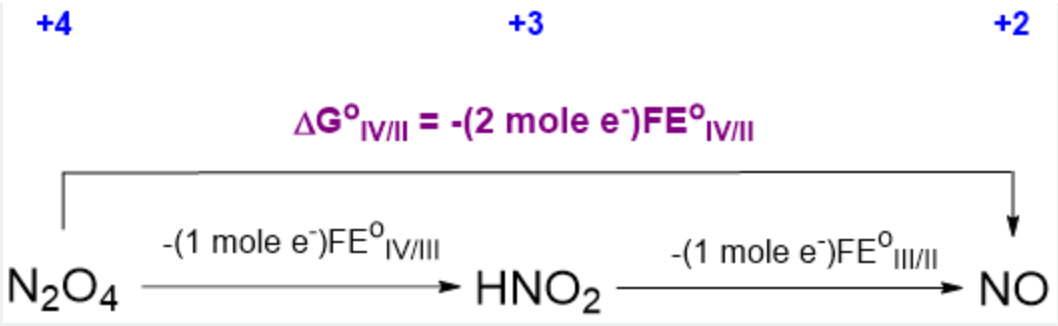


Scheme Runaway argument for \eatSpaces?. Thermodynamic cycle that may be used to determine $E^\circ_{N_2O_4 \rightarrow NO}$.

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 Runaway argument for \eatSpaces?.



Scheme Runaway argument for \eatSpaces?. Thermodynamic cycle expressed in terms of standard potentials.

From Scheme Runaway argument for \eatSpaces? 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 Runaway argument for \eatSpaces? 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.

Answers

Exercise Runaway argument for \eatSpaces?

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 Runaway argument for \eatSpaces?

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 $N_2H_5^+$.

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8.1.4.2: 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 NE°, sometimes expressed as nE°. On this page N will be used in place of n to avoid confusion with the common use of n in redox chemistry to denote the number of electrons involved in individual oxidation or reduction reaction steps.

In Frost diagrams the quantity NE° is used since it is proportional to the standard free energy change for conversion of the free element to that oxidation state.

In NE°

- N is the oxidation state.
- E° is the standard *reduction potential* associated with *interconversion between the free element and that oxidation state*.

For a proof that NE° is proportional to the free energy of an element's oxidation state and more information on how NE° may be calculated, see Note $8.1.4.2.1$ 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 NE° is a measure of thermodynamic stability, the lower its value the more stable the state. Moreover, since NE° measures stability relative to the free element, negative values of NE° indicate that a state is more stable than the element, while positive values indicate that the state is less stable.

Consider the Frost diagram for copper at pH 0 shown in Figure $8.1.4.2.1$.

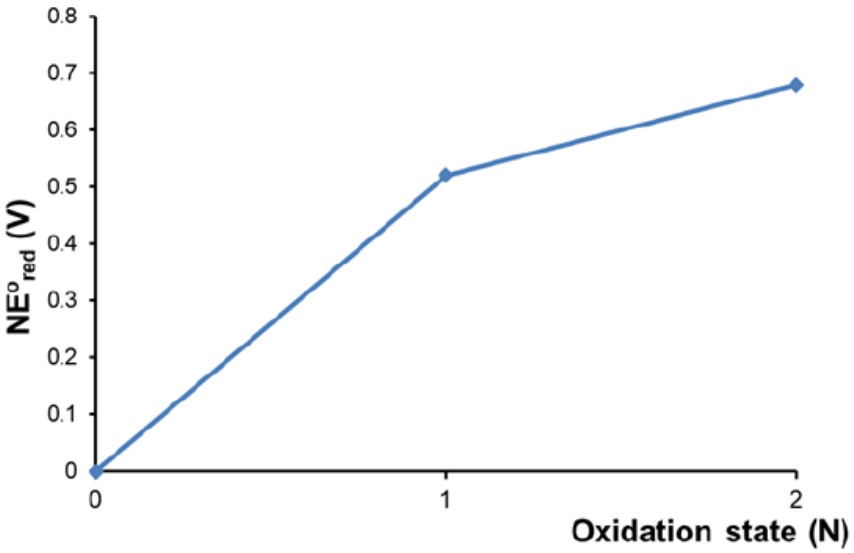


Figure 8.1.4.2.1. Frost diagram for copper in aqueous acid. (CC BY-SA 4.0 International; Stephen Contakes)

As can be seen in Figure 8.1.4.2.1, Cu^{+} and Cu^{2+} are both higher in free energy ($\propto NE^{\circ}$) than free Cu. This is consistent with copper's status as a noble metal that can only be dissolved in acid with the aid of oxidizing agents like O_2, H_2O_2, or NO_3^- (*e.g.,* as in HNO_3).

The acidic Frost diagram of Nickel shown in Figure 8.1.4.2.2 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).

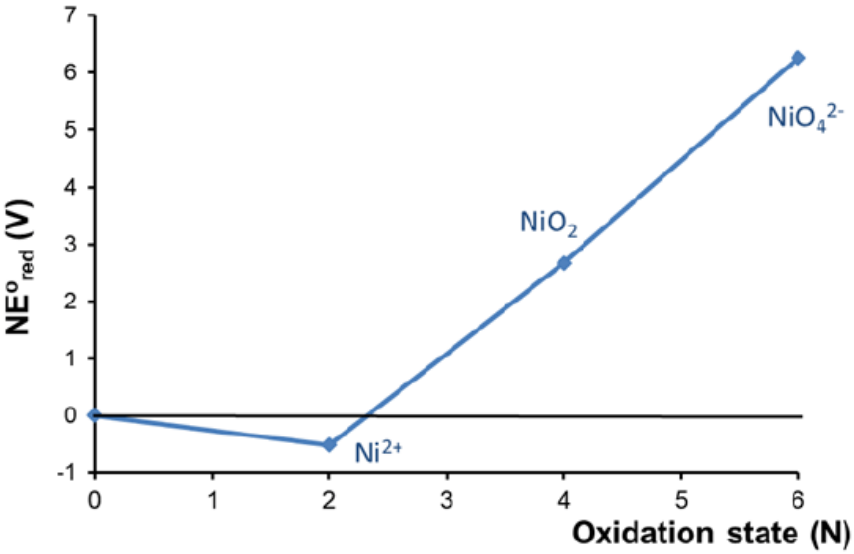


Figure 8.1.4.2.2. Frost diagram for nickel in aqueous acid. (CC BY-SA 4.0 International; Stephen Contakes)

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 8.1.4.2.1. Interpreting a Frost Diagram

Consider the Frost diagram of Cr in acid shown in Figure 8.1.4.2.3. What can be determined about the relative stability of chromium's oxidation states in acid?

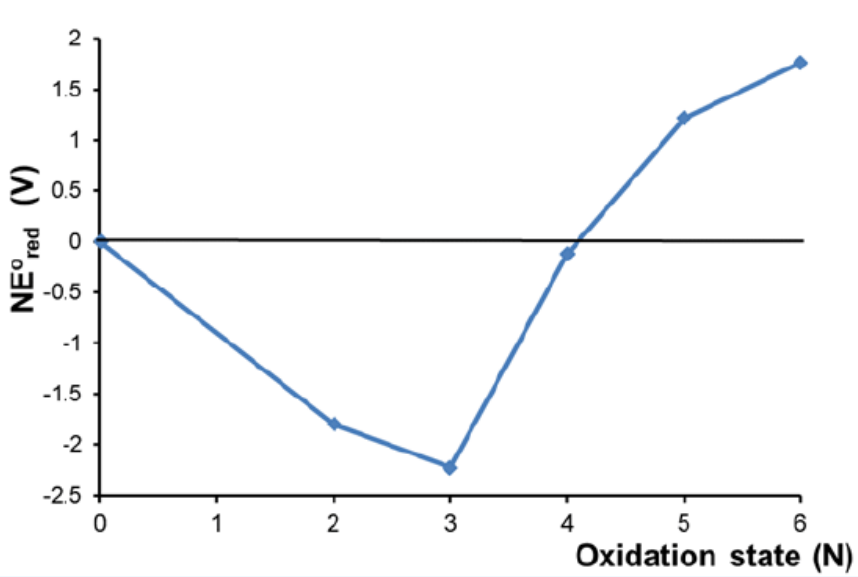


Figure 8.1.4.2.3. Frost diagram for Cr in acidic solution. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

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 8.1.4.2.4.

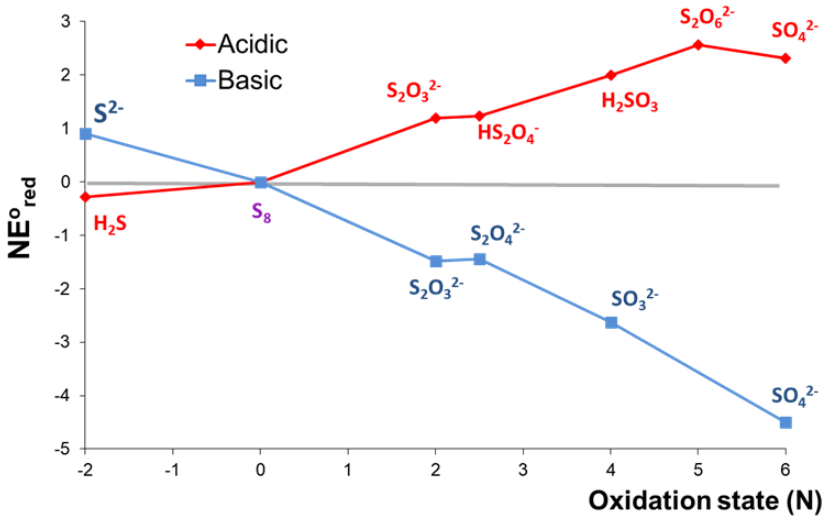


Figure 8.1.4.2.4. Frost diagrams for sulfur at pH 0 and 14. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

As can be seen in Figure 8.1.4.2.4, 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 8.1.4.2.5.

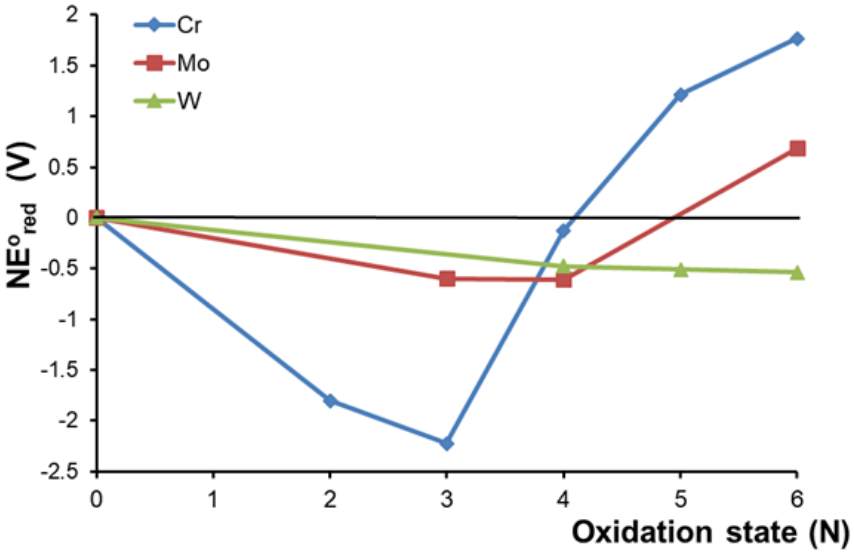


Figure 8.1.4.2.5. Frost diagrams for the group 6 elements at pH 0. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Several trends may be noted from the data in Figure 8.1.4.2.5. 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 8.1.4.2.6.[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).

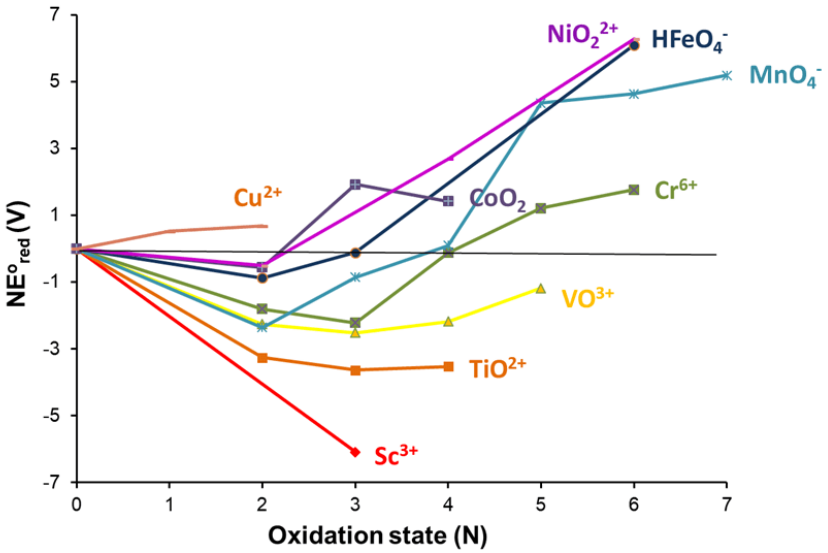


Figure 8.1.4.2.6. Frost diagrams for the first transition series at pH 0. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

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 8.1.4.2.7*a*.

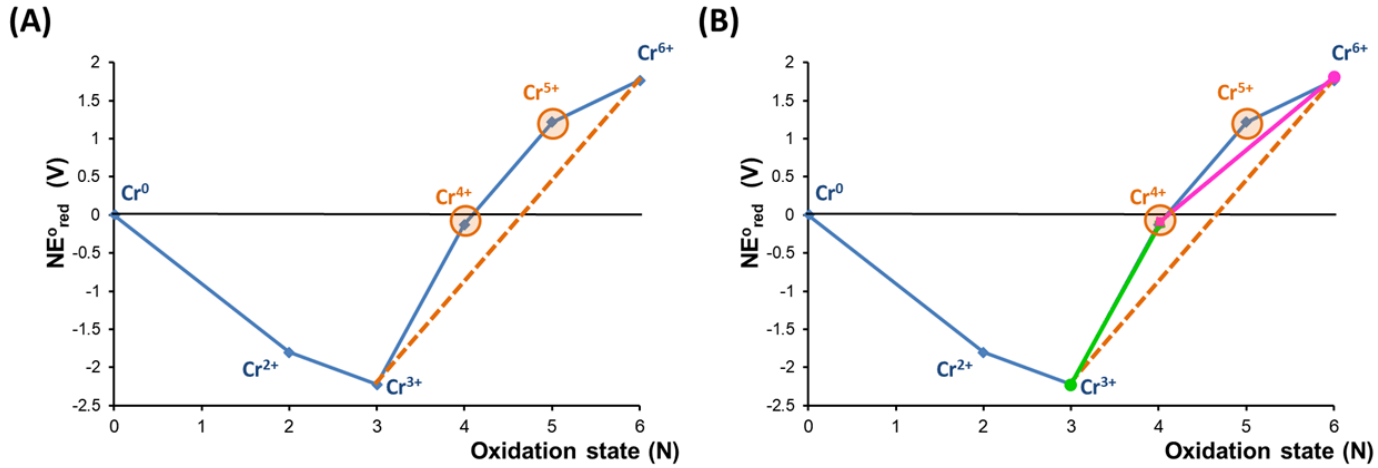


Figure 8.1.4.2.7. (a) Frost diagram for Cr in acidic solution showing that the Cr^{4+} and Cr^{5+} states lie above a tie-line between the Cr^{3+} and Cr^{6+} states. (b) In the case of Cr^{4+}, disproportionation is favored because the $Cr^{4/3+}$ potential (slope of the green tie-line connecting the 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 8.1.4.2.7*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 8.1.4.2.7*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 8.1.4.2.2.

Example 8.1.4.2.2. Systematic identification of Mn redox states that are unstable towards disproportionation in acid.

Consider the Frost diagram of Mn in acid shown in Figure 8.1.4.2.8. Which, if any, of manganese's oxidation states are unstable towards disproportionation at pH 0?

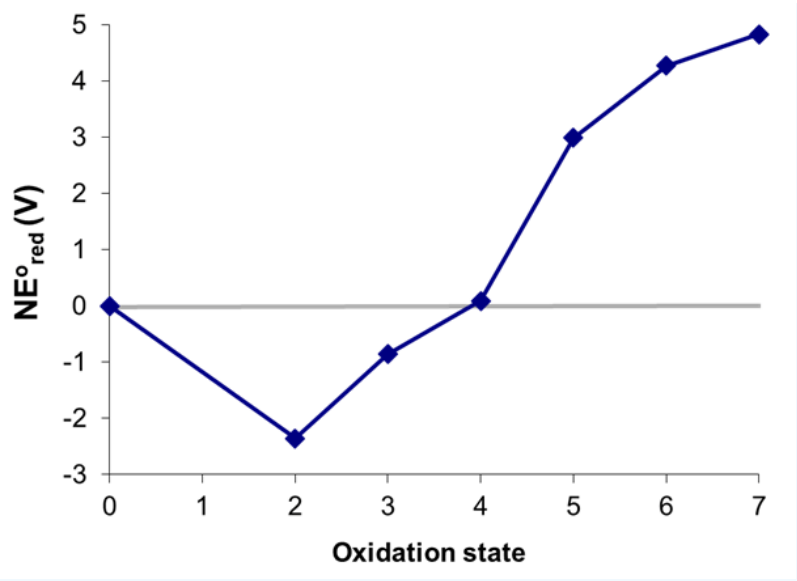
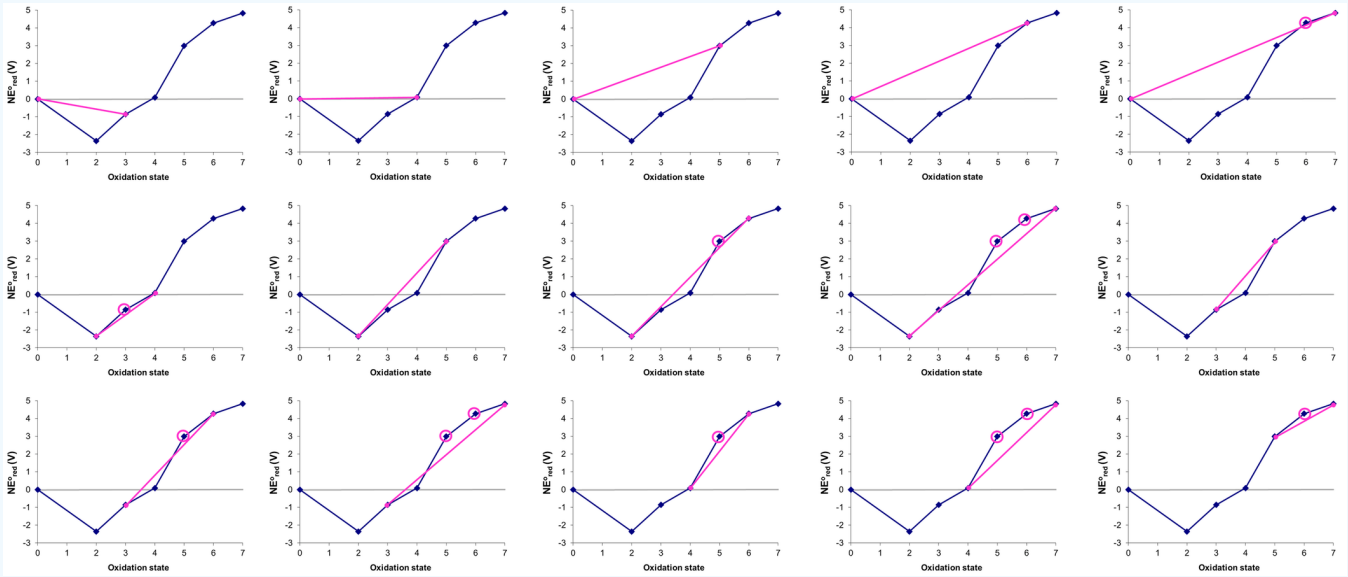


Figure 8.1.4.2.8. Frost diagram for Mn at pH 0. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

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 8.1.4.2.9*a*.

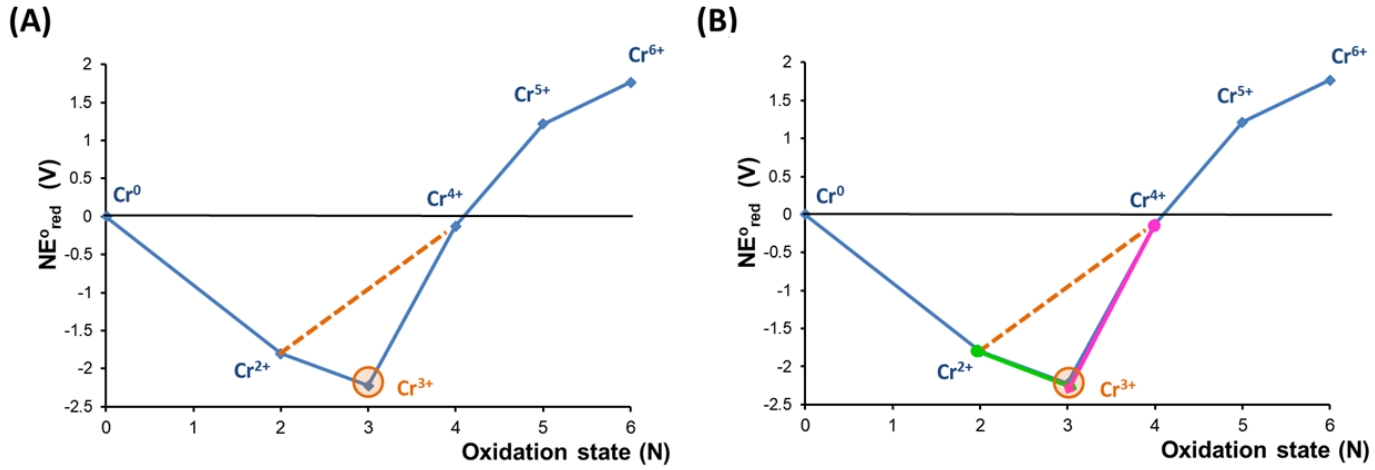


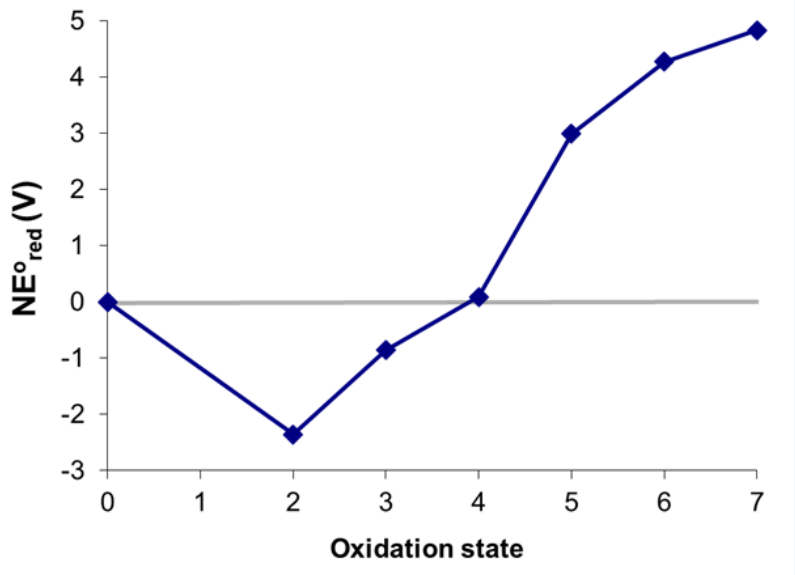
Figure 8.1.4.2.9. (a) Frost diagram for Cr in acidic solution showing that the Cr^{3+} redox state lies below a tie-line between the Cr^{2+} and Cr^{4+} states. (b) The slope of the green line connecting the Cr^{2+} and Cr^{3+} states is less than that of the pink line connecting the Cr^{3+} and Cr^{4+} states. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

As shown in Figure 8.1.4.2.9*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 8.1.4.2.3.

Example 8.1.4.2.3. 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 8.1.4.2.8 of Example 8.1.4.2.2, 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 8.1.4.2.2.

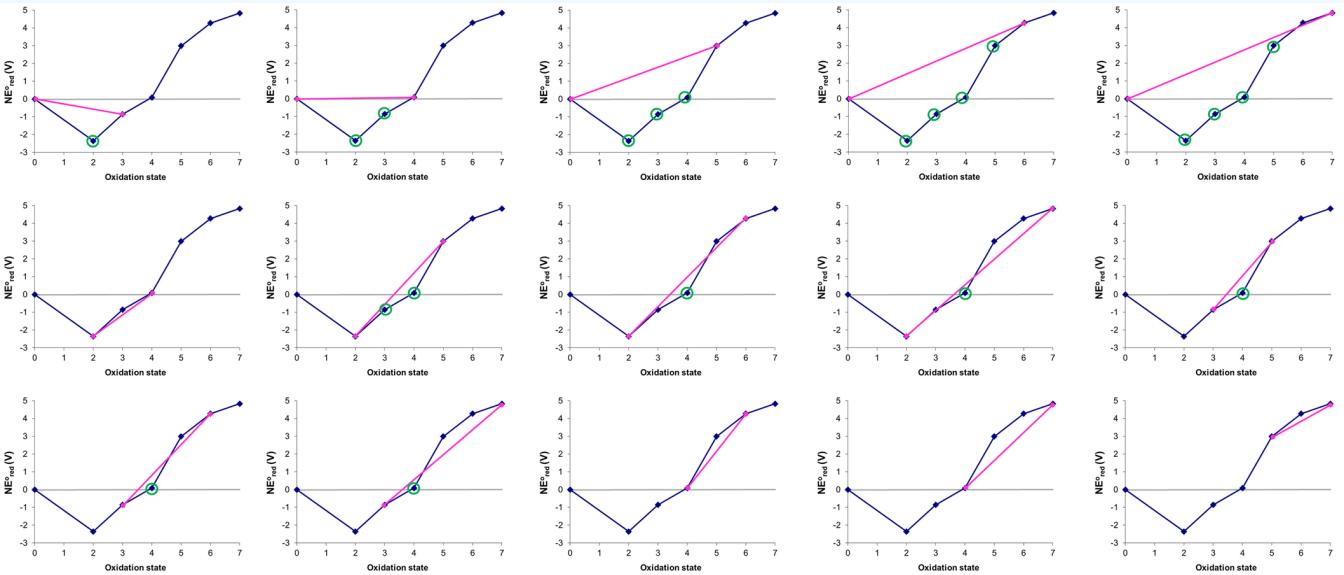


Figure above: the lower energy comproportionation products that species form are circled in green. The comproportionations identified involve the following pairs of oxidation states:

- 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 8.1.4.2.3 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 8.1.4.2.1

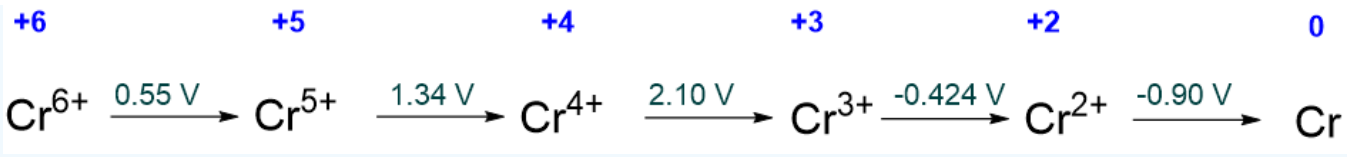
Using the simplified Latimer diagram for Cr in aqueous acid, reproduced below, verify that the disproportionation of Cr^{4+} to Cr^{3+} and Cr^{6+} is thermodynamically spontaneous.



Answer available at the end of this section.

Exercise 8.1.4.2.2

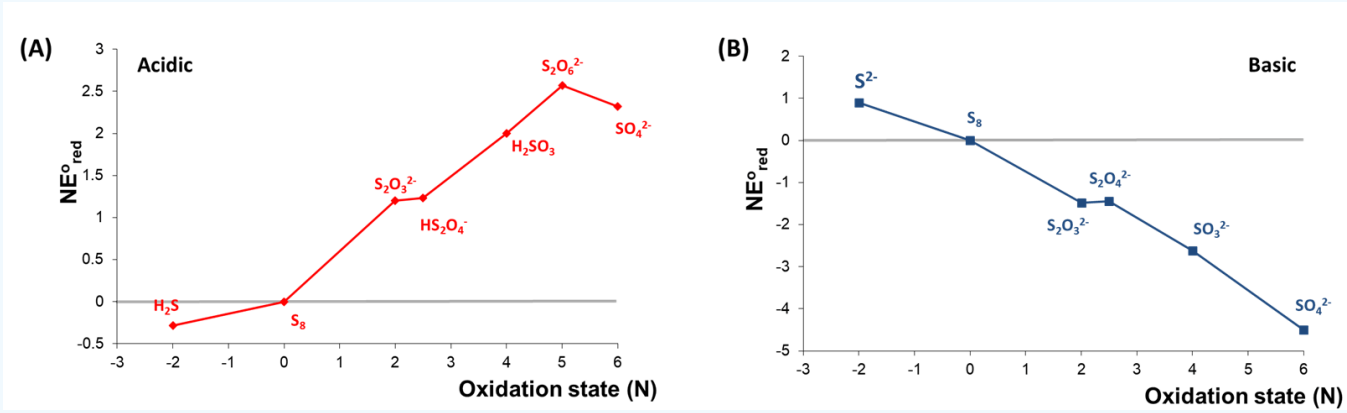
Using the simplified Latimer diagram for Cr in aqueous acid, reproduced below, verify that the comproportionation of Cr^{2+} and Cr^{4+} to Cr^{3+} is thermodynamically spontaneous.



Answer available at the end of this section.

Exercise 8.1.4.2.3. 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 available at the end of this section.

Appendix

Note 8.1.4.2.1. 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

$$E^\circ_{ox} = E^\circ = -E^\circ_{red}$$

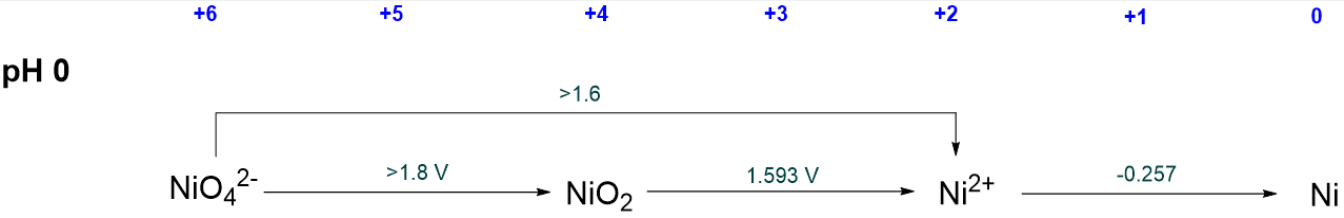
So that for positive oxidation states,

$$\Delta G^\circ_{ox} = -\Delta G^\circ_{red} = -(-nFE^\circ_{red}) = F(NE^\circ)$$

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°:

$$-n_{e^-,NiO_2 \rightarrow Ni} E^\circ_{NiO_2 \rightarrow Ni} = NE^\circ_{Ni \rightarrow NiO_2} = -n_{e^-,NiO_2 \rightarrow Ni^{2+}} E^\circ_{NiO_2 \rightarrow Ni^{2+}} + -n_{e^-,Ni^{2+} \rightarrow Ni} E^\circ_{Ni^{2+} \rightarrow Ni}$$

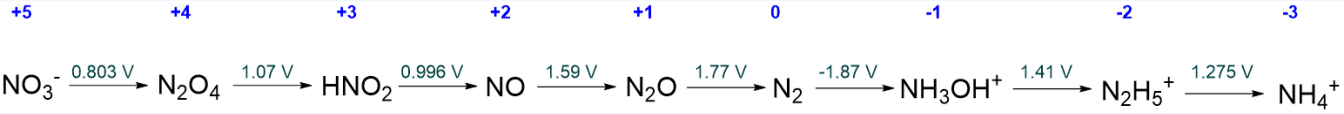
From this expression the value of $NE^\circ_{Ni \rightarrow NiO_2}$ may be calculated by inserting the relevant reduction potentials and number of electrons:

$$NE^\circ_{Ni \rightarrow NiO_2} = 2 \times (+1.593V) + 2 \times (-0.257V) = +2.672V$$

For complex cases it can be helpful to tabulate the calculations, as is done in the following example.

Example 8.1.4.2.1: 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 8.1.4.2.1. 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.

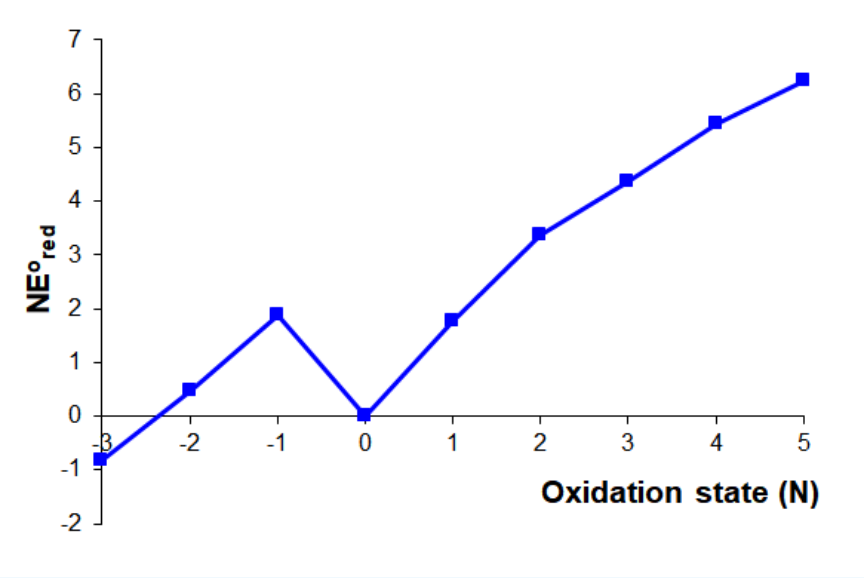
Table 8.1.4.2.1: Calculation of NE° for each oxidation state of nitrogen.

Oxidation State	Step	NE° =	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.

Oxidation State	Step	NE° =	Calculated as the sum of the steps	Notes
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.

Contributors and Attributions

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Answers

Exercise 8.1.4.2.1

The disproportionation of Cr^{4+} to Cr^{3+} and Cr^{6+} is the sum of two processes:

$$Cr^{4+}\text{reduction}: \quad Cr^{4+} + e^- \rightarrow Cr^{3+} \qquad E^\circ_{Cr^{4/3+}} = 2.10\ V$$

$$Cr^{4+}\text{oxidation}: \quad Cr^{4+} \rightarrow Cr^{6+} + 2e^- \qquad E^\circ = -E^\circ_{Cr^{6/4+}}$$

$$\text{Sum}: \quad 3Cr^{4+} + \rightarrow Cr^{6+} + 2Cr^{3+} \qquad E^\circ_{\text{disproportionation}} = E^\circ_{Cr^{4/3+}} - E^\circ_{Cr^{6/4+}}$$

The value of $E^\circ_{Cr^{6/4+}}$ is just the sum of the $Cr^{6/5+}$ and $Cr^{5/4+}$ reduction potentials (+0.55 V + 1.34 V) or +1.89 V. Consequently,

$$E^\circ_{\text{disproportionation}} = E^\circ_{Cr^{4/3+}} \qquad E^\circ_{Cr^{6/4+}} = 2.10\ V - 1.89\ V = +0.21\ V$$

which is spontaneous.

Exercise 8.1.4.2.2

The comproportionation of Cr^{2+} and Cr^{4+} to Cr^{3+} is the sum of two processes:

$$Cr^{4+}\text{reduction}: \quad Cr^{4+} + e^- \rightarrow Cr^{3+} \qquad E^\circ_{Cr^{4/3+}} = +2.10\ V$$

$$Cr^{2+}\text{oxidation}: \quad Cr^{2+} \rightarrow Cr^{3+} + e^- \qquad E^\circ = -E^\circ_{Cr^{3/2+}} = -(-0.424\ V) = +0.424\ V$$

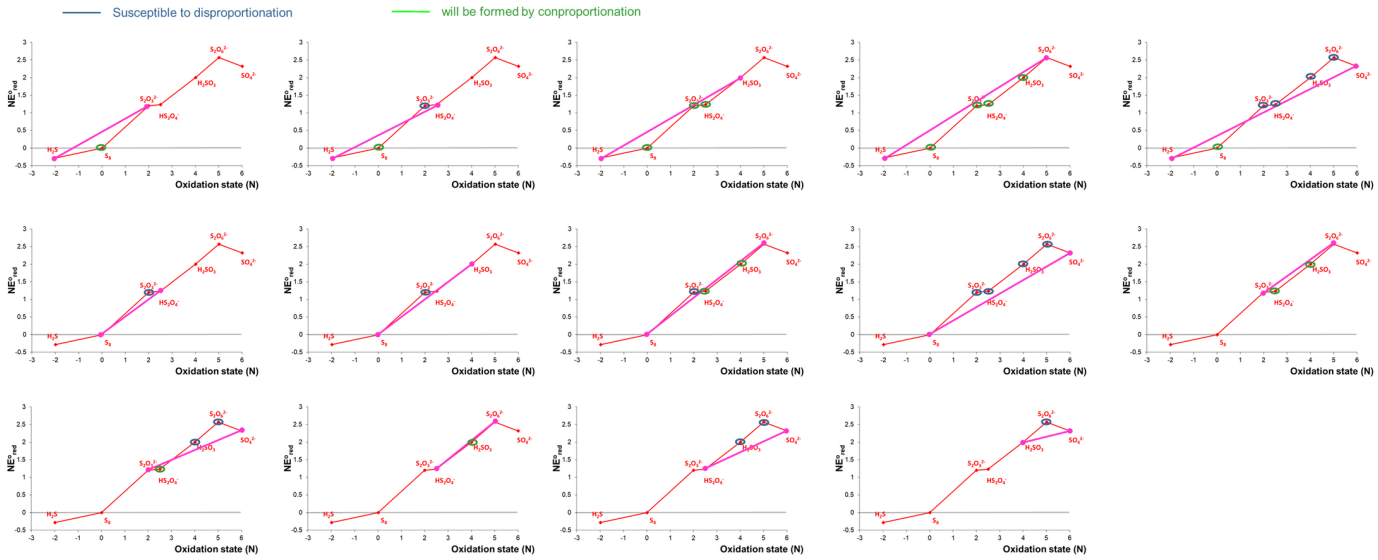
$$\text{Sum}: \quad Cr^{2+} + Cr^{4+} \rightarrow 2Cr^{3+} \qquad E^\circ_{\text{comproportionation}} = +2.10\ V + 0.424\ V = +2.524\ V$$

Since $E^\circ_{\text{comproportionation}}$ is positive, the comproportionation is spontaneous.

Exercise 8.1.4.2.3**. Identifying thermodynamically favored comproportionation and disproportionation reactions.**

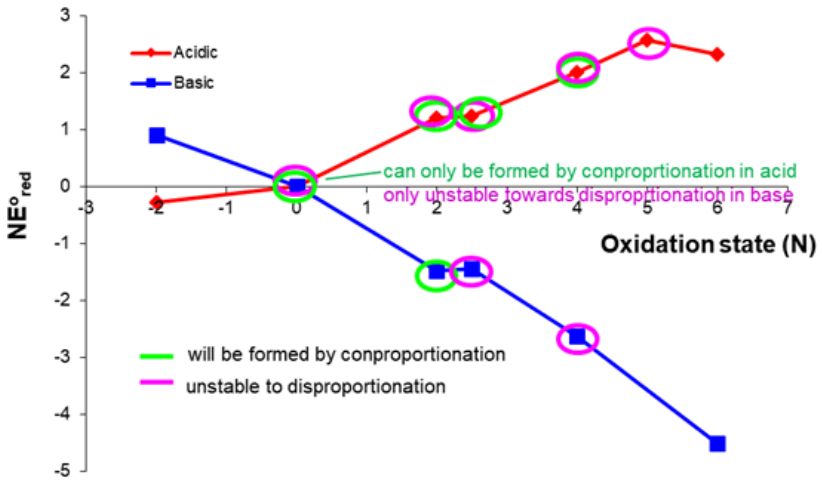
The species that are unstable towards *disproportionation* and *comproportionation* may be identified by constructing tie-lines between nonadjacent redox states and identifying any that fall above and below these lines. Species that are unstable to *disproportionation* will lie above a line; those that 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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8.1.4.3: 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 8.1.4.3.1.

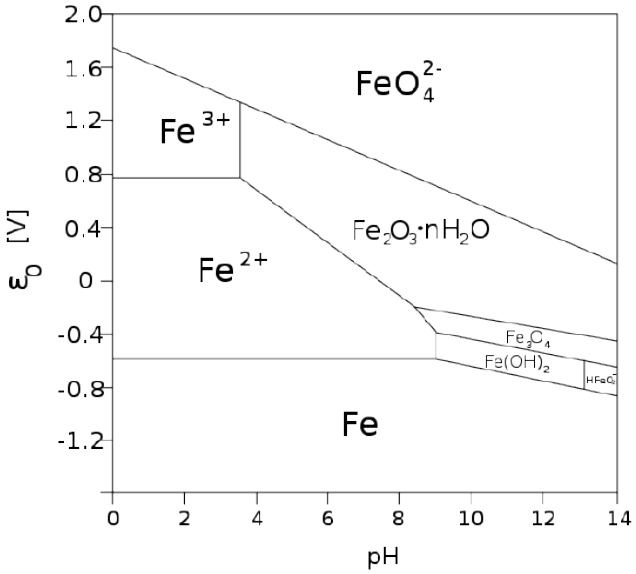


Figure 8.1.4.3.1. Pourbaix diagram for Fe at an unknown Fe concentration. (CC BY-SA 2.5, Andel Früh via Wikipedia)

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 8.1.4.3.2.

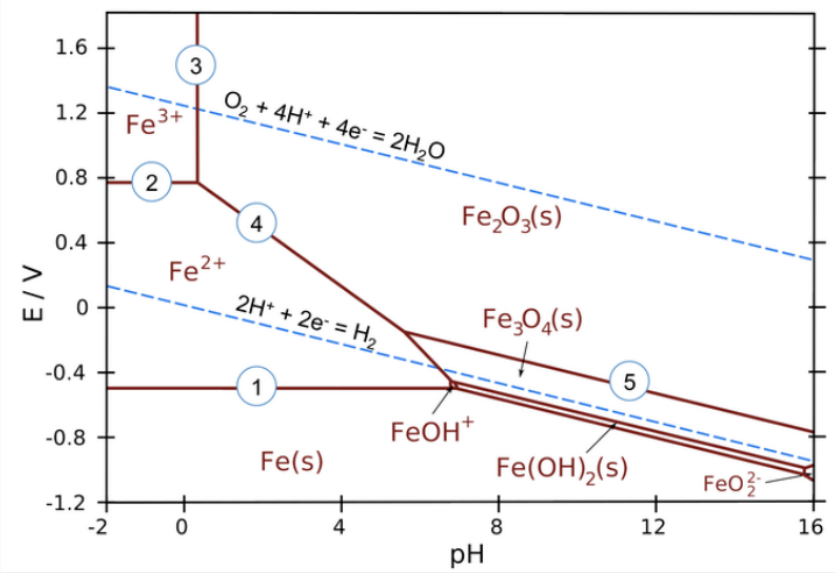


Figure 8.1.4.3.2. Partial Pourbaix diagram for Fe, at a different Fe concentration than the diagram in Figure 8.1.4.3.1. (CC BY-SA 3.0 Unported; Metallos via Wikipedia)

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 8.1.4.3.2. Notice that the diagram also shows equilibrium lines for water reduction

$$2\,\mathrm{H^+} \;+\; 2\,\mathrm{e^-} \;\rightarrow \mathrm{H_2}$$

and oxidation

$$\mathrm{O_2} + 4\,\mathrm{H^+} + 4\,\mathrm{e^-} \;\rightarrow 2\,\mathrm{H_2O}.$$

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 8.1.4.3.2 determines the potential of the system. As can be seen in Figure 8.1.4.3.2, 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 8.1.4.3.1.

Example 8.1.4.3.1

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 8.1.4.3.2 (Do not use the information in Figure 8.1.4.3.1 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 8.1.4.3.1. 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 8.1.4.3.2. In this case the reaction potential when $\frac{Fe^{2+}}{Fe^{3+}}$=1 is $E^\circ_{Fe^{3/2+}}$:

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad E = E^\circ_{Fe^{3/2+}} - \frac{0.05916\ V}{1}\log\frac{[Fe^{2+}]}{[Fe^{3+}]} = E^\circ_{Fe^{3/2+}} - (0.05916\ V)\log 1 = E^\circ_{Fe^{3/2+}}$$

- *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 8.1.4.3.2. 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 8.1.4.3.2. 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.

Contributors and Attributions

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8.2: 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 8.2.1.

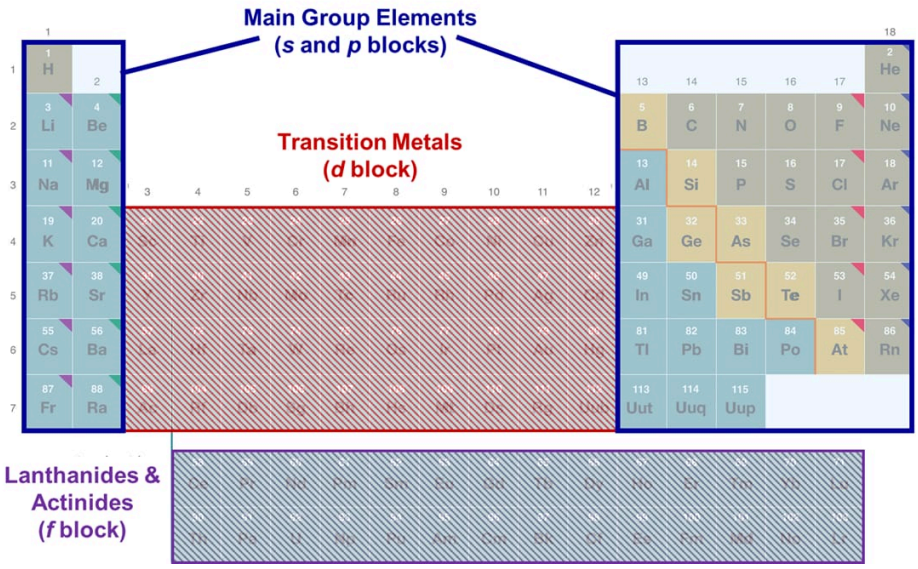


Figure 8.2.1. Location of the main group elements in the periodic table.[1]

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 8.2.1, thirteen of the top 25 chemicals produced in the United States are inorganic main group compounds.

Table 8.2.1**.** Top 25 industrial chemicals produced in the US in 2002.[2]

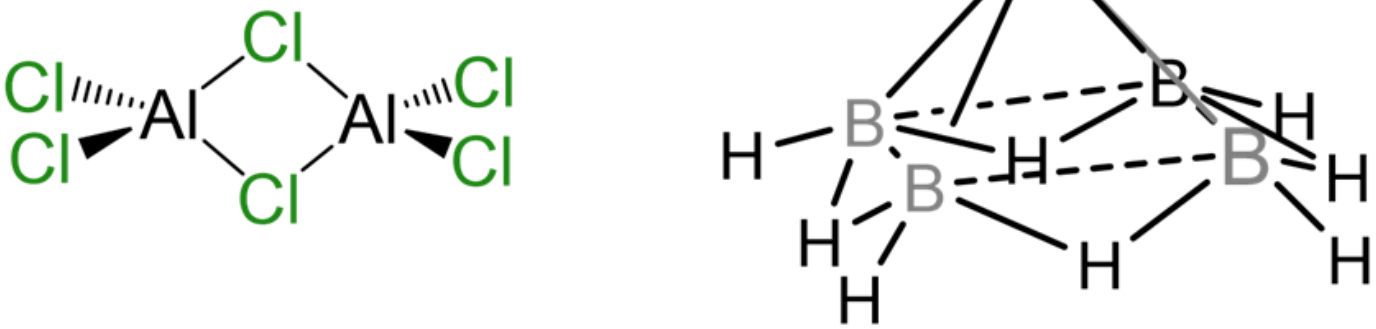
Rank	Name	Formula (Structure)	Billions of Pounds
1	sulfuric acid	H_2SO_4	88.80
2	nitrogen	N_2	58.70
3	oxygen	O_2	42.38
4	ethylene	$H_2C{=}CH_2$	40.41
5	ammonia	NH_3	35.95
6	calcium oxide (lime)	CaO	34.72
7	phosphoric acid	H_3PO_4	25.36
8	sodium hydroxide	NaOH	24.02
9	propylene (propene)	$CH_3CH{=}CH_2$	22.60
10	chlorine	Cl_2	22.28
11	sodium carbonate	Na_2CO_3	20.89
12	urea	$(NH_2)_2C{=}O$	16.84
13	nitric acid	HNO_3	16.08
14	1,2-dichloroethane (ethylene dichloride)	$ClCH_2CH_2Cl$	15.94
15	ammonium nitrate	NH_4NO_3	15.33
16	vinyl chloride	$CH_2{=}CHCl$	13.23
17	benzene	C_6H_6	12.01
18	ethylbenzene	$C_6H_5CH_2CH_3$	10.99
19	carbon dioxide	CO_2	10.91
20	methyl *t*-butyl ether	$CH_3OC(CH_3)_3$	10.86
21	styrene	$C_6H_5CH{=}CH_2$	8.94
22	methanol	CH_3OH	8.73
23	formaldehyde	$H_2C{=}O$	6.98
24	xylenes (mixture)†	$(CH_3)_2C_6H_4$	6.38
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 8.2.**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 8.2.**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

Contributor

Stephen Contakes, Westmont College

The unknown authors of Table 8.2.1 and the periodic table portion of Figure 8.2.1.

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8.3: 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 8.3.1.

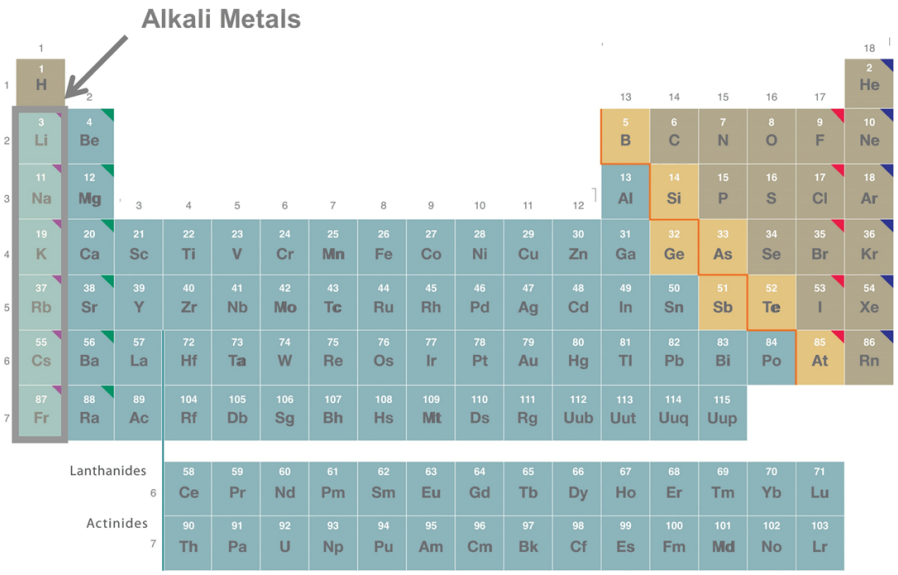


Figure 8.3.1. Position of the alkali metals in the periodic table. (CC-BY-SA-NC 3.0; Anonymous via LibreTexts)

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).

$$2\,\mathrm{NaCl}\,(\mathrm{l}) \rightarrow 2\,\mathrm{Na}\,(\mathrm{l}) + \mathrm{Cl_2}\,(\mathrm{g})$$

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 8.3.2.

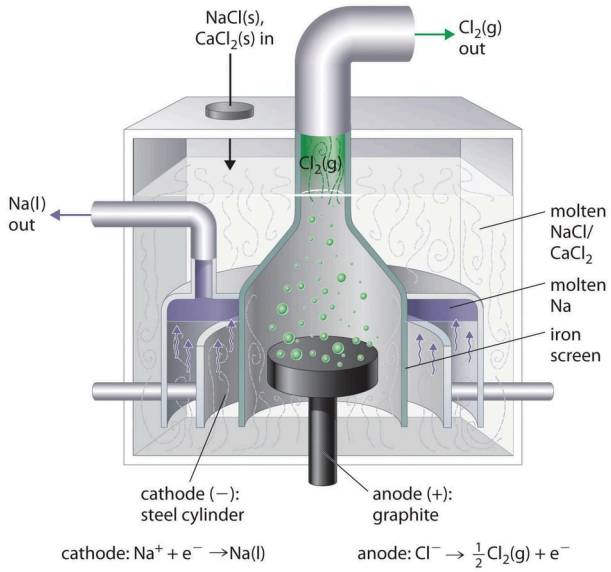


Figure 8.3.2. Downs cell for the electrolysis of molten sodium. (CC-BY-SA-NC 3.0; Anonymous via LibreTexts)

As can be seen from the cell in Figure 8.3.2, 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.

$$\mathrm{KCl + Na \longrightarrow K + NaCl}$$

$$\mathrm{2\,KX + CaC_2 \ \rightarrow 2\,K + CaX_2 + C\ (X = F, Cl)}$$

$$\mathrm{K_2CO_3 + 2\,C \ \rightarrow 2\,K + 3\,CO}$$

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 8.3.3.

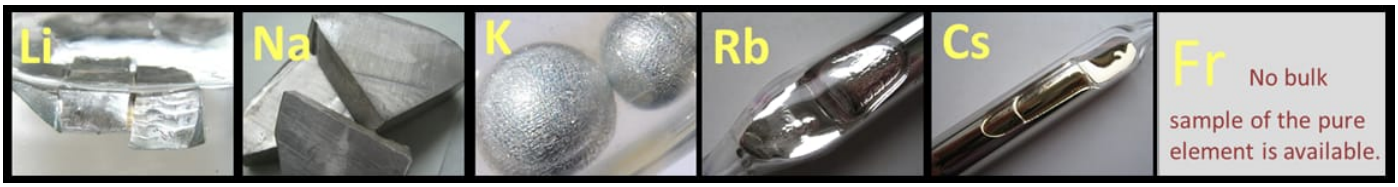


Figure 8.3.3. The alkali metals. Notice that most of the samples are either stored in mineral oil or sealed in glass tubes to prevent ther reoxidation by atmospheric oxygen. The images of the alkali metals are adapted from those at en.Wikipedia.org/wiki/Alkali_metal. Individual image credits for the 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 8.3.1. Further, as can be seen from the data in Table 8.3.1, 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 8.3.1. 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 8.3.2.

Table 8.3.2. 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

Substance	Atomic radius (Angstroms)	Ionization energy (kJ/mol)	Pauling Electronegativity
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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8.3.1: 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 8.3.1.1. As can be seen from the data in Table 8.3.1.1, 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 8.3.1.1**.** 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 8.3.1.1. Nevertheless, as can be seen in Figure 8.3.1.1, 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.

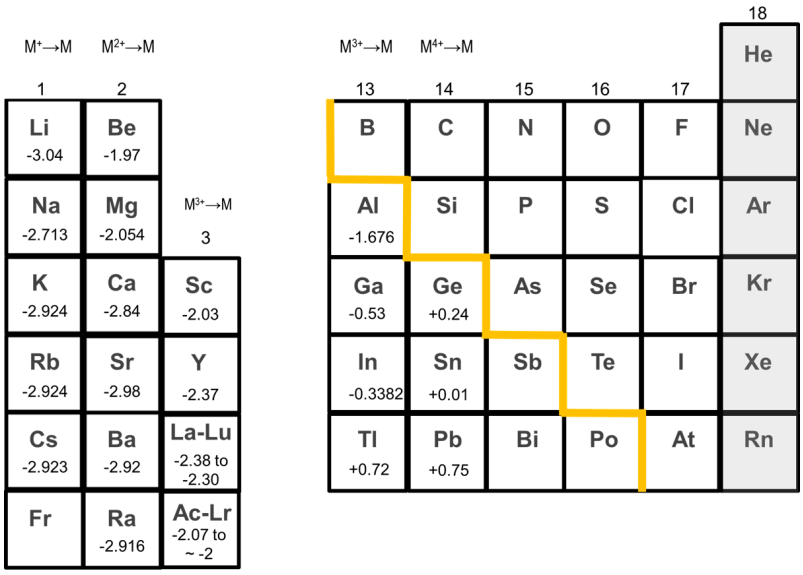


Figure 8.3.1.1. Standard reduction potentials in volts for reduction of selected aqueous cations in acid solution.

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.

$$Na(s)\ \xrightarrow{NH_3}\ Na(NH_3)_6^+\ +\ e^-(solv.) \qquad (\text{at low } Na^+ \text{ concentrations})$$

At higher concentrations of sodium, bronze solutions containing sodide anions (*e.g.* M-) are formed.

$$2\ Na(s)\ \xrightarrow{NH_3}\ Na(NH_3)_6^+\ +\ Na^-(solv.) \qquad (\text{at high } Na^+ \text{ concentrations})$$

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.

$$R-C\equiv C-H\ +\ Na^+(solv.)\ +\ e^-(solv.)\ \longrightarrow\ R-C\equiv C:^-\ Na^+\ +\ \tfrac{1}{2}\ H_2$$

$$Fe(CO)_5 \;+\; 2\ Na^+(solv.) \;+\; 2\ e^-(solv.) \;\longrightarrow\; (Na^+)_2[Fe(CO)_5^{2-}] \;+\; \tfrac{1}{2}\ H_2$$

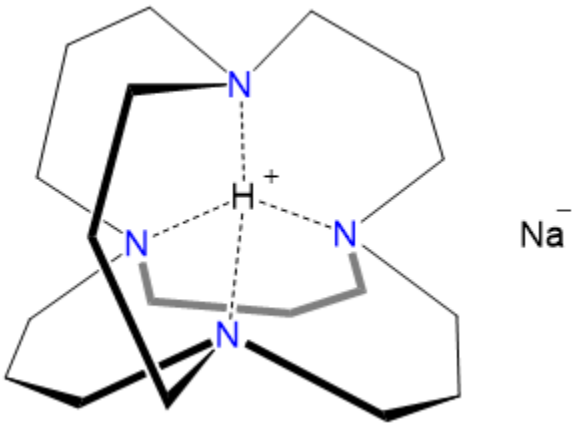
Solid electride salts - *i.e.,* in which the anion is a free electron - may even be prepared by adding a ligand that encapsulates and stabilizes the metal cation and then allowing the solvent to evaporate away from the solvated electron.

$$Na(NH_3)_6^+ \;+\; e^-(solv.) \;+\; \text{encapsulating ligand} \;\underset{-6\ NH_3}{\longrightarrow}\; Na(\text{encapsulating ligand})^+e^-(s)$$

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 8.3.1.2). 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 8.3.1.**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 8.3.1.2A). 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 8.3.1.2B).

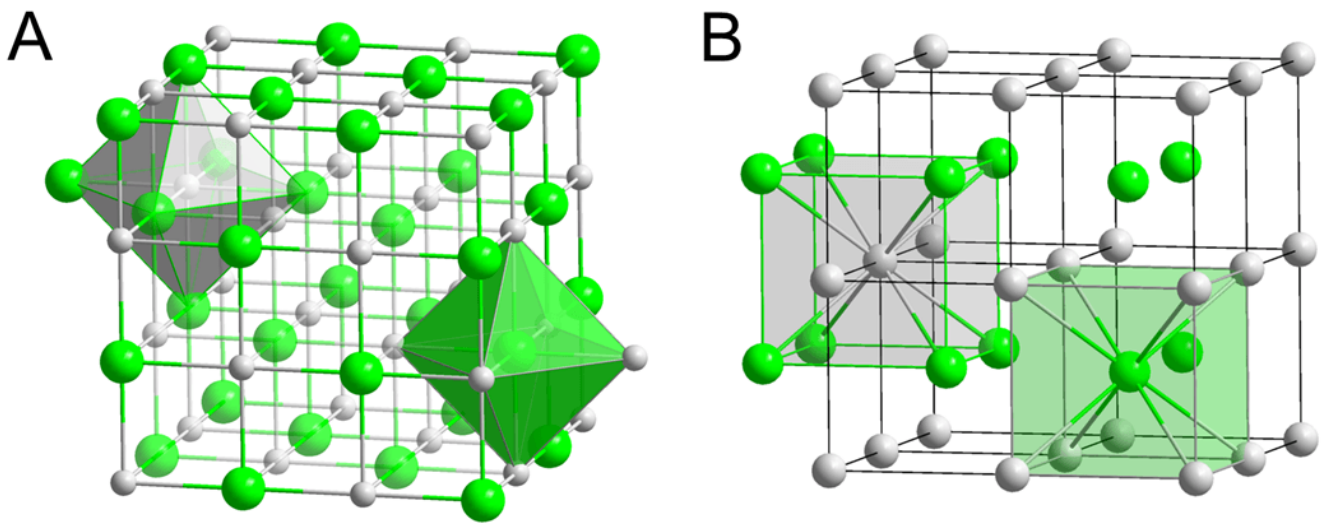


Figure 8.3.1.2. (A) Rock salt structure formed by LiX, NaX, KX, and RbX (X = F, Cl, Br, and I) showing octahedral coordination of six halides about each metal ion. (B) CsCl structure formed by CsCl, CsBr, and CsI showing square coordination of eight halides about each Cs atom. The rock salt structure is by Solid State - Own work, Public Domain, commons.wikimedia.org/w/inde...?curid=38373099 ; the CsCl structure image by Solid State - Own work, Public Domain, commons.wikimedia.org/w/inde...?curid=38373300.

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 8.3.1.3).

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 8.3.1.3. 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 8.3.1.4.

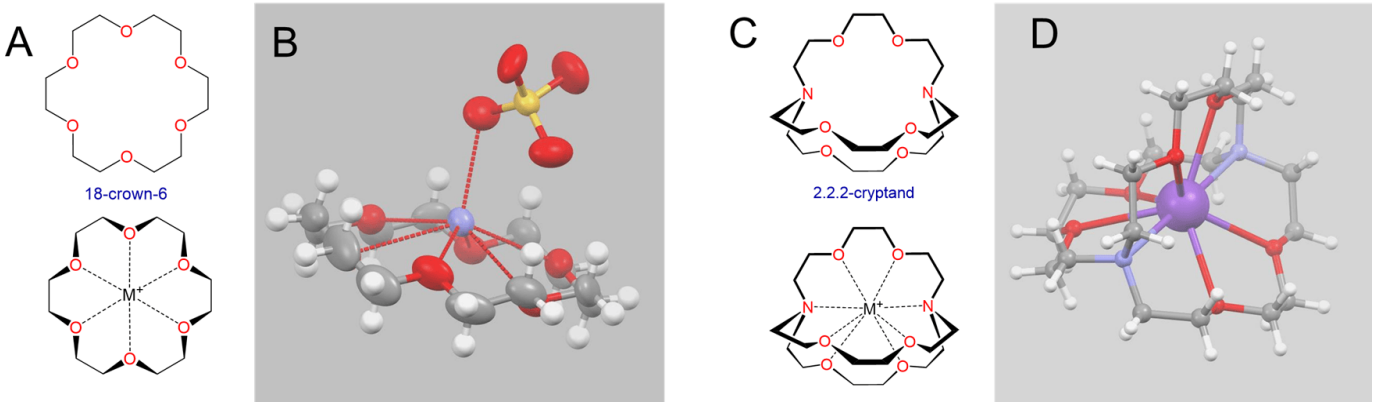
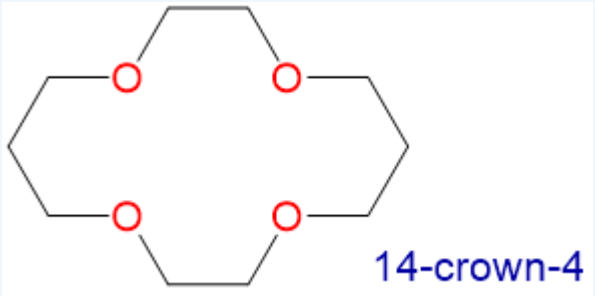
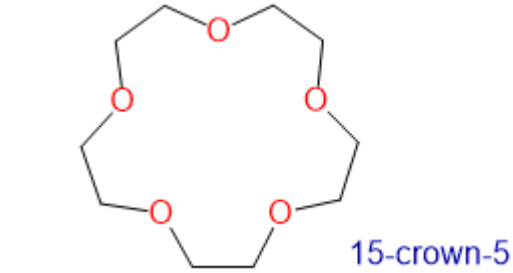
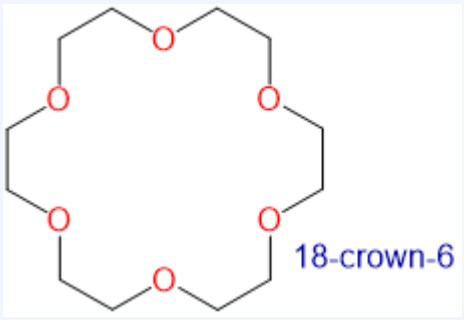
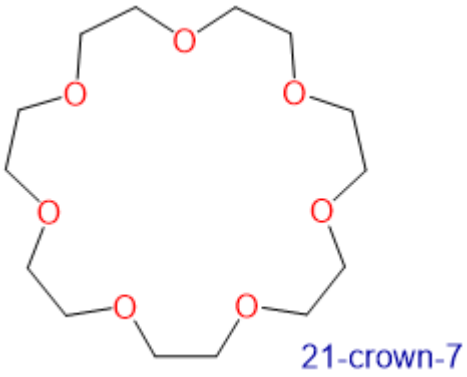


Figure 8.3.1.4. Structures of typical crown ether and cryptand complexes. (A) Cyclic ethers like 18-crown-6 can chelate metal ions through their oxygen lone pairs. They are called crown ethers[3] because they take on a crownlike puckered appearance when bound to the metal, as may be seen from (B) the 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 8.3.1.2, 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 8.3.1.2**.** 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.

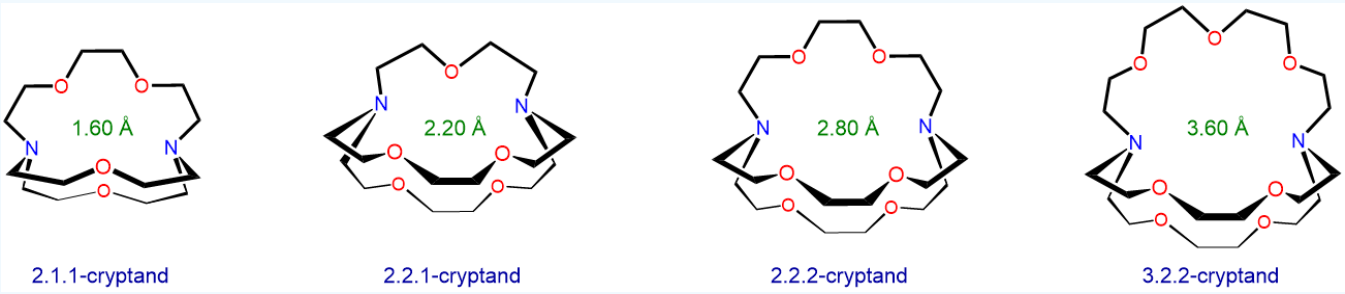
Crown ether	...with a cavity diameter of (in Å)	...preferentially binds	...which has a cation diameter of (in Å)
	1.2-1.5	Li^+	1.36
	1.7-2.2	Na^+	1.94

	2.6-3.2	K^+	2.66
	3.4-4.3	Cs^+	3.34

Exercise 8.3.1.1

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 8.3.1.II. Use the information in Scheme 8.3.1.II and Table 8.3.1.2 along with a cation diameter of 2.98 Å for Rb^+ to predict which alkali metal ion each cryptand will preferentially bind.

Scheme 8.3.1.II. Structures and approximate binding cavity diameters for several cryptands.



Answer available at the end of this section.

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.

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Answers

Exercise 8.3.1.1

The cryptands might be expected to selectively bind the largest ion which fits within the cavity. These predictions are summarized in Table 8.3.1.3.

Table 8.3.1.3**.** 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 Scheme8.3.1.II are of limited utility in predicting the relative binding strengths.

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8.4: 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 8.4.1.

Table 8.4.1**.** 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	$^{1}_{1}\mathrm{H}$	$^{2}_{1}\mathrm{H}$ or D	$^{3}_{1}\mathrm{H}$ 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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8.4.1: 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 1s 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 1s 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 8.4.1.**I**.

Scheme 8.4.1.**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.

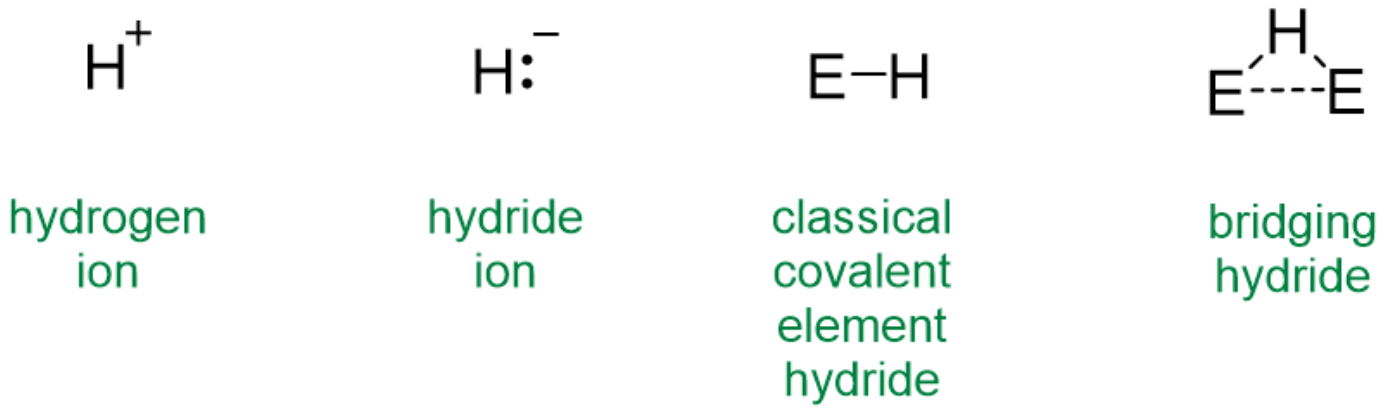


Figure 8.4.1.1).

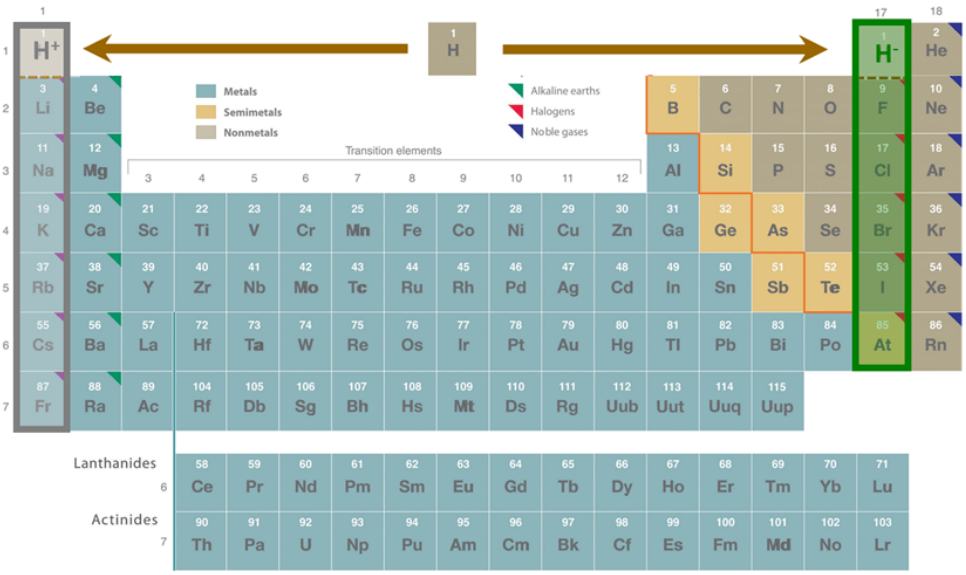


Figure 8.4.1.1. Hydrogen has an ambiguous position in the periodic table. It is usually placed above the alkali metal group, although it could also be placed above the halogens.

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 8.4.1.2.

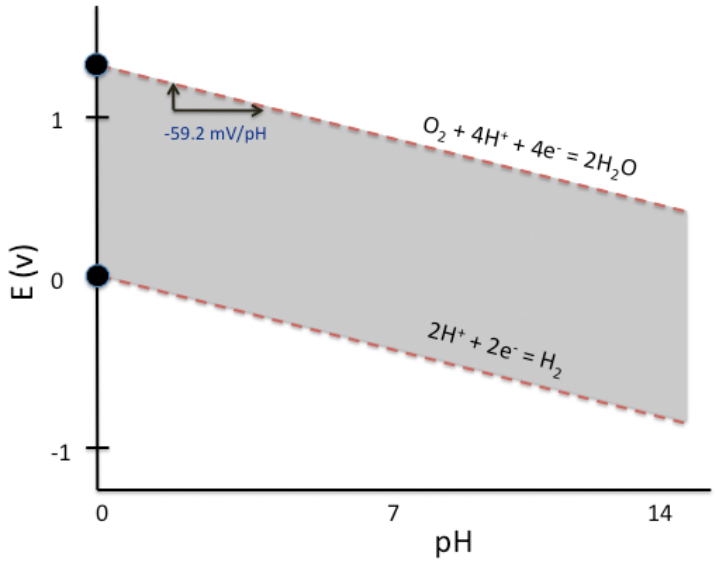


Figure 8.4.1.2. Pourbaix diagram for hydrogen in water. By tem5psu - https://commons.wikimedia.org/wiki/F...2OPourbaix.png, CC BY-SA 3.0, https://commons.wikimedia.org/w/inde...curid=57288471

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.

$$2\ H_2O(l)\ \rightarrow\ 2\ H_2(g)\ +\ O_2(g)$$

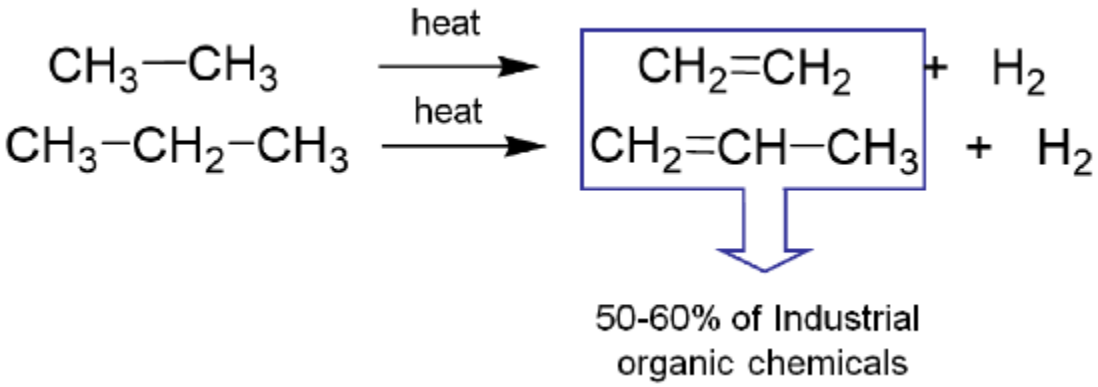
Industrially it is more common to produce hydrogen via **steam reforming** of methane and other hydrocarbons.

$$CH_4(g)\ +\ H_2O(g)\ \xrightarrow{Ni}\ CO(g)\ +\ 3\ H_2(g)\quad \text{(steam reforming)}$$

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.

$$N_2(g)\ +\ 3\ H_2(g)\ \rightarrow\ 2NH_3(g)\quad \text{(Haber}-\text{Bosch process)}$$

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 8.4.1.3, 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**.

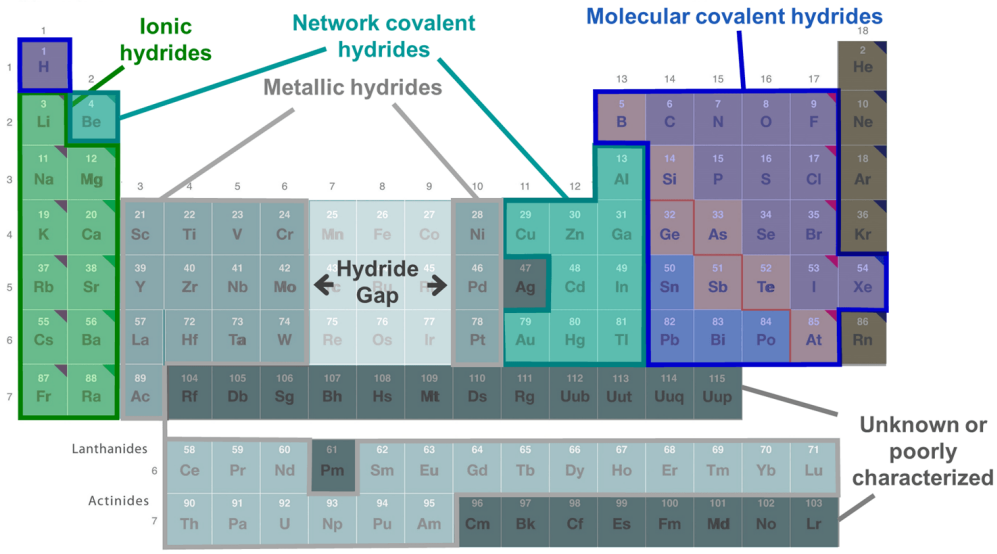


Figure 8.4.1.3. Distribution of the different types of element hydrides across the periodic table. The figure is adapted from the Periodic Table at https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/02._Atoms%2C_Molecules%2C_and_Ions/2.5%3A_The_Periodic_Table

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:

$$NaH(s) + CH_3C \equiv C - H(g) \rightarrow CH_3C \equiv C :^- Na^+ + H_2(g)$$

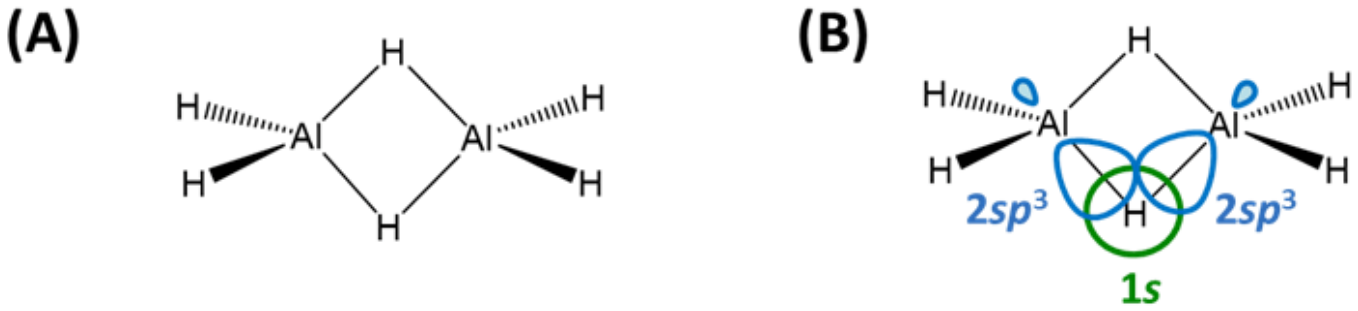
  The $H:^-$ ion in an ionic hydride may in principle act as a nucleophile. However, in practice this application is limited to the less reactive and consequently more selective hydrides of aluminum and boron, both of which are usually classified as intermediate hydrides on account of the covalent character 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 8.4.1.**II**A). These E-H-E bonds are explained as three-center two-electron bonds in valence bond theory)Scheme 8.4.1.**II**B), but may also be described in terms of molecular orbitals (Note 8.4.1.1).

Scheme 8.4.1.**II.** (A) Bridging E-H-E bonds in Al_2H_6 and (B) their valence bond description in terms of overlap between the H 1s and Al sp^3 orbitals.

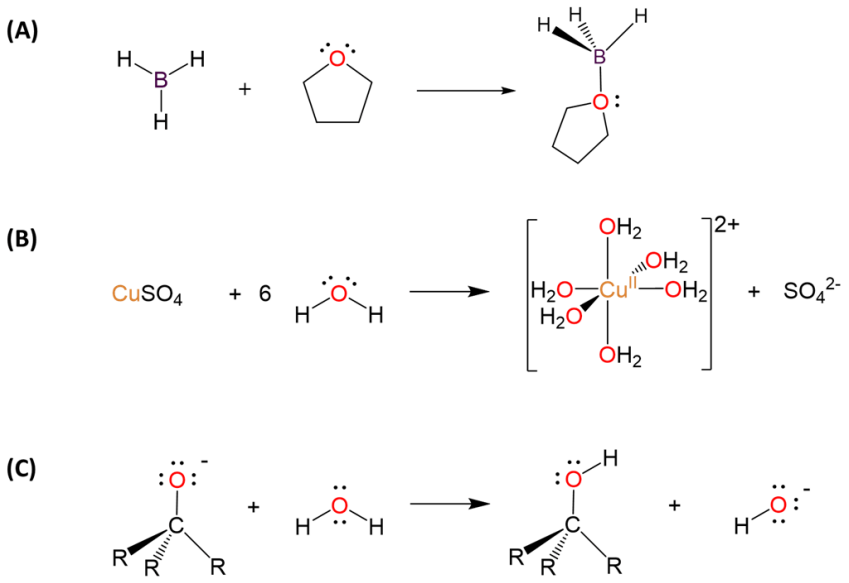


Electron precise and electron rich hydrides are formed by C, N, O, F, and their heavier cogeners. The E-H bonds in these may be described as classical two-center two-electron E-H bonds of Lewis Theory. The electron precise and electron rich hydrides are distinguished in that the electron rich hydrides 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 8.4.1.**III**, electron deficient hydrides tend to function as Lewis acids and electron rich hydrides as Lewis bases and Brønsted acids.

Scheme 8.4.1.**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 8.4.1.IV.

Scheme 8.4.1.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.

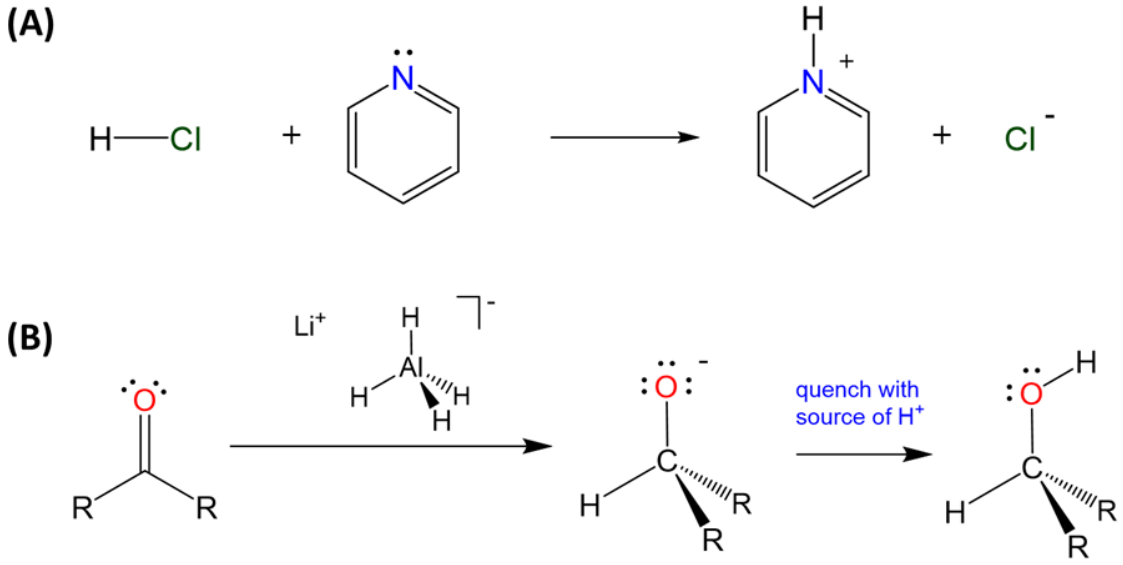


Figure 8.4.1.4, the metals give hydrides of $E^{\delta-} - H^{\delta+}$ bonds, the metalloids (including B) weakly polarized $E^{\delta-} - H^{\delta+}$ bonds and most nonmetals $E^{\delta-} - H^{\delta+}$ bonds.

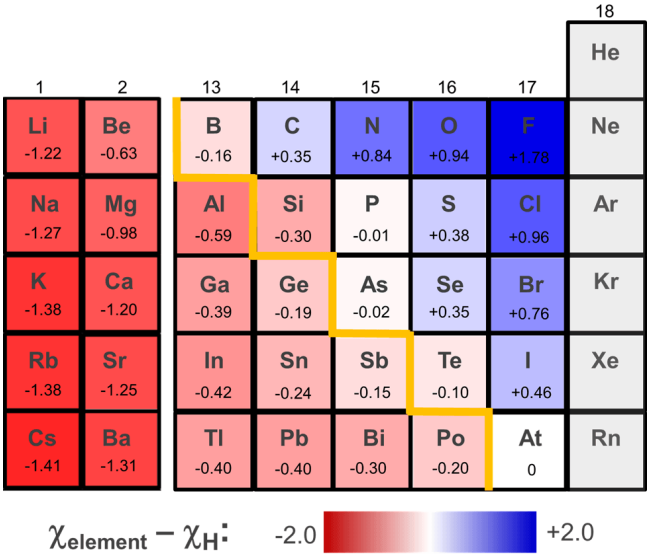


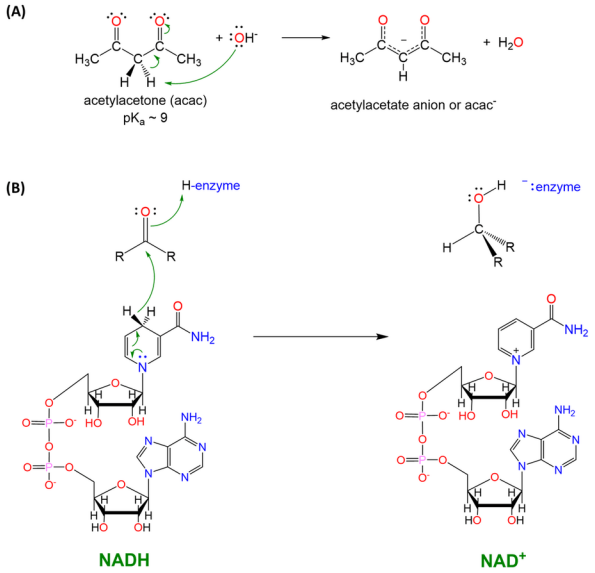
Figure 8.4.1.4. Difference between element and hydrogen Pauling electronegativities. More positive values correspond to positively polarized hydrogen while more negative ones have a larger partial negative charge on hydrogen.

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 8.4.1.4, 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 8.4.1.V).

Scheme 8.4.1.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 8.4.1.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 8.4.1.5.

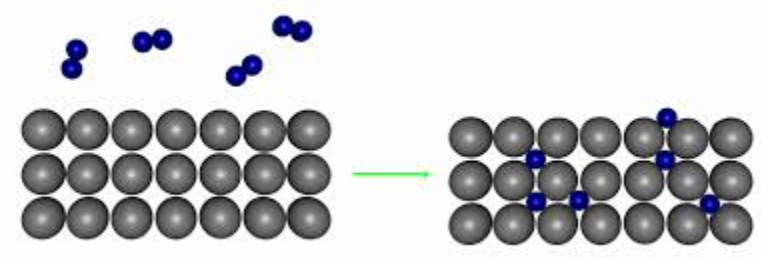


Figure 8.4.1.5. Schematic illustration of the process of formation of an interstitial hydride showing breakup of dihydrogen and its uptake into the metal lattice. The metal lattice expands 10-20% during this process.[1] Taken from https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Map%3A_Inorganic_Chemistry_(Housecroft)/10%3A_Hydrogen/10.7%3A_Binary_Hydrides_-_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. 8.4.1.1. 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 8.4.1.6.

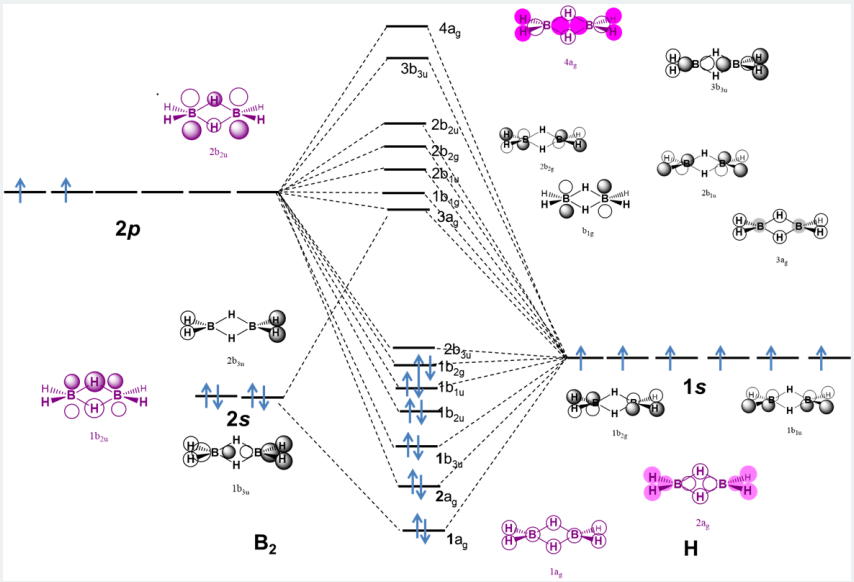


Figure 8.4.1.6. Qualitative MO diagram for diborane. The symmetry adapted bonding and antibonding MOs involved in bridge bonding are shown in violet. The derivation of this diagram is presented in 8.5.1. Properties of the Group 13 Elements and Boron Chemistry.

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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8.5: 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 8.5.1.

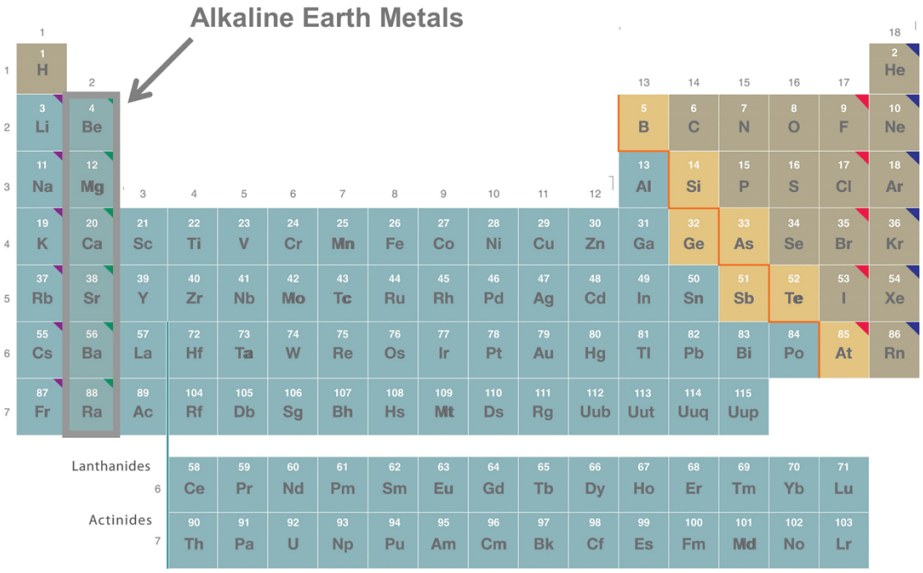


Figure 8.5.1. Position of the alkaline earth metals in the periodic table. Adapted from the periodic table at https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/02._Atoms%2C_Molecules%2C_and_Ions/2.5%3A_The_Periodic_Table.

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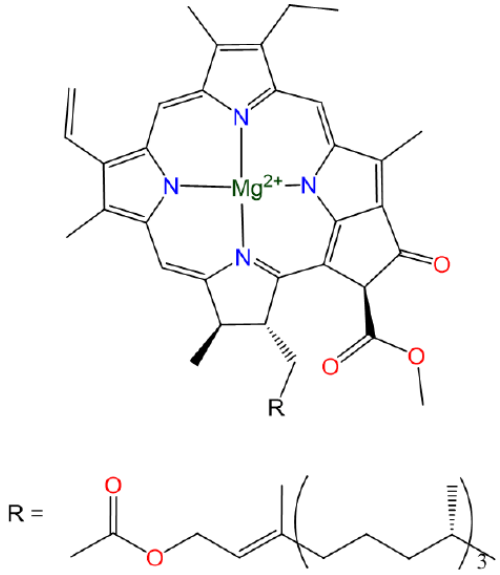
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8.5.1: Preparation and General Properties of the Alkaline Earth Elements

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 8.5.1.1).

Scheme 8.5.1.1**.** 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.

$$2\ MO \xrightarrow{\text{electrolysis}} 2\ M(s) + O_2 \qquad \text{Davy, } (M = Mg,\ Ca,\ 1808)$$

Today Ca, Mg, and the other alkaline earth metals are produced either by electrolysis of their chlorides or chemical reduction by carbon or aluminum.

$$2\ MCl_2 \xrightarrow{\text{electrolysis}} 2\ M(s) + Cl_2 \qquad (M = Be,\ Mg,\ Ca,\ Sr)$$

$$MgO + C \xrightarrow{\text{electrolysis}} Mg(s) + CO$$

$$3\ MO + 2\ Al \xrightarrow{\text{electrolysis}} M(s) + Al_2O_3 \qquad (M = Ca,\ Sr,\ Ra)$$

$$4\ BaO + 2\ Al \xrightarrow{\text{electrolysis}} Ba(s) + BaAl_2O_4$$

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 8.5.1.1. As with the alkali metals, the melting and boiling points decrease down the group as the atomic size increases.

Table 8.5.1.1**.** 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 8.5.1.2, 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 8.5.1.2).

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 8.5.1.2**.** 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

Contributors and Attributions

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8.5.2: 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 8.5.2.2, 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.

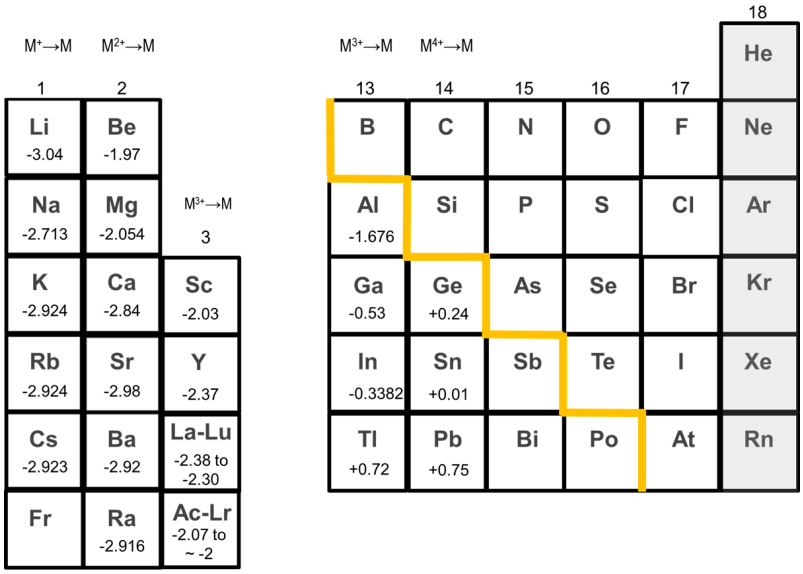


Figure 8.5.2.1. Standard reduction potentials in volts for reduction of selected aqueous cations in acid solution. This figure is a copy of that used in section 8.3.2. Alkali Metals' Chemical Properties. Because of their tendency to form +2 cations, the alkaline earth metals are good reducing agents.

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.

$$MO + H_2O \longrightarrow M(OH)_2 \qquad (M = Be, Mg, Ca, Sr, Ba, \text{ and presumably Ra})$$

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.

$$M^{2+}(aq) + 2\ OH^- \rightarrow M(OH)_2 \qquad (M = Be, Mg, Ca, Sr, Ba, \text{ and presumably Ra})$$

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.

$$M(s) + X_2^- \rightarrow MX_2 \qquad (M = Be, Mg, Ca, Sr, Ba, \text{ and presumably Ra}; X = F, Cl, Br, I)$$

$$M(OH)_2 + 2\ HX \rightarrow MX_2 + 2\ H_2O \qquad (M = Mg, Ca, Sr, Ba, \text{ and presumably Ra}; X = F, Cl, Br, I)$$

$$MO + 2\ HX \rightarrow MX_2 + H_2O \qquad (M = Mg, Ca, Sr, Ba, \text{ and presumably Ra}; X = F, Cl, Br, I)$$

The heavier alkaline earth metals (Mg through Ba) also reduce hydrogen to give hydrides.

$$M(s) + H_2(g) \rightarrow MH_2 \qquad (M = Mg, Ca, Sr, Ba, \text{ and presumably Ra})$$

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.

$$MH_2(s) + H_2O(l) \rightarrow M(OH)_2 + H_2(g) \qquad (M = Mg, Ca, Sr, Ba, \text{ and presumably Ra})$$

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.

$$MCO_3(s) \xrightarrow{\Delta} MO(s) + CO_2(g)$$

$$M(NO_3)_2(s) \xrightarrow{\Delta} MO(s) + 2\ NO_2(g) + O_2(g)$$

Complex factors govern decomposition of the nitrates but, as shown in Table 8.5.2.1, the decomposition of the alkaline earth carbonates shows that on going down the group, carbonate decomposition requires increasingly higher temperatures.

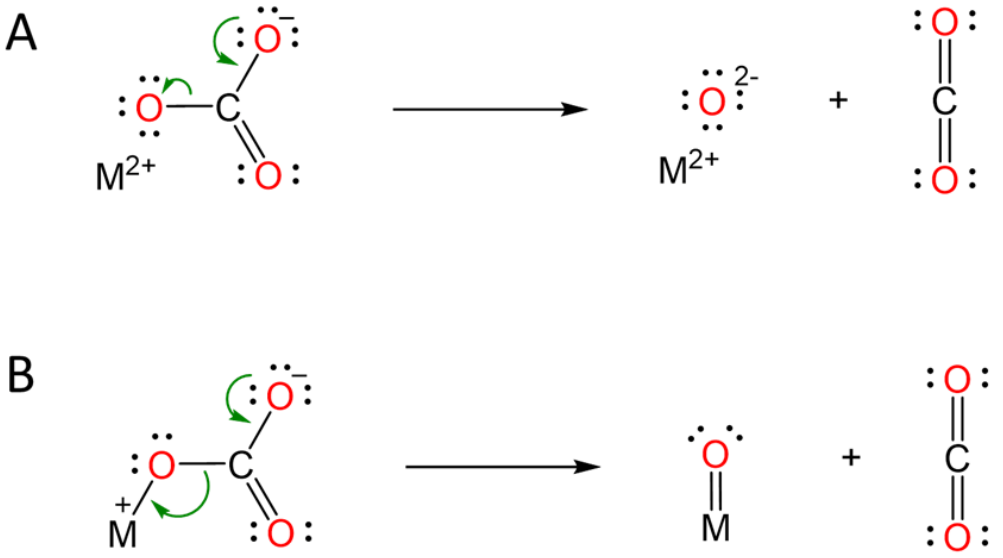
Table 8.5.2.1**.** Decomposition temperatures of alkaline earth carbonates

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 8.5.2.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 8.5.2.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 8.5.2.1

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 available at the end of this section.

Beryllium, and to a lesser extent magnesium, form polar highly covalent compounds.

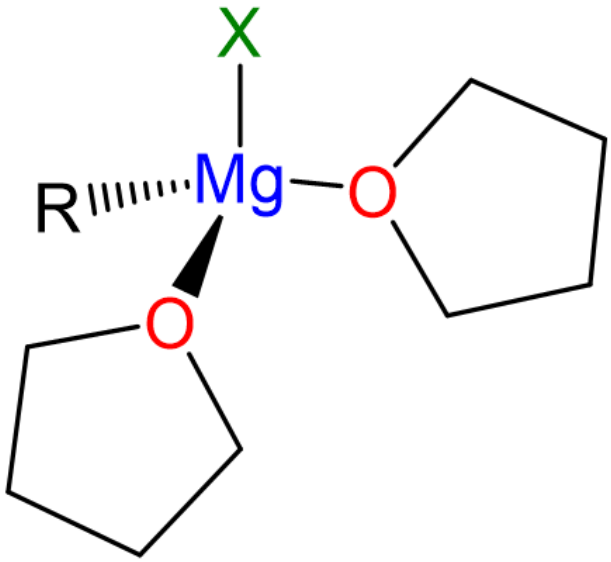
The chemistry of magnesium and beryllium demonstrates the danger of drawing an overly rigorous distinction between elements as metals, nonmetals, and metalloids. This is because both Be and Mg can form compounds with considerable covalent character and, as might be expected from their relative paucity 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.

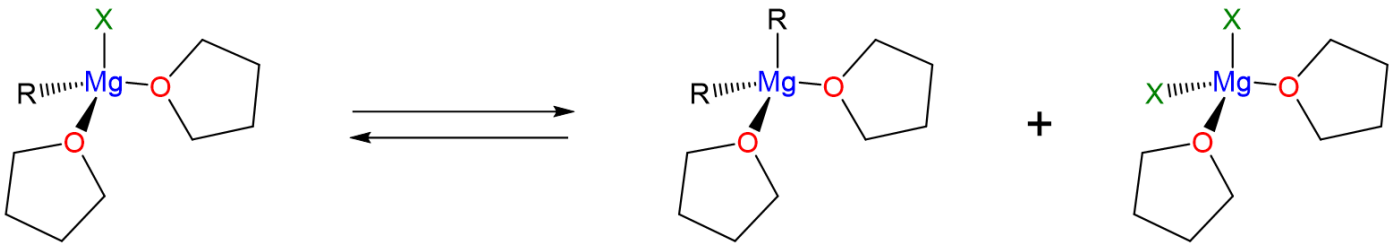
$$Mg(s) \quad + \quad R-X \quad \overset{THF,\text{catalytic } I_2}{\longrightarrow} \quad R-Mg-X$$

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 8.5.2.II.

Scheme 8.5.2.**II.** Structure of monomeric "RMgX" Grignard reagent in THF solution.



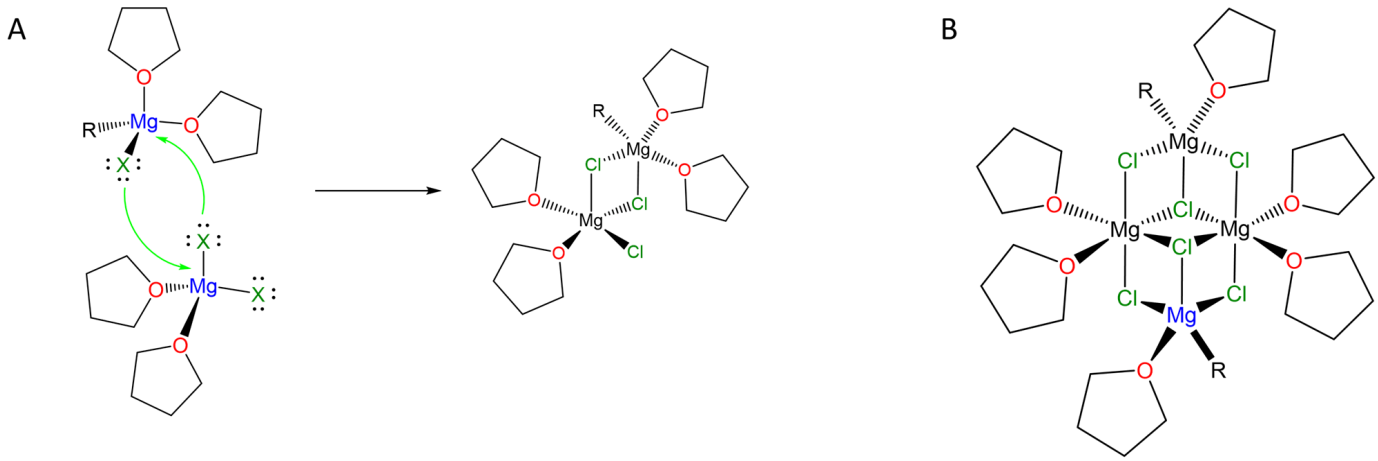
Like molecular compounds, Grignard reagents undergo ligand substitution reactions in solution according to the Schlenk equilibrium.



"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 8.5.2.III.

Scheme 8.5.2.**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 8.5.2.**III**.

Scheme 8.5.2.**III.** Tetrameric Be cluster formed in liquid ammonia. Redrawn from reference 6.

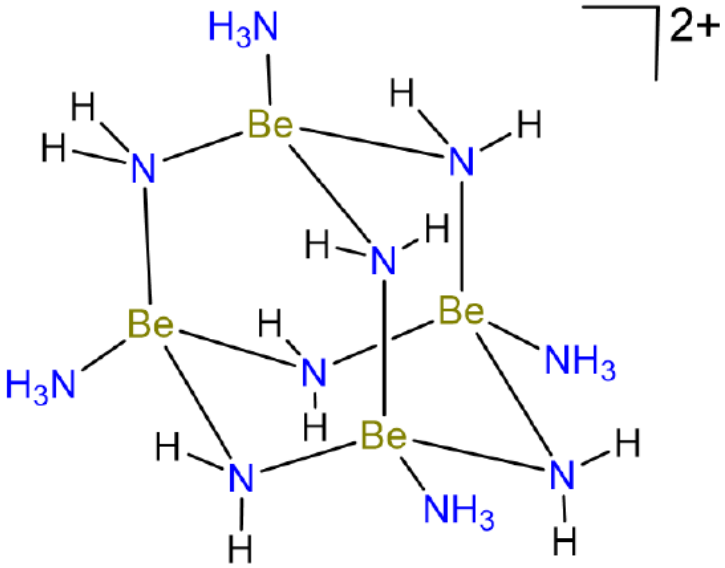


Figure 8.5.2.2. At higher temperatures the polymeric chains dissociate into Be_2Cl_4 dimers and $BeCl_2$ monomers.

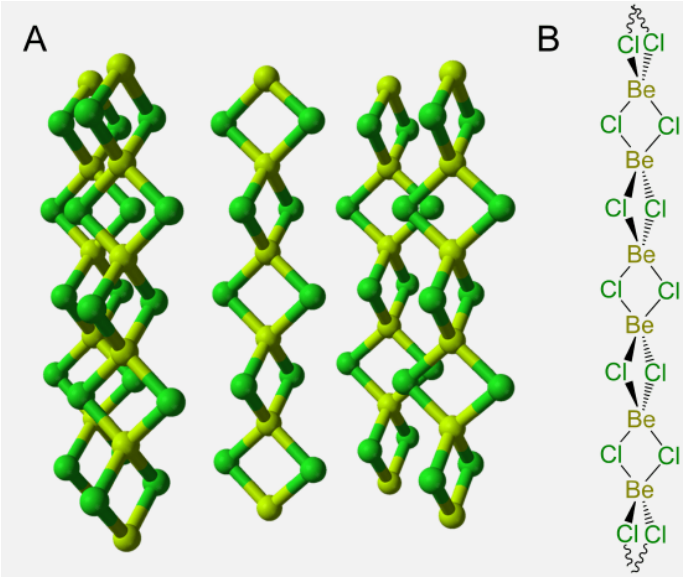


Figure 8.5.2.2. (A) Structure of $BeCl_2$ consisting of (B) polymeric chains of edge-linked $BeCl_4$ tetrahedra. The structure of $BeCl_2$ is by Ben Mills - Own work, Public Domain, commons.wikimedia.org/w/inde...?curid=4759802, who rendered it from X-ray data reported in Rundle, R. E.;Lewis, P.H. *J. 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 8.5.2.IV along with that of $Be_4(NO_3)_6O$, which is thought to possess an anlogous structure.

Scheme 8.5.2.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.

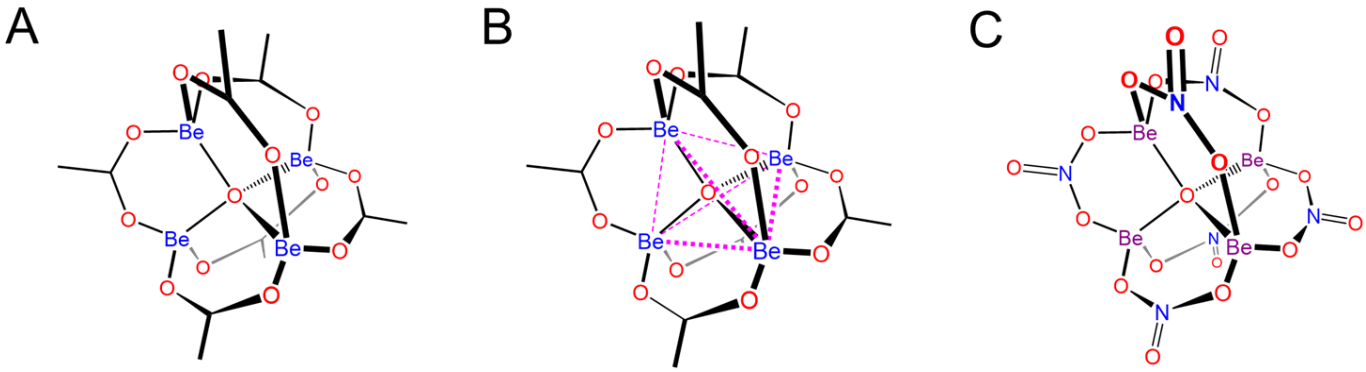


Figure 8.5.2.3.

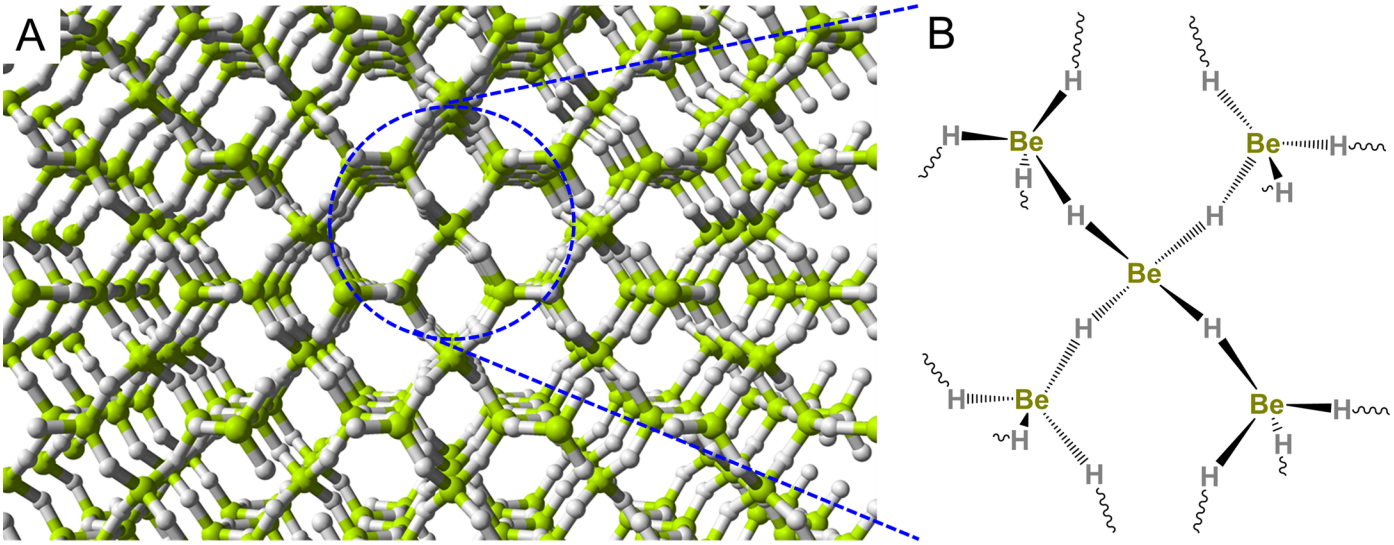
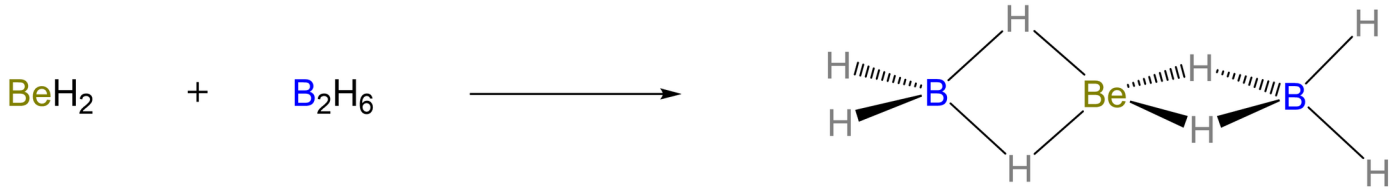


Figure 8.5.2.3. (A) Structure of BeH_2 consisting of (B) a network of BeH_4 tetrahedra linked via 3-center-2-electron Be-H-Be bonds. The structure of BeH_2 is by Ben Mills - Own work, Public Domain, commons.wikimedia.org/w/inde...?curid=3930832, who rendered it from X-ray data reported in Smith, G.S.; 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 8.5.2.V.[7]

Scheme 8.5.2.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.

Contributors and Attributions

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Answers

Exercise 8.5.2.1

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

$$\underset{580\ ^\circ C}{BeSO_4} < \underset{895\ ^\circ C}{MgSO_4} < \underset{1149\ ^\circ C}{CaSO_4} < \underset{1374\ ^\circ C}{SrSO_4} < BaSO_4 < RaSO_4$$

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8.6: 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 8.6.1 .

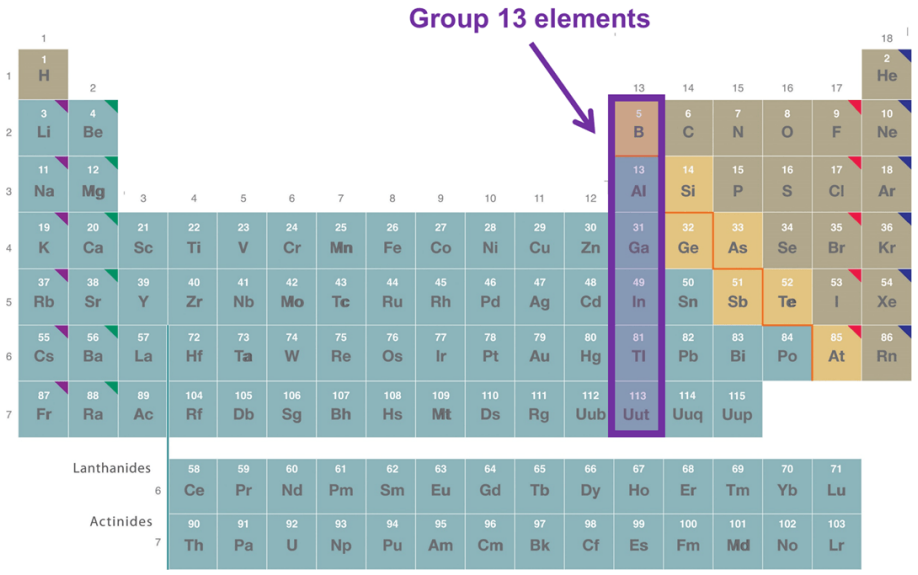


Figure 8.6.1. Position of the group 13 elements in the periodic table. Note that since the periodic table used was developed, element 113 was named Nihonium and given the symbol Nh. Adapted from the periodic table at https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/02._Atoms%2C_Molecules%2C_and_Ions/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.

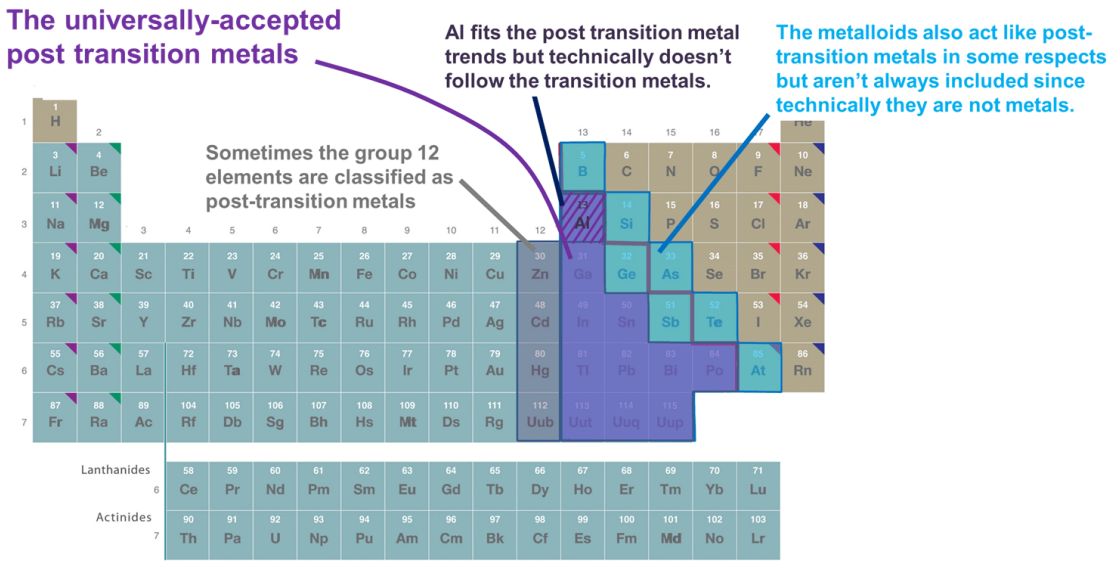


Figure 8.6.2. Some of the elements classified as post transition metals. Those shown in purple are commonly accepted since they are metals and clearly follow the transition metals, while the metals in groups 12 (and sometimes 11), Al, and the metalloids are all sometimes included since they behave like 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.

Contributors and Attributions

Stephen Contakes, Westmont College

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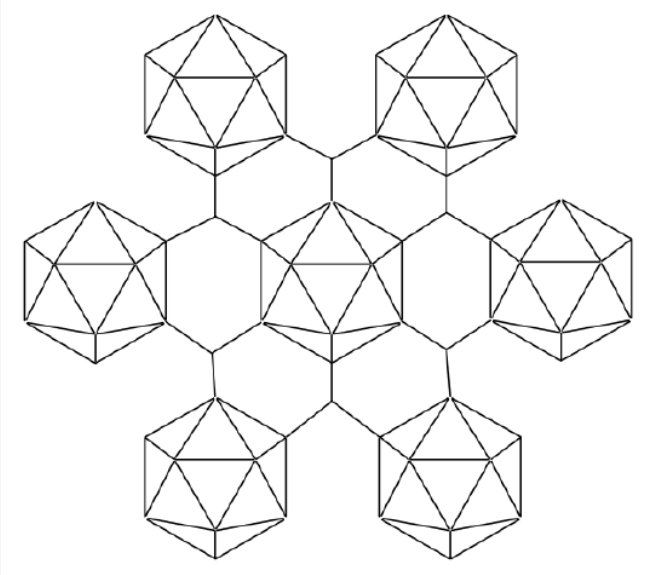
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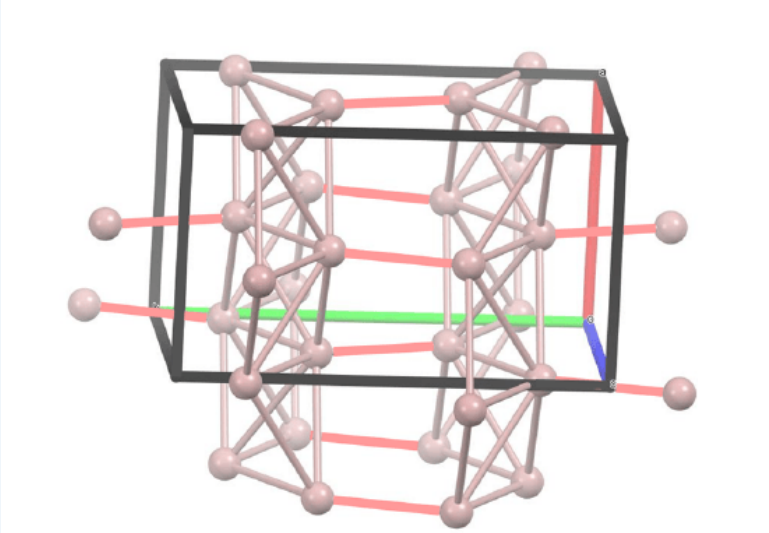
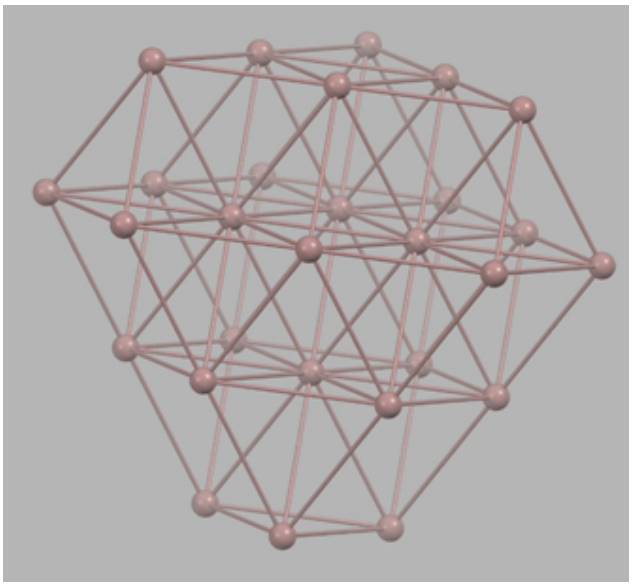
8.6.1: Properties of the Group 13 Elements and Boron Chemistry

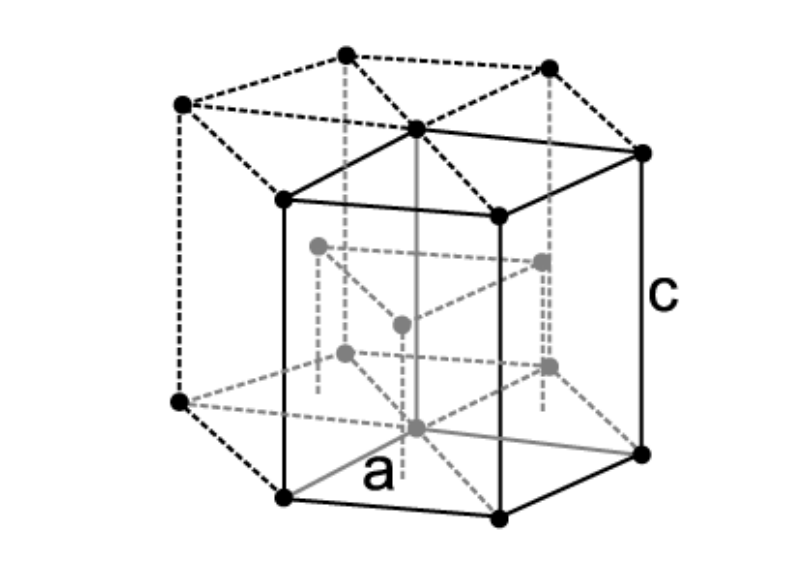
As elements, Boron acts like an electron deficient nonmetal and the other group 13 elements like metals that exhibit varying degrees of covalency.

Selected properties of the Group 13 elements are given in Table 8.6.1.1.

Table 8.6.1.1**.** 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	Ionizat Energ (kJ/m
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
Aluminum or Aluminium,[2] Al	FCC Metal Face-centered cubic crystal structure for aluminium	660	1.61	577

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
Indium, In	Distorted close packed metal 	157	1.78	558

Thallium, Tl	HCP Metal 	304	1.8	589

From the data given in Table 8.6.1.1 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**.

$$2\ Al_2O_3 + 3\ C(s,\ \text{graphite}) \xrightarrow{\text{electrolysis,940–980°C,KF,Na}_2AlF_6} 4\ Al(s) + 3\ CO_2(g)$$

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.

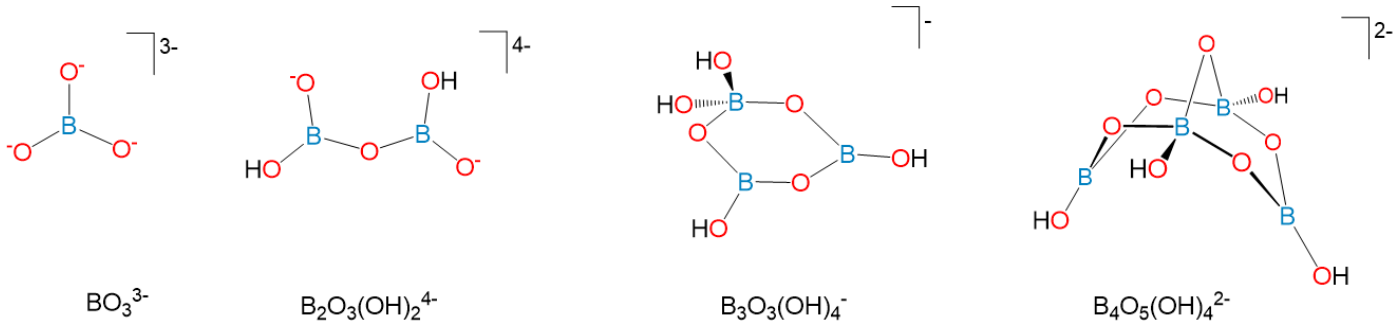
1. **Boron forms ordinary covalent bonds and/or gains electrons to give stable molecules or ions.** For example, while the boron of monomeric BH_3 may not have access to enough valence electrons to achieve a stable octet, it can satisfy its octet by forming an adduct with a Lewis base. A well known example 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 8.6.1.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 8.6.1.II..

Scheme 8.6.1.II. The tetraborate anion.



As illustrated by the structures depicted in Scheme 8.6.1.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 8.6.1.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 8.6.1.**III.**

Scheme 8.6.1.**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.

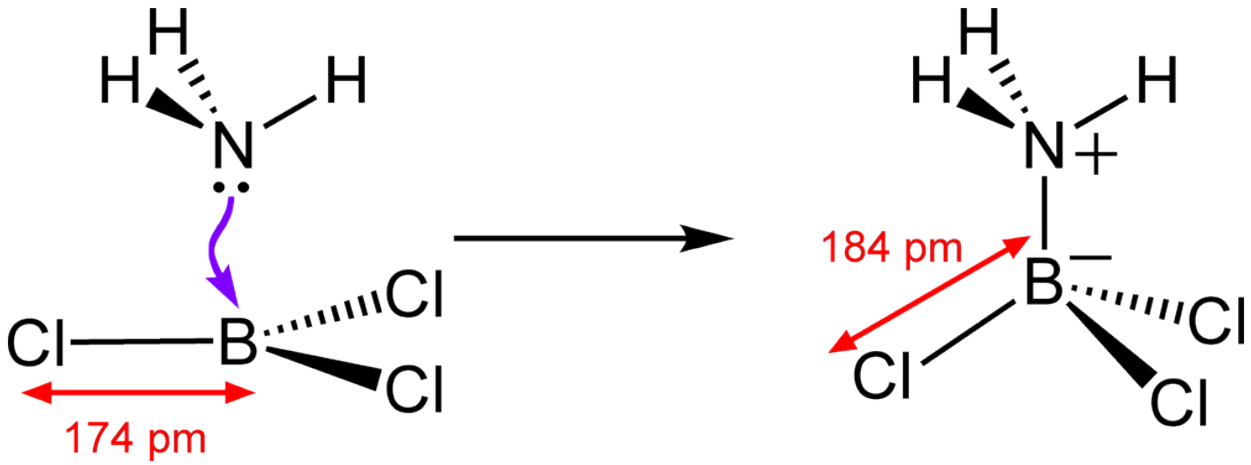


Figure 8.6.1.2C.

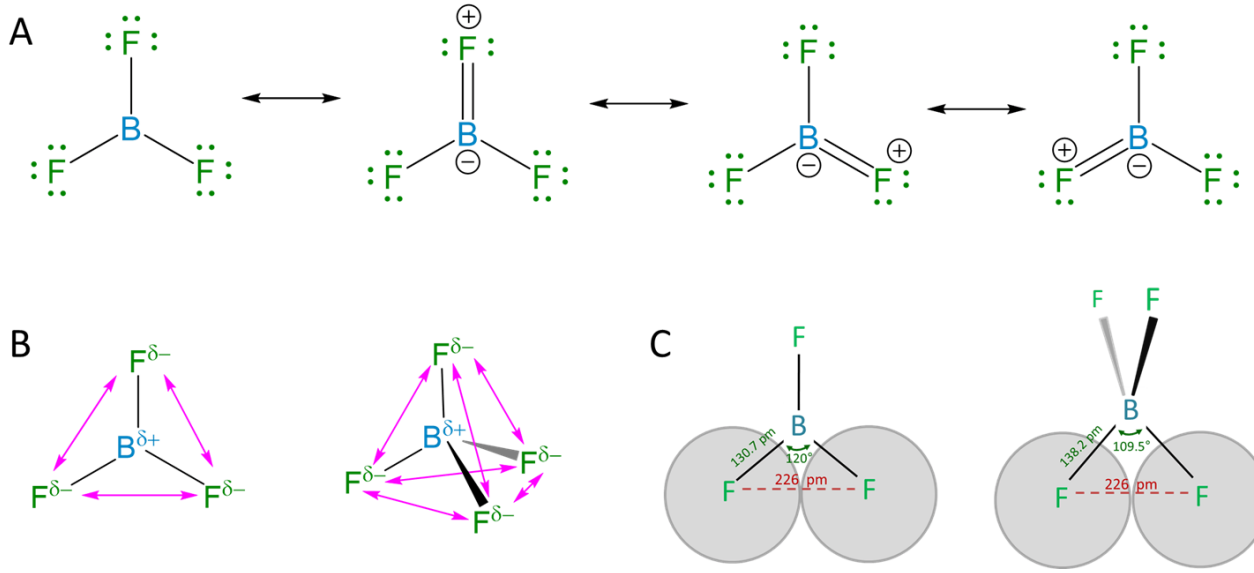


Figure 8.6.1.2. (A) Resonance explanation for short B-F bonds involving contributions from structures in which the partial charges run counter to the expected $B^{\delta+}$-$X^{\delta-}$ polarity based on electronegativity and calculations, the latter of which support (B) an ionic explanation in terms 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 8.6.1.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 8.6.1.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.

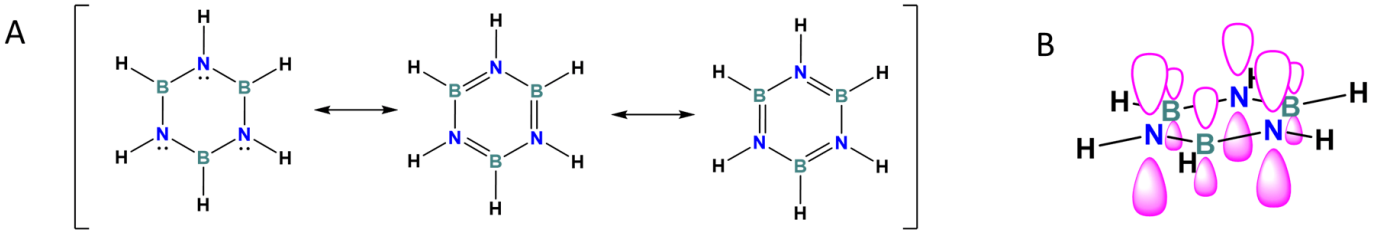


Figure 8.6.1.3A. The B and N in each layer are trigonal planar and arranged in planar layers of interlocking hexagonal rings. As with borazine, the π system is delocalized, although again the electron density is somewhat localized on the N atoms and unlike graphite, hexagonal BN is not a good conductor. 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 8.6.1.3B and 8.6.1.3C. 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.

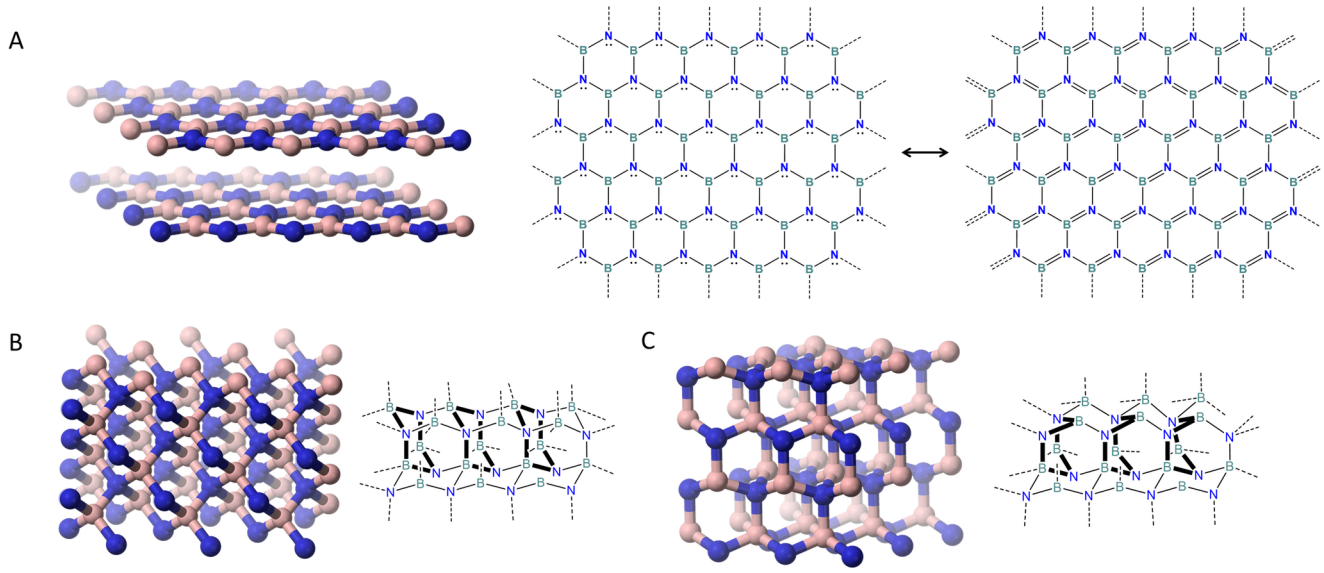


Figure 8.6.1.3. (A) Layered structure of BN along with two resonance structures illustrating the bonding in a boron nitride layer, (B) cubic BN and a schematic depiction emphasizing the linking of layers of chair conformation B_3N_3 rings by chair conformation B_3N_3 rings and (C) Wurtzite-like hexagonal 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.

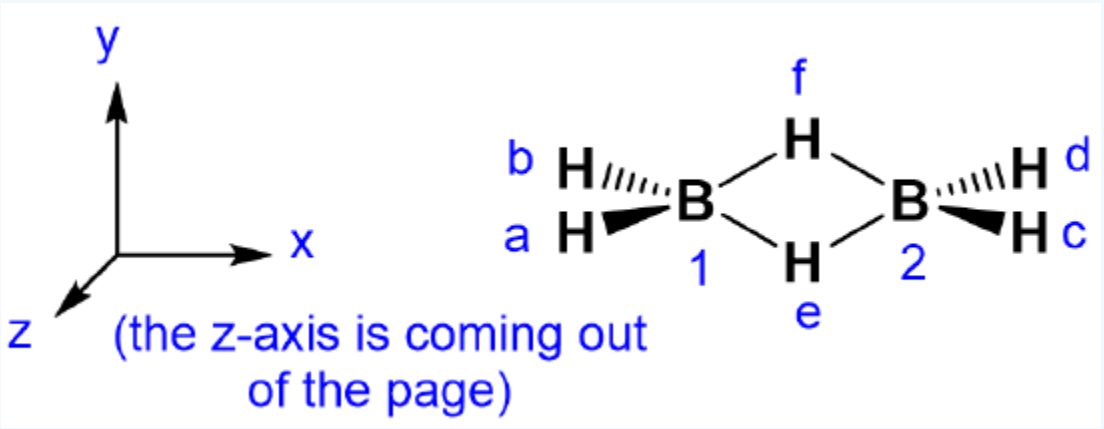


Valence bond and molecular orbital descriptions of the "two-electron three-center" bridge bonds in these molecules have already been given in 8.2.1. Hydrogen's Chemical Properties.

Those who wish to review the MO description of bonding are invited to consider the derivation of the MOs of diborane given in Example 8.6.1.1.

Exercise 8.6.1.1. The molecular orbitals of Diborane

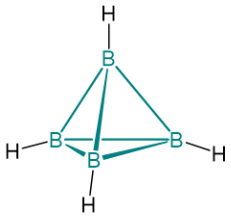
Use the projection operator method to derive MOs for diborane. The structure of diborane is shown below, along with the atom labels and coordinate system which will be used in the answer key.



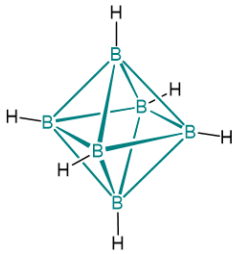
Answer available at the end of this section.

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 8.6.1.V.

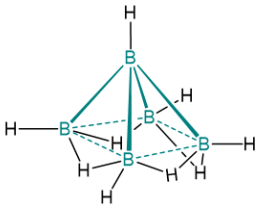
Scheme 8.6.1.V**.** Examples of electron-deficient boron clusters. These consist of a cluster H-B: groups in which the B atoms are held together by sharing electrons among the atoms of the cluster. The B-B and B---B bonds in these images are drawn to help define the cluster shape, in which the B atoms tend to occupy the vertices of a deltahedron.



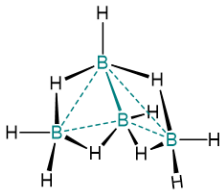
closo-$B_4H_4^{2-}$



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 8.6.1.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 8.6.1.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.

$$B_5H_9 \; + \; MH \; \overset{\text{low T}}{\longrightarrow} \; M^+ \; + \; B_5H_8^- \; H_2 \qquad (M = \text{alkali metal})$$

Many boranes are anionic. The most iconic is icosahedral *closo*-dodecaborate, $B_{12}H_{12}^{2-}$, the structure of which is shown in Figure 8.6.1.3.

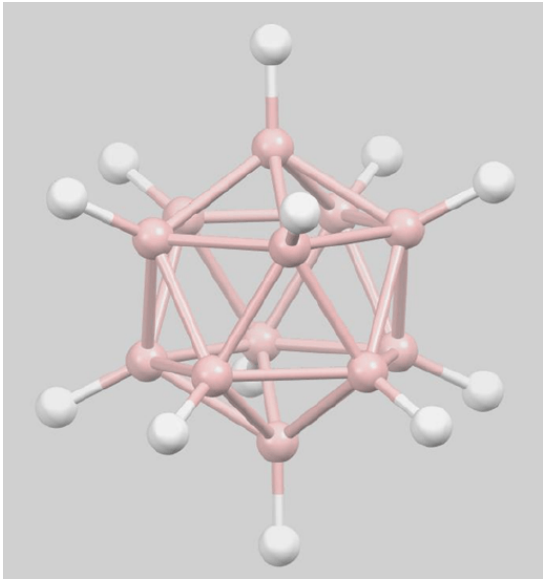
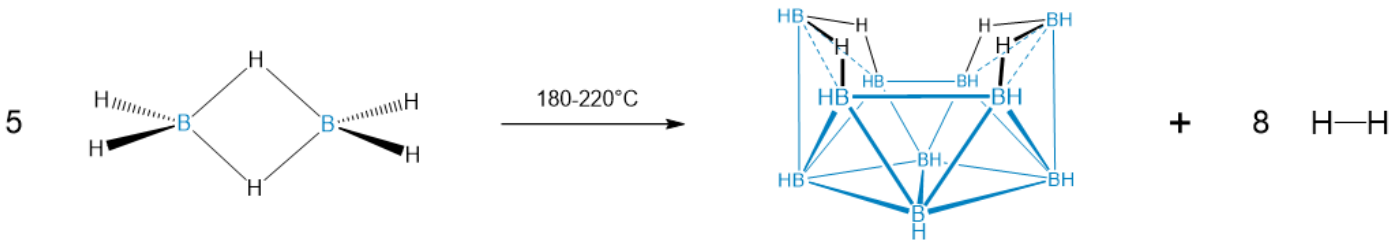


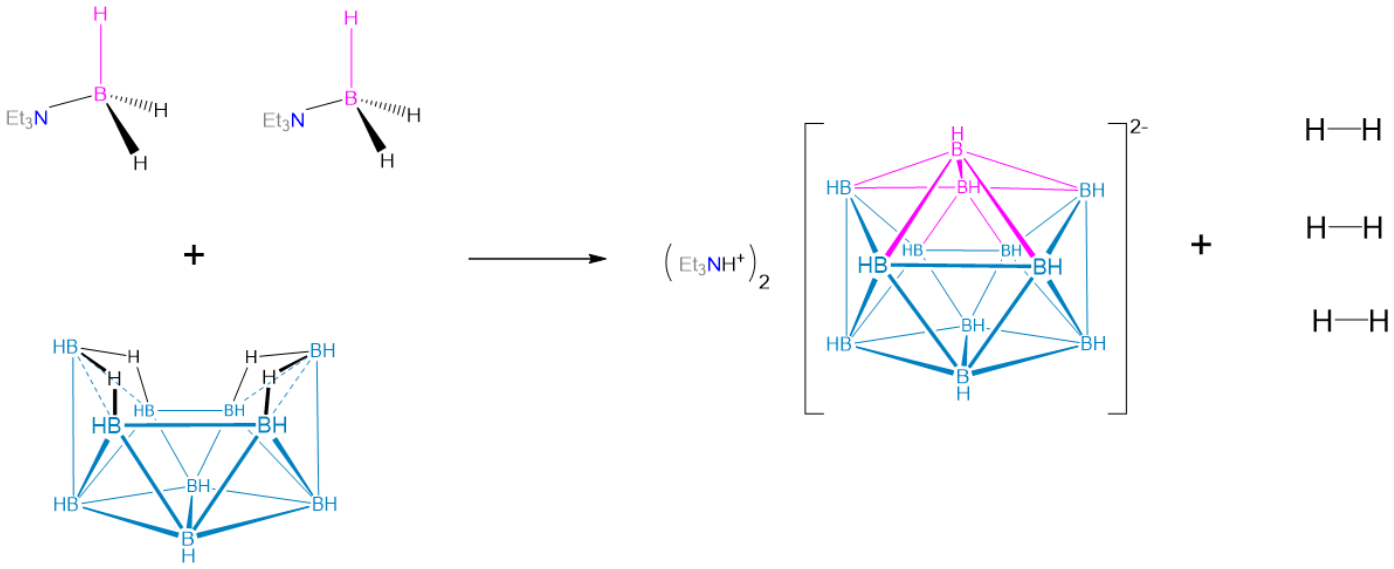
Figure 8.6.1.3. Structure of *closo*-dodecaborate, $B_{12}H_{12}^{2-}$, showing boron atoms in cream and H atoms in white. The diameter of the cluster is similar to that of a benzene ring. Rendered from COD ID: 4306523 as reported in reference 9.

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.

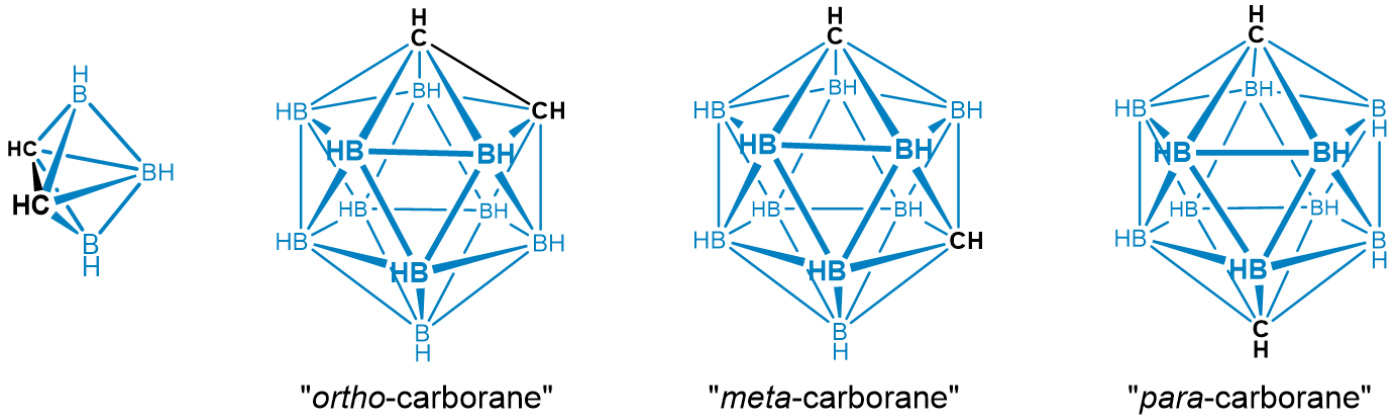


The two missing vertices in the *arachno*- cluster are added by allowing the cluster to react with additional BH_3 units, this time in the form of the Et_3N-BH_3 adduct.



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 8.6.1.VI.

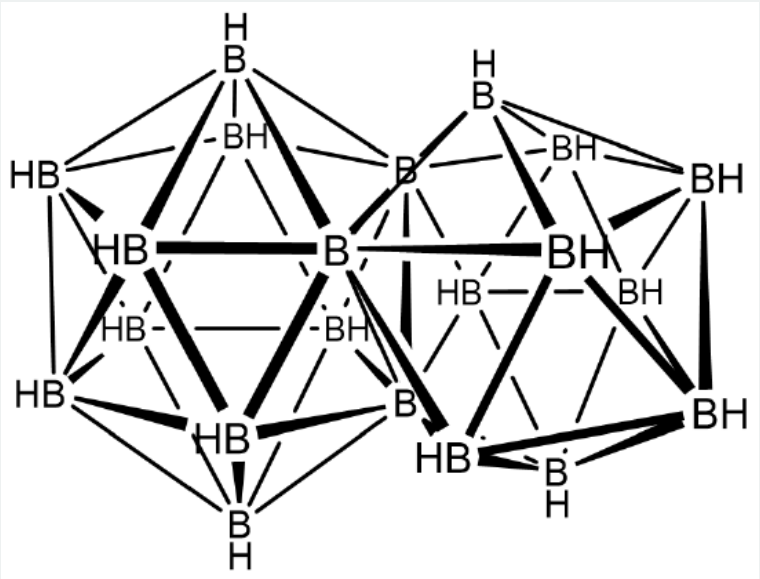
Scheme 8.6.1.VI. Some carborane clusters, including the *ortho*-, *meta*-, and *para*-"carborane", $C_2B_{10}H_{12}$.



Note 8.6.1.1: 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 8.6.1.VI.

Scheme 8.6.1.VII. A face-sharing *conjuncto*- borane.



Note 8.6.1.2: 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 8.6.1.4.

File:Boron neutron capture therapy (bnct) illustration.jpg

Figure 8.6.1.4. Use of neutron capture therapy to destroy cancerous cells. The image is by Pat Kenny (Illustrator) / Public domain.

As can be seen from Figure 8.6.1.4, 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.

3. A. Jain*, S.P. Ong*, G. Hautier, W. Chen, W.D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder, K.A. Persson *(*=equal contributions)*
The Materials Project: A materials genome approach to accelerating materials innovation APL Materials, 2013, 1(1), 011002.

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Contributors and Attributions

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Answers

Exercise 8.6.1.1**. The molecular orbitals of Diborane**

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

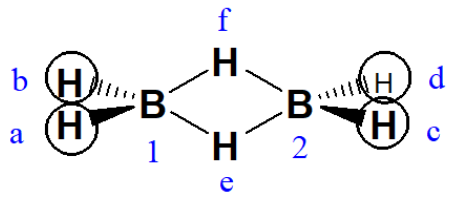
$\Psi(B_{2u})? = [1(H_{1sa}) + (-1)(H_{1sc}) + (1)(H_{1sd}) + (-1)(H_{1sb}) + (1)(H_{1sd}) + (-1)(H_{1sb}) + (-1)(H_{1sa}) + (1)(H_{1sc})]$

$\Psi(B_{2u}) = 0H_{1sa} + 0H_{1sb} + 0H_{1sc} + 0H_{1sd}$ So, there will be no b_{2u} orbital

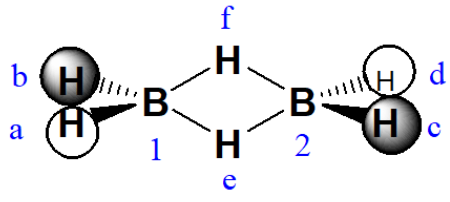
$\Psi(B_{3u})? = [1(H_{1sa}) + (-1)(H_{1sc}) + (-1)(H_{1sd}) + (1)(H_{1sb}) + (-1)(H_{1sd}) + (1)(H_{1sb}) + (1)(H_{1sa}) + (-1)(H_{1sc})]$

$\Psi(B_{3u}) = 2H_{1sa} + 2H_{1sb} - 2H_{1sc} - 2H_{1sd}$ So, there will be one b_{3u} orbital

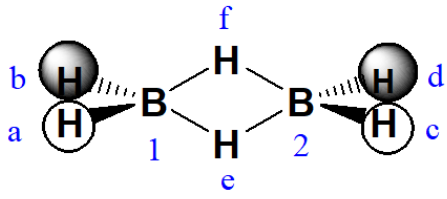
So the first set gives the following terminal hydrogen 1s group orbitals:



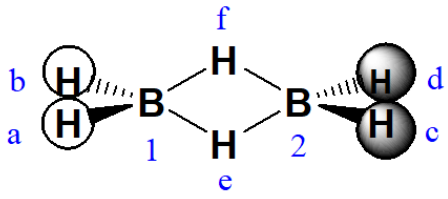
a_g



b_{2g}



b_{1u}



b_{3u}

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

$\Psi(B_{3g})? = [1(H_{1se}) + (-1)(H_{1sf}) + (-1)(H_{1se}) + (1)(H_{1sf}) + (1)(H_{1sf}) + (-1)(H_{1se}) + (-1)(H_{1sf}) + (1)(H_{1se})]$

$\Psi(B_{3g}) = = 0H_{1sa} + 0H_{1sb} + 0H_{1sc} + 0H_{1sd}$ No b_{3g} orbital

$\Psi(A_u)? = [1(H_{1se}) + (1)(H_{1sf}) + (1)(H_{1se}) + (1)(H_{1sf}) + (-1)(H_{1sf}) + (-1)(H_{1se}) + (-1)(H_{1sf}) + (-1)(H_{1se})]$

Ψ (A_u) = $\emptyset H_{1se}$ + $\emptyset H_{1sf}$ 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})]

Ψ (B_{1u}) = $\emptyset H_{1se}$ + $\emptyset H_{1sf}$ So, there will be no b_{1u} orbital

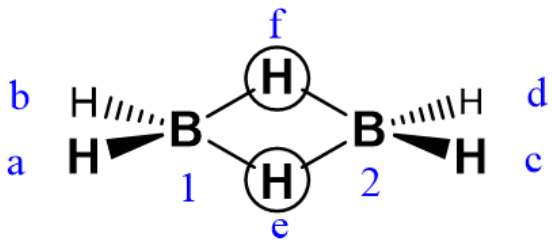
$\Psi(B_{2u})$? = [1(H_{1se}) + (-1)(H_{1sf}) + (1)(H_{1se}) + (-1)(H_{1sf}) + (-1)(H_{1sf}) + (1)(H_{1se}) +(-1)(H_{1sf}) + (1)(H_{1se})]

Ψ (B_{2u}) = 4H_{1se} - 4H_{1sf} So, there will be a b_{2u} orbital

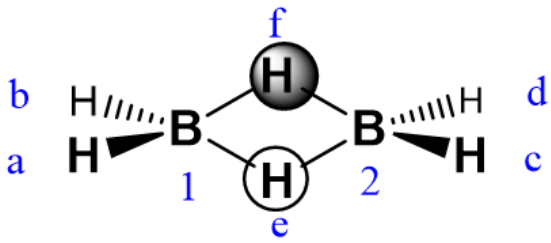
$\Psi(B_{3u})$? = [1(H_{1se}) + (-1)(H_{1sf}) + (-1)(H_{1se}) + (1)(H_{1sf}) + (-1)(H_{1sf}) + (1)(H_{1se}) +(1)(H_{1sf}) + (-1)(H_{1se})]

Ψ (B_{3u}) = $\emptyset H_{1se}$ + $\emptyset H_{1sf}$ So, there will be no b_{3u} orbital

So the second set gives the following bridging hydrogen 1s group orbitals:



a_g



b_{2u}

For Set 3, The B 2s orbitals, taking the 2s 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})]

Ψ (A_g) = 4$B_{s,1}$ + 4$B_{s,2}$ 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})]**

Ψ (B_{1g}) = $\emptyset B_{s,1}$ + $\emptyset B_{s,2}$ 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})]

Ψ (B_{2g}) = $\emptyset B_{s,1}$ + $\emptyset B_{s,2}$ 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})]

Ψ (B_{3g}) = $\emptyset B_{s,1}$ + $\emptyset B_{s,2}$ 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})]

Ψ (A_u) = $\emptyset B_{s,1}$ + $\emptyset B_{s,2}$ 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})]

Ψ (B_{1u}) = $\emptyset B_{s1}$ + $\emptyset B_{s2}$ So, there will be no b_{1u} orbital

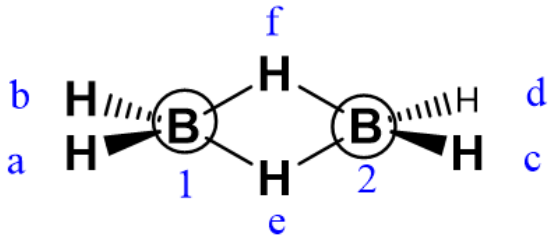
$\Psi(B_{2u})$? = [1(B_{s1}) + (-1)(B_{s2}) + (1)(B_{s2}) + (-1)(B_{s1}) + (-1)(B_{s2}) + (1)(B_{s1}) +(-1)(B_{s1}) + (1)(B_{s2})]

Ψ (B_{2u}) = $\emptyset B_{s1}$ + $\emptyset B_{s2}$ So, there will be no b_{2u} orbital

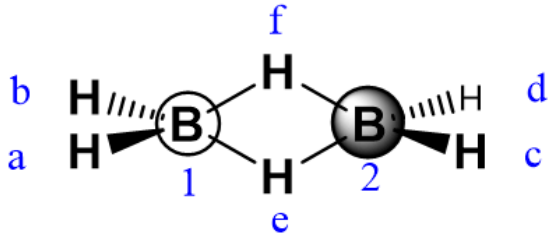
$\Psi(B_{3u})$? = [1(B_{s1}) + (-1)(B_{s2}) + (-1)(B_{s2}) + (1)(B_{s1}) + (-1)(B_{s2}) + (1)(B_{s1}) +(1)(B_{s1}) + (-1)(B_{s2})]

Ψ (B_{3u}) = 4B_{s1} - 4B_{s2} So, there will be one b_{3u} orbital

The boron 2s group orbitals are:



a_g



b_{3u}

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})]

Ψ (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})]

Ψ (B_{1g}) = $\emptyset B_{1px1}$ + $\emptyset B_{1px2}$ 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})]

Ψ (B_{2g}) = $\emptyset B_{1px1}$ + $\emptyset B_{1px2}$ 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})]

Ψ (B_{3g}) = $\emptyset B_{1px1}$ + $\emptyset B_{1px2}$ 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})]

Ψ (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})]

Ψ (B_{1u}) = $0B_{1px1} + 0B_{1px2}$ So, there will be no b_{1u} orbital

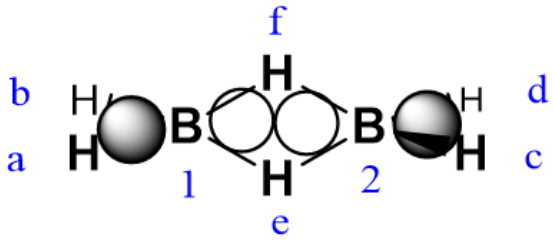
$\Psi(B_{2u})$? = [1($B_{px,1}$) + (-1)(-B_{px2}) + (1)(-B_{px2}) + (-1)(B_{px1}) + (-1)(-B_{px2}) + (1)(B_{px1}) +(-1)(B_{px1}) + (1)(-B_{px2})]

Ψ (B_{2u}) = $0B_{1px1} + 0B_{1px2}$ So, there will be no b_{2u} orbital

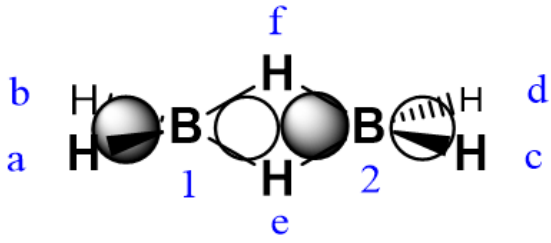
$\Psi(B_{3u})$? = [1($B_{px,1}$) + (-1)(-B_{px2}) + (-1)(-B_{px2}) + (1)(B_{px1}) + (-1)(-B_{px2}) + (1)(B_{px1}) +(1)(B_{px1}) + (-1)(-B_{px2})]

Ψ (B_{3u}) = 4B_{px1} + 4B_{px2} So, there will be one b_{3u} orbital

So the B 2p_x group orbitals are



a_g



b_{3u}

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})]

Ψ (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})]

Ψ (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})]

Ψ (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})]

Ψ (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})]

Ψ (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})]

Ψ (B_{1u}) = $0B_{py1} + 0B_{py2}$; So, there will be no b_{1u} orbital

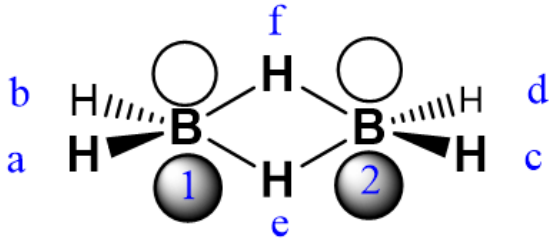
$\Psi(B_{2u})$? =[1(B_{py1}) + (-1)(-B_{py2}) + (1)(B_{py2}) + (-1)(-B_{py1}) + (-1)(-B_{py2}) + (1)(B_{py1}) +(-1)(-B_{py1}) + (1)(B_{py2})]

Ψ (B_{2u}) = 4B_{py1} + 4B_{py2}; So, there will be a b_{2u} orbital

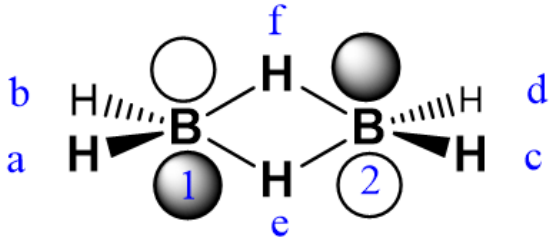
$\Psi(B_{3u})$? = [1(B_{py1}) + (-1)(-B_{py2}) + (-1)(B_{py2}) + (1)(-B_{py1}) + (-1)(-B_{py2}) + (1)(B_{py1}) +(1)(-B_{py1}) + (-1)(B_{py2})]

Ψ (B_{3u}) = $0B_{py1} + 0B_{py2}$; So, there will be no b_{3u} orbital

So the B 2p_y group orbitals are



b_{2u}



b_{1g}

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})]

Ψ (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})]

Ψ (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})]

Ψ (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})]

Ψ (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

$\Psi(B_{1u})? = [1(B_{pz1}) + (1)(B_{pz2}) + (-1)(-B_{pz2}) + (-1)(-B_{pz1}) + (-1)(-B_{pz2}) + (-1)(-B_{pz1}) +(1)(B_{pz1}) + (1)(B_{pz2})]$

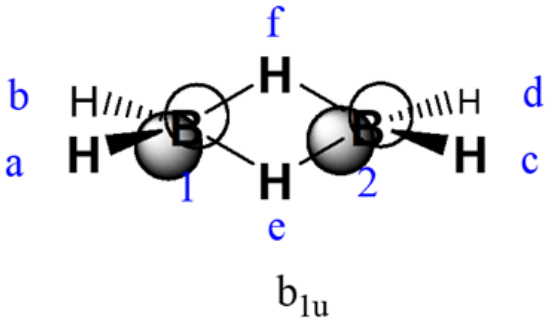
$\Psi\ (B_{1u}) = 4\ B_{pz1} + 4B_{pz2}$ So, there will be a b_{1u} orbital

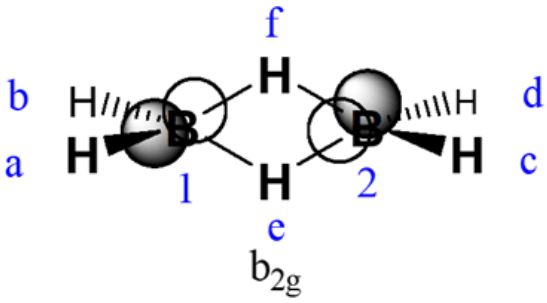
$\Psi(B_{2u})? = [1(B_{pz1}) + (-1)(B_{pz2}) + (1)(-B_{pz2}) + (-1)(-B_{pz1}) + (-1)(-B_{pz2}) + (1)(-B_{pz1}) +(-1)(B_{pz1}) + (1)(B_{pz2})]\Psi\ (B_{2u}) = 0\ B_{pz1} + 0B_{pz2}$ So, there will be no b_{2u} orbital

$\Psi(B_{3u})? = [1(B_{pz1}) + (-1)(B_{pz2}) + (-1)(-B_{pz2}) + (1)(-B_{pz1}) + (-1)(-B_{pz2}) + (1)(-B_{pz1}) +(1)(B_{pz1}) + (-1)(B_{pz2})]$

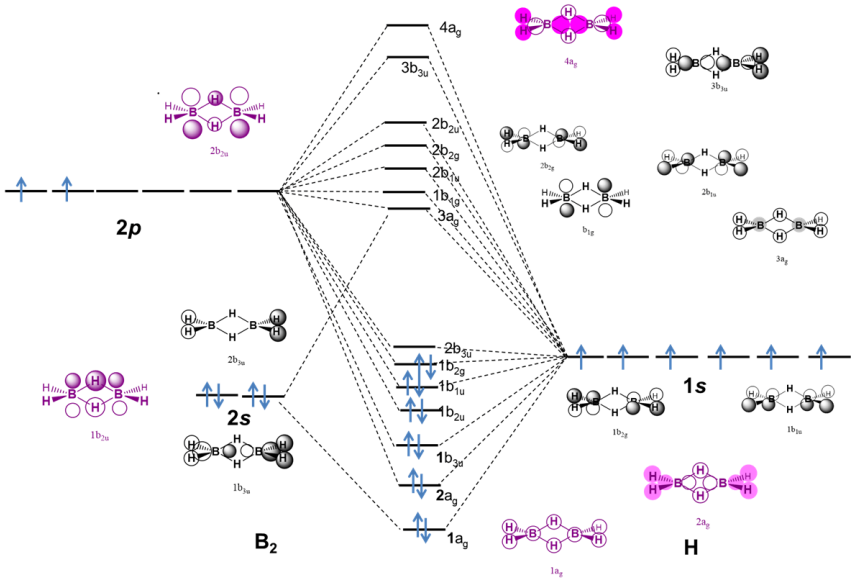
$\Psi\ (B_{3u}) = 0\ B_{pz1} + 0B_{pz2}$ So, there will be no b_{3u} orbital

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.



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8.6.2: 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 8.6.2.1A, 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 8.6.2.1B.

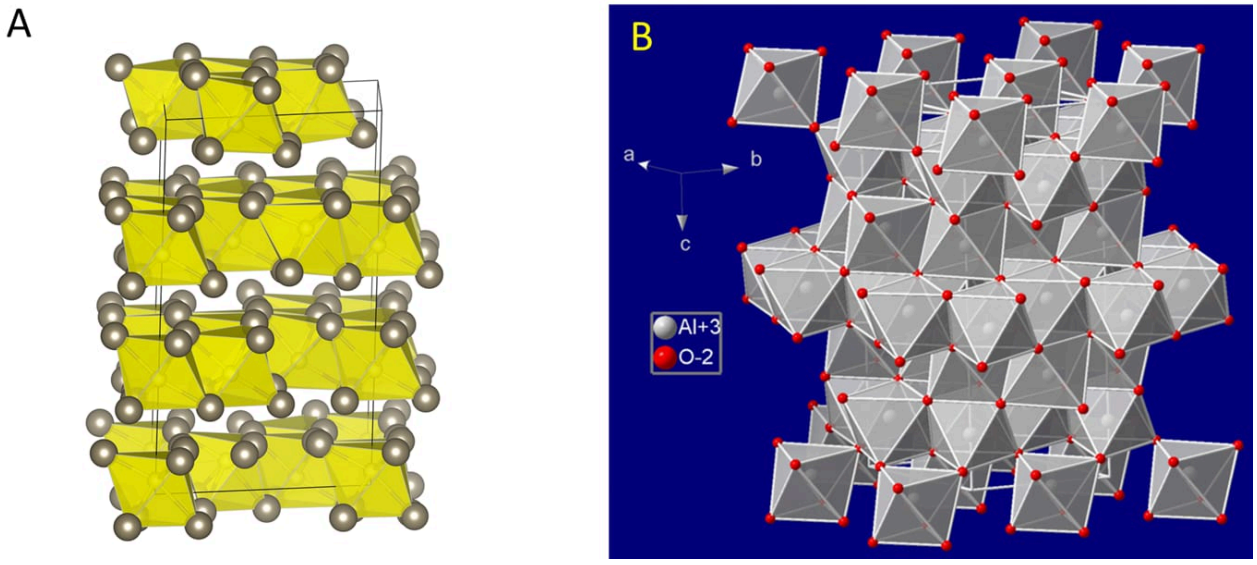


Figure 8.6.2.1. (A) The CdI_2 structure adopted by Tl_2O showing layers of edge-linked Tl_6O octahedra and (B) Corundum Al_2O_3 structure consisting of layers of edge-linked AlO_6 octahedra (in the horizontal) vertex-linked adjacent layers (in the vertical direction). The CdI_2 structure image is by 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 8.6.2.**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 8.6.2.**I.** Two views of the $Al_6O_{18}^{18-}$ anion.

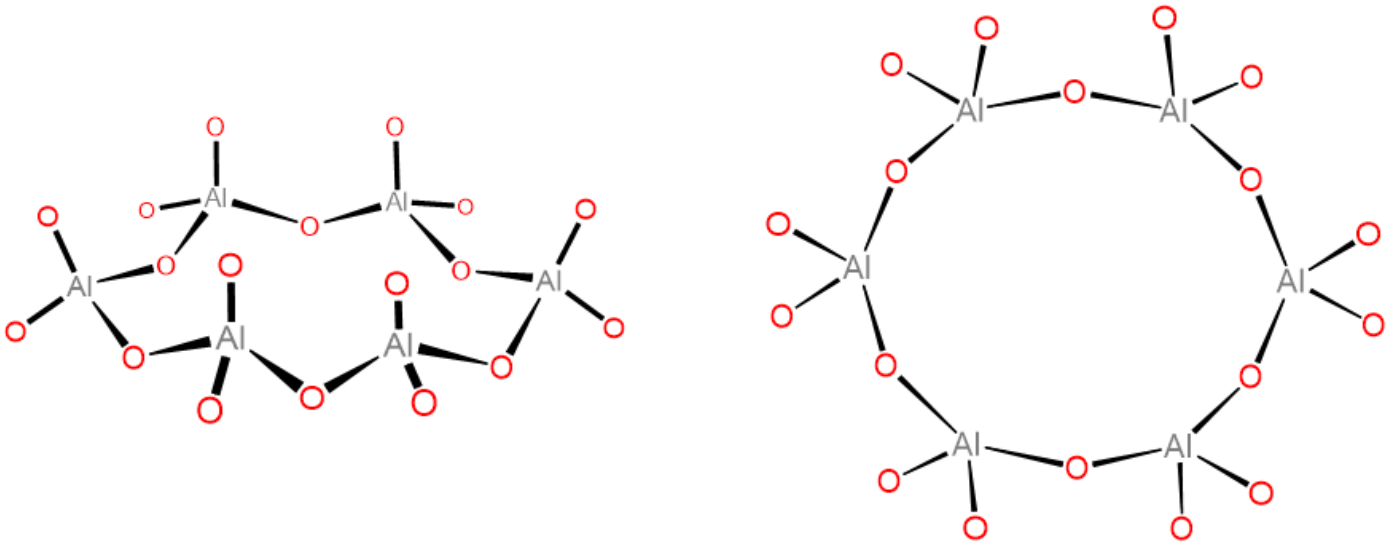


Figure 8.6.2.2 is illustrative. It forms a network structure as a solid, as liquid exists as a E_2X_6 dimer, and in the gas phase is a mixture of dimers and monomers, ultimately giving the monomer only at high temperatures.

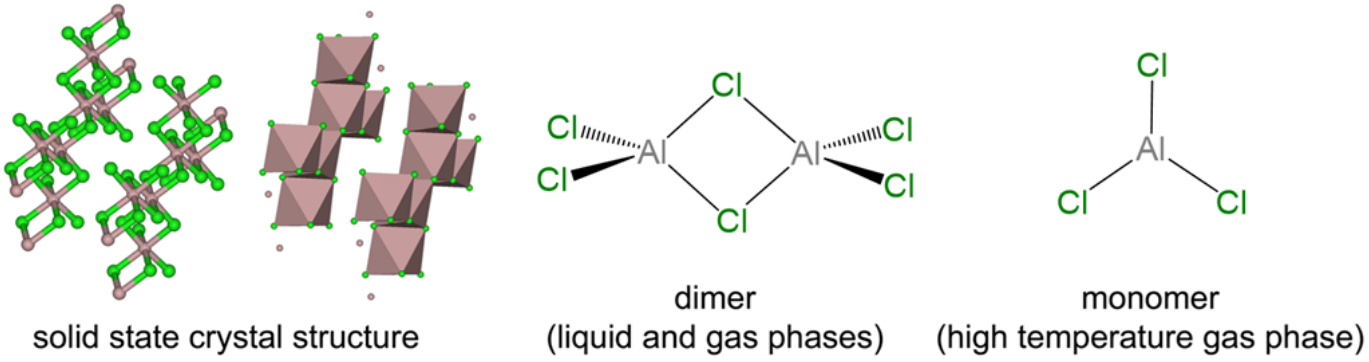
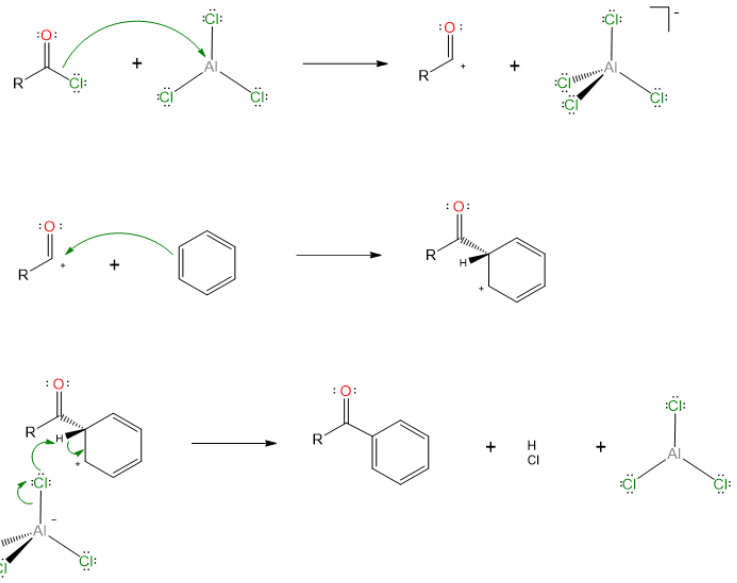


Figure 8.6.2.2. Representative group 13 trihalides. The solid state structure and text are adapted from an image by Benjah-bmm27 taken from https://upload.wikimedia.org/wikipedia/commons/4/42/Aluminium-trichloride-3D-structures.png.

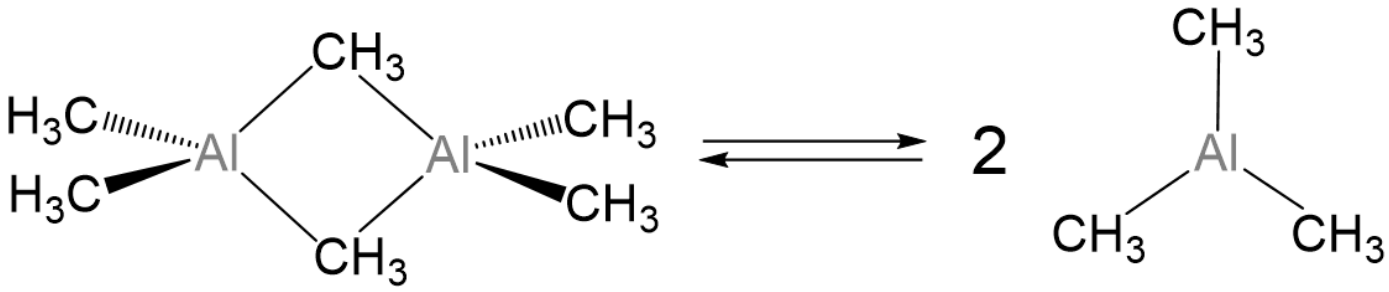
The aluminum trihalides are effective Lewis acids. This property serves as the basis for their use as a catalyst in Friedel-Crafts alkylations and acylations. In these reactions, $AlCl_3$ acts as a Lewis base to abstract a chloride ion from an alkyl or acyl halide, generating a carbon-based cation that can add to an aromatic ring in an electrophilic aromatic substitution reaction (Scheme 8.6.2.**II**).

Scheme 8.6.2.**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 8.6.2.**II**) for smaller alkyl groups, shifting towards monomer with bulky ones.

Scheme 8.6.2.**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 8.6.2.3A. 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 8.6.2.3.

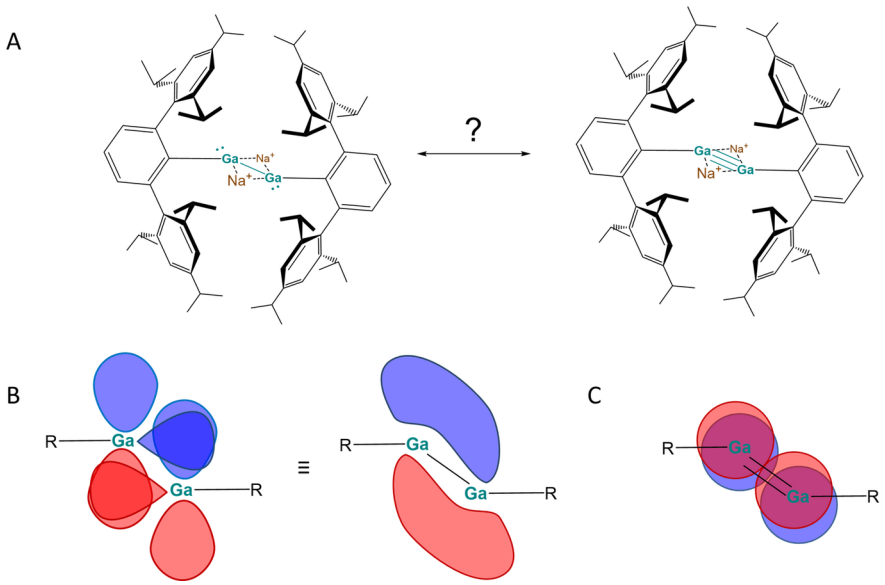


Figure 8.6.2.3. (A) Two Lewis depictions of possible bonding arrangements in Robinson's Gallyne, in which the bond between the Ga atoms has been proposed to consist of (B) an overlap between σ type and *p* orbitals on the two Ga atoms, equivalent to the σ bond and a Klinkhammer-type slipped π bond. (C) 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 8.6.2.4.

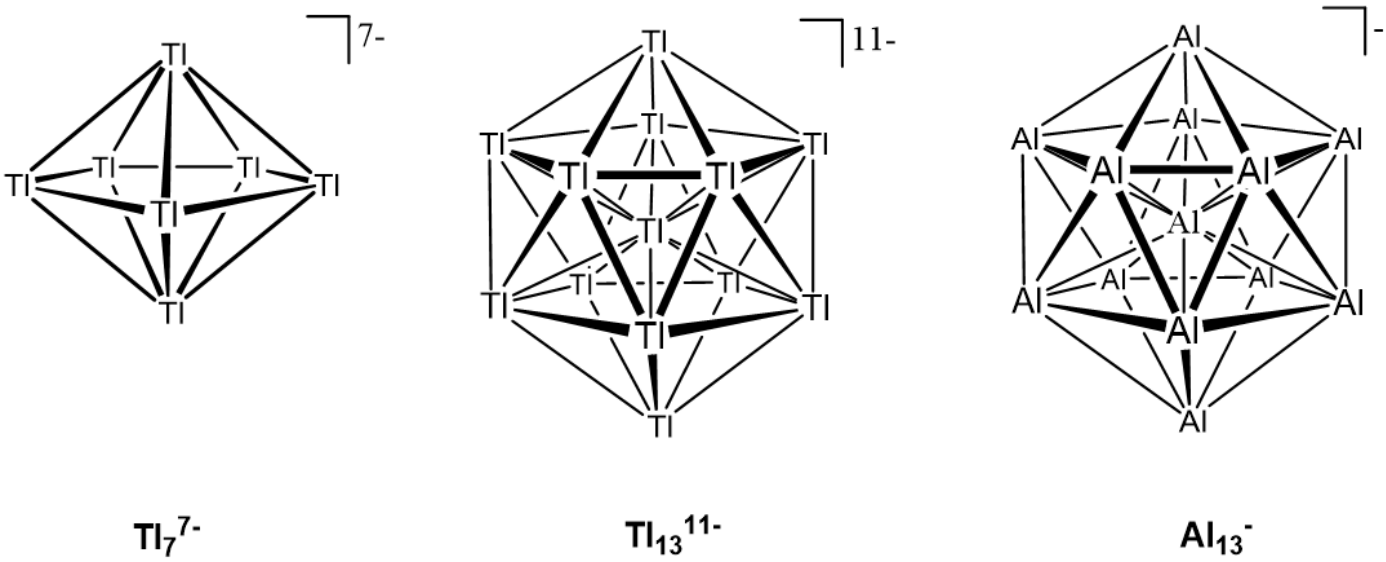


Figure 8.6.2.4. Structures of some naked metal clusters. The shapes of these are often analogous to those of stable boranes, although in many of them, one of the atoms occupies the cluster interior.

As may be seen from the structures in Figure 8.6.2.4, 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**

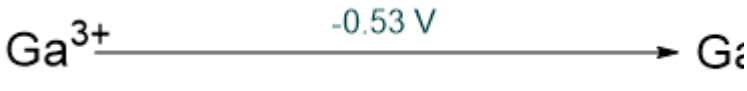
Metalloid clusters consist of a small particle of metal surrounded by ligands. Some such Al and Ga clusters even contain upwards of 69 atoms. Examples include clusters with formulas $[Al_{69}\{N(SiMe_3)_2\}_{18}]^{3-}$ and $[Al_{77}N(SiMe_3)_2\}_{20}]^{2-}$. The structure of a relatively small example is given in Figure 8.6.2.5.

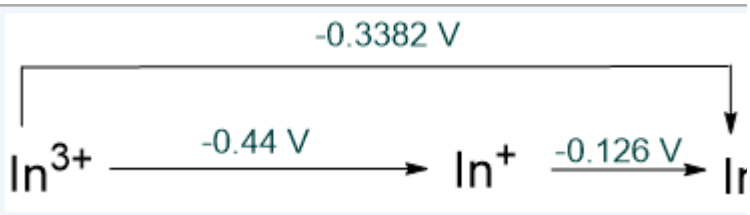
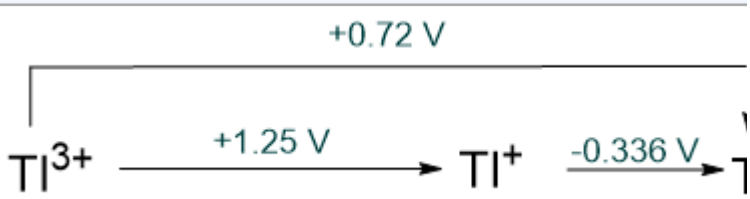
Figure 8.6.2.5. Structure of $Cp^*_{10}Al_{50}$ ($Cp^* = C_5(CH_3)_5^-$). By Smokefoot - Own work, CC BY-SA 4.0, commons.wikimedia.org/w/inde...curid=87686580

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 8.6.2.1.

Table 8.6.2.1**.** 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 8.6.2.1, 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 ns 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 8.6.2.**III**.

Scheme 8.6.2.**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 ns orbitals become lower in energy on going down a group of the periodic table. As may be seen from the energies given in Figure 8.6.2.6, the energy of the ns 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.

key: s orbitals
p orbitals
d orbitals
units: eV

H -13.61																	He -24.59
Li -5.39	Be -9.32											B -14.05 -8.30	C -19.43 -10.66	N -25.56 -13.18	O -32.38 -15.85	F -40.17 -18.65	Ne -48.47 -21.59
Na -5.14	Mg -7.65											Al -11.32 -5.98	Si -14.89 -7.78	P -18.84 -9.65	S -22.71 -11.62	Cl -25.23 -13.67	Ar -29.24 -15.82
K -4.34	Ca -6.11	Sc -6.60 -7.92	Ti -7.12 -9.22	V -7.32 -10.11	Cr -7.46 -10.75	Mn -7.84 -11.14	Fe -7.91 -11.66	Co -8.10 -12.12	Ni -8.22 -12.93	Cu -8.42 -13.47	Zn -9.39 -17.30	Ga -12.61 -5.93	Ge -16.05 -7.54	As -18.94 -9.17	Se -21.37 -10.82	Br -24.37 -12.49	Kr -27.51 -14.22
Rb -4.18	Sr -5.70	Y -6.70 -6.49	Zr -7.31 -8.31	Nb -7.22 -8.86	Mo -7.24 -9.14	Tc -7.21 -9.25	Ru -7.13 -9.31	Rh -7.28 -9.45	Pd -7.44 -9.58	Ag -7.58 -12.78	Cd -8.99 -17.86	In -11.89 -5.60	Sn -14.56 -7.01	Sb -16.74 -8.41	Te -18.71 -9.79	I -20.89 -11.18	Xe -23.40 -12.56
Cs -3.90	Ba -5.21	La -7.04 -5.28	Hf -7.52 -6.14	Ta -8.45 -7.58	W -8.52 -8.76	Re -8.76 -9.70	Os -8.82 -10.00	Ir -8.83 -10.22	Pt -8.75 -10.37	Au -9.22 -11.86	Hg -10.44 -15.59	Tl -13.14 -5.47	Pb -15.12 -6.81	Bi -17.52 -8.15	Po -20.05 -9.42	At -22.69 -10.71	Rn -25.47 -12.03
Fr ?	Ra ?	Ac ?															

Figure 8.6.2.6. 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 8.6.2.2 and bond energies given in Table 8.6.2.3.[15]

Table 8.6.2.2**.** 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 8.6.2.3**.** 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 8.6.2.3, 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 8.6.2.7A, 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.

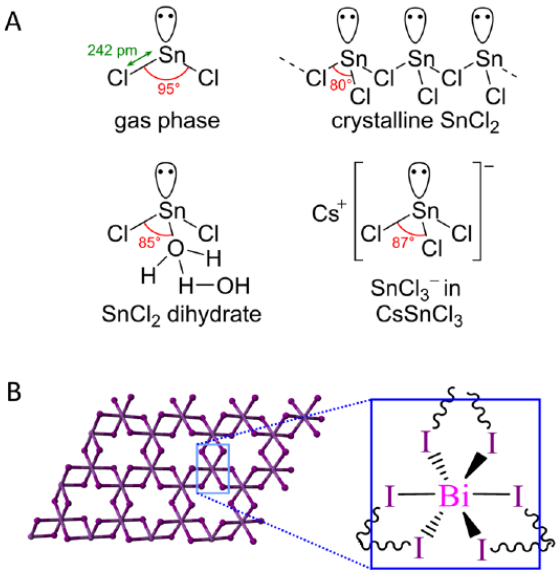


Figure 8.6.2.7. (A) Steroechemically active inert pairs in $SnCl_2$ and several of its Lewis base adducts. (B) Stereochemically inert lone pairs in BiI_3. The $SnCl_2$ image is by Hbf878 - Own work, CC0, commons.wikimedia.org/w/inde...curid=64768302. The BiI_3 image is adapted from the structure drawn 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 8.6.2.7B, 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 8.6.2.8).

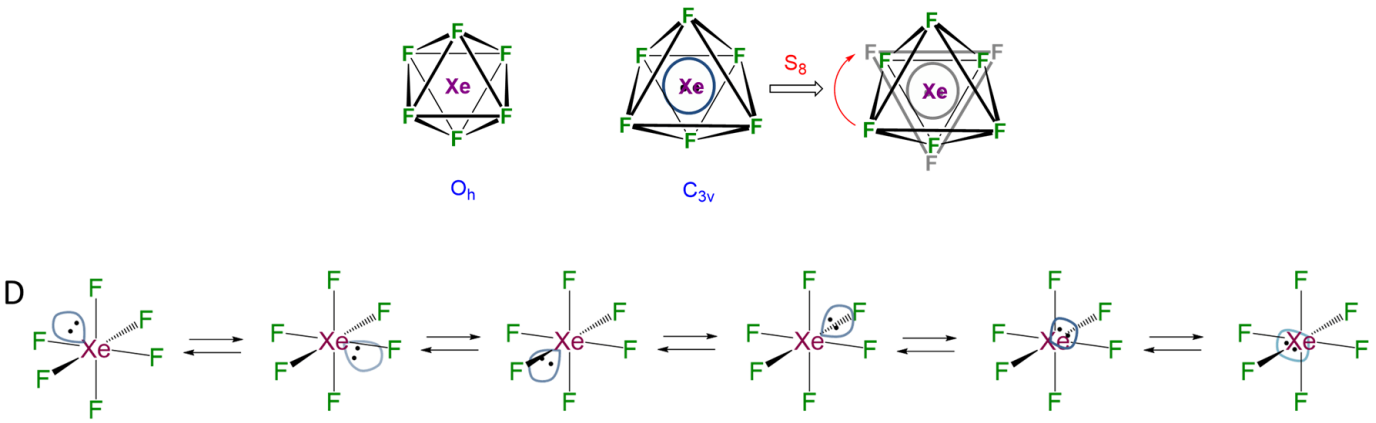


Figure 8.6.2.8. The appearance of stereochmeical inactivity on the part of the inert pair in BiI_3 can likely be explained in terms of fluxional behavior similar to that believed to take place in XeF_6. (A) If the lone pair of XeF_6 were stereochemically inactive, the compound would possess true O_h 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.

Notes and References

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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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8.7: 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 8.7.1.

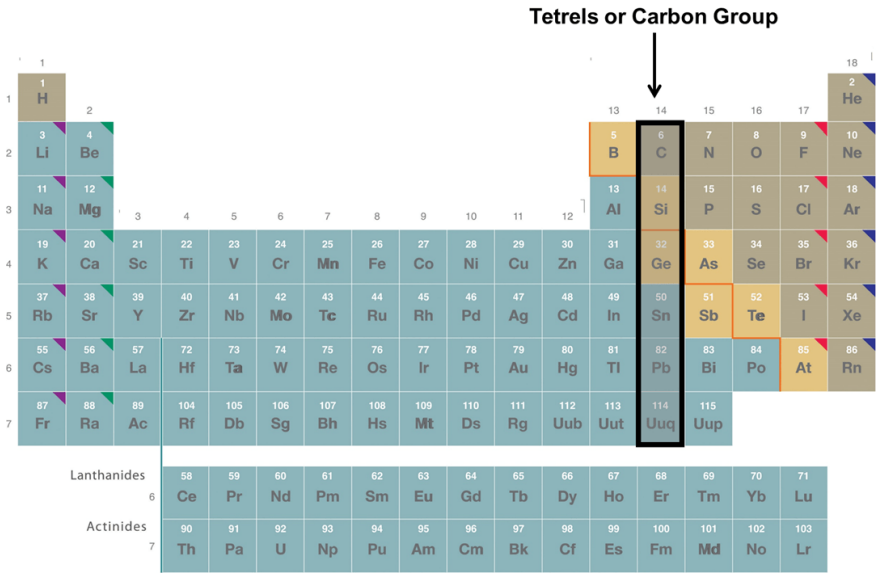


Figure 8.7.1. The Group 14 elements. Note that since the periodic table used was developed element 115 was named Flerovium and given the symbol Fl. Adapted from the periodic table at https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/02._Atoms%2C_Molecules%2C_and_Ions/2.5%3A_The_Periodic_Table

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8.7.1: 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 8.7.1.1.

Table 8.7.1.1: 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
***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.					

Property	Carbon	Silicon	Germanium	Tin	Lead
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 8.7.1.1, 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 8.7.1.1 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

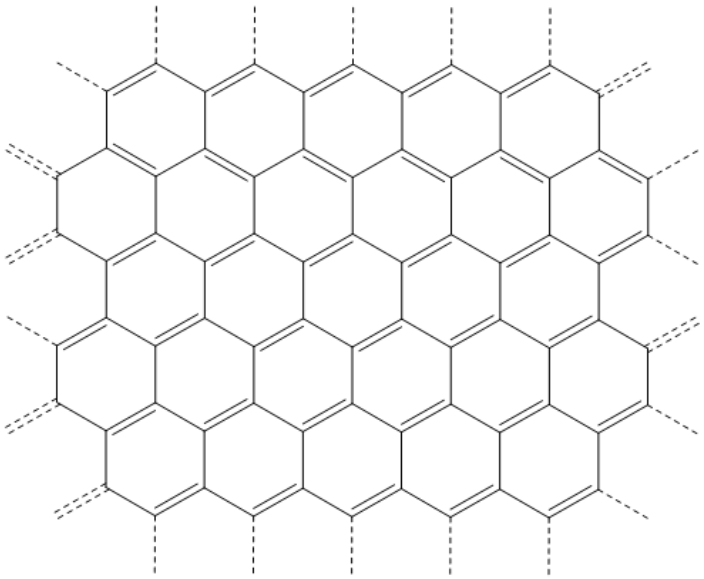
Carbon's ability to form strong multiple bonds enables it to form a host of molecular and network covalent allotropes. Some of these allotropes have been known since ancient times; some are a focus of much active research. The major classes of allotropes include:

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 8.7.1.**I**.

Scheme 8.7.1.**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 pi 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 8.7.1.1. 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 8.7.1.1b).

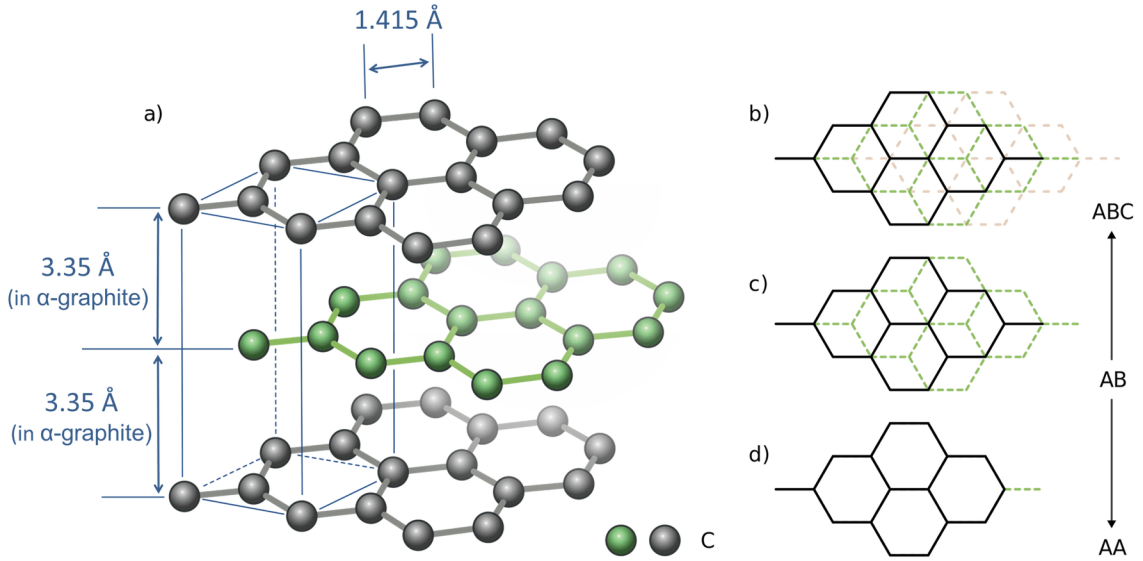


Figure 8.7.1.1. Graphite structures. (a) Structure of α-graphite showing the offset of adjacent graphene layers that alternate in an AB pattern along with (b-d) additional stacking arrangements of the graphene layers. The AB stacking arrangement corresponds to α-graphite and the ABC arrangement to β-graphite. 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 8.7.1.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 8.7.1.2.

Figure 8.7.1.2. 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 8.7.1.3. 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).

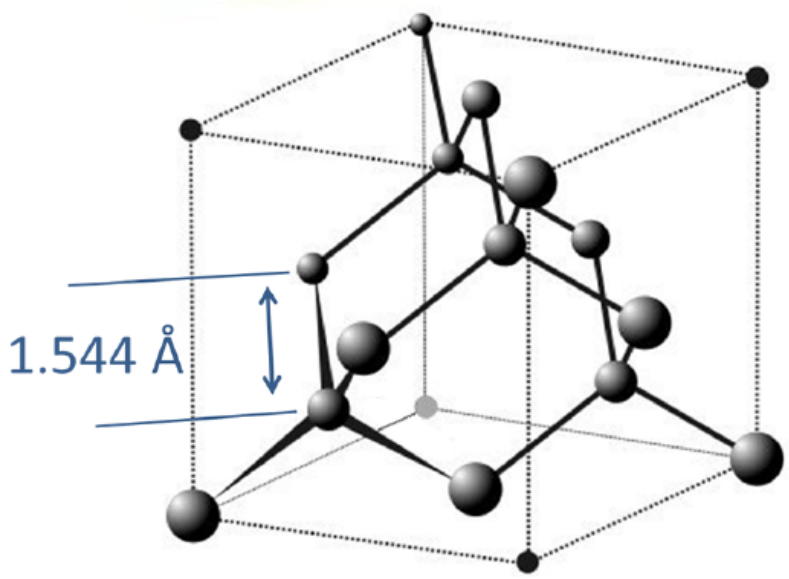


Figure 8.7.1.3. Diamond structure. The image is extracted and slightly modified from Diamond_and_graphite.jpg: by User:Itubderivative work: Materialscientist (talk) - Diamond_and_graphite.jpgFile:Graphite-tn19a.jpg, CC BY-SA 3.0, commons.wikimedia.org/w/inde...?curid=7223557.

4. Fullerenes. Since the late 1980s discovery of the sixty-carbon European football (soccer ball) shaped buckminsterfullerene shown in Figure 8.7.1.4A, 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 8.7.1.4B.

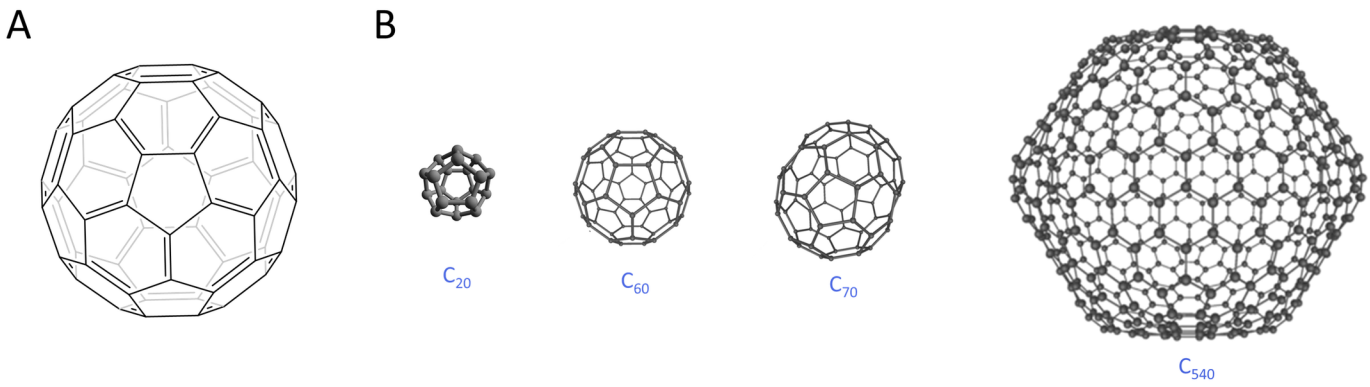
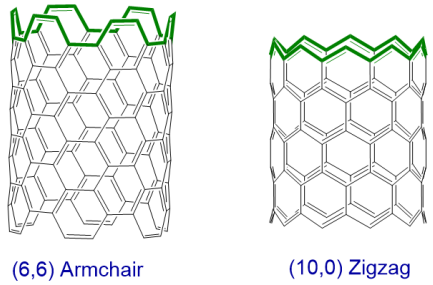


Figure 8.7.1.4**.** Structures of several fullerenes: (A) buckminsterfullerene, C_{60}, named after the American architect Buckminster Fuller, who popularized the use of geodesic domes; (B) C_{70}, and (C) C_{540}. The image of C_{20} is taken from By Perditax - Own work, CC0, commons.wikimedia.org/w/inde...curid=15480223; the 3D images of 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 8.7.1.5. These exist in different arrangements classified according to how the graphite sheet is oriented relative to the nanotube axis.



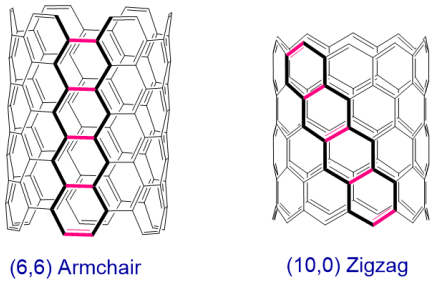


Figure 8.7.1.5. An example of an armchair and a zigzag nanotube. Note that contrary to what some textbooks claim, armchair and zigzag nanotubes do not represent different nanotube conformations but rather different configurations of carbons in a nanotube.

As shown in Figure 8.7.1.6, 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 8.7.1.7, 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 8.7.1.7, bottom).

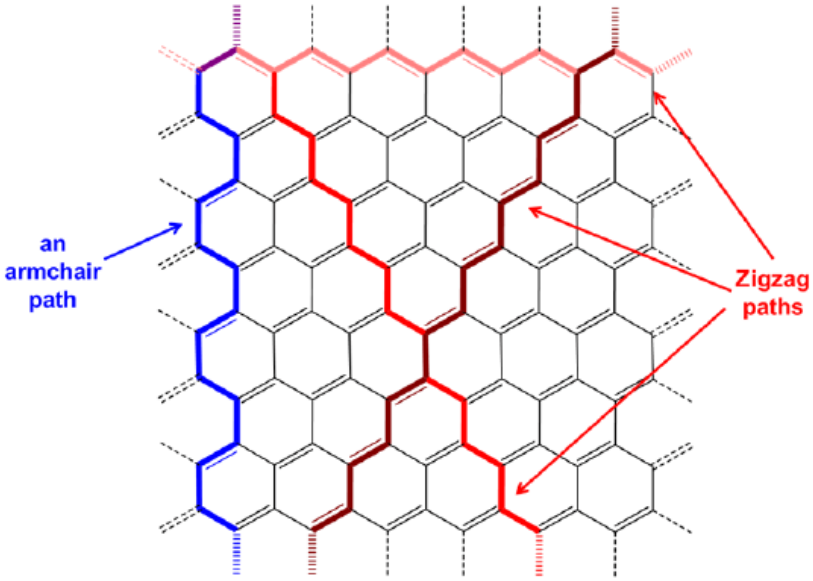


Figure 8.7.1.6. Connected paths of bonds in a graphene sheet are classified as involving armchair paths or zigzag paths.

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 8.7.1.7, 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.

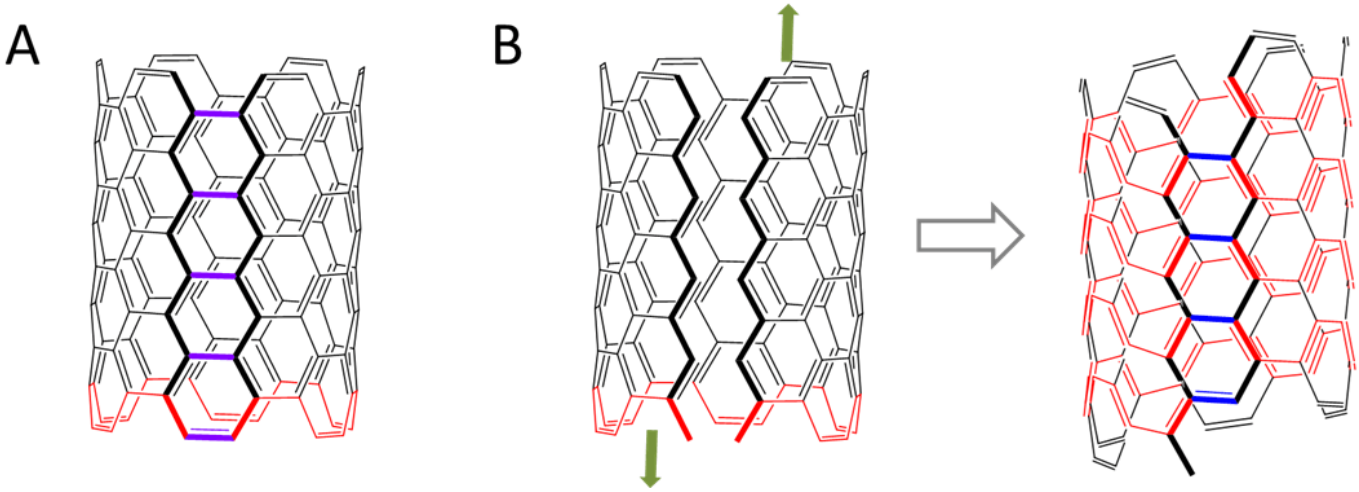


Figure 8.7.1.7. (A) The armchair and zigzag paths that define a nanotube as armchair or zigzag wrap form circular paths in an ordinary nanotube. In a helical nanotube the paths are coiled in a helix arrangement. (B) Such helical nanotubes may be thought of as formed by connecting the zigzag ends of a 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** 8.7.1.8**.**

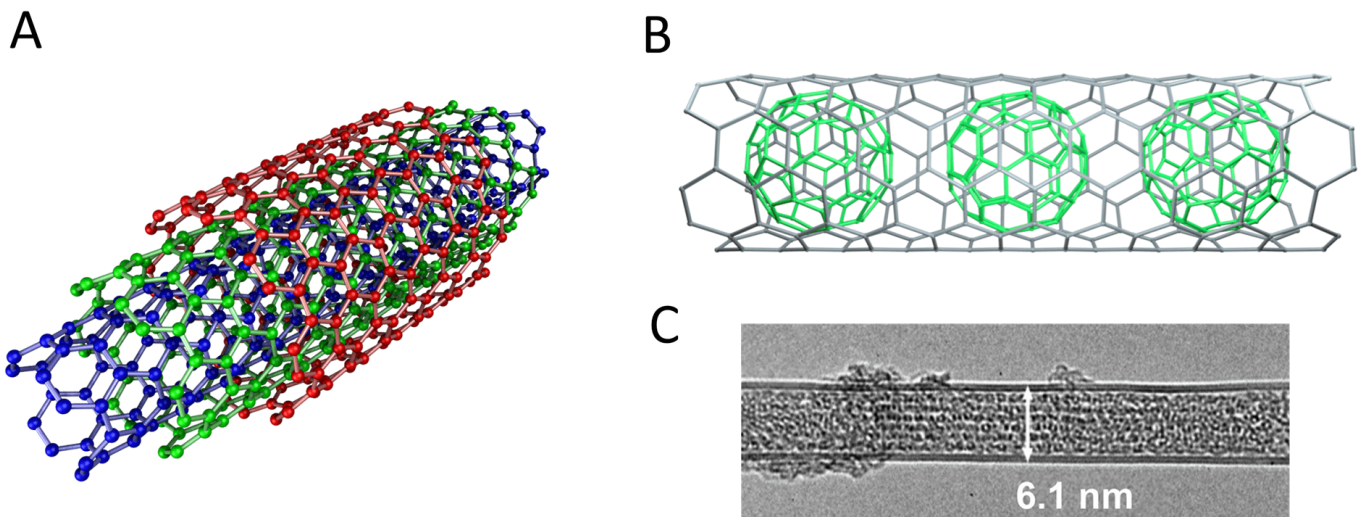


Figure 8.7.1.8. (A) Model of a triple wall carbon nanotube; (B) Carbon peapod structure consisting of C_{60} chains in a single walled carbon nanotube; (C) TEM image of a 6.1 nm wide double walled carbon nanotube filled with C_{60} molecules (for reference a 6-membered aromatic ring is ~0.00025 nm wide). 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 8.7.1.9.
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.

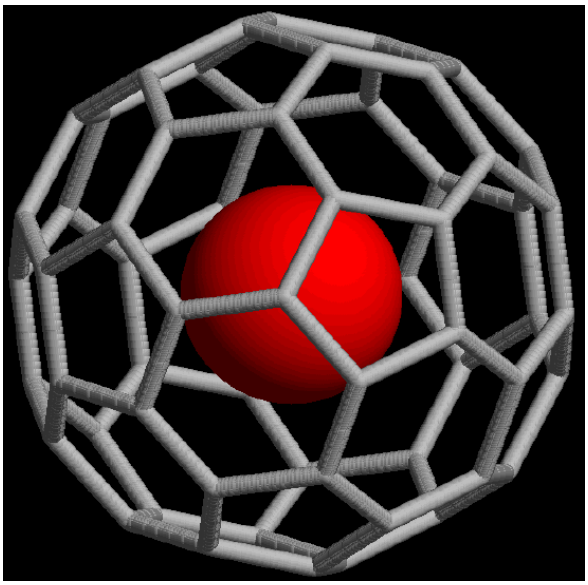


Figure 8.7.1.9. Model of an endohedral complex of buckminsterfullerene, M@C_{60}. Such complexes can form in conjunction with oxidation of the metal and reduction of the fullerene and so might be described as $M^{z+}@C_{60}^{z-}$. However, many examples of neutral endohedral complexes are also known, 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 8.7.1.10.

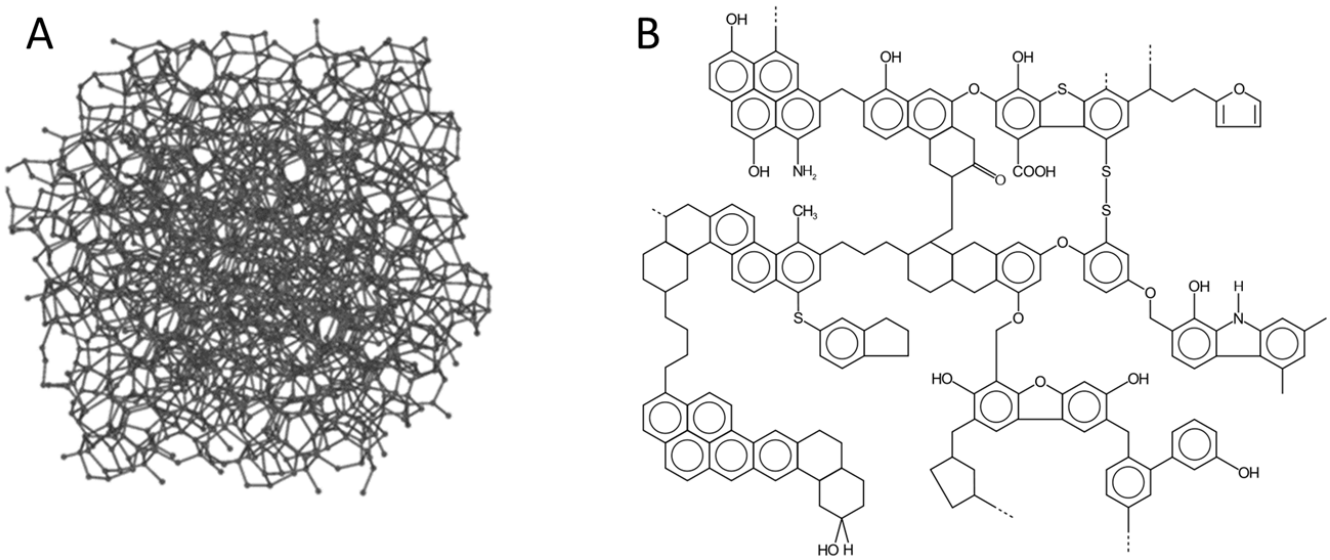


Figure 8.7.1.10. Models illustrative of the molecular structure of (A) amorphous carbon and (B) coal. Although the presence of non-carbon material is most apparent in the structure of coal, neither are not true allotropes since they contain C-H bonds and other organic material. The image of amorphous 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** 8.7.1.11**.**

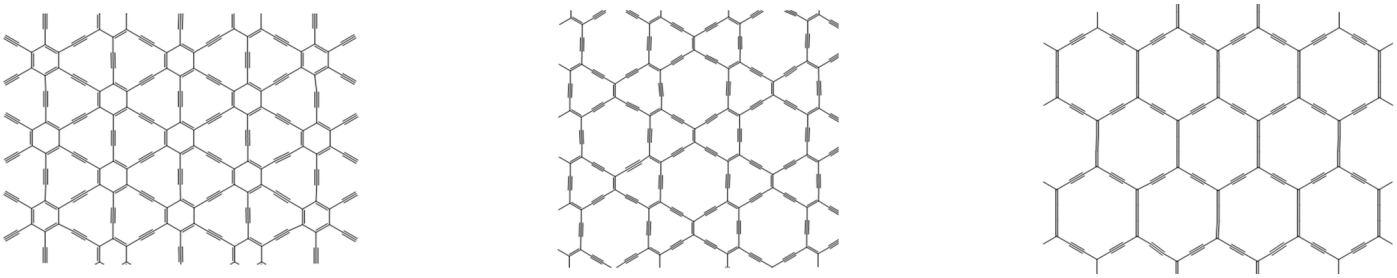


Figure 8.7.1.11. A variety of graphyne structures that have been proposed as theoretically stable. As of July 2020 no sample of stable graphyne has been made experimentally.

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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8.7.2: Inorganic Compounds of the Group 14 Elements

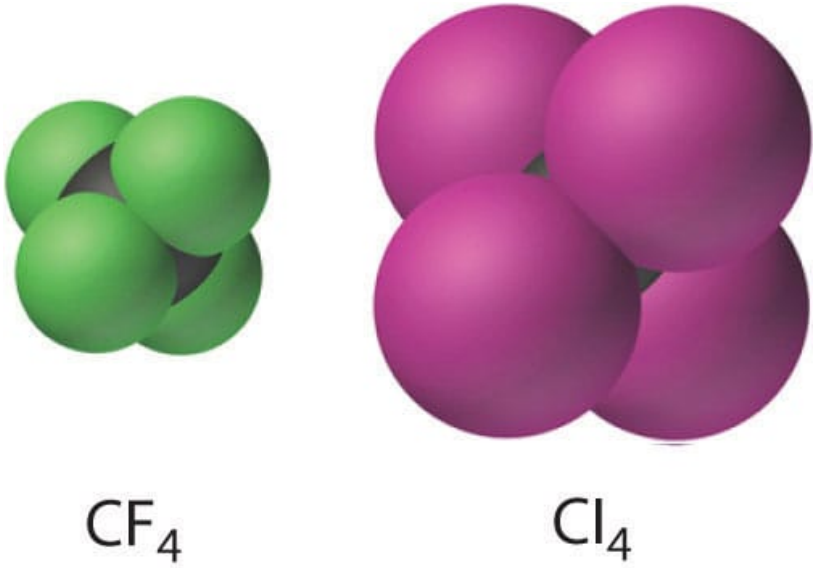
Reactions and Compounds of Carbon

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:

$$CH_{4(g)} + 4X_{2(g)} \rightarrow CX_{4(l,s)} + 4HX_{(g)} \tag{8.7.2.1}$$



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:

$$\mathrm{HCO_2H(l)} \xrightarrow{\mathrm{H_2SO_4(l)}} \mathrm{CO(g) + H_3O^+(aq) + HSO_4^-} \tag{8.7.2.2}$$

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:

$$\mathrm{CO(g) + Cl_2(g)} \xrightarrow{\Delta} \mathrm{Cl_2C{=}O(g)} \tag{8.7.2.3}$$

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):

$$\mathrm{C(s) + 2S(g)} \xrightarrow{\Delta} \mathrm{CS_2(g)} \tag{8.7.2.4}$$

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 8.7.2.1

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 8.7.2.1

Predict the products of the reactions and write a balanced chemical equation for each reaction.

a. C(s) + excess O_2(g) $\xrightarrow{\Delta}$
b. C(s) + H_2O(l) →
c. $NaHCO_3$(s) + H_2SO_4(aq) →

Answer

a. C(s) + excess O_2(g) $\xrightarrow{\Delta}$ CO_2(g)
b. C(s) + H_2O(l) → no reaction
c. $NaHCO_3$(s) + H_2SO_4(aq) → 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.

YouTube Video

This interactive element is not available in this format. Visit the link or scan the QR code to access it online.

View this YouTube Video online

Video 8.7.2.1*: 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):

$$MX_{4(s,l)} + 2H_2O_{(l)} \rightarrow MO_{2(s)} + 4HX_{(aq)} \tag{8.7.2.5}$$

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 8.7.2.3). 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.

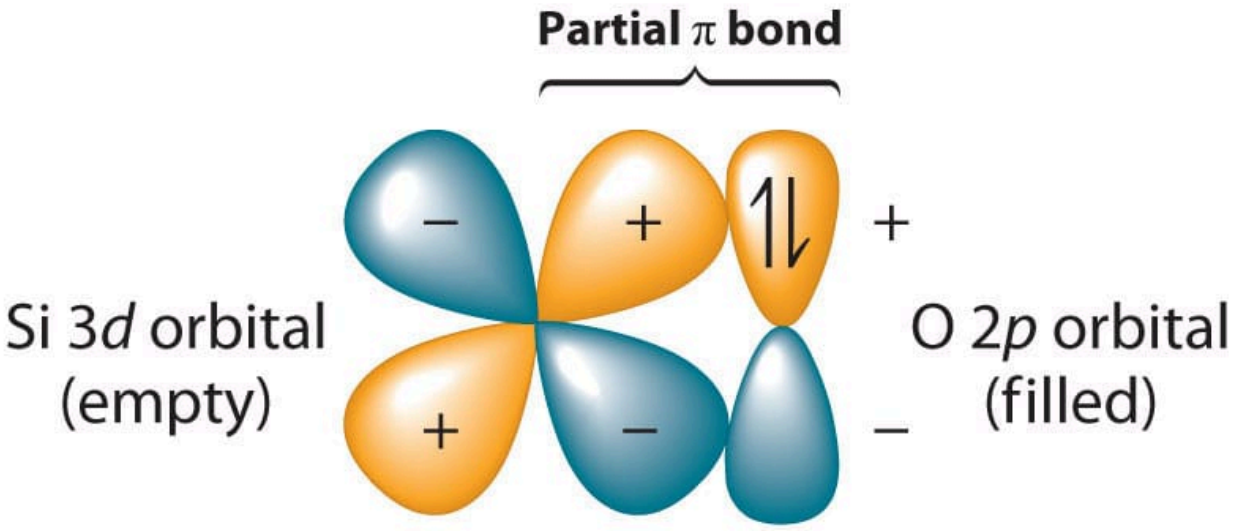
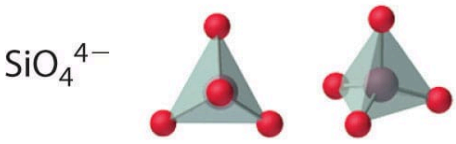


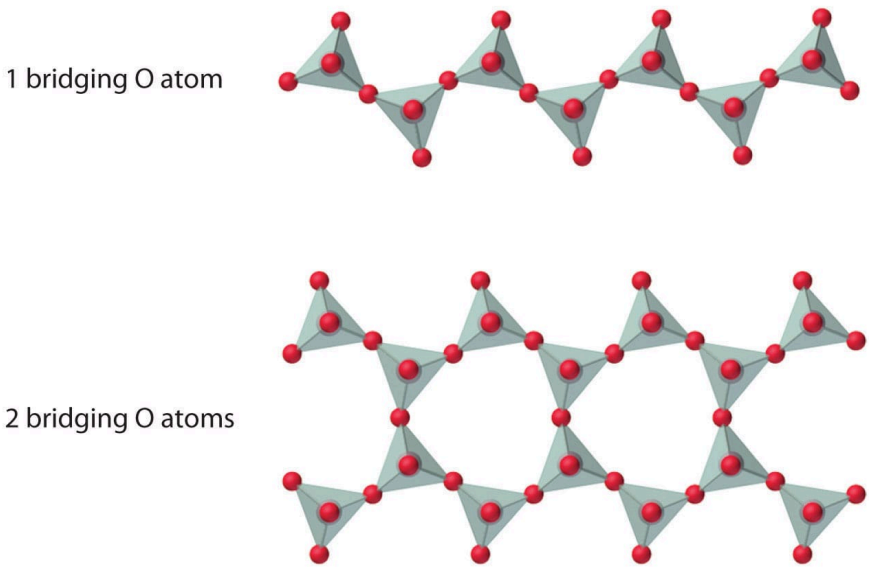
Figure 8.7.2.3: π Bonding between silicon and oxygen. Silicon has relatively low-energy, empty 3d orbitals that can interact with filled 2p hybrid orbitals on oxygen. This interaction results in a partial π bond in which both electrons are supplied by oxygen, giving the Si–O bond partial double bond 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 8.7.2.4). 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.

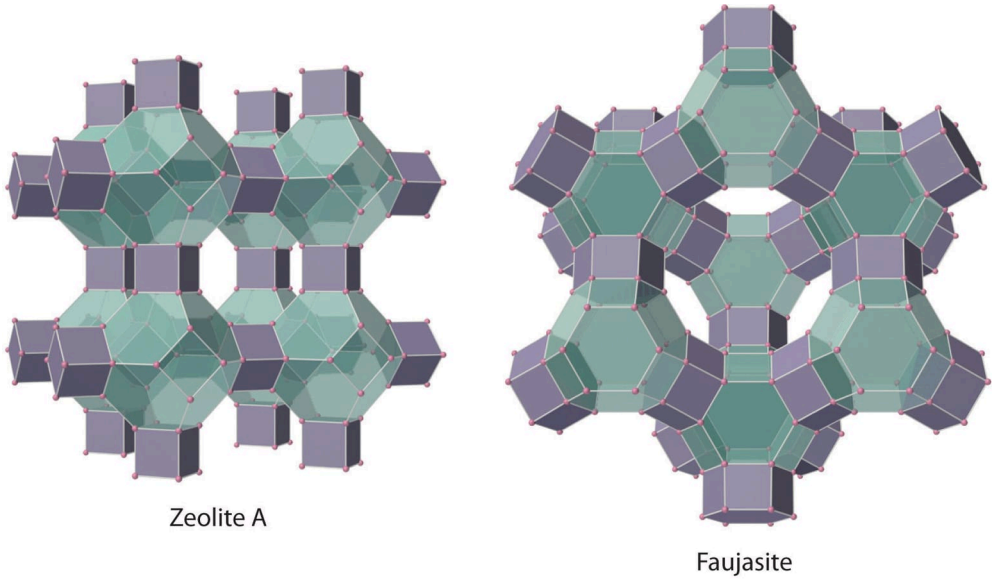


Figure 8.7.2.4: Zeolites are aluminosilicates with large cavities connected by channels. The cavities normally contain hydrated cations that are loosely bound to the oxygen atoms of the negatively charged framework by electrostatic interactions. The sizes and arrangements of the channels and cavities 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):

$$3Si_{(l)} + 2N_{2(g)} \rightarrow Si_3N_{4(s)} \tag{8.7.2.6}$$

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:

$$Mg_2Si_{(s)} + 4H^+_{(aq)} \rightarrow 2Mg^{2+}_{(aq)} + SiH_{4(g)} \tag{8.7.2.7}$$

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.

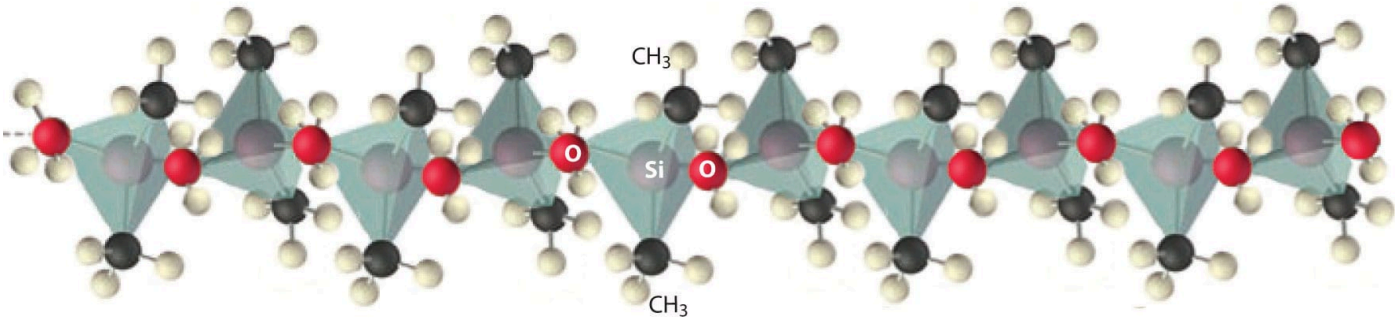


Figure 8.7.2.5 Silicones are polymers with long chains of alternating silicon and oxygen atoms. The structure of a linear silicone polymer is similar to that of quartz, but two of the oxygen atoms attached to each silicon atom are replaced by the carbon atoms of organic groups, such as the methyl groups (–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 8.7.2.5). 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 8.7.2.2

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 8.7.2.2

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. $PbO_2(s) \xrightarrow{\Delta} PbO(s) + \frac{1}{2}O_2(g)$
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.

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8.7.3: 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).

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8.7.4: 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).

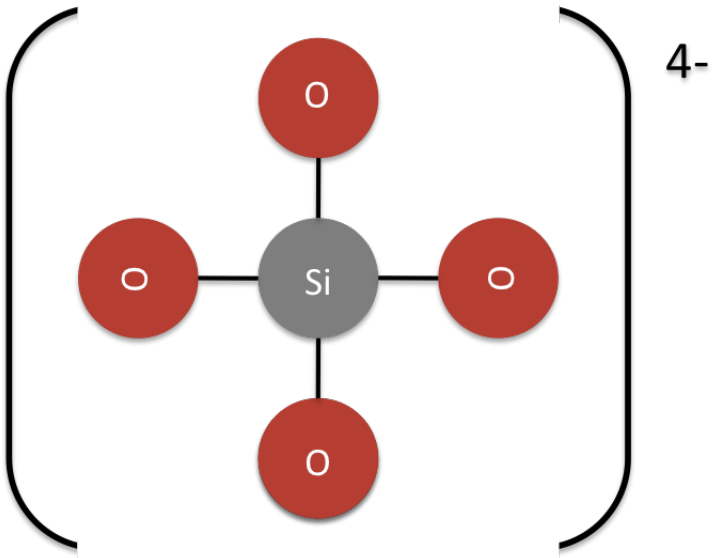


Figure 2: The net charge of silica is minus 4

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.

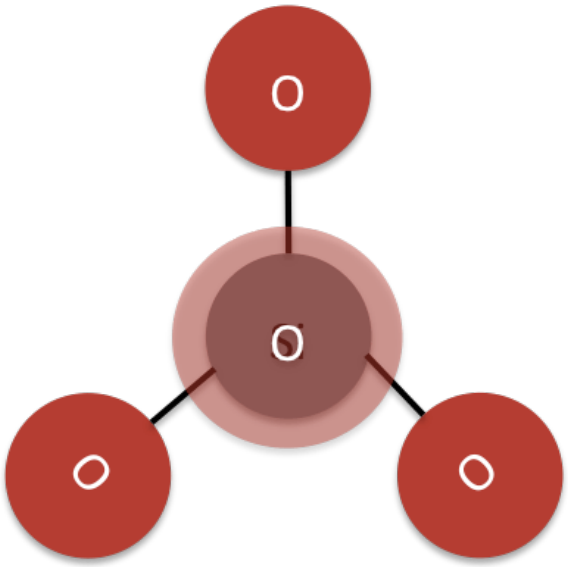


Figure 3: This is a representation of the tetrahedral silica complex

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-}.

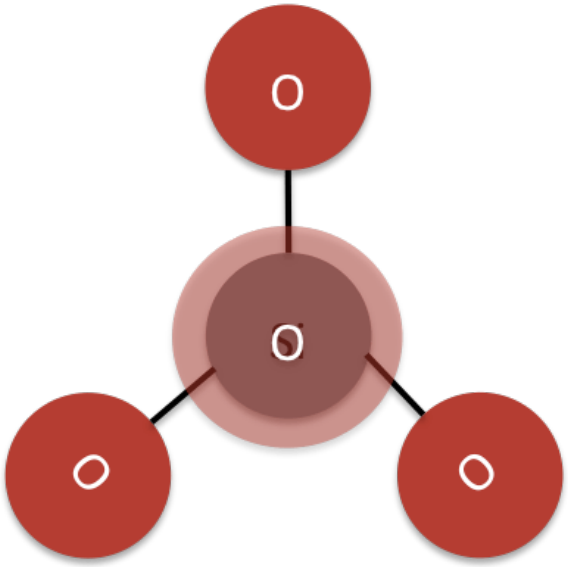


Figure 4: The core of a nesosilicate

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)

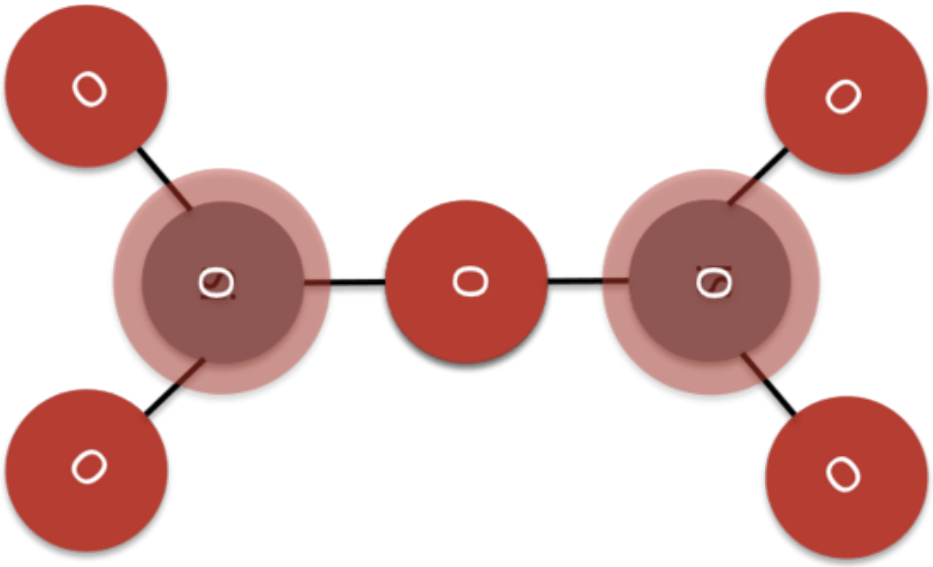


Figure 5: The core of a sorosilicate

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)

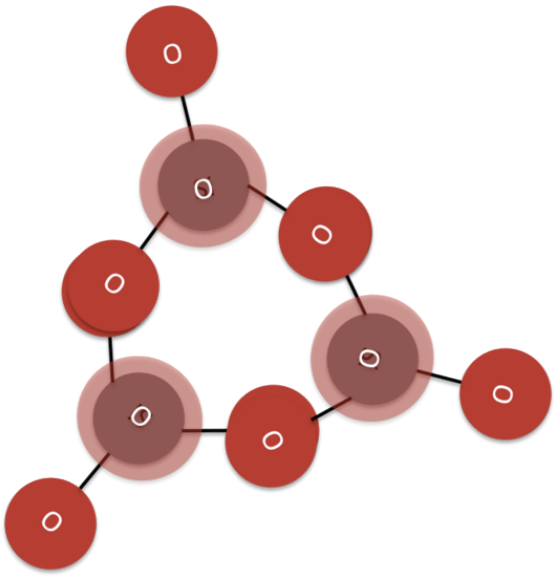


Figure 6: The core of a cyclosilicate

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.

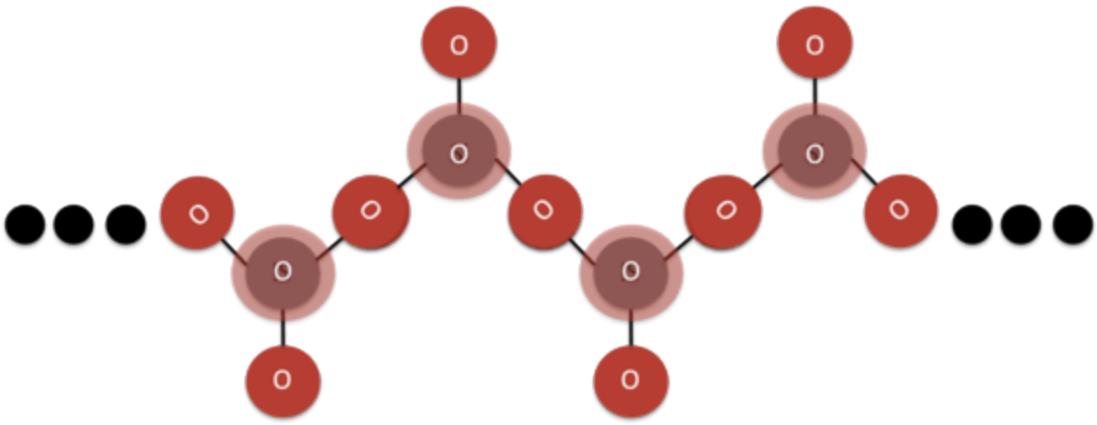


Figure 7: The core of a single chain inosilicate

The mineral group pyroxenes are examples of single chain inosilicates.

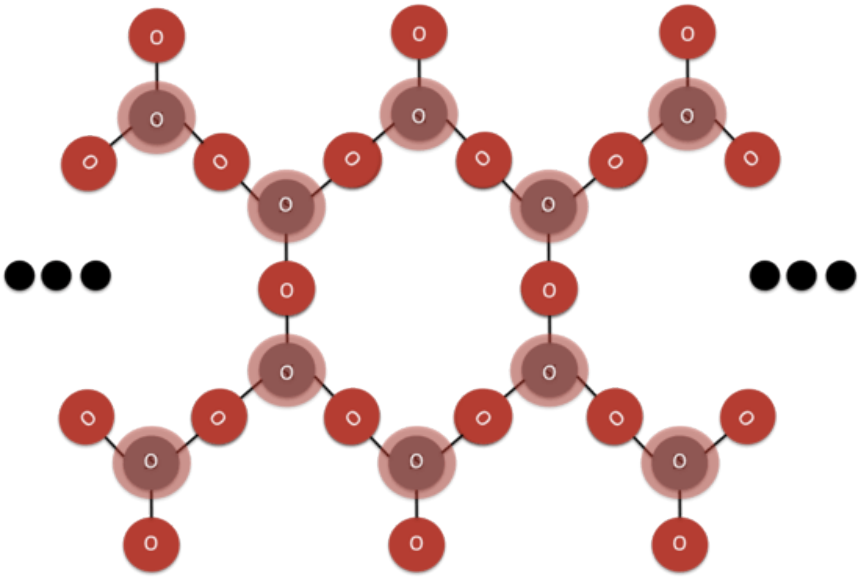


Figure 8: The core of a double chain inosilicate

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.

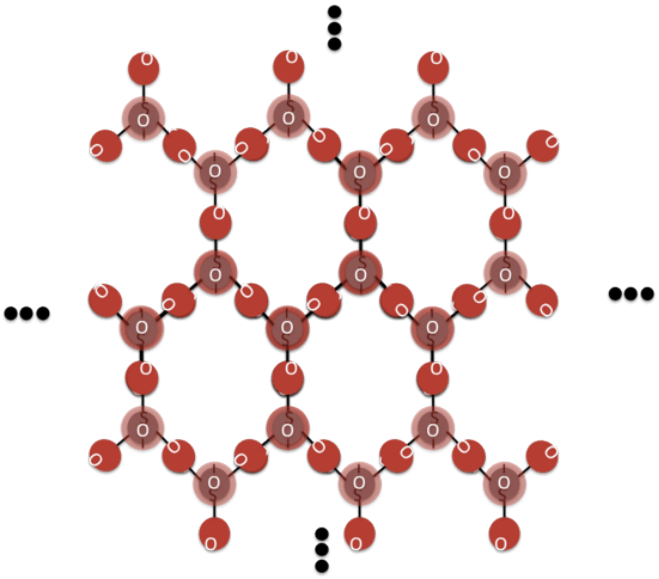


Figure 9: The core of phyllosilicate

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)

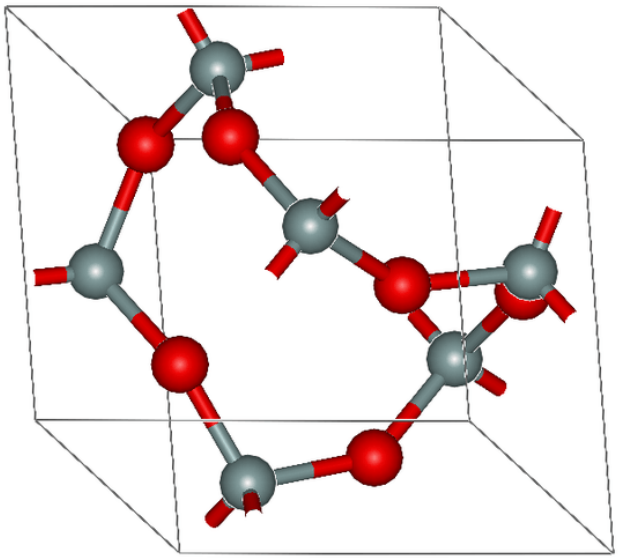


Figure 10: The 3d core of tectosilicate

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).

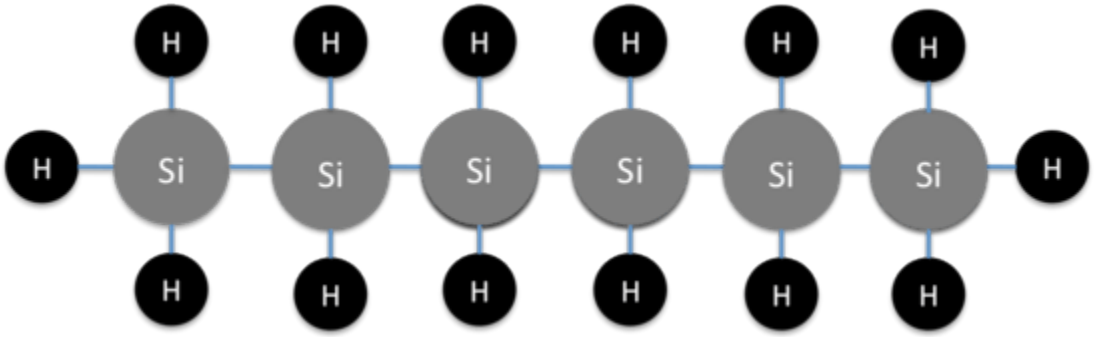


Figure 11: The largest silane, hexasilane

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)

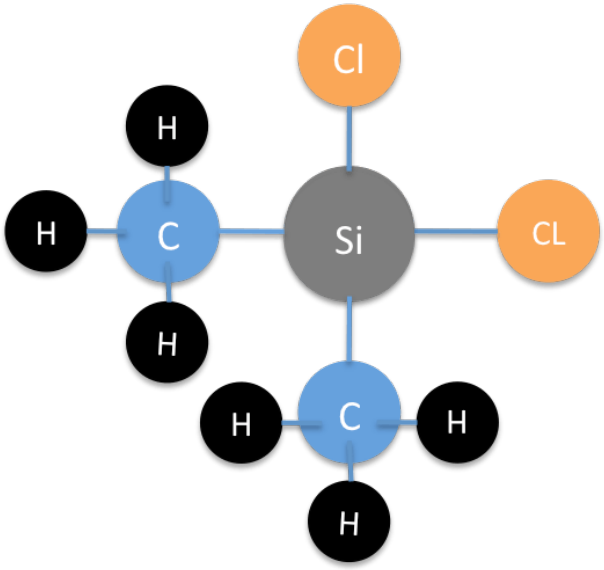


Figure 12: The organosilane, dichlorodimethylsilane

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)

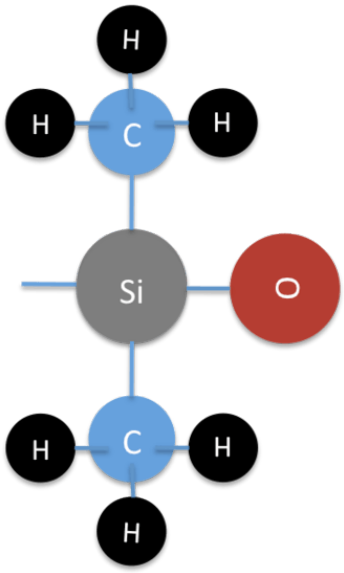


Figure 13: The core unit of a silicone

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.

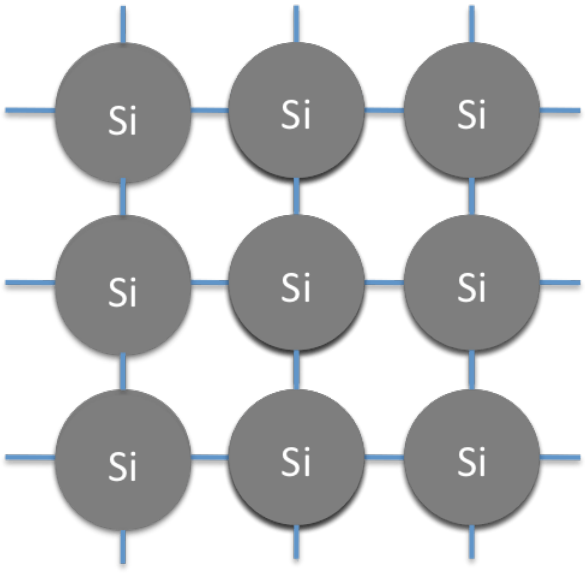


Figure 15: An example of a silicon lattice

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)

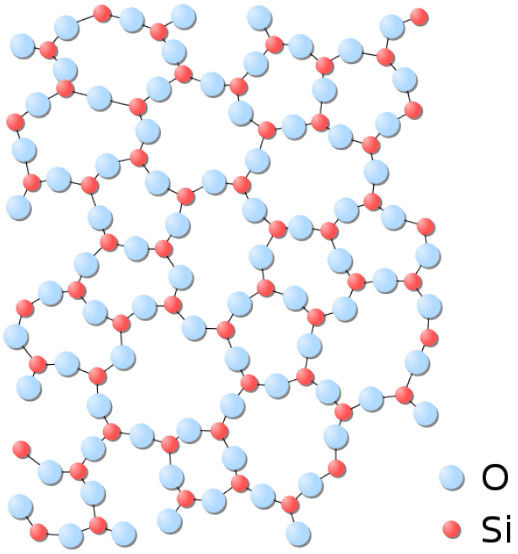


Figure 16: Non-crystalline silica

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: 1 oxide O_2

How does a silicate tetrahedral balance its charge if not bonded with another silicate?

Ans: By bonding to positively charged metals.

Carbon is to organic compounds as silica is to:

Ans: minerals

How big is the largest silicon-hydrogen compound?

Ans: The largest silane is hexasilane, with six silicon atoms and fourteen hydrogens.

Why is silicon important to computers?

Ans: It is used to make semiconductors.

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8.7.4.1: 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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8.7.4.2: 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.

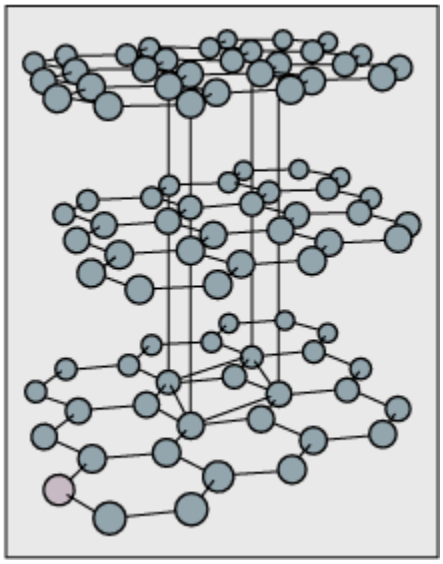
Group 14 Elements C, Si, Ge, Sn, Pb

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.

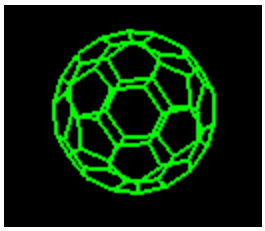
- Carbon - The element of organic chemistry and life.
- Silicon - The element of information technology.
- Germanium - The element of transistor bases.
- Tin and lead - Elements known to alchemists.

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,

$$SiO_2 + 2\,C \rightarrow Si_{(l)} + 2\,CO \qquad \text{at } 3300\ K$$

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,

$$\mathrm{SiO_2 + 4\,Mg \ \rightarrow Mg_2Si + 2\,MgO}$$

$\mathrm{Mg_2Si}$ is a compound, and it reacts with water to form silane.

Silane, $\mathrm{SiH_4}$, can be produced by reacting $\mathrm{Mg_2Si}$ with acids

$$\mathrm{Mg_2Si + 4\,H_2O \ \rightarrow 2\,Mg(OH)_2 + SiH_4}$$

and $\mathrm{SiH_4}$ is ignited when it contacts air, being much more reactive than methane,

$$\mathrm{SiH_4 + O_2 \ \rightarrow SiO_2 + H_2O}$$

In a basic solution, $\mathrm{SiH_4}$ reacts with water to give $\mathrm{SiO(OH)_3{}^-}$,

$$\mathrm{SiH_4 + OH^- + 3\,H_2O \ \rightarrow SiO(OH)_3{}^- + 4\,H_2}$$

Silicon Halides

Silicon tetrafluoride is formed when glass ($\mathrm{SiO_2}$) is exposed to HF, and when Si reacts with $\mathrm{F_2}$,

$$\mathrm{SiO_2 + 4\,HF_{(aq)} \ \rightarrow 2\,H_2O + SiF_{4(g)}}$$
$$\mathrm{Si + 2\,F_2 \ \rightarrow SiF_{4(g)}}$$

When chlorine passes through hot sand ($\mathrm{SiO_2}$) and carbon, $\mathrm{SiCl_4}$ is produced,

$$\mathrm{SiO_2 + C + 2\,Cl_2 \ \rightarrow 2\,CO + SiCl_{4(g)}}$$

$\mathrm{SiCl_4}$ and $\mathrm{SiF_4}$ react with water to give silicic acid,

$$\mathrm{SiCl_4 + 4\,H_2O \ \rightarrow 4\,HCl + Si(OH)_{4(aq)}},$$
$$\mathrm{SiF_4 + 4\,H_2O \ \rightarrow 4\,HF + Si(OH)_{4(aq)}}.$$

Silicone Polymers

Silicones are polymers with the general formula $\mathrm{(R_2SiO_2)_n}$ or $\mathrm{(RSiO_3)_n}$, (R = $\mathrm{CH_3}$, $\mathrm{C_2H_5}$, $\mathrm{C_6H_5}$, etc). The chain is held together by $\mathrm{Si{-}O{-}Si}$ bonds. A simple one is $\mathrm{((CH_3)_2SiO_2)_n}$,

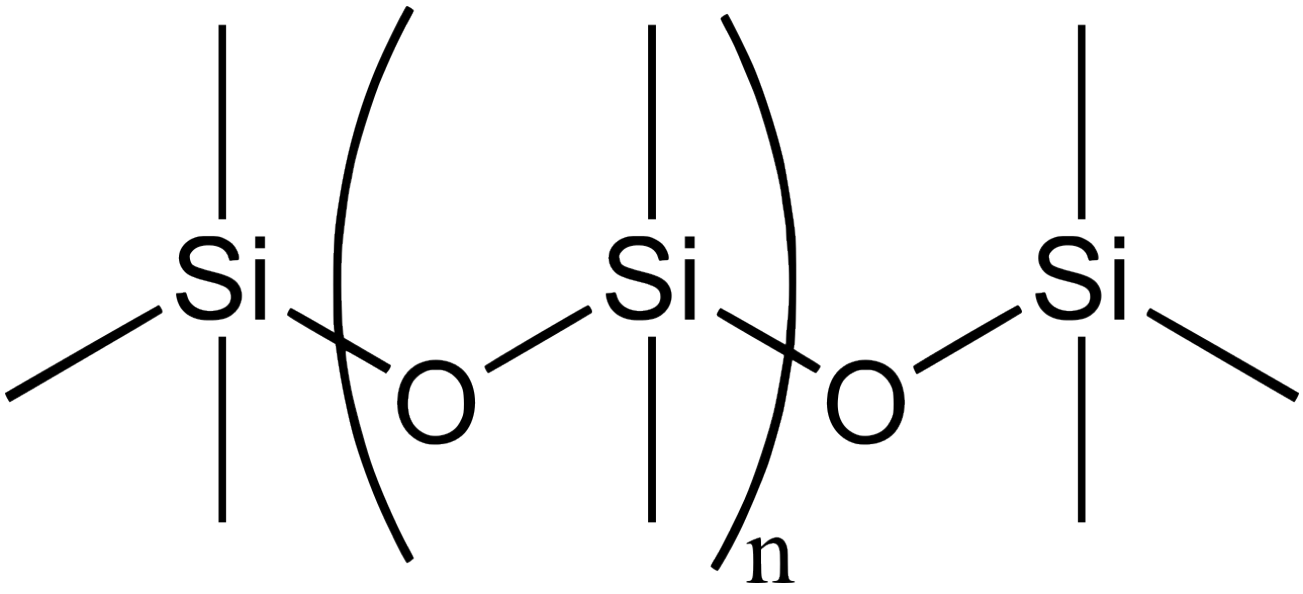


Figure 2: *Chemical structure of the silicone polydimethylsiloxane (PDMS).*

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. $\mathrm{B\ Al\ Ga\ In\ Tl}$
   b. $\mathrm{C\ Si\ Ge\ Sn\ Pb}$
   c. $\mathrm{N\ P\ As\ Sb\ Bi}$
   d. $\mathrm{O\ S\ Se\ Te\ Po}$
   e. $\mathrm{F\ Cl\ Br\ I\ At}$
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: $\mathrm{SiO_2}$, C or Mg?**
5. **Which is stable towards air: methane or silane?**
6. **Give the name of polymers whose chains are held together by $\mathrm{Si{-}O{-}Si}$ 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 $\mathrm{C_{60}}$ being the most common.

3. *Answer* . . .$\mathrm{CaC_2}$
   Hint…
   The reaction to produce acetylene gas is

   $$\mathrm{CaC_2 + H_2O \ \rightarrow C_2H_2 + Ca(OH)_2}$$

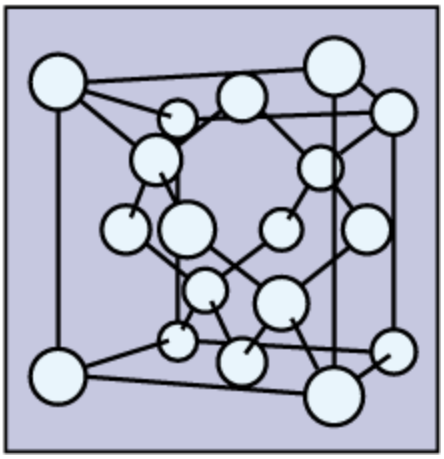
   Acetylene is still an important industrial gas, as raw material for polymers.

4. *Answer* …C
   Hint…
   Carbon or coke is used for silicon metal, because $\mathrm{Mg_2Si}$ 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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8.7.5: 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 8.7.5.1: 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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8.7.6: 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

Arrange the following in order of decreasing ionization energy: Sn, Si, Pb, I, In.

Answer: Si> I > Sn > In > Pb

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8.7.7: 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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8.7.7.1: Lead Acetate

Lead Acetate

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8.7.7.2: 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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8.8: Group 15

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8.8.1: The Group 15 Elements

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8.8.2: Compounds of the Group 15 Elements

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8.9: 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.

8.9.1: General Properties and Reactions

8.9.1.1: Nitrogen Group (Group 5) Trends

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8.9.1: 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.

Contributors and Attributions

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8.9.1.1: 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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8.9.2: 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.

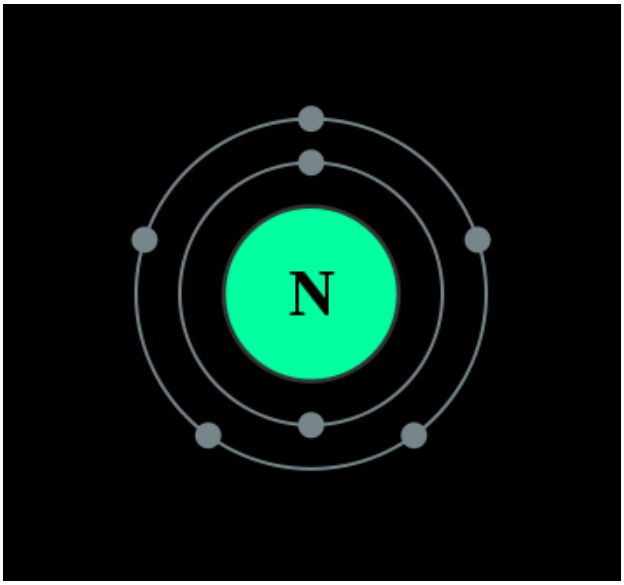


Figure 8.9.2.1 : *A Bohr diagram of the nitrogen atom.*

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 $8.9.2.2$: *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.

$$3Mg + N_2 \rightarrow Mg_3N_2 \tag{8.9.2.1}$$

When mixed with water, nitride will form ammonia; the nitride ion acts as a very strong base.

$$N^{3-} + 3H_2O_{(l)} \rightarrow NH_3 + 3OH^-_{(aq)} \tag{8.9.2.2}$$

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:

$$N_2 + 3H_2 \rightarrow 2NH_3 \tag{8.9.2.3}$$

Ammonia is a base and is also used in typical acid-base reactions.

$$2NH_{3(aq)} + H_2SO_4 \rightarrow (NH_4)_2SO_{4(aq)} \tag{8.9.2.4}$$

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.

$$N_2O_5 + H_2O \rightarrow 2HNO_{3(aq)} \tag{8.9.2.5}$$

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

  $N_2 + 3H_2$ → $2NH_3$(Haber process)

  $H_2N_2O_2$ → 2HNO

  $2NH_3 + CO_2$ → $(NH_2)_2CO + H_2O$

  $2Mg + 3N_2$ → Mg_3N_2

  $N_2H_5 + H_2O$ → 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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8.9.3: 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 Edit section

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 1.3x10^{-22} and 5.8x10^{-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 $\mathrm{P_4}$ 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, $\mathrm{P_4O_6}$ when air supply is limited, and $\mathrm{P_4O_{10}}$ when sufficient air is present.

Diphosphorus (P_2)

Diphosphorus (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 (N_2).

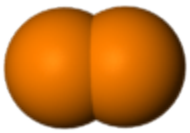


Figure 2: Diphosphorus molecule. (CC-SA-BY 3.0; Wikipedia)

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.

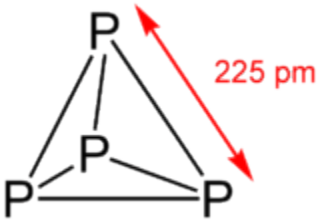


Figure 3: Structure of white phosphorus. (CC-SA-BY 3.0; Wikipedia)

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".



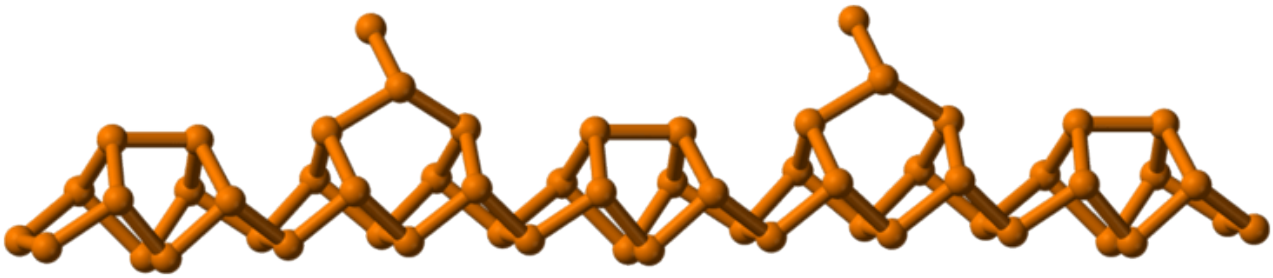


Figure 5. Structure of Violet Phosphorus. (CC-SA-BY 3.0; Wikipedia)

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.

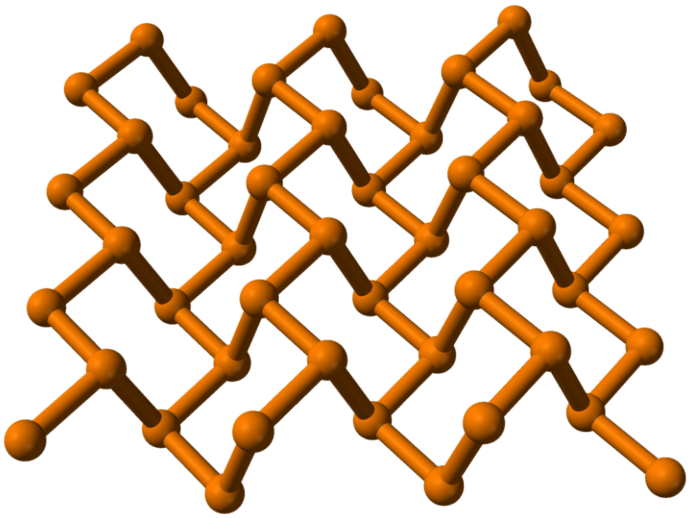


Figure 6. Ball-and-stick model of a sheet of phosphorus atoms in black phosphorus. (CC-SA-BY 3.0; Wikipedia)

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.

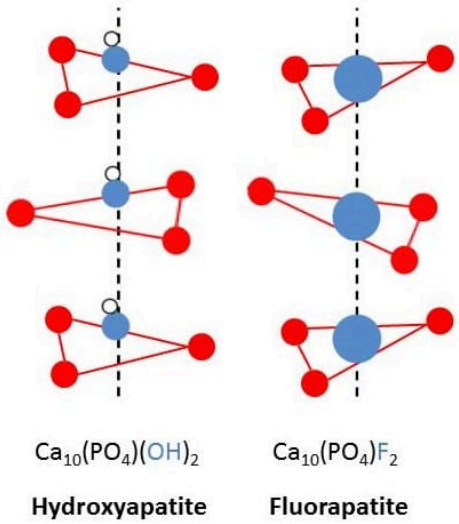


Figure 6: (left) Fluoride ions (F^-) replace hydroxyl groups (OH^-) in hydroxyapatite to form fluorapatite in the tooth enamel. (right) A portion of the apatite crystal lattice is depicted showing the replacement of hydroxide by fluoride (big blue circles). (Public Domain; Delmar Larsen).

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}:

$$2\,Ca_3(PO_4)_2 + 6\,SiO_2 \rightarrow P_4O_{10} + 6\,CaSiO_3 \tag{8.9.3.1}$$

P_4O_{10} can be reduced by carbon:

$$P_4O_{10} + 10\,C \rightarrow P_4 + 10\,CO. \tag{8.9.3.2}$$

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:

$$P_4 + 5\,O_2 \rightarrow P_4O_{10} \tag{8.9.3.3}$$

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:

$$P_4 + 3\,O_2 \rightarrow P_4O_6 \tag{8.9.3.4}$$

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:

$$P_4 + 5\,O_2 \rightarrow P_4O_{10} \tag{8.9.3.5}$$

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,

$$P_4O_{10} + 6\,H_2O \rightarrow 4\,H_3PO_4 \tag{8.9.3.6}$$

Phosphoric acid is a polyprotic acid, and it ionizes in three stages:

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \tag{8.9.3.7}$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \tag{8.9.3.8}$$

$$HPO_4^{2-} \rightarrow H^+ + PO_4^{3-} \tag{8.9.3.9}$$

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
$H_3PO_4 + H_2O \rightarrow H_3O^+ + H_2PO^{4-}$	$K_{a1}=7.5\text{x}10^{-3}$
$H_2PO_4^- + H_2O \rightarrow H_3O^+ + HPO_4^{2-}$	$K_{a2}=6.2\text{x}10^{-8}$
$H_2PO_4^- + H_2O \rightarrow H_3O^+ + PO_4^{3-}$	$K_{a3}=2.14\text{x}10^{-13}$
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).

References Edit section

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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 $\mathrm{P_4O_{10}}$ reacts with water? Give the formula of the product.
3. What is the phosphorus-containing product when $\mathrm{PCl_3}$ 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* $\mathrm{H_3PO_4}$

$$\mathrm{P_4O_{10} + 6\,H_2O \rightarrow 4\,H_3PO_4}$$

3. *Answer* $\mathrm{H_3PO_3}$

$$\mathrm{PCl_3 + 3\,H_2O \rightarrow H_3PO_3 + 3\,HCl}$$

   This is a weaker acid than $\mathrm{H_3PO_4}$.

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8.9.4: Chemistry of Arsenic (Z=33)

Figure 1: Sample of solid Arsenic. from Wikipedia.

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8.9.5: 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 s*tibnite* 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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8.9.6: 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^{o}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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8.9.7: 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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8.10: Group 16

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8.10.1: The Group 16 Elements

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8.10.1.1: Compounds of the Group 16 Elements

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8.10.1.2: The Group 16 Elements

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8.11: 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.

8.11.1: General Properties and Reactions

8.11.1.1: Oxygen Group (Group VIA) Trends

8.11.2: Chemistry of Oxygen (Z=8)

8.11.2.1: Ozone

8.11.2.1.1: Important properties of ozone

8.11.2.1.2: Ozone Layer and Ozone Hole

8.11.3: Chemistry of Sulfur (Z=16)

8.11.4: Chemistry of Selenium (Z=34)

8.11.5: Chemistry of Tellurium (Z=52)

8.11.6: Chemistry of Polonium (Z=84)

8.11.7: Chemistry of Livermorium (Z=116)

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8.11.1: 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 8.11.1.1: 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 8.11.1.1: 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

	Oxygen	Sulfur	Selenium	Tellurium	Polonium
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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8.11.1.1: 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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8.11.2: 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:

$$\mathrm{CO_2 + H_2O + h\nu \rightarrow organic\ compounds + O_2}$$

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

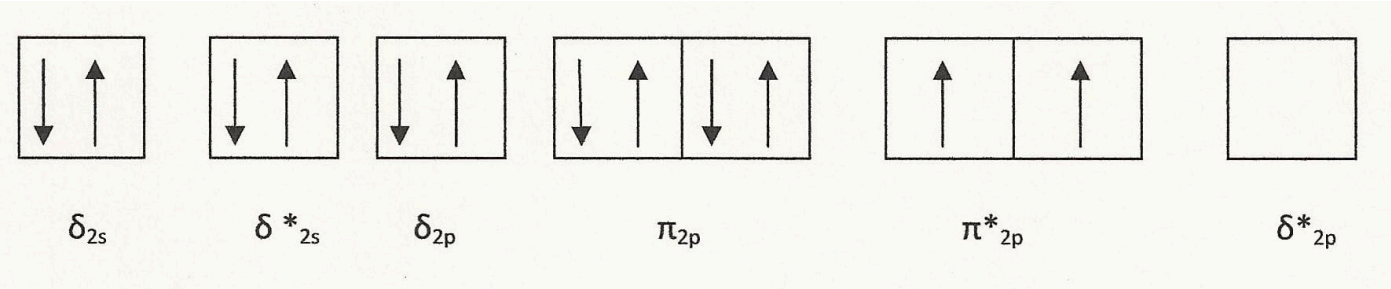
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Magnetic Properties of Oxygen

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.

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Video $8.11.2.1$***:*** *A chemical demonstration of the paramagnetism of molecular oxygen, as shown by the attraction of liquid oxygen to magnets.*

As shown in Video $8.11.2.1$, 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.

$$4\,\mathrm{Li} + \mathrm{O_2} \rightarrow 2\,\mathrm{Li_2O} \tag{8.11.2.1}$$

Sodium: Reacts with oxygen to form a white mixture of sodium oxide and sodium peroxide. The reactions are shown below.

- Sodium oxide:

$$4\,\mathrm{Na} + \mathrm{O_2} \rightarrow 2\,\mathrm{Na_2O} \tag{8.11.2.2}$$

- Sodium peroxide:

$$2\,\mathrm{Na} + \mathrm{O_2} \rightarrow \mathrm{Na_2O_2} \tag{8.11.2.3}$$

Potassium: Reacts with oxygen to form a mixture of potassium peroxide and potassium superoxide. The reactions are shown below.

- Potassium peroxide:

$$2\,\mathrm{K} + \mathrm{O_2} \rightarrow 2\,\mathrm{K_2O_2} \tag{8.11.2.4}$$

- Potassium superoxide:

$$\mathrm{K} + \mathrm{O_2} \rightarrow \mathrm{KO_2} \tag{8.11.2.5}$$

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.

$$\mathrm{Ba\,(s)} + \mathrm{O_2\,(g)} \rightarrow \mathrm{BaO_2\,(s)} \tag{8.11.2.6}$$

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.

$$\mathrm{O_2\,(g) + F_2\,(g)\ \rightarrow F_2O_2\,(g)} \tag{8.11.2.7}$$

Group 18: Some would assume that the Noble Gases would not react with oxygen. However, xenon does react with oxygen to form $\mathrm{XeO_3}$ and $\mathrm{XeO_4}$. The ionization energy of xenon is low enough for the electronegative oxygen atom to "steal away" electrons. Unfortunately, $\mathrm{XeO_3}$ 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:

$$2Sn_{(s)} + O_{2(g)} \rightarrow 2SnO_{(s)} \tag{8.11.2.8}$$

$$4Fe_{(s)} + 3O_{2(g)} \rightarrow 2Fe_2O_{3(s)} \tag{8.11.2.9}$$

$$4Al_{(s)} + 3O_{2(g)} \rightarrow 2Al_2O_{3(s)} \tag{8.11.2.10}$$

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.

$$C_8H_{18}(l) + 25/2\ O_2(g) \rightarrow 8CO_2(g) + 9H_2O(l)\ \Delta H_o = -5.48 \times 10^3\ kJ$$

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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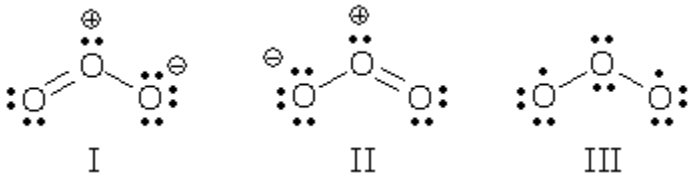
8.11.2.1: Ozone

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.

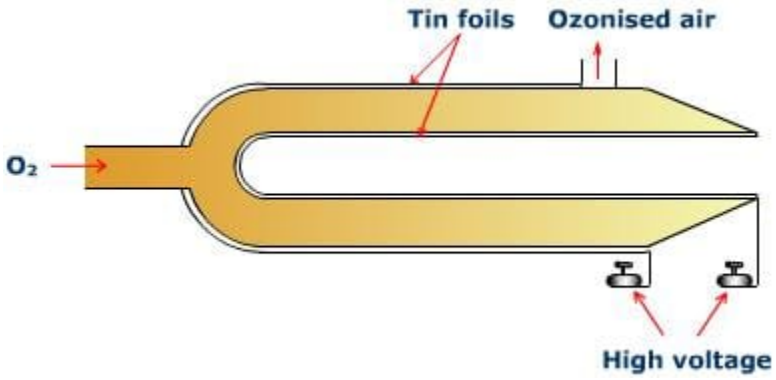


Figure 1: Siemen's ozonizer

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%.

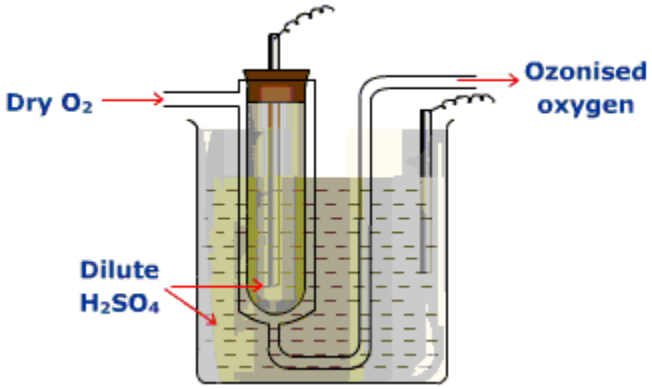


Figure 2: Brodie's ozonizer

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.

$$\mathrm{O_2} \xrightarrow{h\nu} \mathrm{O^{\cdot} + O^{\cdot}}$$

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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8.11.2.1.1: Important properties of ozone

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8.11.2.1.2: 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., $\mathrm{CFCl_3}$ and $\mathrm{CF_2Cl_2}$) 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.

$$\mathrm{CF_2Cl_2 + h\nu \rightarrow CF_2Cl^{\cdot} + Cl^{\cdot}} \tag{8.11.2.1.2.1}$$

Chlorine atoms, being highly reactive, react with ozone ($\mathrm{O_3}$):

$$\mathrm{Cl^{\cdot} + O_3 \ \rightarrow ClO^{\cdot} + O_2} \tag{8.11.2.1.2.2}$$

The monoxide of chlorine further reacts with another molecule of $\mathrm{O_3}$:

$$\mathrm{ClO^{\cdot} + O_3 \ \rightarrow Cl^{\cdot} + 2\,O_2} \tag{8.11.2.1.2.3}$$

The chlorine atom so obtained reacts with another ozone molecule. Hence, steps 8.11.2.1.2.2 and 8.11.2.1.2.3 are repeated again and again, and lead to the depletion of the concentration of ozone.

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8.11.3: 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 $\mathrm{H_2SO_4}$.
- Explain properties and applications of $\mathrm{H_2S}$.

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 8.11.3.1: 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^{o} 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 ^{o}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.

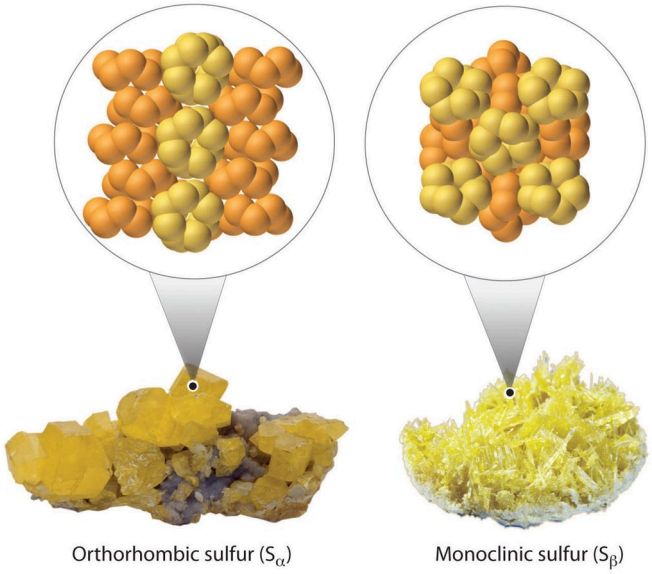


Figure 8.11.3.2: Two allotropes of sulfur.

While oxygen has fewer allotropes than sulfur, including O, $\mathrm{O_2}$, $\mathrm{O_3}$, $\mathrm{O_4}$, $\mathrm{O_8}$, 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:

$$\begin{array}{ll} \mathrm{O{-}O} & 142\ k\,\mathrm{J/mol} \\ \mathrm{S{-}S} & 268\ k\,\mathrm{J/mol} \\ \mathrm{O{=}O} & 499\ k\,\mathrm{J/mol} \\ \mathrm{S{=}S} & 352\ k\,\mathrm{J/mol} \end{array}$$

This means that $\mathrm{O{=}O}$ is stronger than $\mathrm{S{=}S}$, while $\mathrm{O{-}O}$ is weaker than $\mathrm{S{-}S}$. So, in sulfur, single bonds are favored and catenation is easier than in oxygen compounds. It seems that the reason for the weaker $\mathrm{S{=}S}$ 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: $\mathrm{Se{=}Se}$ has an even weaker bond enthalpy of $272\,\mathrm{kJ/mol}$.

> What happens when the solid sulfur melts? The $\mathrm{S_8}$ 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 $\mathrm{O_2}$ giving a blue flame (Figure 8.11.3.1):

$$\mathrm{S + O_2 \ \rightarrow SO_2}$$

$\mathrm{SO_2}$ is produced whenever a metal sulfide is oxidized. It is recovered and oxidized further to give $\mathrm{SO_3}$, for production of $\mathrm{H_2SO_4}$. $\mathrm{SO_2}$ reacts with $\mathrm{H_2S}$ to form $\mathrm{H_2O}$ and S.

$$\mathrm{2SO_2 + O_2 \rightleftharpoons 2SO_3}$$

$$\mathrm{SO_3 + H_2O \rightleftharpoons H_2SO_4 \ \ (a\ valuable\ commodity)}$$

$$\mathrm{SO_3 + H_2SO_4 \rightleftharpoons H_2S_2O_7 \quad (pyrosulfuric\ acid)}$$

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, H_2S, is a diprotic acid. The equilibria below,

  $$H_2S \rightleftharpoons HS^- + H^+$$
  $$HS^- \rightleftharpoons S^{2-} + H^+$$

  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 (H_2SO_4). Sulfur dioxide (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 (H_2SO_3), which contributes to the acid rain problem.

- **Sulfuric acid**, H_2SO_4, is produced by reacting 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.

$$C_{12}H_{22}O_{11}(s) \rightarrow 12C(s) + 11H_2O(l)$$

(Concentrated sulfuric acid used in forward reaction to remove H and O atoms.)

Applications of Sulfuric Acid

- as a strong acid for making HCl and $\mathrm{HNO_3}$.
- 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 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).

$$2Cu^{2+}_{(aq)} + 5I^-_{(aq)} \rightarrow 2CuI_{(s)} + I^-_{3(aq)}$$

$$I^-_{3(aq)} + 2S_2O^{2-}_{3(aq)} \rightarrow 3I^-_{(aq)} + S_4O^{2-}_{6(aq)}$$

  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, 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 ($\mathrm{FeS_2}$, known as fool's gold because of its golden color). The most common sulfate-containing mineral is gypsum, $\mathrm{CaSO_4 \cdot 2H_2O}$, 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.

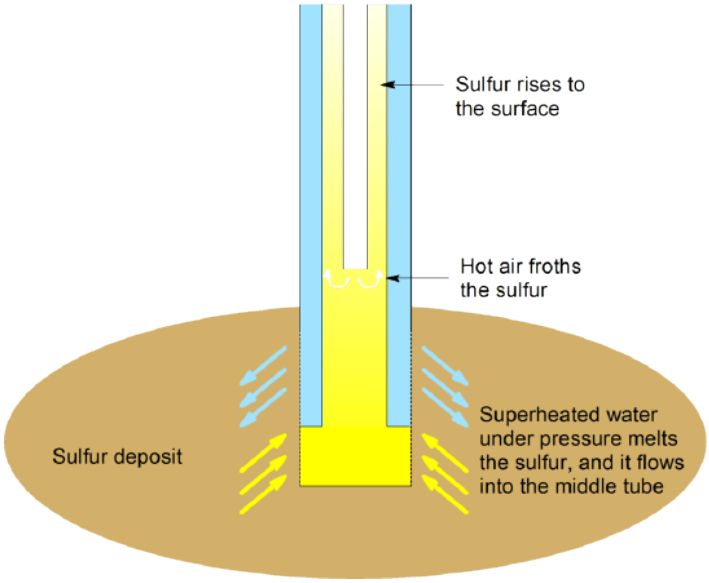


Figure 8.11.3.1: Pictorial representation of the Frasch process. Adapted from Wolfgang Nehb, Karel Vydra (2005), "Sulfur", Ullmann's Encyclopedia of Industrial Chemistry, Weinheim: Wiley-VCH. (Public Domain; Rifleman 82)

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. $\mathrm{CaCO_3 \rightarrow CaO + CO_2}$
   b. $\mathrm{SO_2 + H_2O \rightarrow H_2SO_3}$
   c. $\mathrm{BaO + CO_2 \rightarrow BaCO_3 \rightarrow BaSO_3}$ upon reaction with $\mathrm{SO_2}$
   d. $\mathrm{CaCO_3 + H_2O \rightarrow Ca(OH)_2 + CO_2}$
   e. $\mathrm{CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2 \rightarrow CaSO_4}$ upon oxidation
7. Give the formula of thiosulfate ion.
8. What is the oxidation state of S in $\mathrm{SF_6}$, $\mathrm{H_2SO_4}$, $\mathrm{NaHSO_4}$, $\mathrm{SO_4^{2-}}$, and $\mathrm{SO_3}$?
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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8.11.4: 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.

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8.11.5: 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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8.11.6: 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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8.11.7: 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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8.12: Group 17 (The Halogens)

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8.12.1: Compounds of the Group 17 Elements (Halogens)

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8.12.2: The Group 17 Elements (Halogens)

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8.13: 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.

8.13.1: Physical Properties of the Halogens

8.13.1.1: Atomic and Physical Properties of Halogens

8.13.1.2: General Properties of Halogens

8.13.1.3: Halogen Group (Group 17) Trends

8.13.1.4: Physical Properties of the Group 17 Elements

8.13.2: Chemical Properties of the Halogens

8.13.2.1: Halide Ions as Reducing Agents

8.13.2.2: Halogens as Oxidizing Agents

8.13.2.3: Interhalogens

8.13.2.4: More Reactions of Halogens

8.13.2.5: Oxidizing Ability of the Group 17 Elements

8.13.2.6: Testing for Halide Ions

8.13.2.7: The Acidity of the Hydrogen Halides

8.13.3: Chemistry of Fluorine (Z=9)

8.13.4: Chemistry of Chlorine (Z=17)

8.13.4.1: The Manufacture of Chlorine

8.13.5: Chemistry of Bromine (Z=35)

8.13.6: Chemistry of Iodine (Z=53)

8.13.7: Chemistry of Astatine (Z=85)

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8.13.1: Physical Properties of the Halogens

Some chemical and physical properties of the halogens are summarized in Table 8.13.1.1. 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 8.13.1.1: 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	red-brown liquid	blue-black solid
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 electronegativity, χ^P	3.98	3.16	2.96	2.66

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.

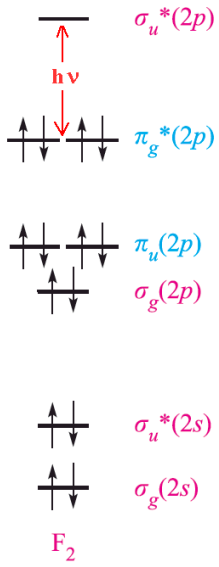


Figure 8.13.1.1***:*** *Molecular orbital diagram for fluorine.*

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).

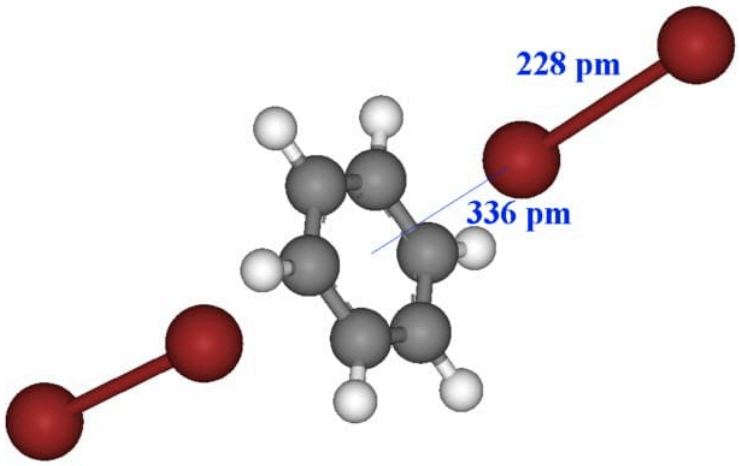


Figure 8.13.1.2***:*** *Structure of dibromine and benzene complex*

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]

$$R_3P + Br_2(Et_2O, N_2/r.t.) \rightarrow R_3PBr_2 \tag{8.13.1.1}$$

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.

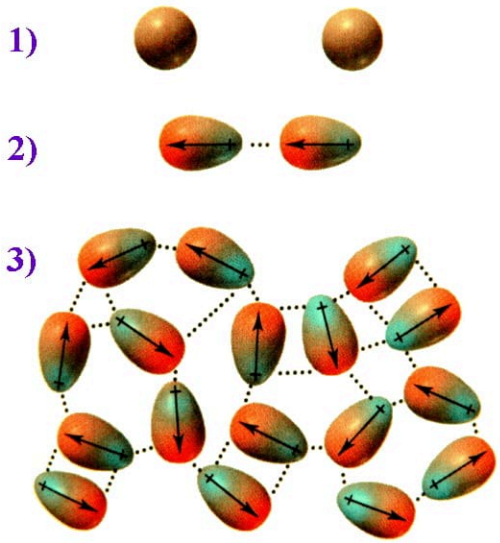


Figure 8.13.1.3***:*** *On average the electron cloud for molecules can be considered to be spherical in shape. When two non-polar molecules approach, attractions or repulsions between the electrons and nuclei can lead to distortions in their electron clouds (i.e., dipoles are induced). When more molecules 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.

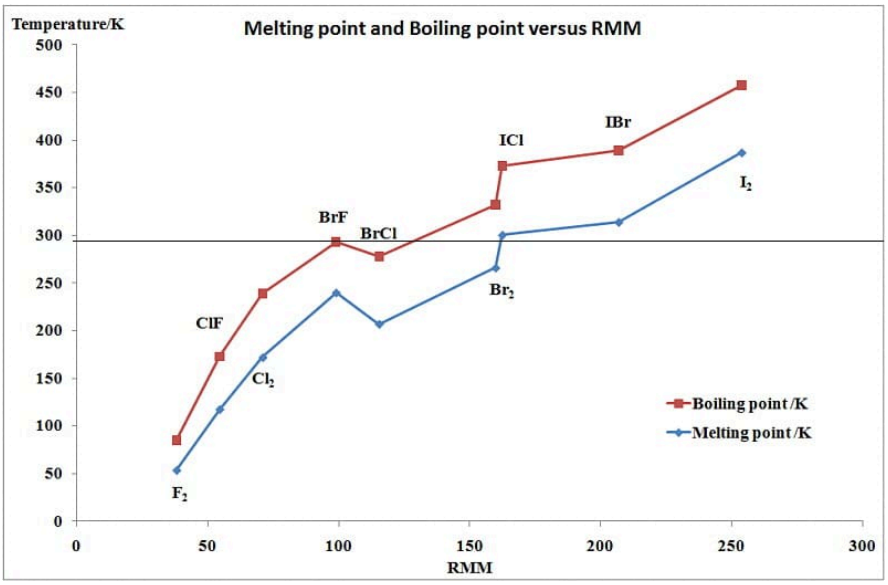


Figure 4:

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:

$$½X_{2(g)} \rightarrow X_{(g)} \tag{8.13.1.2}$$

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

$$X_{(g)} + e^- \rightarrow X^-_{(g)} \tag{8.13.1.3}$$

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.

$$X^-_{(g)} + H_2O \rightarrow X^-_{(aq)} \tag{8.13.1.4}$$

The overall reaction is then:

$$½X_{2(g)} \rightarrow X^-_{(aq)} \tag{8.13.1.5}$$

Table 8.13.1.2

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:

$$X_2 + H_{2(g)} \rightarrow 2HX_{(g)} \tag{8.13.1.6}$$

In water, the halogens disproportionate according to:

$$X_2 + H_2O_{(l)} \rightarrow HX_{(aq)} + HXO_{(aq)} \tag{8.13.1.7}$$

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:

$$3Cl_{2(g)} + 6OH^-_{(aq)} \rightarrow ClO^-_{3(aq)} + 5Cl^-_{(aq)} + 3H_2O(l) \tag{8.13.1.8}$$

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 8.13.1.3: 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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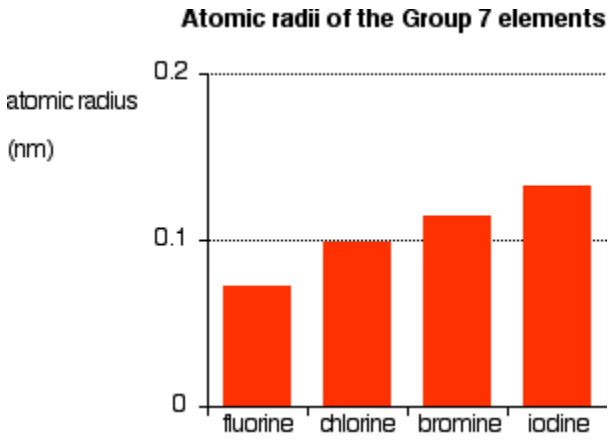
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8.13.1.1: Atomic and Physical Properties of Halogens

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

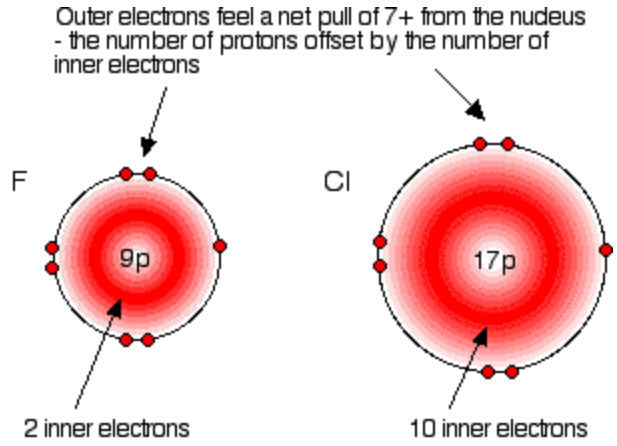
The radius of an atom is determined by:

- 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.

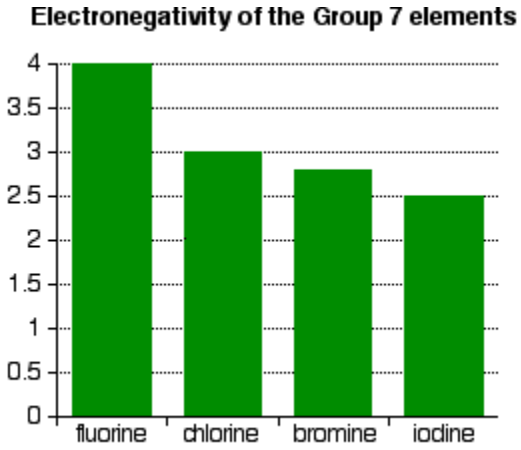


This is true for all the atoms in Group 7: the outer electrons experience a net charge of +7..

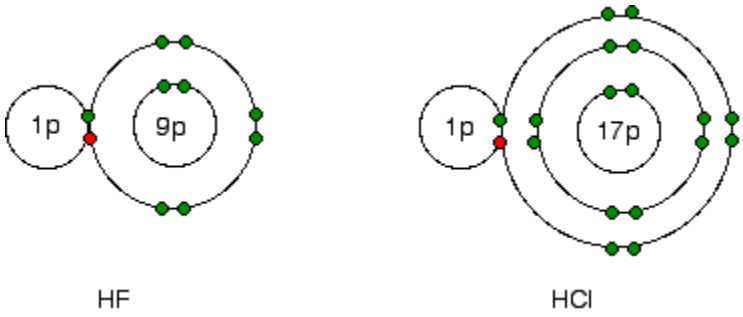
The only factor affecting the size of the atom is therefore the number of layers of inner electrons surrounding the atom. More layers take up more space due to electron repulsion, so atoms increase in size down the group.

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

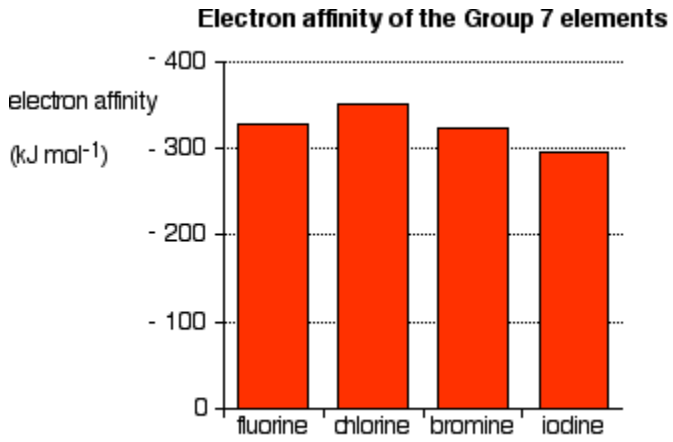
The first electron affinity is the energy released when 1 mole of gaseous atoms each acquire an electron to form 1 mole of gaseous 1- ions. In other words, it is the energy released in the following process:

$$X(g) + e^- \rightarrow X^-(g)$$

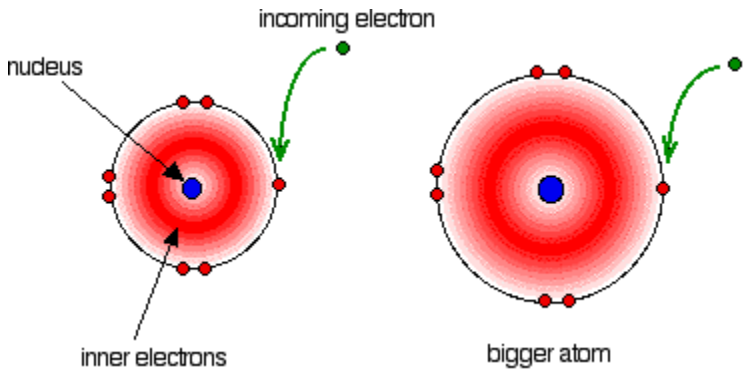
First electron affinities have negative values by convention. For example, the first electron affinity of chlorine is -349 kJ mol^{-1}. The negative sign indicates a release of energy.

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.



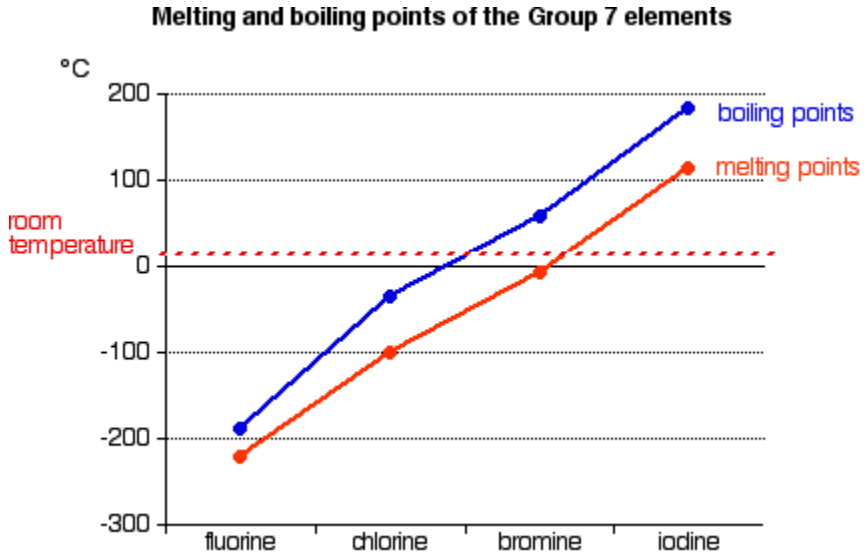
In the larger atom, the attraction from the more positive nucleus is offset by the additional screening electrons, so each incoming electron feels the effect of a net +7 charge from the center.

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

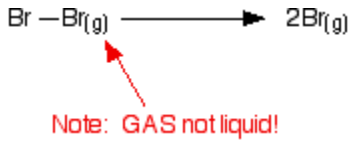
The halogens are much more soluble in organic solvents such as hexane than they are in water. Both hexane and the halogens are non-polar molecules, so the only intermolecular forces between them are van der Waals dispersion forces. Because of this, the attractions broken (between hexane molecules and 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:

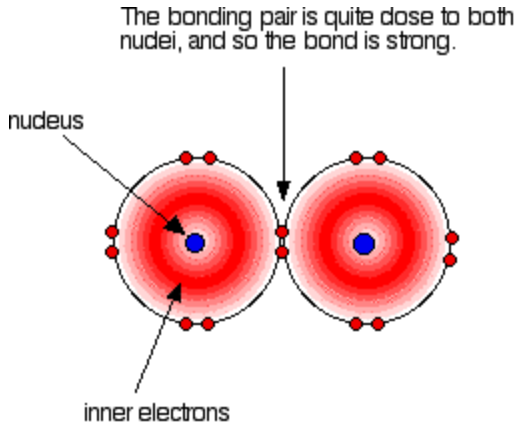
$$Cl-Cl(g) \rightarrow 2Cl(g)$$

Although bromine is a liquid, the bond enthalpy is defined in terms of gaseous bromine molecules and atoms, as shown below:

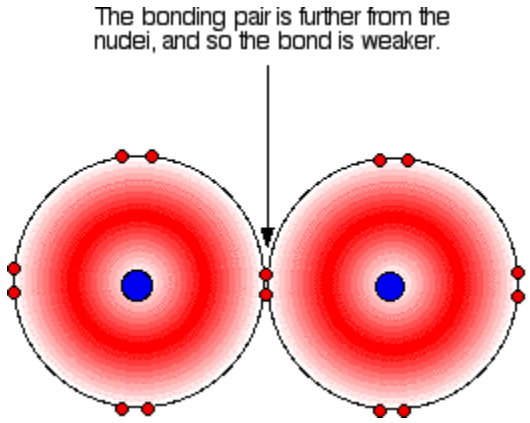


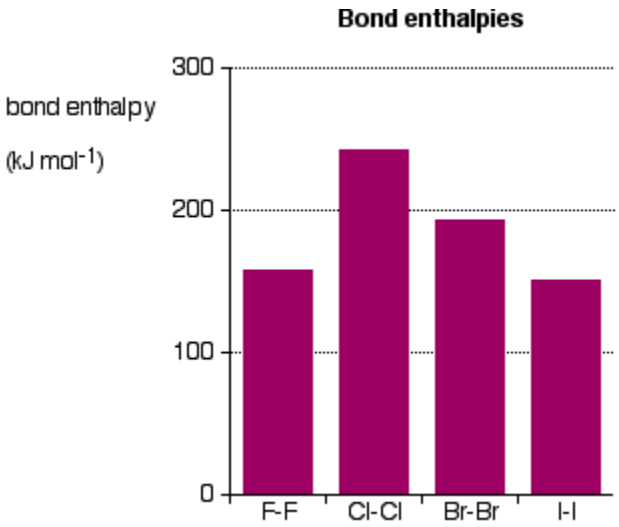
Bond enthalpy in the halogens, $X_2(g)$

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.

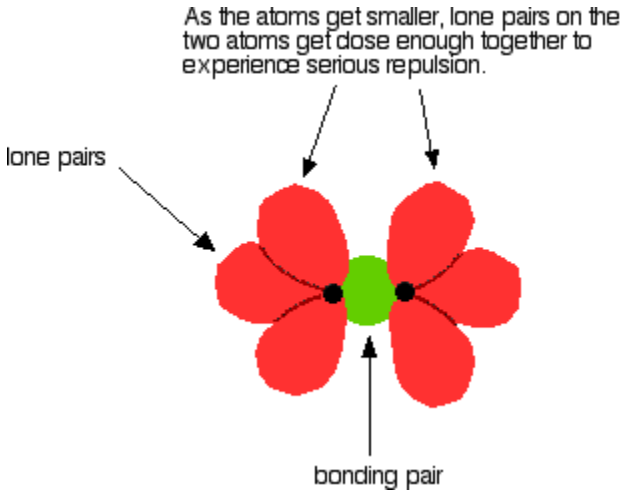




As is clear from the figure above, the bond enthalpies of the Cl-Cl, Br-Br and I-I bonds decreases as predicted, but the F-F bond enthalpy deviates.

Because fluorine atoms are so small, a strong bond is expected—in fact, it is remarkably weak. There must be another factor for consideration.

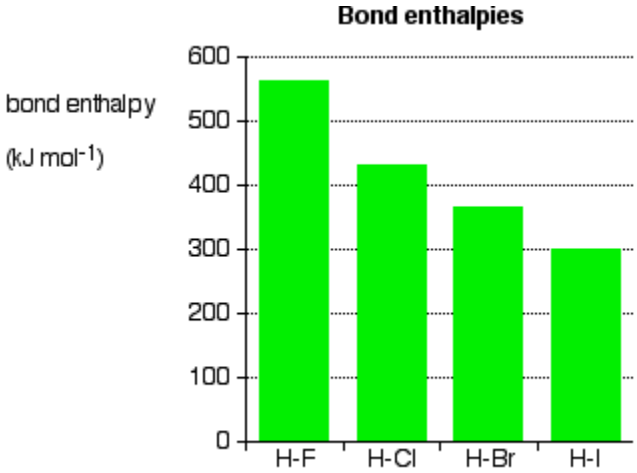
In addition to the bonding pair of electrons between the two atoms, each atom has 3 lone pairs of electrons in the outer shell. If the bond is very short,as in F-F, the lone pairs on the two atoms are close enough to cause significant repulsion, illustrated below:



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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8.13.1.2: 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

Halogen	Covalent Radius (pm)	Ionic (X-) radius (pm)
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

Halogen	Electron Affinity (kJ/mol)
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

Compound	Uses
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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1. Hill, Graham, and John Holman. Chemistry in Context. 5th ed. United Kingdom: Nelson Thornes, 2000. 224-25.
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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8.13.1.3: 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.

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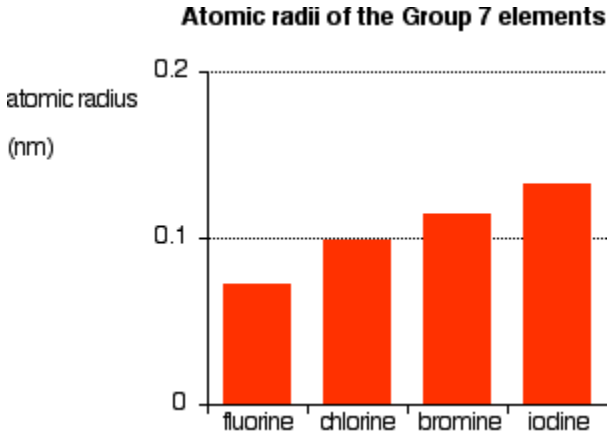
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8.13.1.4: Physical Properties of the Group 17 Elements

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).

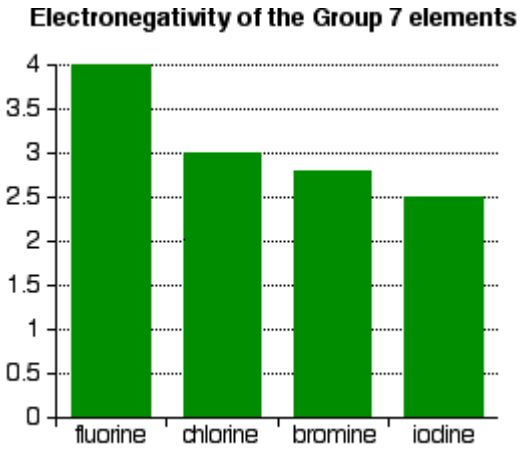
Trends in Atomic Radius

You can see that the atomic radius increases as you go down the group.

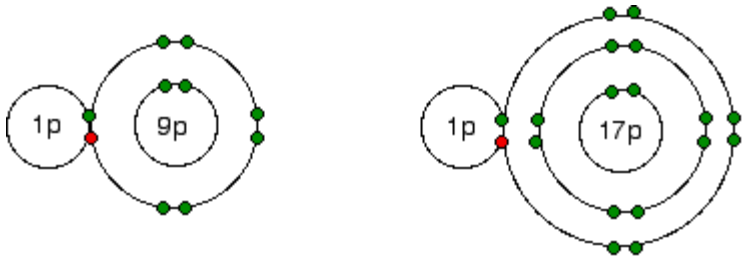


The radius of an atom is governed by

- 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.



HF HCl

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.

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8.13.2: 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

8.13.2.1: Halide Ions as Reducing Agents

8.13.2.2: Halogens as Oxidizing Agents

8.13.2.3: Interhalogens

8.13.2.4: More Reactions of Halogens

8.13.2.5: Oxidizing Ability of the Group 17 Elements

8.13.2.6: Testing for Halide Ions

8.13.2.7: The Acidity of the Hydrogen Halides

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8.13.2.1: 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.

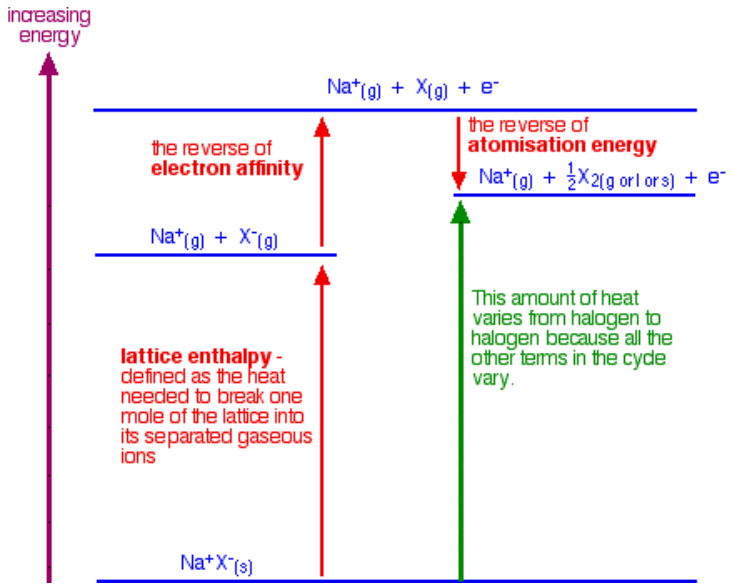
A more detailed explanation

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.

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8.13.2.2: 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:

$$\mathrm{Cl_2 + 2\,I^-} \rightarrow \mathrm{2\,Cl^- + I_2}$$

- 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.

$$\mathrm{2\,F_2 + 2\,H_2O} \rightarrow \mathrm{4\,HF + O_2}$$

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:

$$\mathrm{Cl_2 + 2\,Br^-} \rightarrow \mathrm{2\,Cl^- + Br_2}$$

The bromine forms an orange solution. As shown below, chlorine can also oxidize iodide ions to iodine:

$$\mathrm{Cl_2 + 2\,I^-} \rightarrow \mathrm{2\,Cl^- + I_2}$$

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.

$$\mathrm{Br_2 + 2\,I^-} \rightarrow \mathrm{2\,Br^- + I_2}$$

Iodine won't oxidize any of the other halide ions, except possibly the extremely radioactive and rare astatide ions.

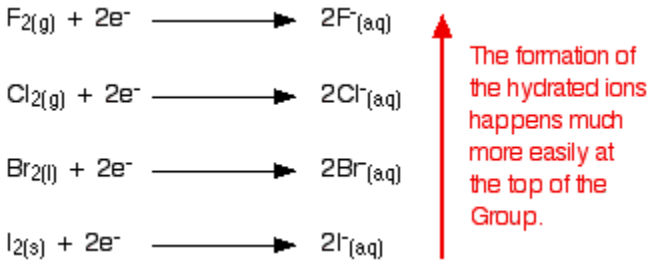
To summarize

- 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., $\mathrm{Cl^-}$). 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

	atomization energy (kJ mol^{-1})	electron affinity (kJ mol^{-1})	hydration enthalpy (kJ mol^{-1})	overall (kJ mol^{-1})
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.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

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8.13.2.3: 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

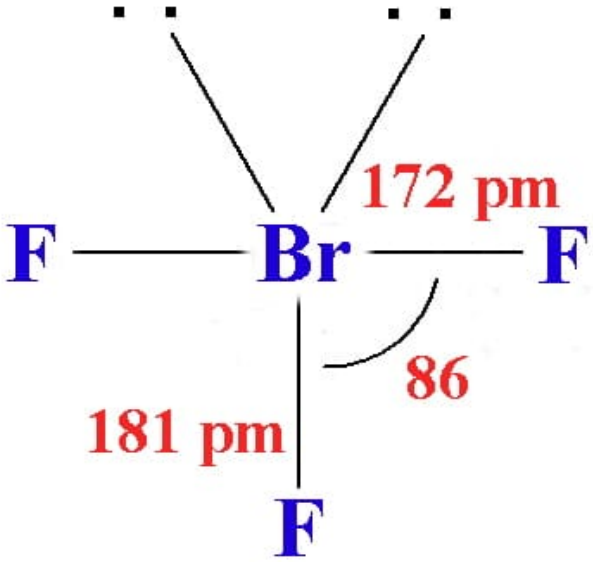
Some properties of interhalogen compounds are listed below. They are all prepared by direct combination of the elements, although since in some cases more than one product is possible, the conditions may be varied by altering the temperature and relative proportions. For example, under the same conditions, difluorine reacts with dichlorine to give ClF, with dibromine to give BrF_3, but with diiodine to give IF_5.

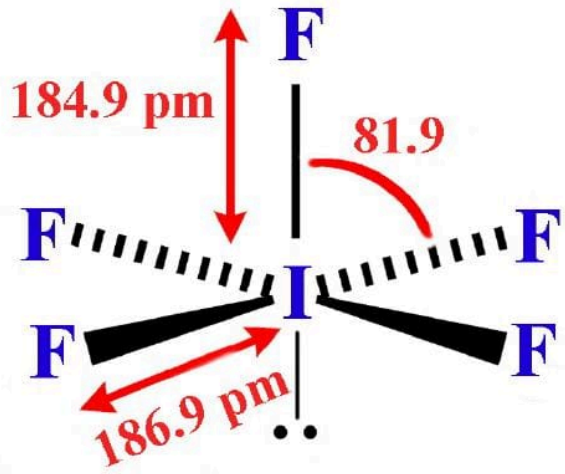
Compound	ClF	BrF	BrCl	ICl	IBr	ClF_3	BrF_3	IF_3	I_2Cl_6	ClF_5	BrF_5	
Appearance at 298K	Colorless gas	Pale brown gas	impure	Red solid	Black solid	Colorless gas	Yellow liquid	Yellow solid	Orange solid	Colorless gas	Colorless liquid	Co li
Stereochemistry	linear	linear	linear	linear	linear	T-shaped	T-shaped	T-shaped	planar	square-based pyramid	square-based pyramid	sc b py
Melting point /K	117	~240	dissoc.	300(a)	313	197	282	245 (dec)	337 (sub)	170	212.5	2
Boiling point /K	173	~293	~278	~373	389	285	399	-	-	260	314	
$\Delta_f H°(298\ K)$ /kJ mol^{-1}	-50.3	-58.5	14.6	-23.8	-10.5	-163.2	-300.8	~-500	-89.3	-255	-458.6	-8
Dipole moment for gas-phase molecule /D	0.89	1.42	0.52	1.24	0.73	0.6	1.19	-	0	-	1.51	

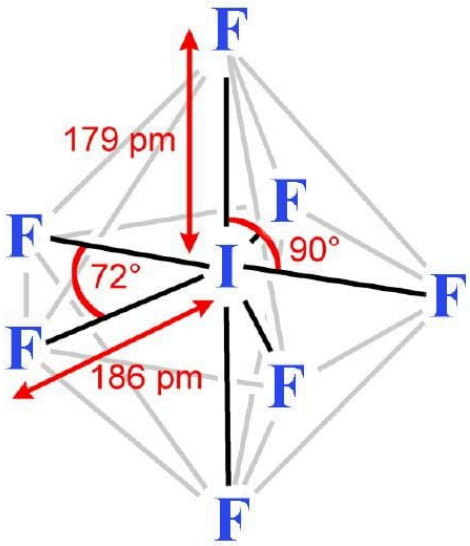
Bond distances in gas-phase molecules except for IF_3 and I_2Cl_6 / pm	163	176	214	232	248.5	160 (eq), 170 (ax)	172 (eq), 181 (ax)	187 (eq), 198 (ax)	238 (terminal) 268 (bridge)	172 (basal), 162 (apical)	178 (basal), 168 (apical)	(b (a

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:

$$\mathrm{U} + 3\,\mathrm{ClF_3} \longrightarrow \mathrm{UF_6} + 3\,\mathrm{ClF}$$

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 --> 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:

$$2\,\mathrm{ICl} \rightarrow \mathrm{I^+} + \mathrm{ICl_2^-}$$

Interhalogen compounds are more reactive than normal halogens, except for fluorine.

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8.13.2.4: 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.

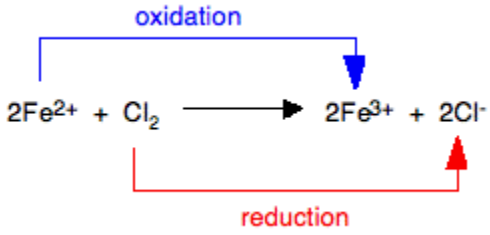
$$Fe + 2I_2 \rightarrow FeI_2$$

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.

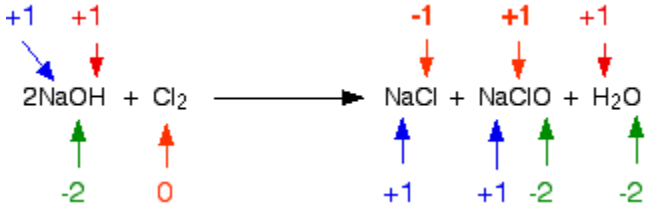
The reaction of chlorine with cold sodium hydroxide solution

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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8.13.2.5: 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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8.13.2.6: Testing for Halide Ions

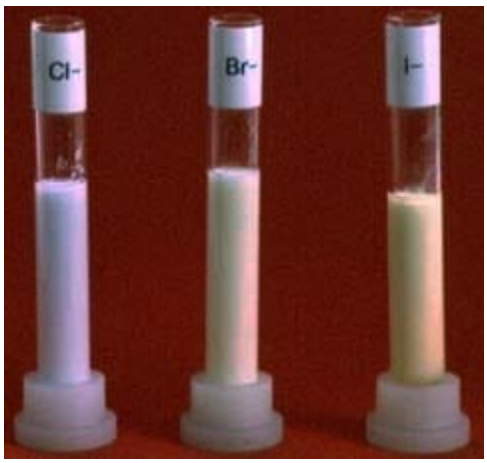
This page discusses the tests for halide ions (fluoride, chloride, bromide and iodide) using silver nitrate and ammonia.

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.

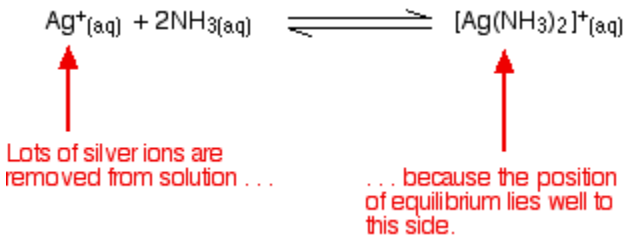
Essentially, the product of the ionic concentrations is never greater than the solubility product value. Enough solid is always precipitated to lower the ionic product to the solubility product. The table below lists solubility products from silver chloride to silver iodide (a solubility product for 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.

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

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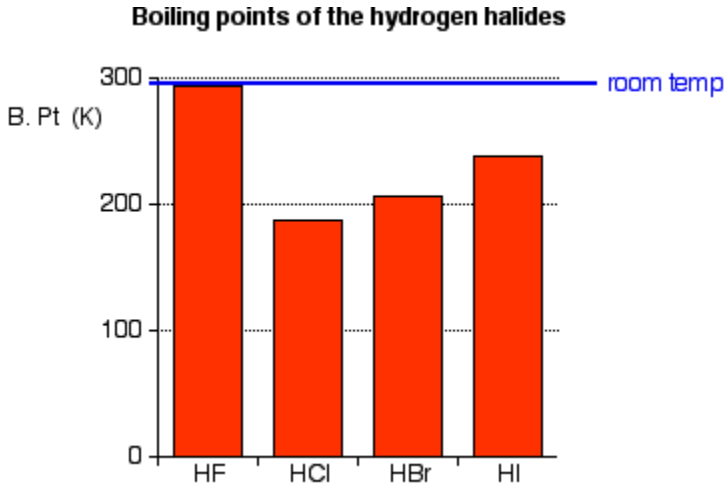
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8.13.2.7: The Acidity of the Hydrogen Halides

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.

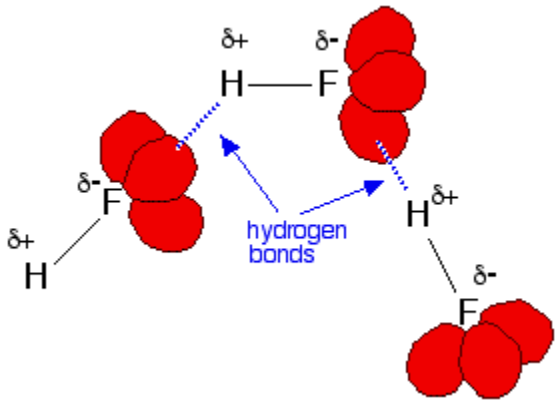
Physical properties

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.

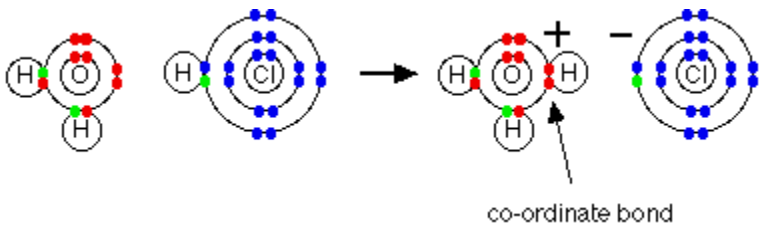
The acidity of the hydrogen halides

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

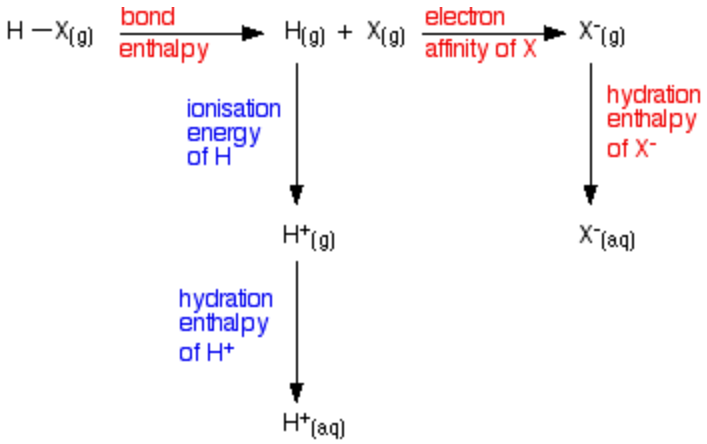
Because the fluorine atom is so small, the bond enthalpy (bond energy) of the hydrogen-fluorine bond is very high. The chart below gives values for all the hydrogen-halogen bond enthalpies:

	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:

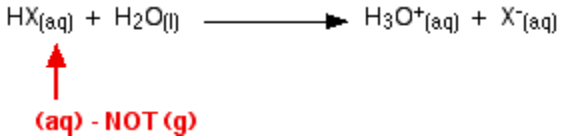
	bond enthalpy of HX (kJ mol^{-1})	**electron affinity of X (kJ mol^{-1})**	**hydration enthalpy of X$^-$ (kJ mol^{-1})**	**sum of these (kJ mol^{-1})**
HF	+562	-328	-506	-272
HCl	+431	-349	-364	-282
HBr	+366	-324	-335	-293
HI	+299	-295	-293	-289

There is virtually no difference in the total HF and HCl values.

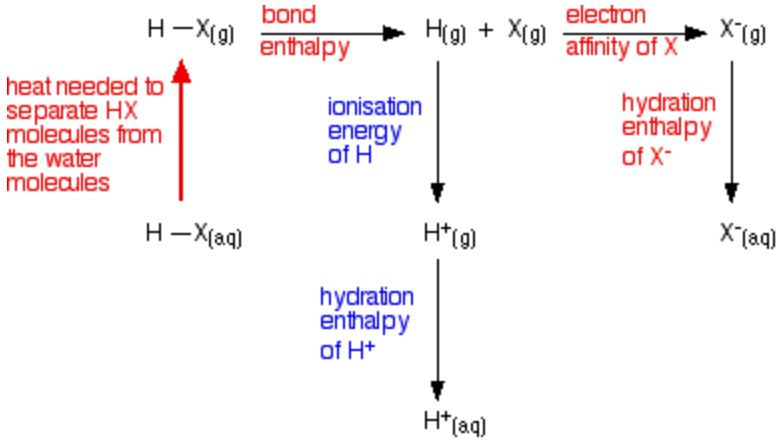
The large bond enthalpy of the H-F bond is offset by the large hydration enthalpy of the fluoride ion. There is a very strong attraction between the very small fluoride ion and the water molecules. This releases a lot of heat (the hydration enthalpy) when the fluoride ion becomes wrapped in water molecules.

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.

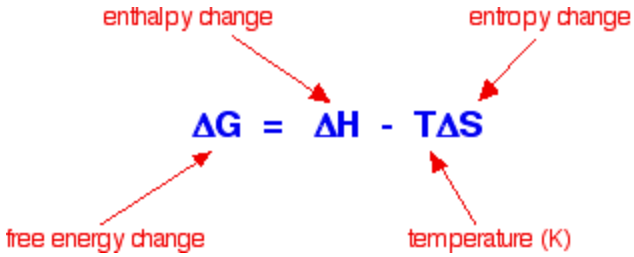
Entropy and free energy considerations

The free energy change, not the enthalpy change, determines the extent and direction of a reaction.

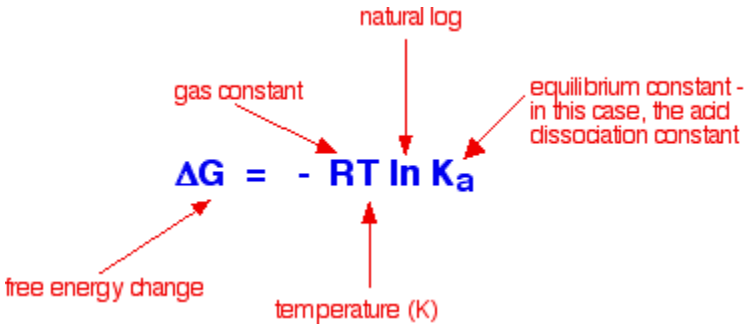
Free energy change is calculated from the enthalpy change, the temperature of the reaction and the entropy change during the reaction.

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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8.13.3: 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).

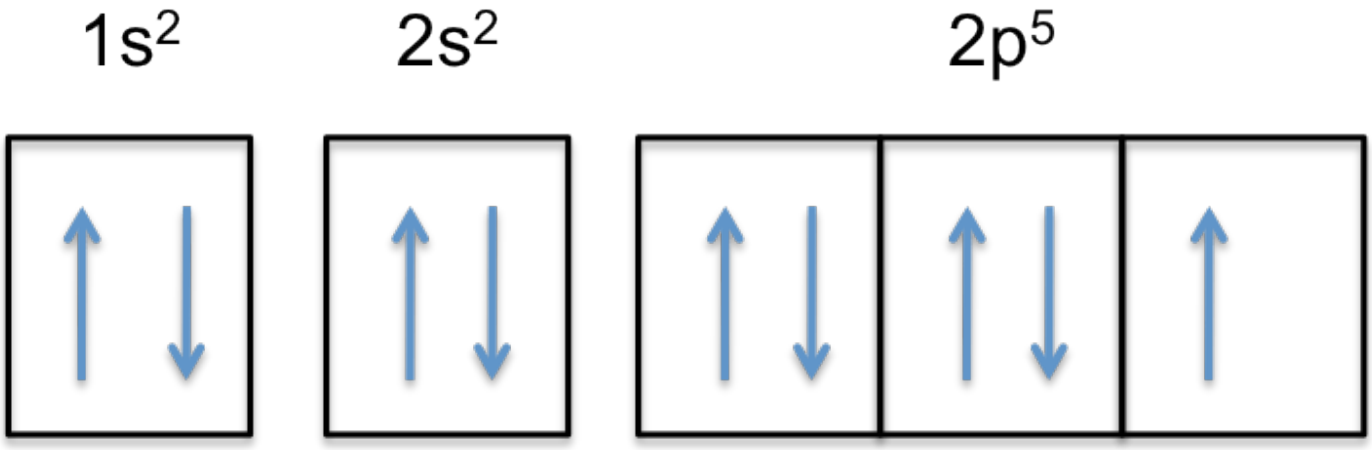


Figure 2: Electronic configuration of fluorine

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).

References

1. Newth, G. S. Inorganic Chemistry. Longmans, Green, and Co.:New York, 1903.
2. Latimer, Wendell M., Hildebrand, Joel H. Reference Book of Inorganic Chemistry. The Macmillan Company: New York, 1938.

Problems

(Highlight to view answers)

1. Q. What is the electron configuration of fluorine? of F^-?

A. $1s^2 2s^2 2p^5$

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

2. Q. Is fluorine usually oxidized or reduced? explain.

A. Fluorine is usually reduced because it accepts an electron from other elements since it is so electronegative.

3. Q. What are some common uses of fluorine?

A. Toothpaste, plastics, rocket fuels, glass etching, etc.

4. Q. Does fluorine form compounds with nonmetals? if so, give two examples, one of them being of an oxide.

A. OF_2, ClF

5. Q. What group is fluorine in? (include name of group and number)

A. 17, Halogens

Contributors and Attributions

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8.13.4: 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]$3s^2 3p^5$
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. $H_2S + 4Cl_2 + 4H_2O \rightarrow H_2SO_4 + 8HCl$
b. $2Sb + 3Cl_2 \rightarrow 2SbCl_3$

2) The electron configuration of chlorine is: $1s^2 2s^2 2p^6 3s^2 3p^5$

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.

References

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8.13.4.1: 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:

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \tag{8.13.4.1.1}$$

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:

$$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^- \tag{8.13.4.1.2}$$

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:

$$4OH^-_{(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)} + 4e^- \tag{8.13.4.1.3}$$

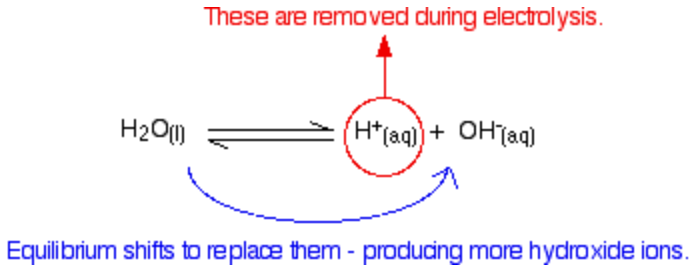
The chlorine must be purified by removing this oxygen.

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:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \tag{8.13.4.1.4}$$

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.

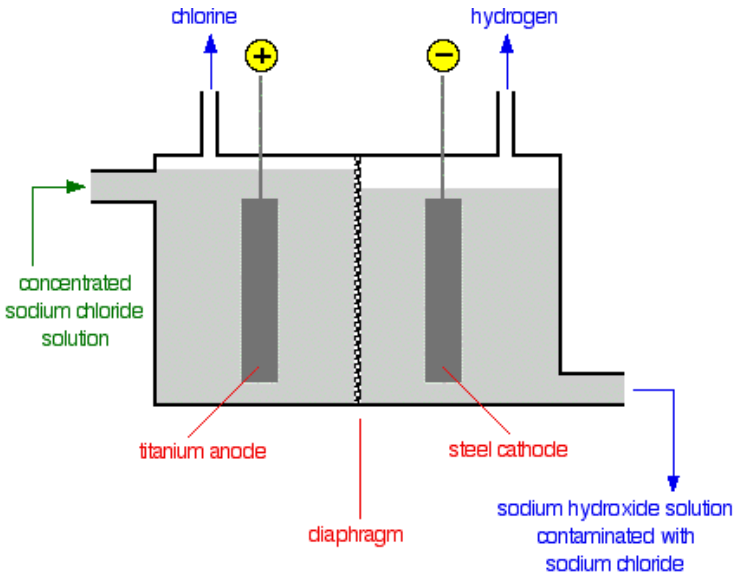


Figure 1: The diaphragm cell

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.

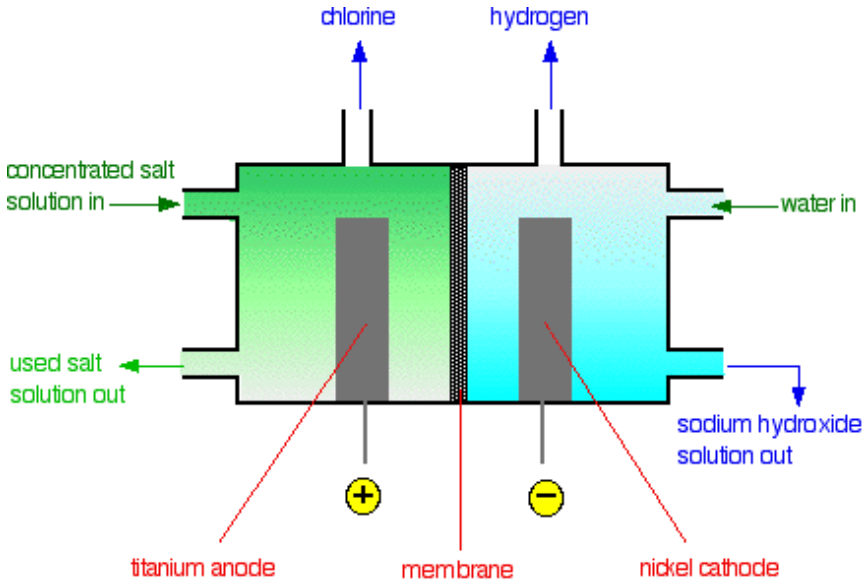


Figure 2: The membrane cell

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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8.13.5: 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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8.13.6: 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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8.13.7: 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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8.14: 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.

8.14.1: History, usage, properties, and distribution of the elements

8.14.2: Properties of Nobel Gases

8.14.2.1: Noble Gas (Group 18) Trends

8.14.3: Chemistry of the Group 18 (Noble Gas) Elements

8.14.4: Reactions of Nobel Gases

8.14.5: Chemistry of Helium (Z=2)

8.14.6: Chemistry of Neon (Z=10)

8.14.7: Chemistry of Argon (Z=18)

8.14.8: Chemistry of Krypton (Z=36)

8.14.9: Chemistry of Radon (Z=86)

8.14.10: Chemistry of Xenon (Z=54)

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8.14.1: History, usage, properties, and distribution of the elements

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8.14.2: 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 1800th 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

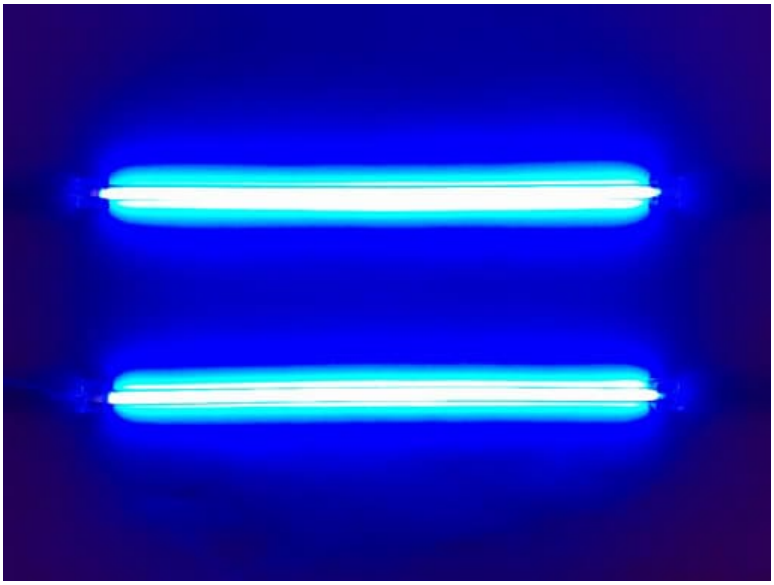
Helium

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

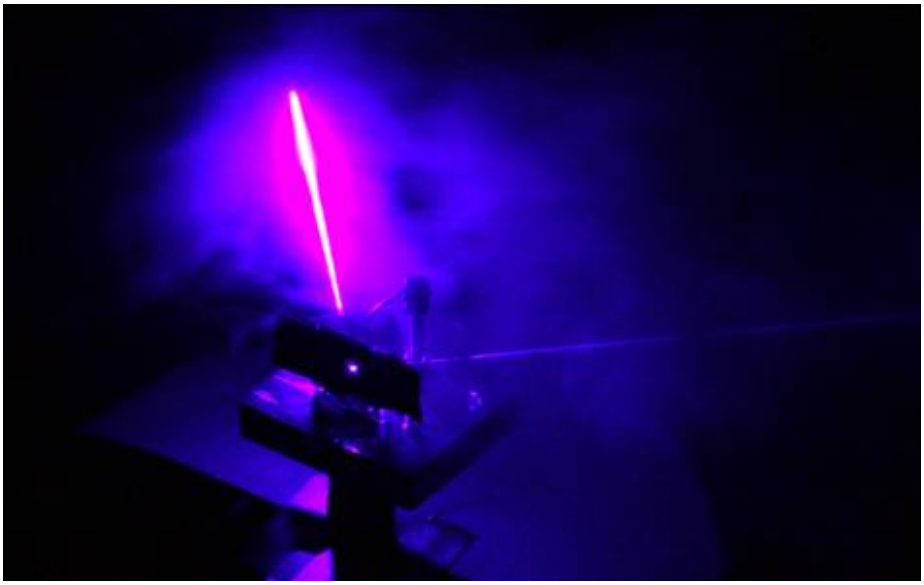
Argon has a large number of applications in electronics, lighting, glass, and metal fabrications. Argon is used in electronics to provide a protective heat transfer medium for ultra-pure silicon crystal semiconductors and for growing germanium. Argon can also fill fluorescent and incandescent light bulbs, 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_4: en.Wikipedia.org/wiki/XeF4
- Wikipedia article on XeF_6: en.Wikipedia.org/wiki/XeF6
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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
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- 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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8.14.2.1: 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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8.14.3: Chemistry of the Group 18 (Noble Gas) Elements

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8.14.4: 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

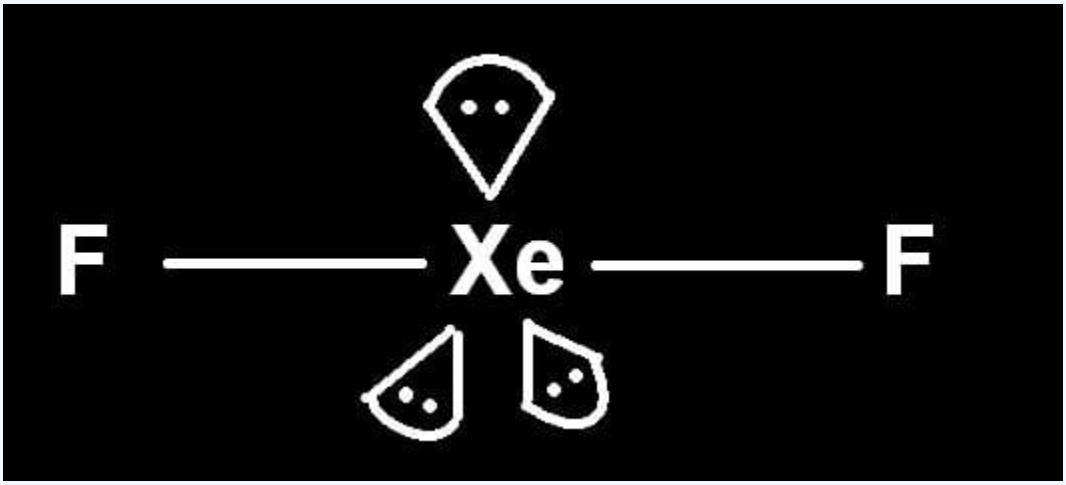
Noble gases are odorless, colorless, nonflammable, and monotonic gases that have low chemical reactivity.

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)

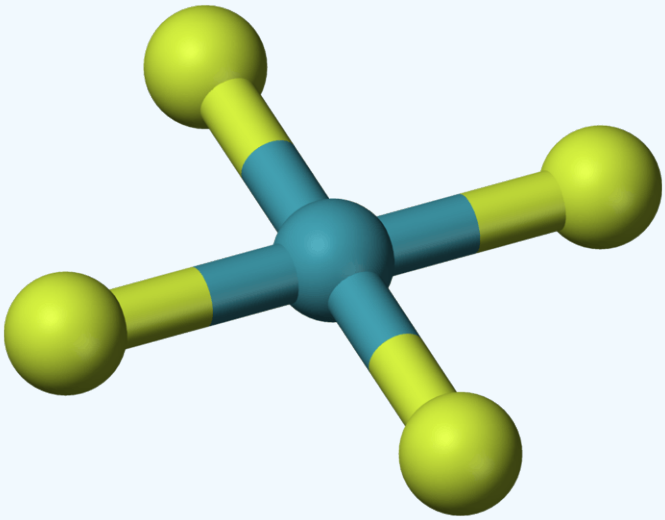




Figure: On Oct. 2, 1963, Argonne announced the creation of xenon tetrafluoride, the first simple compound of xenon, a noble gas widely thought to be chemically inert.

- Colorless Crystals
- Square planar geometry
- Discovered in 1963

Xenon Hexafluoride (XeF_6)

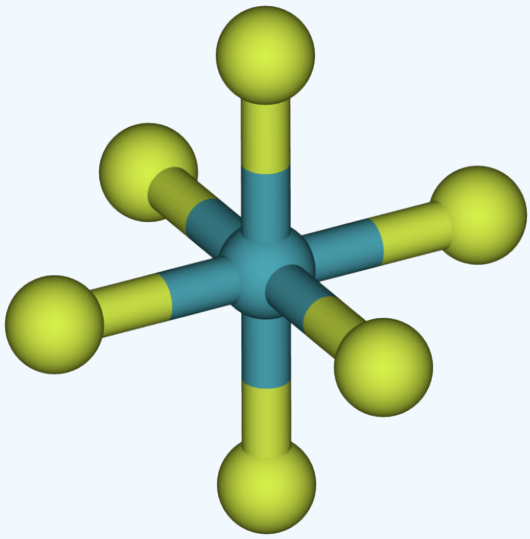
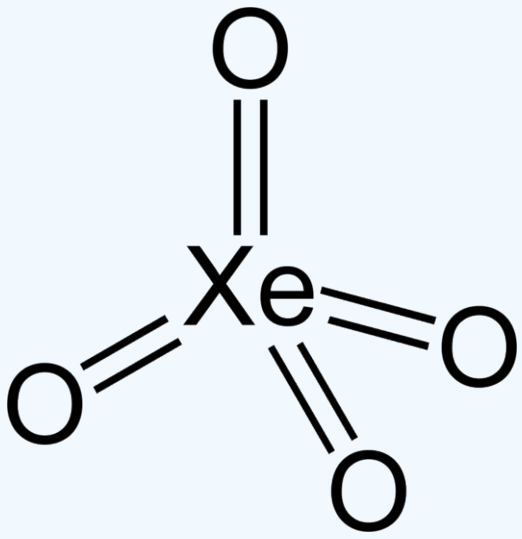


Figure used with permission from Wikipedia.

- 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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8.14.5: 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	7x10^{-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

- en.Wikipedia.org/wiki/Helium
- 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 _____.

Contributors and Attributions

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8.14.6: Chemistry of Neon (Z=10)

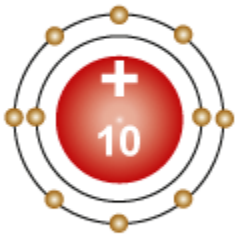


Figure 1: Electron Diagram of Neon. Image courtesy of xxx

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8.14.7: 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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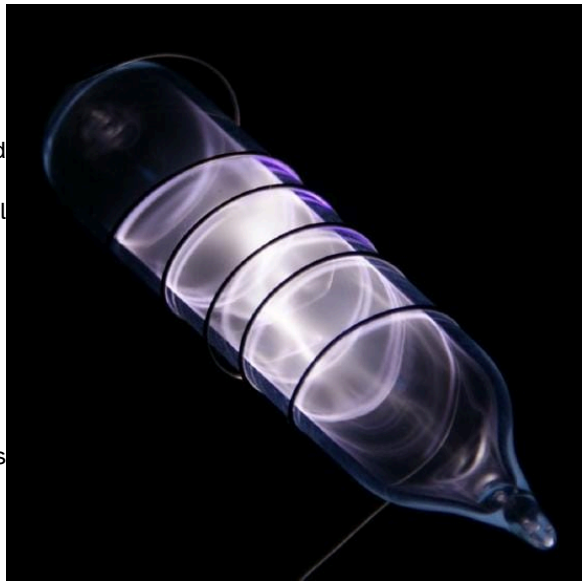
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8.14.8: Chemistry of Krypton (Z=36)

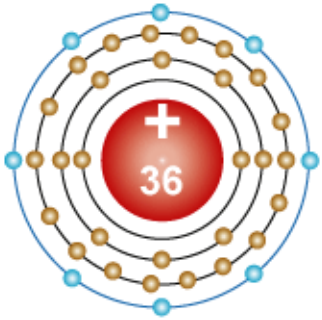
Krypton is one of the six Noble Gas elements (Group 18), which are widely known for their relative "inertness" and difficulty in forming chemical compounds with any other elements, due to these elements having full valence shells. Contrary to original thinking, however, Krypton has been made to react 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.

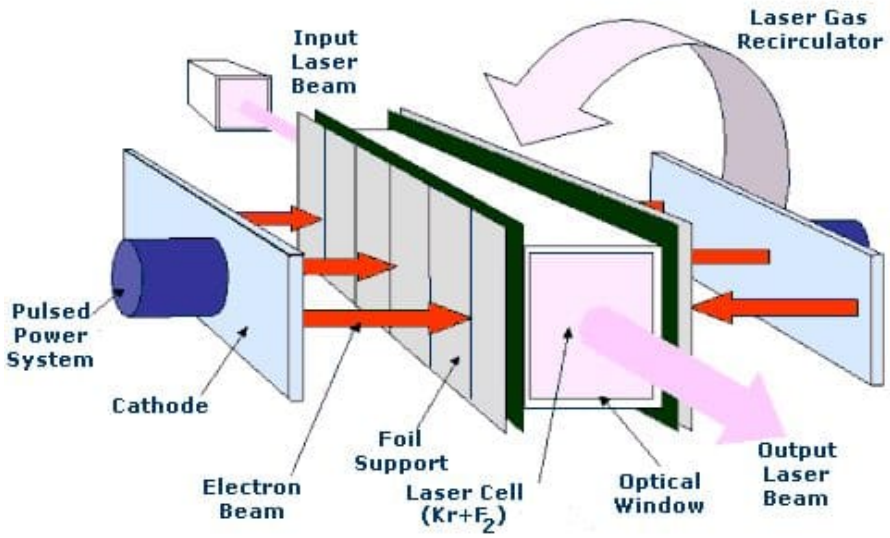
$$Kr_{(g)} + F_{2(g)} \rightarrow KrF_{2(g)}$$

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

References

1. Newton, David E. *Chemical Elements: From Carbon to Krypton*.2nd Volume. Detriot, MI: UXL, 1999. Print.
2. Codd, Sarah L., and Joseph D. Seymour. *Magnetic Resonance Microscopy: Spatially Resolved NMR Techniques and Applications* . Bozeman, MT: Wiley, John & Sons, Incorporated, 2009. Print.
3. Sykes, A.G. *Advances in Inorganic Chemistry*. 46. San Diego, CA: Academic Press, 1999. Print.

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8.14.9: 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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8.14.10: 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.

Contributors and Attributions

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8.P: Problems

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9: COORDINATION CHEMISTRY I - STRUCTURE AND ISOMERS

Coordination compounds are important to all areas of chemistry, engineering, the life and environmental sciences, and beyond. In the synthetic laboratory catalytic amounts of coordination compounds enable organic chemists to synthesize new compounds selectively and in high yield under mild conditions. Applied industrially, coordination compound catalysts serve as vital catalysts that facilitate the conversion of raw petrochemical or bio-derived feedstocks into useful industrial and consumer products. Without them life as we know it would be impossible, as many biochemical systems are coordination complexes. Examples include the hemoglobin that transports oxygen around our bodies and the myoglobin that stores it, the photosystems that harvest light and use light energy in photosynthesis, the constituents of the respiratory chain, and many of the enzymes involved in the expression and transmission of genetic information. In studying coordination chemistry you are about to take your first steps into a vast and exciting world.

9.1: Prelude to Coordination Chemistry I - Structure and Isomers

9.2: History

9.3: Nomenclature and Ligands

9.4: Isomerism

9.5: Coordination Numbers and Structures

9.6: Coordination Frameworks

9.P: Problems

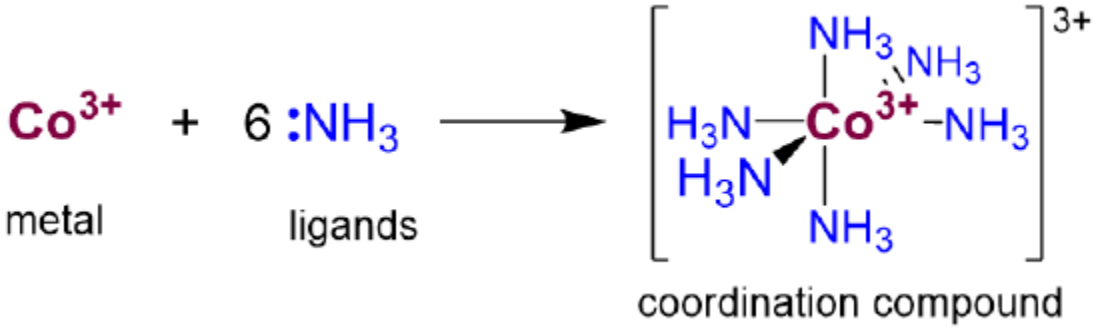
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9.1: Prelude to Coordination Chemistry I - Structure and Isomers

What is a coordination compound?

Coordination compounds consist of one or more **metals** bound to one or more Lewis base **ligands**. For example, hexammineruthenium (3+) ion is a coordination complex in which six ammonia ligands coordinate a Co^{3+} ion, as shown in Scheme 9.1.1.



Scheme 9.1.1: Formation of hexammineruthenium(3+) ion from Co^{3+} and NH_3. (CC BY 4.0; Stephen Contakes)

Such complexes are called coordination complexes because the ligand-metal bond may be thought of as a **coordinate covalent bond** in which both of the bonding electrons come from the ligand, which is then said to **coordinate** the metal. This coordinate covalent model is a very useful formalism for understanding the basic features of coordination chemistry, although it does not always accurately reflect the actual details of the bonding in every coordination complex. Nevertheless, even in those cases where the simple coordinate covalent bond model breaks down, the coordinate covalent bond concept supplies the language sophisticated models employ to describe the more complex bonding involved.

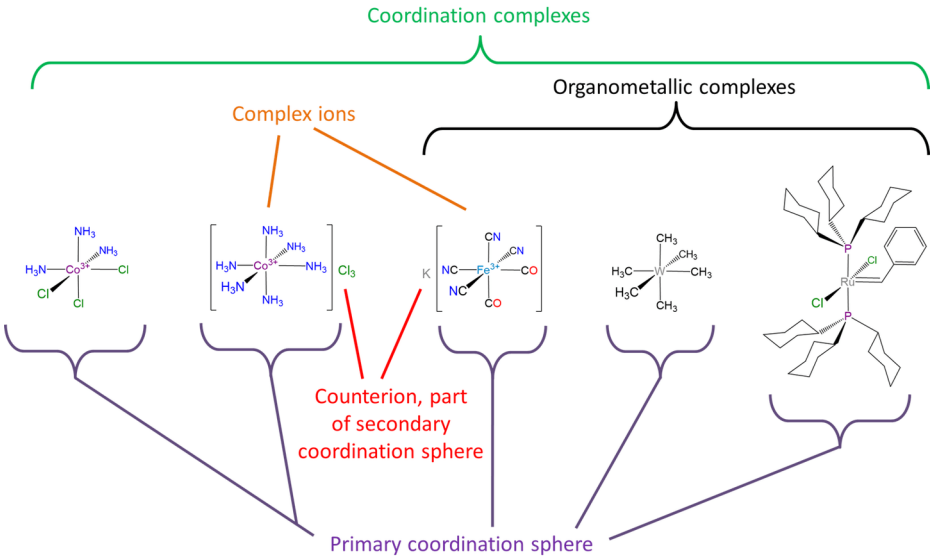
Additional important terms

Some of the common widely used terms that follow from the coordinate covalent model of bonding in coordination complexes include:

- Coordination compounds are also called **coordination complexes**, **metal complexes**, or just **complexes**. The term **complex** refers to coordination compounds' composite nature, in that they may be thought of as comprising multiple ligand and metal ion parts that can be restored by breaking the coordinate covalent bonds holding the complex together. This is in contrast to inorganic or organic molecules which are more commonly thought about as whole molecules held together by the sharing of electrons contributed by all the atoms.
- Coordination complexes that are ions are called **complex ions.**
- Ligands bound to the coordination complex are said to reside in the **primary** or **inner coordination sphere**. These bound ligands are not readily exchangeable, in contrast to nearby counterions and solvent molecules, which are said to reside in the **secondary** or **outer coordination sphere**.
- The portion of the complex contributing the electron pairs is said to be the **donor** and the portion which receives them the **acceptor**. In conventional coordination compounds the ligand is the donor and the metal the acceptor. In these cases it would be equally convenient to refer to the ligand donor as the Lewis base and the metal acceptor as the Lewis acid. However, in more complex bonding scenarios there may be multiple electron pair donation and acceptance interactions taking place between each pair of atoms and donor-acceptor language will be more convenient.
- The number of ligand sites donating lone pairs to the central atom is referred to as the **coordination number**. For most complexes this will just be equal to the number of ligand atoms bound to the metal. In simple complexes it is just equal to the number of ligands. For instance, the cobalt in Scheme 9.1.1 has a coordination number of six.
- Although technically compounds with metal-carbon bonds are coordination complexes, the term coordination complex is

sometimes used to refer to complexes which do not possess metal-carbon bonds in their primary coordination sphere. Complexes which possess metal-carbon bonds are called **organometallic compounds** instead. The use of the terms organometallic and coordination to distinguish organometallic compounds from other types of coordination compounds is often convenient since many organometallic ligands engage in more than simple σ donor-acceptor coordinate covalent bond formation with the metal center. However, this is true of some wholly inorganic ligands too, so it should always be kept in mind that organometallic compounds are just a type of coordination compound and that inorganic ligands can in principle be tuned to interact with a metal center in much the same way an organic ligand does.

A summary of some of the concepts and terms used to describe coordination compounds is given in Scheme 9.1.2.



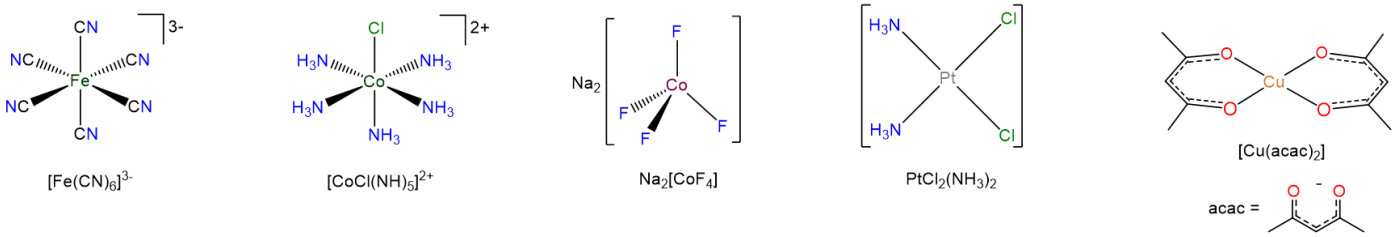
Scheme 9.1.2: Some terms used to describe coordination compounds. (CC BY 4.0; Stephen Contakes)

The formulae of coordination complexes

The way the formulae of coordination complexes are written reflects the fact that it is often convenient to think of coordination compounds as a composite of metals and ligands. When writing the formula of a complex

- the atoms of a ligand are not added to those of the rest of the compound. Instead, the ligand atoms are kept together, if necessary by enclosing the ligand formula in parentheses or giving an abbreviation for the ligand.
- For complex ions the metal and ligands are enclosed in square brackets. Sometimes this is also done for neutral coordination compounds as well. In either case the brackets enclose those parts of the compound which comprise the primary coordination sphere; anything else is in the secondary coordination sphere outside.

A careful perusal of the examples in Scheme 9.1.3 should make the important features of this system clear.



Scheme 9.1.3: Formulae of coordination compounds and complex ions. (CC BY 4.0; Stephen Contakes)

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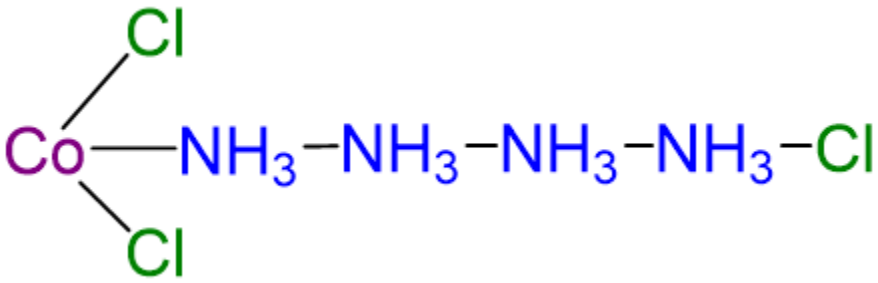
9.2: History

History of the Coordination Compounds

Coordination compounds have been known and used since antiquity; one of the oldest synthetic pigments is the blue pigment Egyptian blue, a copper complex of formula $CaCuSi_4O_{10}$ used by the Egyptians since the third Millenium B.C. (in ancient China the Ba analogue, Han blue, was discovered independently). The blue color of Egyptian blue is due to interlocked $Cu(Si_2O_7)_4$ units in which each copper is coordinated by four O atoms in a square planar arrangement. Later, in 1706, the Berlin painter Diesbach would discover another deep blue pigment, Prussian blue: $KFe_2(CN)_6$.

Despite their long use, the chemical nature of coordination compounds was unclear for a number of reasons. For example, many compounds called "double salts" were known, such as $AlF_3 \cdot 3\,KF$, $Fe(CN)_2 \cdot 4\,KCN$, and $ZnCl_2 \cdot 2\,CsCl$, which were combinations of simple salts in fixed and apparently arbitrary ratios. Why should $AlF_3 \cdot 3\,KF$ exist but not $AlF_3 \cdot 4\,KF$ or $AlF_3 \cdot 2\,KF$? And why should a 3:1 KF:AlF_3 mixture have different chemical and physical properties than either of its components? Similarly, adducts of metal salts with neutral molecules such as ammonia were also known—for example, $CoCl_3 \cdot 6\,NH_3$, which was first prepared sometime before 1798. Like the double salts, the compositions of these adducts exhibited fixed and apparently arbitrary ratios of the components. For example, $CoCl_3 \cdot 6\,NH_3$, $CoCl_3 \cdot 5\,NH_3$, $CoCl_3 \cdot 4\,NH_3$, and $CoCl_3 \cdot 3\,NH_3$ were all known and had very different properties, but despite all attempts, chemists could not prepare $CoCl_3 \cdot 2\,NH_3$ or $CoCl_3 \cdot NH_3$.

Although the chemical composition of such compounds was readily established by existing analytical methods, their chemical nature was puzzling and highly controversial. The major problem was that what we now call valence (i.e., the oxidation state) and coordination number were thought to be identical. As a result, highly implausible (to modern eyes at least) structures were proposed for such compounds. Of these the most influential was the Blomstrand-Jørgensen chain theory of bonding in coordination compounds, which predicted the "Chattanooga choo-choo" model for $CoCl_3{\cdot}4NH_3$ shown in Scheme 9.2.I.



Scheme 9.2.I. Blomstrand-Jørgensen chain theory model of bonding in $CoCl_3{\cdot}4NH_3$.

Nevertheless, this theory was not wholly illogical and, in fact, explained much of the analytical data on coordination compounds available to chemists of the time. This data included the electrical conductivity of aqueous solutions of these compounds, which was roughly proportional to the number of ions formed per mole, and the number of free chloride ions present, which could be determined by precipitating them gravimetrically as AgCl. In the case of $CoCl_3{\cdot}4NH_3$, two ions and one chloride were produced when the compound was dissolved in water, which Jørgensen was able to explain using the chain structure shown above by postulating that chlorides attached to NH_3 could dissociate while those attached to Co could not. The modern theory of coordination chemistry, which overthrew the chain theory, is based largely on the work of Alfred Werner (1866–1919; Nobel Prize in Chemistry in 1913). In a series of careful experiments carried out in the late 1880s and early 1890s, he examined the properties of several series of metal halide complexes with ammonia. For example, five different "adducts" of ammonia with $PtCl_4$ were known at the time: $PtCl_4{\cdot}nNH_3$ (n = 2–6). Some of Werner's original data on these compounds are shown in Table 9.2.1. Werner's data on $PtCl_4{\cdot}6NH_3$ in Table 9.2.1 showed that all the chloride ions were present as free chloride. In contrast, $PtCl_4{\cdot}2NH_3$, was a neutral molecule that did not give free chloride ions when dissolved in water.

Alfred Werner (1866–1919)

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

Table 9.2.1: Werner's Data on Complexes of Ammonia with $PtCl_4$

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

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

$$[Pt(NH_3)_6]Cl_4 \rightarrow [Pt(NH_3)_6]^{4+}(aq) + 4Cl^-(aq) \tag{9.2.1}$$

$$[Pt(NH_3)_5Cl]Cl_3 \rightarrow [Pt(NH_3)_5Cl]^{3+}(aq) + 3Cl^-(aq) \tag{9.2.2}$$

$$[Pt(NH_3)_4Cl_2]Cl_2 \rightarrow [Pt(NH_3)_4Cl_2]^{2+}(aq) + 2Cl^-(aq) \tag{9.2.3}$$

$$[Pt(NH_3)_3Cl_3]Cl \rightarrow [Pt(NH_3)_3Cl_3]^{+}(aq) + Cl^-(aq) \tag{9.2.4}$$

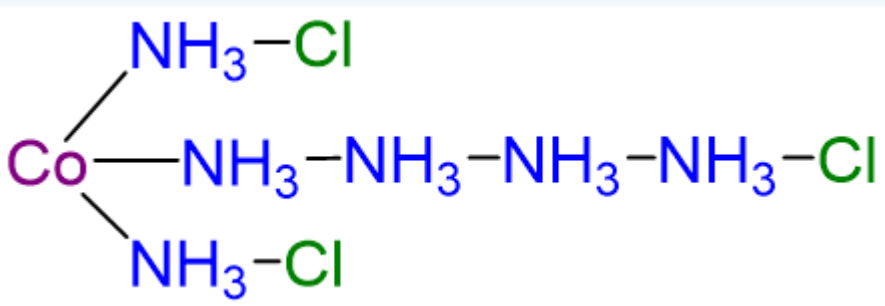
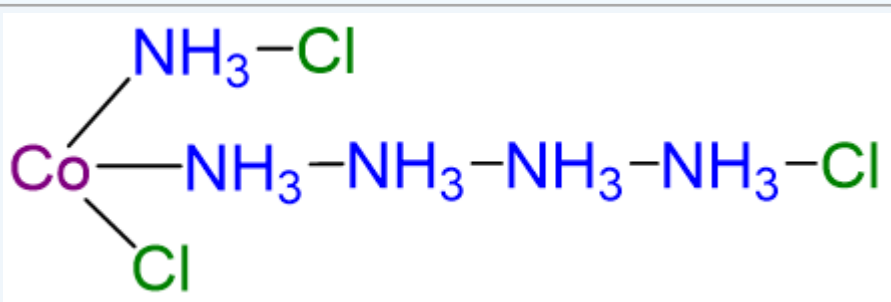
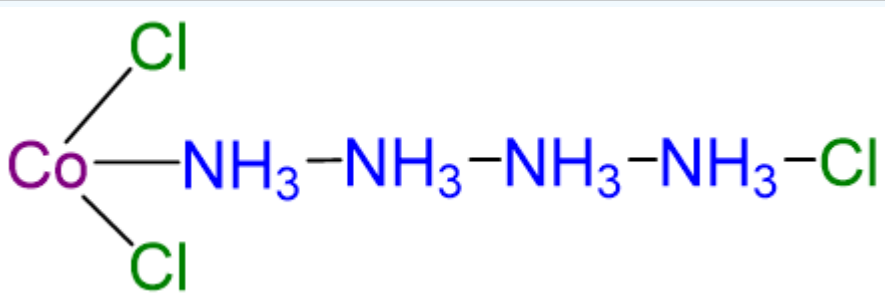
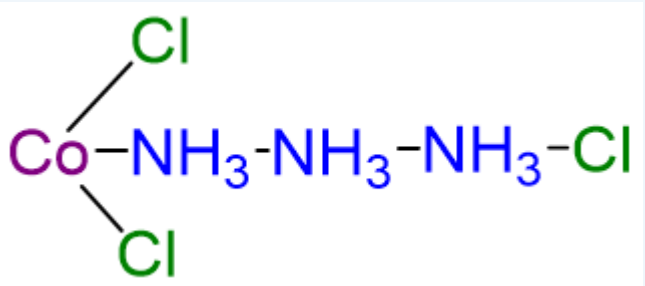
$$[Pt(NH_3)_2Cl_4] \rightarrow [Pt(NH_3)_2Cl_4]^{0}(aq) \tag{9.2.5}$$

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

Exercise 9.2.1. The $CoCl_3 xNH_3$ series.

The series $CoCl_3 \cdot xNH_3$ was particularly important in establishing the correctness of Werner's coordination theory over the rival chain theory. By ~1900 conductivity measurements suggested that the members of the series gave the number of ions shown in Table 9.2.1.

Table 9.2.1. The CoCl3·xNH3 series according to coordination theory, chain theory, and experiment.

Compound	Color	Werner formulation	Blomstrand-Jørgensen chain theory formulation	I s
$CoCl_3 \cdot 6NH_3$	yellow	$[Co(NH_3)_6]Cl_3$		4
$CoCl_3 \cdot 5NH_3$	violet	$[Co(NH_3)_5Cl]Cl_2$		3
$CoCl_3 \cdot 4NH_3$	green	$[Co(NH_3)_4Cl_2]Cl$		2
$CoCl_3 \cdot 3NH_3$	orange	$[Co(NH_3)_4Cl_3]$		(

What does this data suggest about the relative explanatory power of Werner's coordination theory and chain theory? Explain.

Answer available at the end of this section.

What ultimately convinced Jørgensen of the correctness of Werner's coordination model over his own chain theory was how Werner's explanation of the structure of cobalt coordination complexes using an octahedral coordination geometry explained the existence of isomers in Co complexes containing Cl and NH_3 ligands. In the case of $[Co(NH_3)_4Cl_2]Cl$ two isomers were known: one red and the other green. Because both compounds had the same chemical composition and the same number of groups of the same kind attached to the same metal, there had to be something different about the arrangement of the ligands around the

metal ion. Werner's key insight was that the six ligands in $[Co(NH_3)_4Cl_2]Cl$ had to be arranged at the vertices of an octahedron because that was the only structure consistent with the existence of two, and only two, stereoisomers (Figure 9.2.1). His conclusion was also corroborated by the existence of two and only two stereoisomers of the next compound in the series: $Co(NH_3)_3Cl_3$.

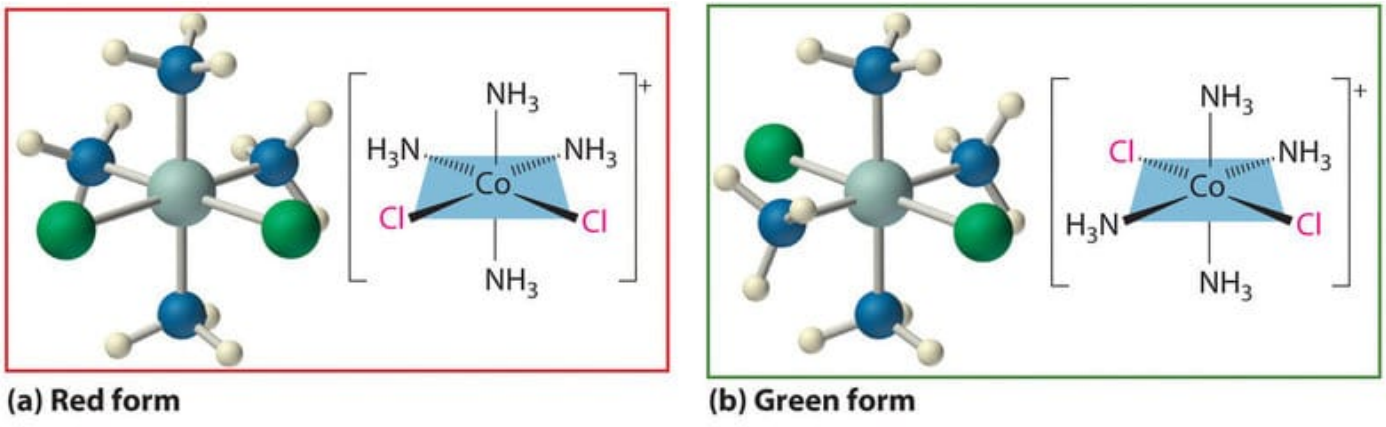


Figure 9.2.1. The $[Co(NH_3)_4Cl_2]^+$ ion can have two different arrangements of the ligands, which results in different colors: if the two Cl^- ligands are next to each other (*cis*), the complex is red (a), but if they are opposite each other (*trans*), the complex is green (b).

Example 9.2.1: Why did Werner propose an octahedral geometry for 6-coordinate complexes?

In Werner's time, many complexes of the general formula MA_4B_2 were known, but no more than two different compounds with the same composition had been prepared for any metal. To confirm Werner's reasoning that this suggests these complexes possess an octahedral geometry, calculate the maximum number of different structures possible for six-coordinate MA_4B_2 complexes with each of the three most symmetrical possible structures the ligands will form about the central metal - a hexagon, a trigonal prism, and an octahedron.

Assuming that the absence of evidence for additional compounds in this case serves as reasonable circumstantial evidence for their absence, what does the fact that no more than two forms of any MA_4B_2 complex were known suggest about the three-dimensional structures of these complexes?

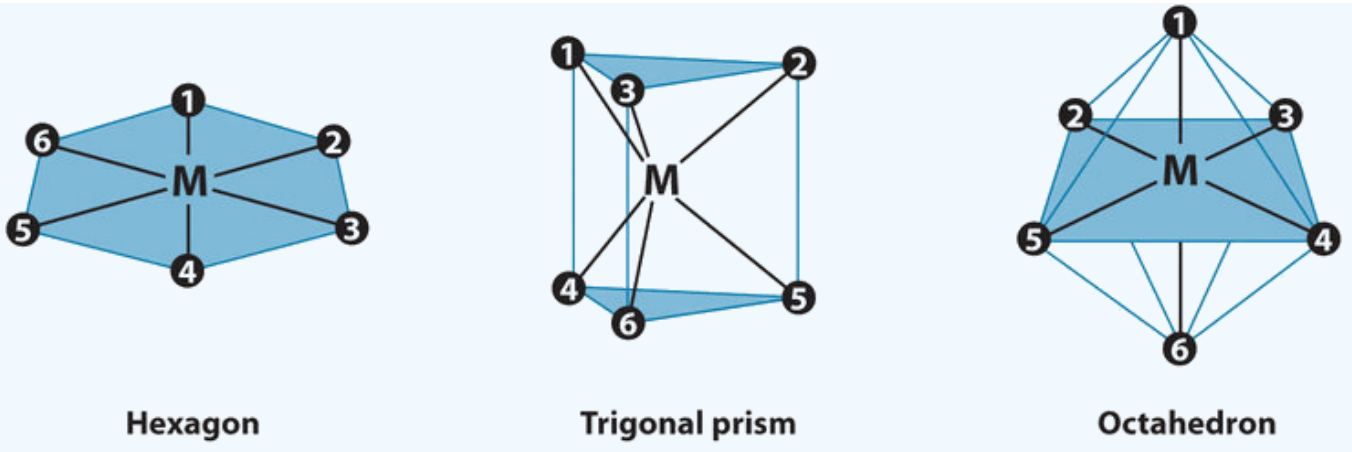
Solution

In this problem you are given

- the stochiometry of the complexes, MA_4B_2
- three possible coordination geometries - hexagonal, trigonal prismatic, and octahedral.

In order to calculate the number of isomers that could be present for each geometry it is best to follow a systematic approach. Since there are fewer B type ligands than A type ligands, the easiest way to do this for each geometry is to start by placing a B ligand at one vertex and then to determine how many different positions are available for the second B ligand.

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



For the hexagon, we place the first B ligand at position 1. There are now **three** possible places for the second B ligand:

- position 2 (or 6)
- position 3 (or 5)
- position 4

The (1, 2) and (1, 6) arrangements are chemically identical because the two B ligands are adjacent to each other. The (1, 3) and (1, 5) arrangements are also identical because in both cases the two B ligands are separated by an A ligand. Those of you who remember your ogranic chemistry might recognize that this situation is formally analogous to the *ortho*-, *meta*-, and *para*-isomerism in disubstituted benzenes.

Turning to the trigonal prism, we place the first B ligand at position 1. Again, there are three possible choices for the second B ligand:

- at position 2 or 3 on the same triangular face
- position 4 (on the other triangular face but adjacent to 1)
- position 5 or 6 (on the other triangular face but not adjacent to 1).

The (1, 2) and (1, 3) arrangements are chemically identical, as are the (1, 5) and (1, 6) arrangements.

In the octahedron, however, if we place the first B ligand at position 1, then we have only two choices for the second B ligand:

- position 2 (or 3 or 4 or 5)
- position 6.

In the latter, the two B ligands are at opposite vertices of the octahedron, with the metal lying directly between them. Although there are four possible arrangements for the former, they are chemically identical because in all cases the two B ligands are adjacent to each other.

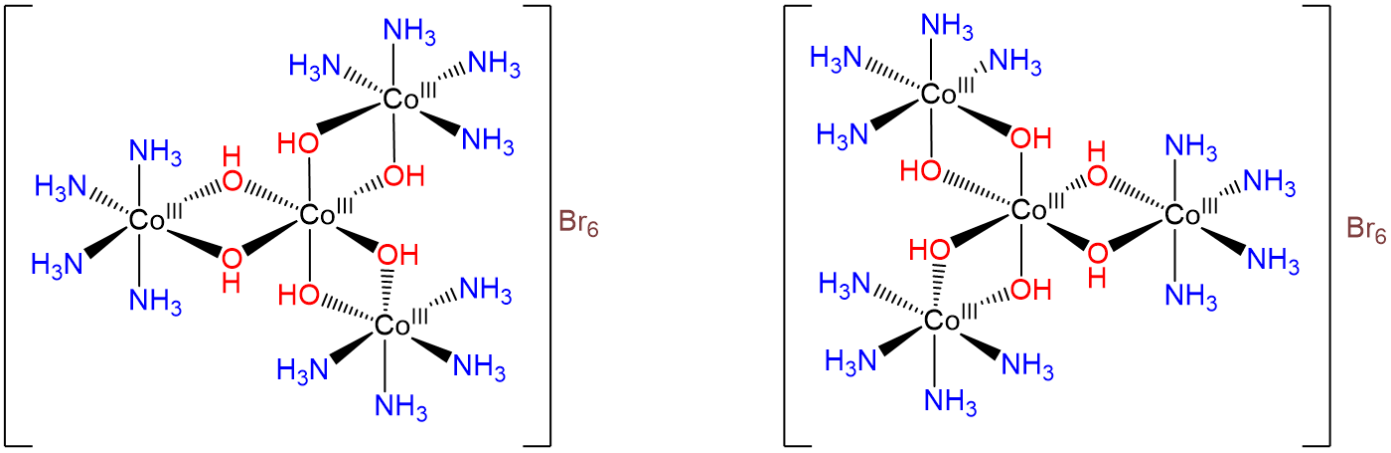
The number of possible MA_4B_2 arrangements for the three geometries is thus: hexagon, 3; trigonal prism, 3; and octahedron, 2. The fact that only two different forms were known for all MA_4B_2 complexes that had been prepared suggested that the correct structure was the octahedron but did not prove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

Exercise 9.2.1

Determine the maximum number of structures that are possible for a four-coordinate MA_2B_2 complex with either a square planar or a tetrahedral symmetrical structure.

Answer available at the end of this section.

Even Werner's explanation of isomerism in coordination complexes in terms of octahedral and other recognized coordination geometries did not convince all chemists until he was able to resolve a racemic mixture of *d*- and *l*-$[Co\{Co(NH3)_4(OH)_2\}_3]$ into its enantiomers, which are shown in Scheme 9.2.**II**. By doing so Werner demonstrated to chemists of his time (virtually none of whom knew group theory) that tetrahedral carbon atoms were not required for chirality; D_3 octahedral complexes were also chiral.



Scheme 9.2.II: d- and l-enantiomers of $[Co\{Co(NH3)_4(OH)_2\}_3]$, colloquially referred to as hexol. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Answers

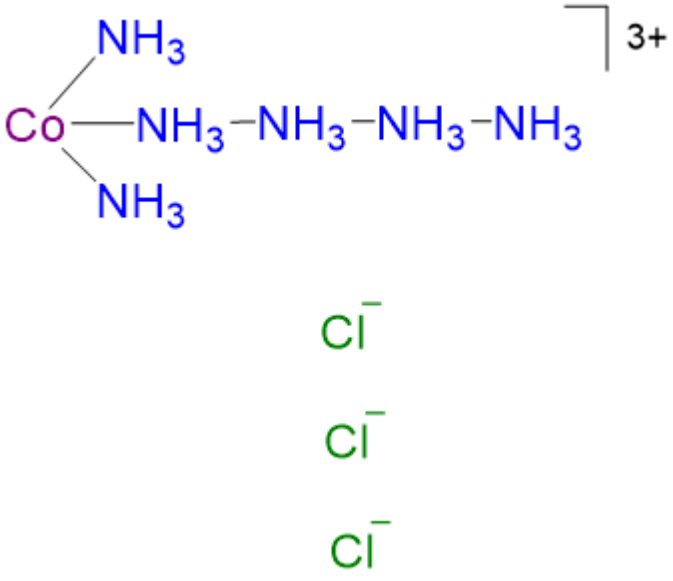
Exercise 9.2.1**. The $CoCl_3xNH_3$ series.**

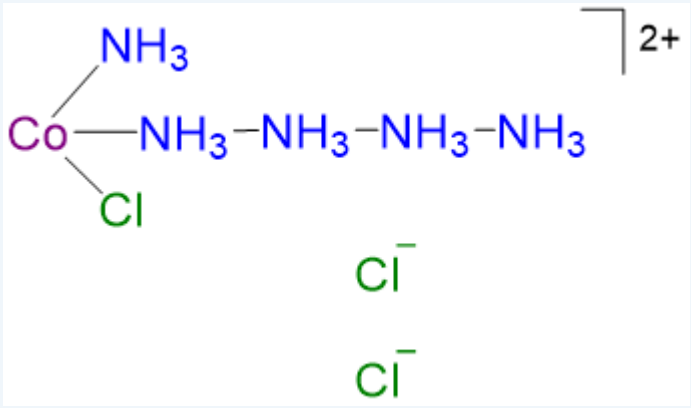
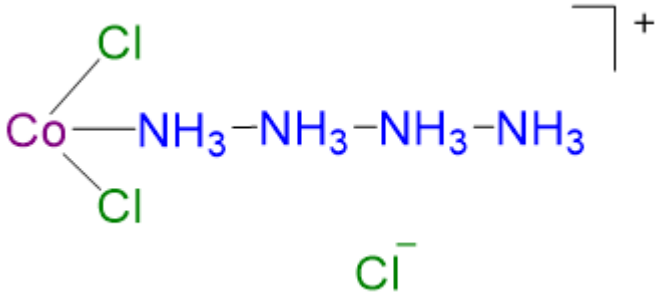
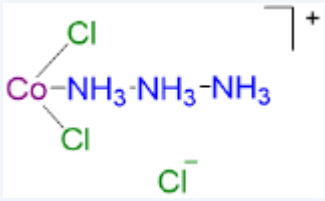
Remember that

- chain theory predicts that the number of ions is the number formed when the Cl atoms bound in a chain with NH_3 dissociate.
- coordination theory predicts the number of ions based on the number of complex ions and their counterions.

Based on this the predictions of coordination theory and chain theory can be compared with the experimental data, as is done in Table 9.2.2.

Table 9.2.2*: Comparison of ions predicted for the $CoCl_3{\cdot}xNH_3$ series by coordination theory and chain theory with the number obse experimentally.*

Compound	Color	Ions predicted by Werner's coordination theory	Number of ions predicted by coordination theory	Ions predicted by Blomstrand-Jørgensen chain theory	Numbe of ion predict by cha theor
$CoCl_3{\cdot}6NH_3$	yellow	$[Co(NH_3)_6]^{3+}$ Cl^- Cl^- Cl^-	4		4

Compound	Color	Ions predicted by Werner's coordination theory	Number of ions predicted by coordination theory	Ions predicted by Blomstrand-Jørgensen chain theory	Numbe of ion predict by cha theory
$CoCl_3 \cdot 5NH_3$	violet	$[Co(NH_3)_5Cl]^{2+}$ Cl^- Cl^-	3		3
$CoCl_3 \cdot 4NH_3$	green	$[Co(NH_3)_4Cl_2]^+$ Cl^-	2		2
$CoCl_3 \cdot 3NH_3$	orange	None	0		2

As can be seen by comparing the number of ions predicted by coordination and chain theory in Table 9.2.2, coordination theory successfully explains all the observed ion counts, while chain theory fails to explain the lack of ions observed for $CoCl_3 \cdot 3NH_3$.

Nevertheless, as is often the case when developing theoretical models using data from real experimental investigations, these observations did not convince Jørgensen, who could point to the experimental difficulty of determining the number of ions present from solution conductivity data.

Exercise 9.2.1

square planar, 2; tetrahedral, 1

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- 24.1: Werner's Theory of Coordination Compounds by Anonymous is licensed CC BY-NC-SA 4.0.

9.3: Nomenclature and Ligands

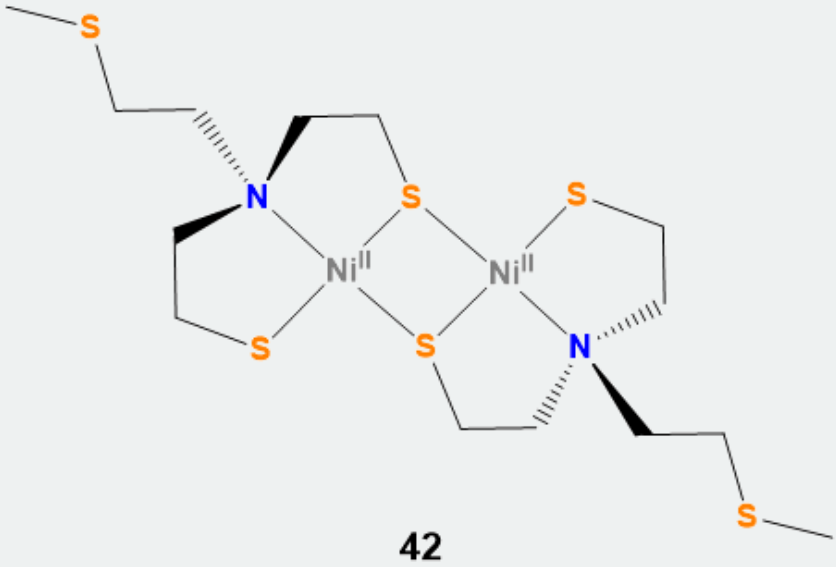
Systems of nomenclature and formulae are intended as tools, to be employed insofar as they are useful

There are well-established rules for both naming and writing the formulae of coordination compounds. The purpose of these rules is to facilitate clear and precise communication among chemists. As with all such rules, some are more burdensome than others to employ, and some serve more crucial roles in the communication process while others are more peripheral - and all are poorly used in the service of pedantic tyranny, especially when used against those who are otherwise doing good work. For this reason, you are urged to approach the rules in a spirit of generosity towards others in

- naming and writing formulas as reasonably accurately as you can so that ligands and metals are where readers expect them and thus can understand what you mean more easily.
- being gracious towards the many professional inorganic chemists who adhere loosely to some of the rules you are about to learn.
- recognizing that in cases when a structure is particularly complex and a picture may make be particularly useful, you should supply one (See the note below).

Note 9.3.1: Sometimes the most helpful name to give a compound is 42.

Even though the IUPAC nomenclature rules permit specification of even the most complex structures, it is often much easier and more effective to supply a numbered structure that can be referred to instead of the IUPAC name. Consider bis{[(μ-2-mercaptoethyl)(2-mercaptoethyl)-methylthioethylaminato (2-)]Nickel(II)}. Which is easier, to expect readers and hearers to work out the structure from that name or to just refer them to compound **42** in Scheme 9.3.I?



42

Scheme 9.3.I. Structure of bis{[(μ-2-mercaptoethyl)(2-mercaptoethyl)-methylthioethylaminato (2-)]Nickel(II)}. The authors of the synthesis of this compound in Inorganic syntheses1 may have had to figure out an IUPAC name for this compound but if you have this scheme in your paper and your instructor is OK with it you can just call it **42**

Coordination Complexes are named as the ligand derivatives of a metal

A variety of systems have been used for naming coordination compounds since the development of the discipline in the time of Alfred Werner. In this section the most common approaches as they are currently used by practicing chemists will be described. Those who need a more thorough and accurate acquaintance with the full IUPAC nomenclature rules are encouraged to consult

the IUPAC brief guide to inorganic nomenclature followed by complete guidelines, commonly known as the IUPAC red book. If those are still not enough a careful read of note 9.3.1 is suggested.

The systems for naming coordination compounds used at present are additive, meaning that they consider coordination compounds as comprising a central metal to which are added ligands. To specify the structure and bonding in this metal-ligand complex then involves:

1. when there are several different ways of attaching the metal and ligands, specifying the structural or stereoisomer
2. systematically listing the ligands in a way that, as necessary, conveys information about how they are linked to the metal and their stereochemistry
3. providing the identity of the metal and its oxidation state, or if the oxidation state is unclear, at least the overall charge on the complex
4. specifying any counterions present

Since the stereochemistry of coordination compounds forms the subject of the next section, in this section it will be addressed by simply giving the prefixes that designate stereochemistry as if they were self-evident. Do not worry about these for now. They will make sense after you have learned more about stereochemistry in the next section. At that time, you can go back over the examples in that section to solidify your understanding of how to name coordination compounds.

However, in order to name coordination compounds accurately you will need to learn how to think about and name ligands first.

Ligands

Ligands are classified based on whether they bind to the metal center through a single site on the ligand or whether they bind at multiple sites. Ligands that bind through only a single site are called **monodentate** from the Latin word for tooth; in contrast, those which bind through multiple sites are called **chelating** after the Greek $\chi\alpha\lambda\epsilon$ for "claw". These relationships are summarized in Figure 9.3.1.

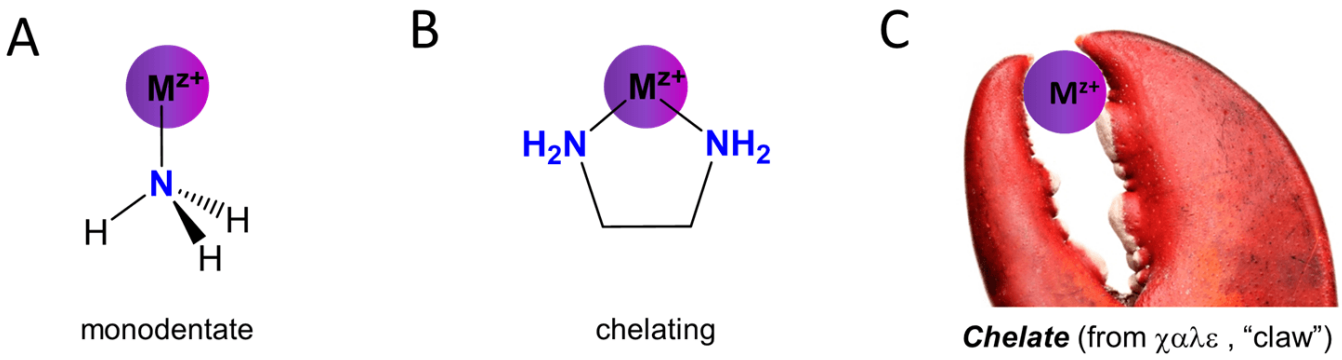
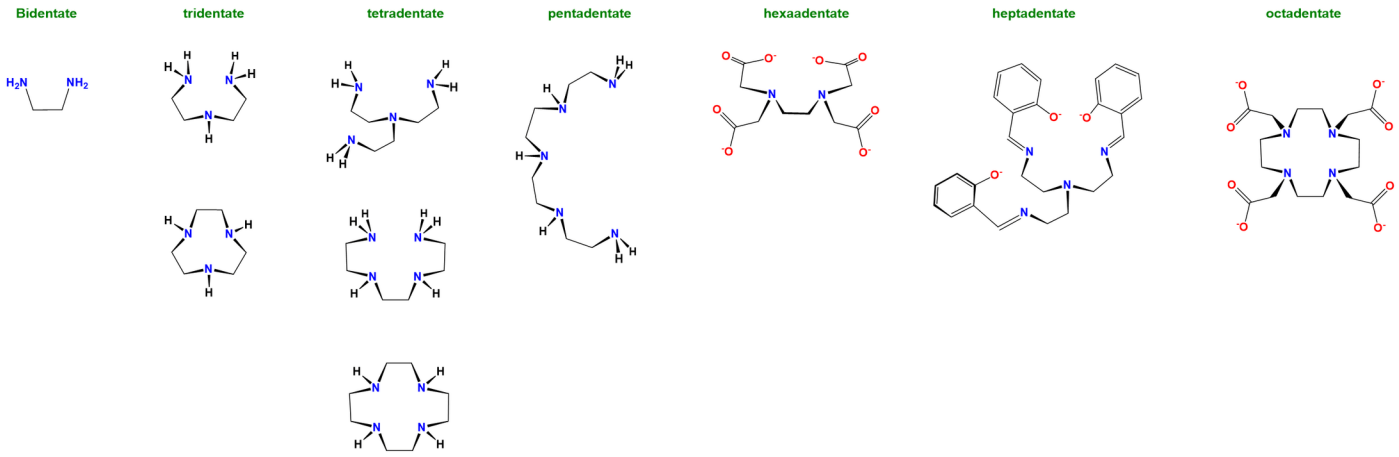


Figure 9.3.1. (A) Ammonia is a monodentate ligand while (B) ethylene diamine is a chelating ligand owing to its capacity to bind metals via its two amine functional groups. (C) Chelating ligands act like a lobster claw in attaching to the metal via multiple sites. The lobster claw image is adapted from https://www.clipart.email/download/1127636.html. Otherwise this work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Following naturally from the classification of non-chelating ligands as monodentate, chelating ligands are further classified according to the number of sites which they can use to bind a metal center. This number of binding sites is called the denticity and ligands are referred to as monodentate (non- chelating), bidentate, tridentate, etc., based on the number of sites available. Ligands with two binding sites have a denticity of two and are said to be bidentate; those with three are tridentate, four tetradentate, and so on. To illustrate this classification system examples of chelating ligands classified according to denticity are given in Scheme 9.3.I.

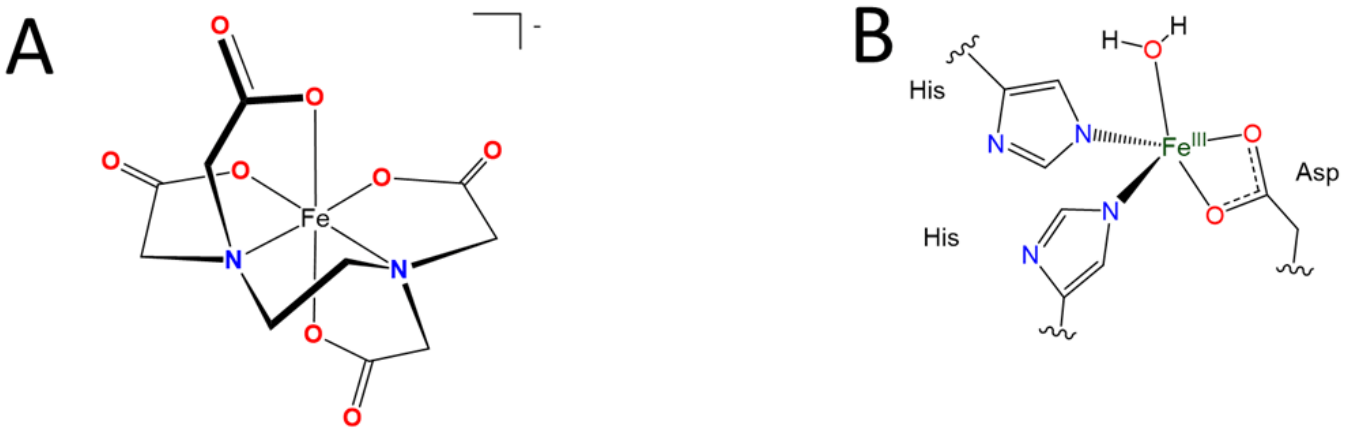
Scheme 9.3.I. A selection of chelating ligands classified according to denticity.



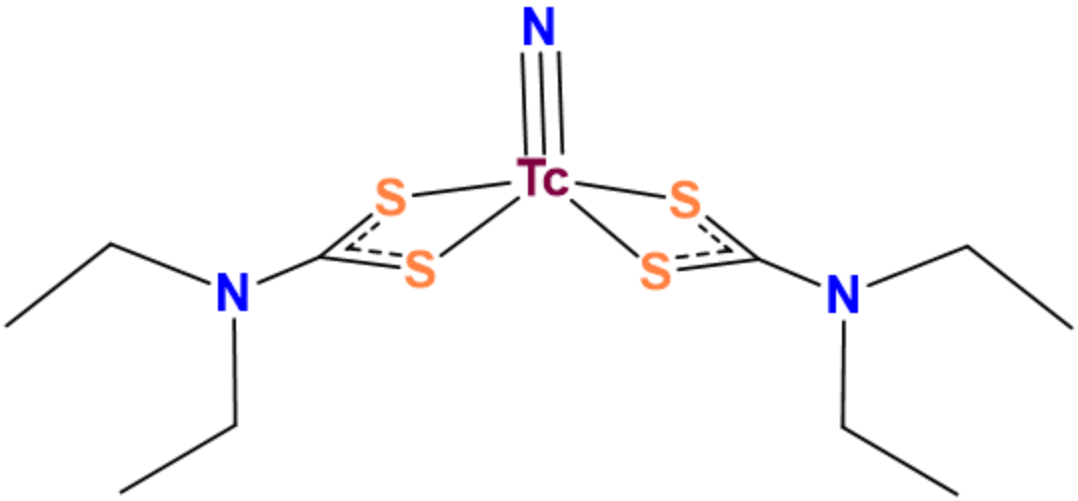
Scheme 9.3.IIA. Because only one oxygen per carboxylate *typically* binds, only one is counted when assigning a ligand's denticity. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Although only one carboxylate oxygen *usually* binds to a metal, it is still possible to bind for both oxygens to bind to a single metal. As shown in Scheme 9.3.IIB, complexes in which both carboxylates bind to a metal are known, and in fact are common in the active sites of some enzymes. It is just that the binding of both oxygens gives a strained four-membered ring that is usually unstable.

Scheme 9.3.**II.** (A) Only one oxygen per carboxylate counts towards the denticity of EDTA since on binding the other oxygen generally points away from the metal center, as in the structure of $Fe(EDTA)^-$. (B) In some enzyme active sites both oxygens of a carboxylic acid (aspartate or Asp in this example) bind to a metal. The aspartate carboxylic acid group is bidentate while the EDTA carboxlic acid groups in A are monodentate. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.



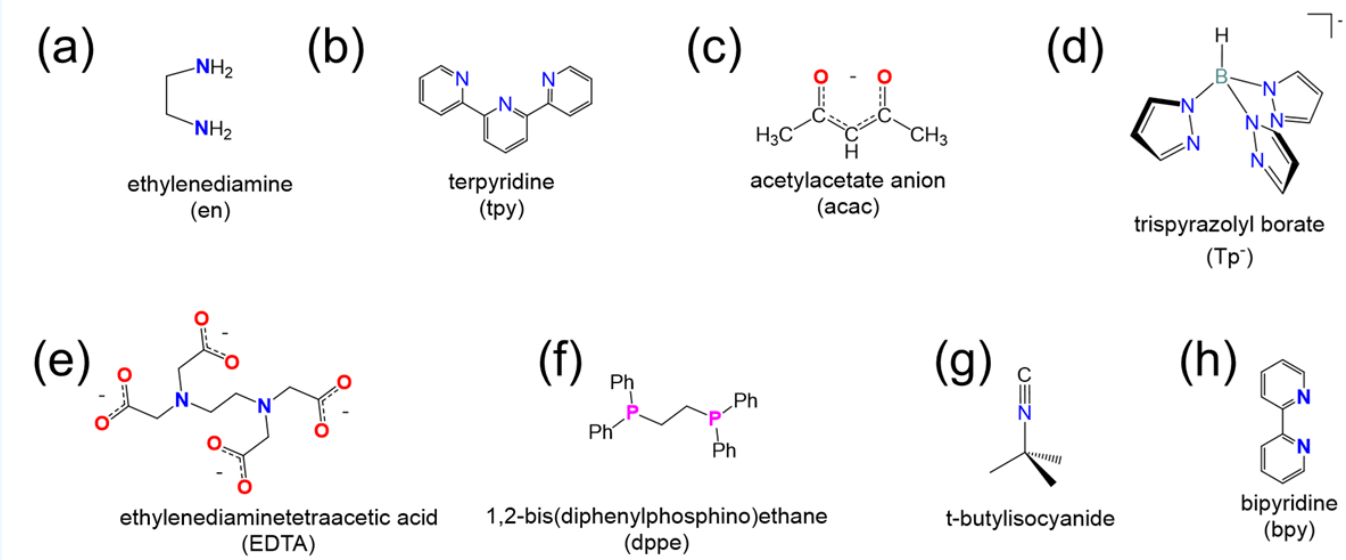
Scheme 9.3.**III.** As in this complex, dithiocarbamates commonly bind metals through both sulfur atoms. Consequently, dithiocarbamates are classified as bidentate. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.



Because of these factors it is technically more correct to say that carboxylates *usually act as* monodentate ligands and dithiocarbamates bidentate ones than it is to say that carboxylates *are* monodentate ligands and dithiocarbamates bidentate ones. So in other words the ligand classifications presented here just represent common binding modes.

Exercise 9.3.1

Determine the denticity of each ligand in the list below and classify them as monodentate, tridentate, etc.



Answer available at the end of this section.

This experimentally-based classification of dithiocarbamates as bidentate and carboxylates as monodentate can be confusing to a beginner. Fortunately, such experimentally based classifications are embedded in the lists of common monodentate ligands as given in Table 9.3.1 and common chelating ligands in Table 9.3.2.

A perusal of the ligands in Table 9.3.1 reveals that several can bind to a metal in multiple ways. For example, thiocyanate, SCN^- can bind metals through its S or N atoms. Such ligands are called **ambidentate ligands**. In naming an ambidentate ligand, the atom through which it attaches to the metal is commonly specified after the ligand name using the italicized element symbol or, more formally, a κ followed by the italicized element symbol. An example is given in Scheme 9.3.I.[2]

Scheme 9.3.**I.** Two possible binding modes of nitrite acting as a ligand.[3]

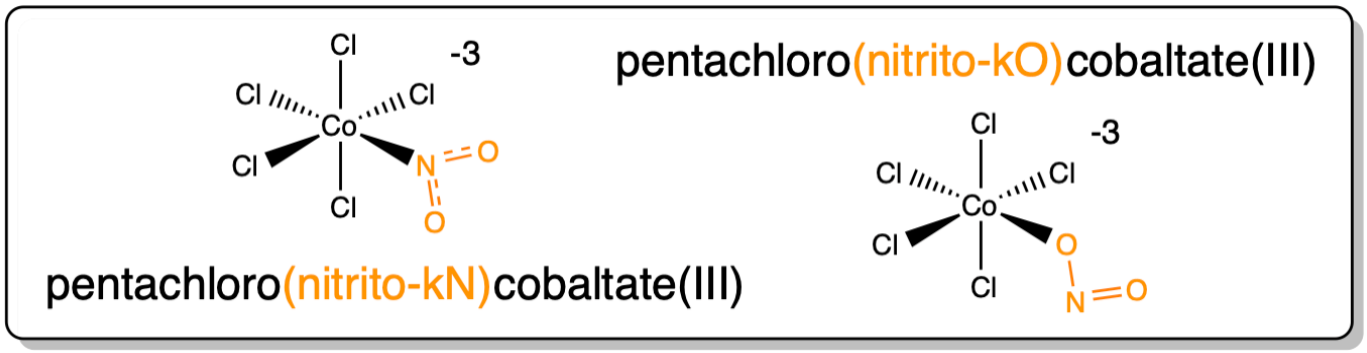
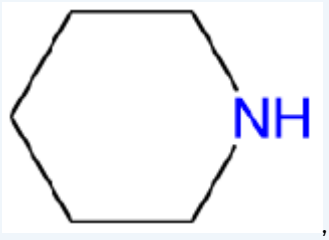
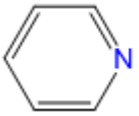
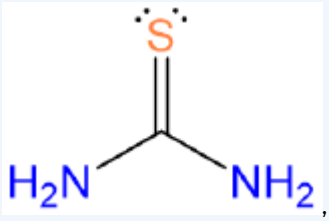


Table 9.3.1. *Common monodentate ligands. Most chemists still prefer common names over the IUPAC ones.*

Ligand	Common name	IUPAC name
H^- (H ligands are always considered anions for naming purposes)	hydrido	hydrido
F^-	fluoro	fluorido
Cl^-	chloro	chlorido
Br^-	bromo	bromido
I^-	iodo	iodido
CN^-, as M-CN	cyano	cyanido or cyanido-κC or cyanido-*C*
CN^-, as M-NC	isocyano	isocyanido or cyanido-κN or cyanido-*N*
CH_3NC	methylisocyanide	methylisocyanide
N_3^-	azido	azido
SCN^-, *e.g.* thiocyanate as M-SCN	thiocyanato	thiocyanato-κS or thiocyanato-*S*
NCS^-, *e.g.* thiocyanate as M-NCS	isothiocyanato	thiocyanato-κN or thiocyanato-*N*
$CH_3CO_2^-$	acetato	ethanoato
N^{3-}	nitrido	nitrido
NH^{2-}	imido	azanediido
NH_2^-	amido	azanido
NH_3	ammine	ammine
RNH_2, R_2NH, R_3N	alkylamine, dialkylamine, trialkalyamine (*e.g.* methylamine for CH_3NH_2)	alkylamine, dialkylamine, trialkalyamine (*e.g.* methylamine for CH_3NH_2)

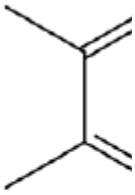
Ligand	Common name	IUPAC name
 piperidine, abbreviated pip	piperidine	piperidine
 , pyridine, abbreviated py	pyridine	pyridine
CH_3CN, acetonitrile, abbreviated MeCN	acetonitrile	acetonitrile
P^{3-}	phosphido	phosphido
PH_3	phosphine	phosphane
PR_3	trialkylphosphine (*e.g.* trimethylphosphine for Me_3P)	trialkylphosphane (*e.g.* trimethylphosphane for Me_3P)
PAr_3	triarylphosphine (*e.g.* triphenylphosphine for Ph_3P)	triarylphosphine (*e.g.* triphenylphosphane for Ph_3P)
 , dimethylsulfoxide or DMSO or dmso	dimethylsulfoxide (sometimes called dimethylsulfoxo but this usage is rare and violates the nomenclature rules for neutral ligands)	(methanesulfinyl)methane or dimethyl(oxido)sulfur
 , thiourea or tu	thiourea	thiourea
O^{2-}	oxo	oxido
OH^-	hydroxo	hydroxido
H_2O	aqua	aqua
S^{2-}	sulfo	sulfo

Ligand	Common name	IUPAC name
HS^-	hydrosulfido	hydrosulfido
RS^-	alkanethiolate (*e.g.* ethanthiolate for EtS^-)	thioalkanoate
H_2S	hydrogen sulfide	hydrogen sulfide
R_2S	alkylsulfanylalkane (*e.g.* ethylsulfanylethane for Et_2S)	dialkyl sulfide
O_2	dioxygen	dioxygen
O_2^-, superoxide	superoxido	dioxido(1-) or superoxido
O_2^{2-}, peroxide	peroxido	dioxido(2-) or peroxido
N_2	dinitrogen	dinitrogen
NO (are always considered neutral for naming purposes)	nitrosyl	nitrosyl
CO	carbonyl	carbonyl
CS	thiocarbonyl	thiocarbonyl
SO, as M-SO	sulfino	sulfur monoxide-κS or sulfur monoxide-S
NO_2, as M-NO_2	nitryl	nitrogen dioxide-κN or nitrogen dioxide-*N*
CO_3^{2-}	carbonato	carbonato
NO_2^-, as M-NO_2	nitro or nitrito-*N*	nitrito-κ*N* or nitrito-*N*
NO_2^-, as M-ONO	nitrito or nitrito-*O*	nitrito-κ*O* or nitrito-*O*
NO_3^-	nitrato	nitrato
SO_3^{2-}	sulfito	sulfito
SO_4^{2-}	sulfato	sulfato
$S_2O_3^{2-}$, as M-S-SO_2-O^-	thiosulfato-*S*	thiosulfato-κS or thiosulfato-*S*
$S_2O_3^{2-}$, as M-O-SO_2-S^-	thiosulfato-*O*	thiosulfato-κ*O* or thiosulfato-*O*

Table 9.3.2. *Common chelating ligands organized by denticity. Most chemists use the common names and abbreviations to describe*

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or a metal)
bidentate ligands			
acetylacetonato	2,4-pentanediono	acac	

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or a metal)
R-BINAP and *S*-BINAP	*R*- or *S*-2,2'-bis(diphenylphosphino)-1,1'-binapthyl	BINAP	
2,2'-bipyridine	2,2'-bipyridine	bpy or bipy	
cyclooctadiene	1,5-cyclooctadiene	COD	(binding to t
dialkyldithiocarbamato	dialkylcarbamodithiolato	$R_2NCS_2^-$ or dtc	

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or a metal)
dimethylgloximato	butanedienedioxime	Hdmg or DMG	
diphenylphosphinoethane or 1,2-(diphenylphosphino)ethane	Ethane-1,2-diylbis(diphenylphosphane)	dppe	
ethylenediamine	Ethane-1,2-diamine	en	
ethylenedithiolato	Ethane-1,2-dithiolato	$C_2H_2S_2^{2-}$	
nacnac	*N*,*N*'-diphenyl-2,4-pentanediiminato	nacnac	

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or a metal)
oxalato	oxalato	ox	
1,10-phenanthroline or *o*-phenanthroline	1,10-phenanthroline	phen or *o*-phen	
phenylpyridinato	2-phenylpyridinato-C^2,*N* or 2-phenylpyridinato-κC^2,*N*	ppy	
tridentate ligands			
triazacyclononane	1,4,7-triazacyclononane	tacn	

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or a metal)
diethylenetriamine	1,4,7-triazaheptane	dien	
pyrazoylborato (scorpionate)	hydrotris(pyrazo-1-yl)borato	Tp	
terpyridine or 2,2';6',2"-terpyridine	$1^2,2^2:2^6,3^2$-terpyridine or 2,6-bis(2-pyridyl)pyridine, tripyridyl, 2,2′:6′,2″-terpyridine	tpy or terpy	
tetradentate ligands			
β, β', β"-triaminotriethylamine	β, β', β"-tris(2-aminoethyl)amine	tren	

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or a metal)
triethylenetetramine	1,4,7,10-tetraazadecane	trien	
corroles	variable and generally not used	cor or Cor	
12-crown-4	1,4,7,10-tetraoxacyclododecane	12-crown-4	
tetramethylcyclam	1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane	TMC or cyclam	

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or a metal)
cyclam	1,4,8,11-tetraazacyclotetradecane	cyclam	
cyclen	1,4,7,10-tetraazacyclododecane	cyclen	
tris(2-pyridylmethyl)amine	1-pyridin-2-yl-*N*,*N*-bis(pyridin-2-ylmethyl)methanamine	tpa or TPA	
phthalocyanines	variable and generally not used	variable, usually a modified Pc	

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or a metal)
porphyrins	variable and generally not used	variable, usually a modified por, Por, or P (e.g. TPP = tetraphenylporphyrin)	
salen	2,2'-ethylenebis(nitrilomethylidene)diphenoxido	salen	
pentadentate ligands			
15-crown-5	1,4,7,10,13-Pentaoxacyclopentadecane	15-crown-5	
tetraethylenepentamine	1,4,7,10,13-pentaazatridecane	tepa or TEPA	
hexadentate ligands			

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or a metal)
18-crown-6	1,4,7,10,13,16-hexaoxacyclooctadecane	18-crown-6	
2,1,1-cryptand	4,7,13,18-Tetraoxa-1,10-diazabicyclo[8.5.5]icosane	2,1,1-crypt or [2.1.1]-cryptand kryptofix 211 and variations thereof	
ethylenediaminetetraaceto	2,2′,2″,2‴-(Ethane-1,2-diyldinitrilo)tetraaceto	EDTA, edta, Y^{4-}	
heptadentate ligands			
2,2,1-cryptand	4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]icosane	2,2,1-crypt or [2.2.1]-cryptand kryptofix 221 and variations thereof	
octadentate ligands			

Common Ligand name	IUPAC ligand name	abbreviation (if applicable)	structure or a metal)
2,2,2-cryptand	4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosan	2,2,2-crypt or [2.2.2]-cryptand kryptofix 222 and variations thereof	
pentetato acid or diethylenetriaminepentaacetato or DTPA	2-[bis[2-[bis(carboxylatomethyl)amino]ethyl]amino]acetato	DTPA	
DOTA or tetraxetan	1,4,7,10-Tetraazacyclododecane-1,4,7,10-tetraacetic acid	Dota, DOTA	

Rules for Naming Coordination Compounds

As explained above, the name of a coordination compound communicates

- as appropriate, information about isomerism
- systematically listing the ligands in a way that as necessary conveys information about their oxidation state and how they are linked to the metal
- the identity of the metal and its oxidation state
- any counterions present

Before going into these rules it is worth pointing out a few things.

1. It is easiest to learn these rules by starting with one or two of the rules, learning how to apply them, and then adding additional rules one at a time. To that end, instructors who wish to use a more programmed approach may find it convenient to first direct their students to this page which focuses on getting the names of the ligands and metal right, without worrying about isomerism or stereochemistry.

2. The rules also assume some familiarity with common coordination geometries and patterns of isomerism in metal complexes. Thus it might be easiest to learn about common coordination geometries first, followed by common patterns of isomerism in metal complexes before beginning this section. If you decide to dive right in to this section you might find it helpful to know that when applying nomenclature and formula rules most textbooks *assume*

- complexes in which the metal has a coordination number of six are octahedral
- complexes in which the metal has a coordination number of five are trigonal bipyramidal
- complexes in which Pt^{II} , Pd^{II} , or Rh^{I}, or Ir^{I} have a coordination number of four are square planar
- other complexes in which the metal has a coordination number of four are tetrahedral

Like all assumptions these don't always work in real life but they should be good enough to get you through your first inorganic chemistry course.

For the pedants among you, note that the complexes given as examples and in exercises on this page have been selected for pedagogical utility. Although many are well-known compounds, others are hypothetical.

Now on to the rules.

Rule 1: If ions are present, name the cation first, followed by the anion.

Examples:

$K_2[Pt^{II}Cl_4]$ potassium tetrachloroplatinate(2-)

$[Co^{III}(NH_3)_6](NO_3)_3$ hexaamminecobalt(3+) nitrate

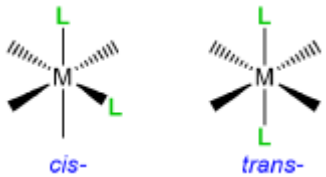
$[Co^{III}(NH_3)_6][Cr^{III}(C_2O_4)_3]$ hexaamminecobalt(3+) tris(oxalato)chromium(3-)

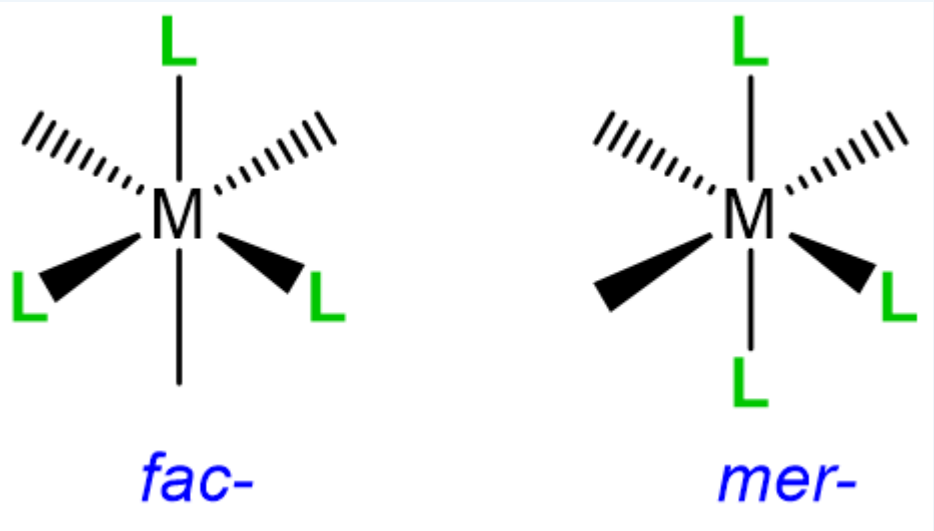
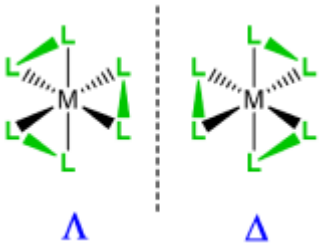
Rule 2: When multiple isomers are possible, designate the particular isomer in italics at the front of the name of each complex

If you have not yet learned about isomerism in coordination compounds skip this rule for now and return to it after you have.

When a complex might exist as one of two stereoisomers, prefixes are commonly used to designate which isomer is present. The most common cases are listed in Table 9.3.3.

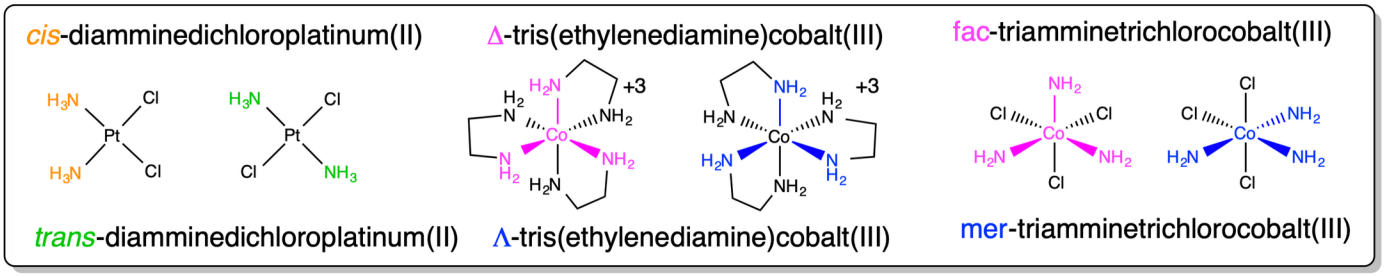
Table 9.3.3. *Prefixes used to specify isomerism about a metal center when naming and writing coordination compounds' formulae.*

Type of isomerism	Graphical reminder	Prefixes
Geometric, *cis-* , *trans-*		*cis-* or *trans-*

Type of isomerism	Graphical reminder	Prefixes
Geometric, *fac- /mer-*		*fac-* or *mer-*
Enantiomers, Λ-, Δ-		Λ- or Δ-

Examples of how isomerism about a metal center is designated are given in Scheme 9.3.II.

Scheme 9.3.II. Application of nomenclature rules for stereosimerism about a metal.[3]



There are a number of other cases where it might be advisable to specify the stereochemistry of a complex. These cases involve specifying

- the coordination geometry about a metal center (octahedral, trigonal prismatic, tetrahedral, square planar, etc.)
- the geometry cannot be unambigouously described by a single *cis/trans* or *fac/mer* relaionship of ligands

These cases may also be handled by using a designator to specify the coordination geometry and, as necessary, giving the position of ligated atoms in terms of designated numbered positions for that geometry. See the IUPAC red book for details as such cases fall outside the scope of what is normally advisable for an undergraduate course.

Rule 3: Specify the identity, number, and as appropriate, isomerism of the ligands present in alphabetical order by ligand name.

Before specifying the metal, the ligands are written as prefixes of the metal.

In specifying the ligands several rules are followed.

1. The ligands are written in alphabetical order by the ligand name only; symbols are not considered and prefixes do not count in determining alphabetical order.

   Example: In the name of the complex ion $[Co(NH_3)_5Cl]^{2+}$, pentamminechlorocobalt(II), the ammine ligand is named before the chloro ligand because the order is alphabetical by the ligand name by virtue of which ammine comes before chloro.

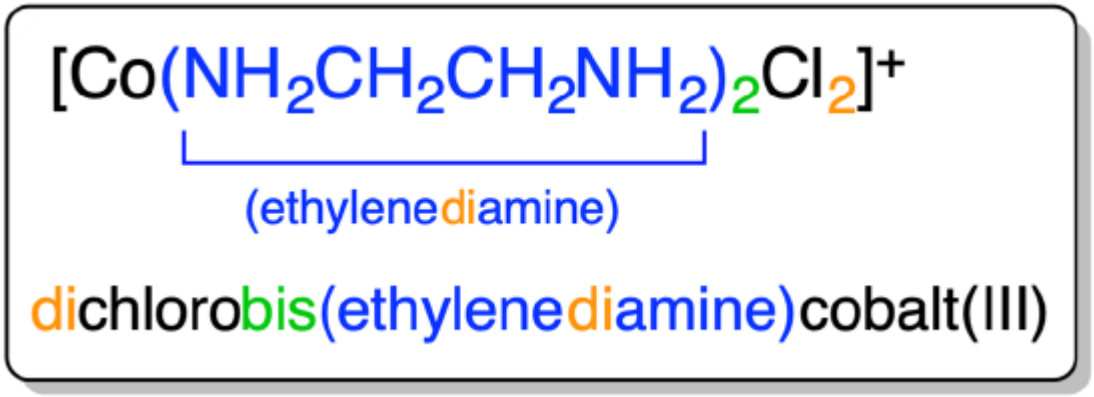
2. Prefixes are used to indicate the number of each ligand present. Specifically, *di-*, *tri-*, *tetra-* , *penta-*, *hexa-*, *etc.* prefixes are used to indicate multiple ligands of the same type EXCEPT when the ligand is polydentate or its name already has a *di-*, *tri-*, *tetra-* etc. In that case *bis-*,*tris-*, *tetrakis-*, etc. are used instead. These prefix rules are summarized in Table 9.3.3.

Table 9.3.3. *Prefixes used to specify the number of a given ligand present.*

Number of identical ligands	prefix used when the ligand name is simple	prefix used when the ligand is polydentate or its name already has a *di-*, *tri-*, *tetra-* etc.
2	di-	bis-
3	tri-	tris-
4	tetra-	tetrakis-
5	penta-	pentakis-
6	hexa-	hexakis-
7	hepta-	heptakis-
8	octa-	octakis-
9	nona-	nonakis-
10	deca-	decakis-

An example of the application of the prefix rule is given in Scheme 9.3.III.

Scheme 9.3.III. Example of the use of prefixes to specify the number of ligands of each type in a complex.[3]



3. Ligand names are based on their charge.

   - Neutral and cationic ligand names are the same as the names of their neutral compounds with two caveats:

     i. names that involve spaces should either be put in parentheses or the spaces should be eliminated (preferred)

        Example: cis-dichlorobis(**dimethyl sulfoxide**)platinum(II) or *cis*-dichlorobis(**dimethylsulfoxide**)platinum(II)

     ii. A few ligands are given common names.

- H_2O = aqua
- NH_3 = ammine (notice that there are two n's)
- CO = carbonyl
- CS = thiocarbonyl
- NO = nitrosyl

- For anionic ligands, the vowel at the end of their anion names is changed to an -"o"

  Examples: Cl^- = chloro, NH_2^- = amido, N_3^- = azido

  Caveat: some anionic ligands have common names that may also be used

  Examples:

  I^- = iodo or iodino

  CN^- = cyano or cyanido

  O^{2-} = oxo or oxido

The IUPAC and common names of many ligands are given in Tables 9.3.1. and 9.3.2.

4. When an ambidentate ligand is present, the atom through which it is bound to the metal is indicated by giving either its element symbol or a κ and its element symbol in italics after the ligand name.

   Example:

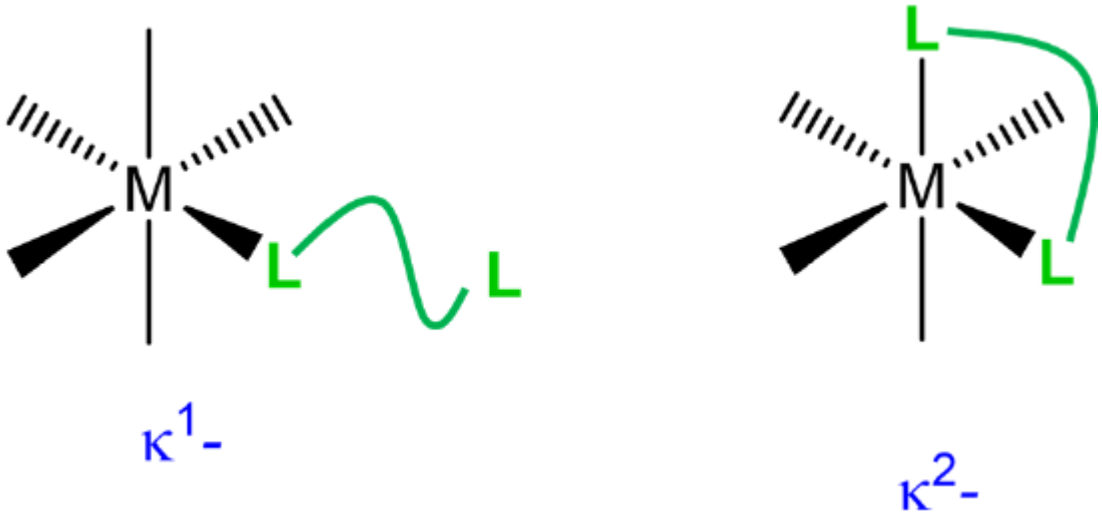
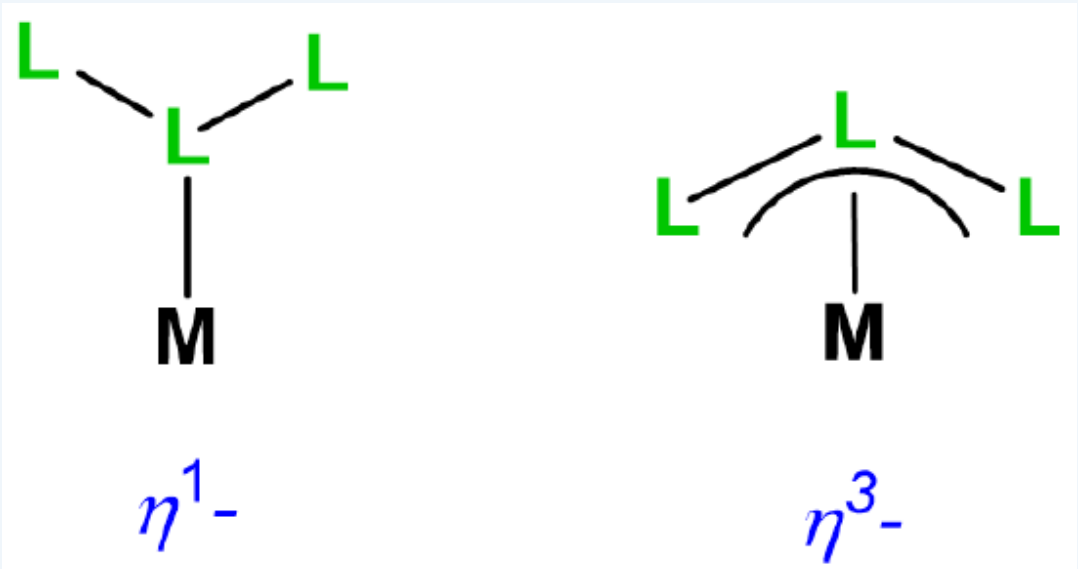
   M-SCN is thiocyanato-S or thiocyanato-κS

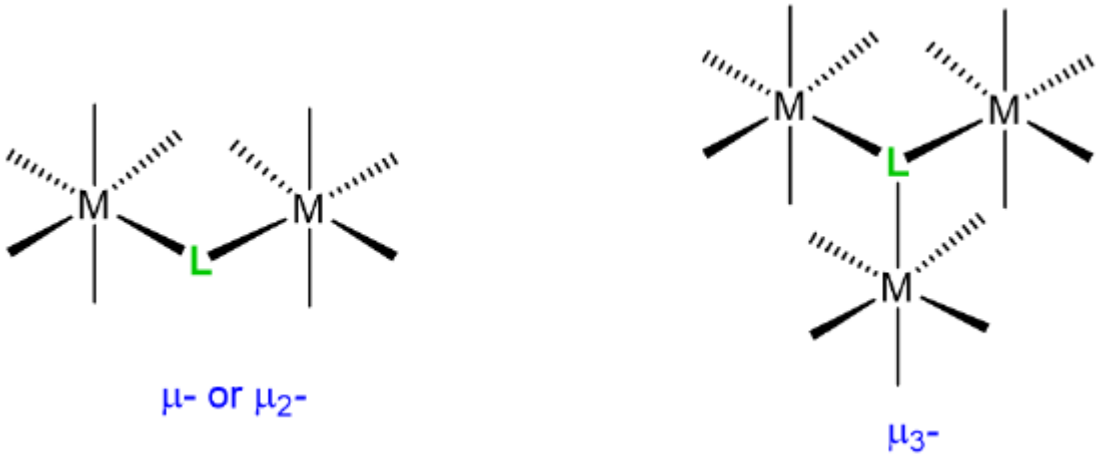
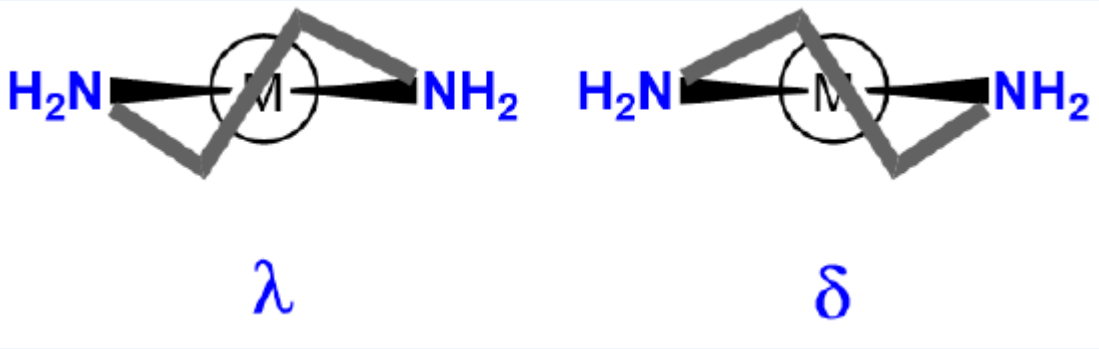
   M-NCS = thiocyanato-*N or* thiocyanato-κ*N*

   The use of κ and an element symbol to indicate how a ligand and metal are linked is called a **k-term**. More complex k-terms might also involve specifying the atoms by number, though their use is outside the scope of this text.

5. As appropriate, additional information about the way a ligand is bound to the metal center and/or its stereochemistry is specified using a prefix. The prefixes to provide linkage and stereochemistry for ligands are given in Table 9.3.4.

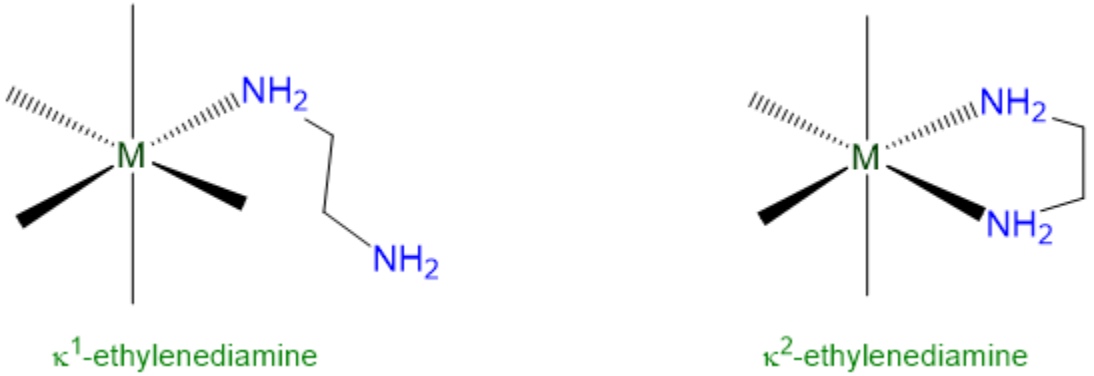
Table 9.3.4. *Prefixes used to specify ligands' isomerism when naming and writing coordination compounds' formulae. Some of these types of isomerism will be discussed in later pages.*

Type of isomerism	Graphical reminder	Prefixes
when a multidentate ligand binds through less than the full number of atoms		κ^n where the numb of attache atoms; us when the attached atoms are not direct connecte a chemica bond. The metal-liga bonding usually involves σ -type coordinat
hapticity		η^n where the numb of attache atoms; us when the coordinat atoms are connecte by bonds. Usually th metal-liga bonding involves π -type coordinat In speech =monoha η^2=dihapt η^3=trihap etc.

Type of isomerism	Graphical reminder	Prefixes
bridging ligands		μ_n where the numb of atoms bridged. T number n usually omitted when n =2
chelating ligand ring twist		λ- or δ-

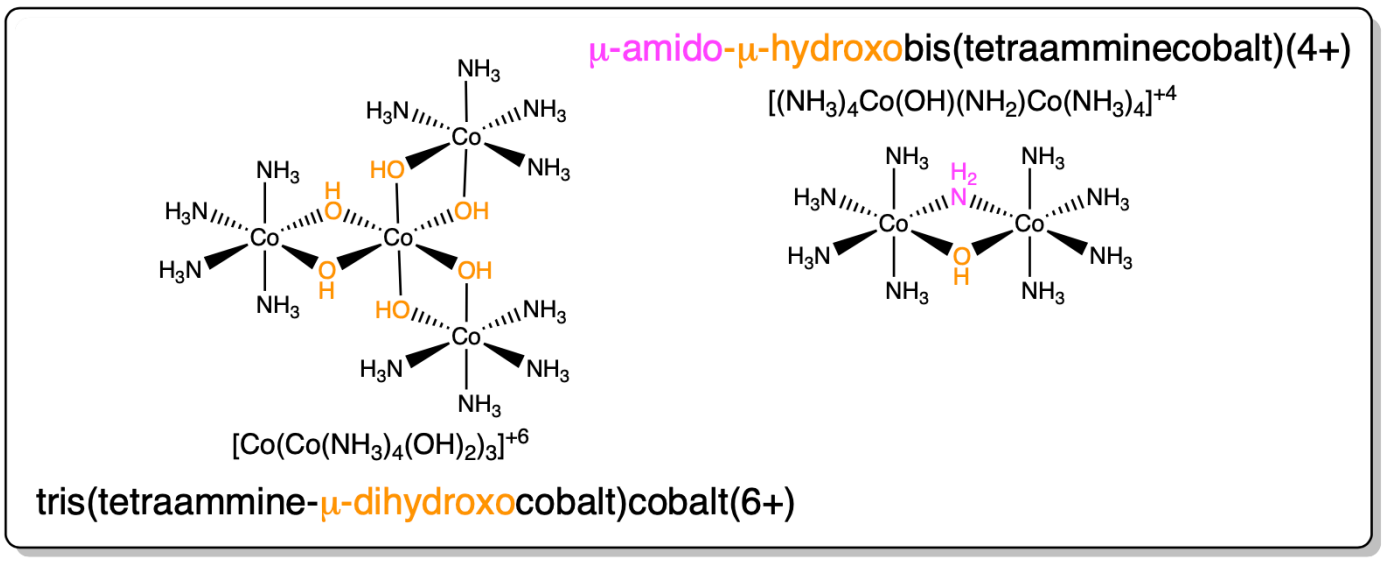
A example showing how the nomenclature rule is applied to a ligand that can have two coordination modes is given in Scheme 9.3.IV.

Scheme 9.3.IV**.** Use of the κ notation to specify the number of attached groups in a multidentate ligand.



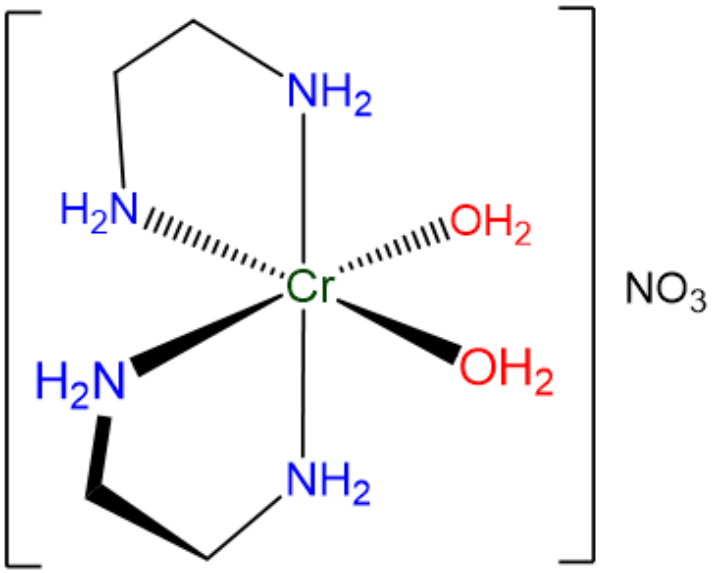
Scheme 9.3.V. The names of the complexes follow the rules described in 9.2.6: multinuclear coordination complexes.

Scheme 9.3.V**.** Use of the μ notation to specify bridging ligands in metal complexes.[3]



6. If desired, parentheses *may* be used to delineate a ligand name to make it easier to identify in the name of the complex. This can be particularly helpful when the entire name contains a lot of information to keep track of. An example is given in Scheme 9.3.VI.

   Scheme 9.3.VI**.** When naming the complex shown, *cis*-diaquabis(ethylenediamine)chromium(III) nitrate is easier to read than *cis*-diaquabisethylenediaminechromium(III) nitrate.



Rule 4: Specify the identity of the metal

- In neutral and cationic complexes the metal's name is used directly

  - *e.g.* as in hexammineruthenium(III) for $[Ru(NH_3)_6]^{3+}$

- In anionic complexes, *-ate* replaces *-ium*, *-en*, or *–ese* or adds to the metal name,

  e.g., as in hexachloromanganate(IV) for $MnCl_6^{2-}$

- In anionic complexes of some metals a Latin-derived name is used instead of the element's English name. These names are

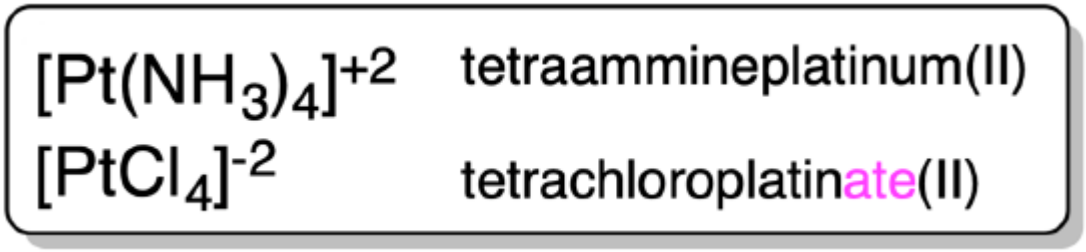
given in Table 9.3.5.

Table 9.3.5. Latin terms for select metal Ions. Redrawn from this page describing the nomenclature of coordination complexes.

Transition Metal	Latin
Copper	Cuprate
Gold	Aurate
Iron	Ferrate
Lead	Plumbate
Silver	Argentate
Tin	Stannate

An example of the application of the metal naming rules is given in Scheme \sf{{9{.}3{.}\eatSpaces{VII} \endSpaces}}\).

Scheme 9.3.VII. Example of the application of the metal specification rules to a cationic and an anionic platinum complex.[3]



Rule 5: Specify the oxidation state of the metal.

Two different systems are used to specify the oxidation state of the metal.

1. In the **Stock system** the metal's oxidation state is indicated in Roman numerals after the metal name.

   Examples:

   $[CoCl(NH_3)_5]Cl_2$ = pentamminechlorocobalt(III) chloride

   $[PtBr_2(bpy)]$ = dibromobipyridineplatinium(II)

   $K[Ag(SCN)_2]$ = potassium di-S-thiocyanatoargentate(I)

2. In the **Ewing-Bassett system** the charge on the complex is specified in Arabic numerals after the complex name. This provides a way of specifying a complex even when the oxidation state of the metal isn't known and, in cases where it is known, the value of the metal's oxidation state may be inferred from the complex ion's charge.

   $[CoCl(NH_3)_5]Cl_2$ = pentamminechlorocobalt(2+) chloride

   $[PtBr_2(bpy)]$ = dibromobipyridineplatinium(0)

   $K[Ag(SCN)_2]$ = potassium di-S-thiocyanatoargentate(1-)

Summary of rules for naming coordination complexes.

A graphical summary of the **rules for naming complexes** along with a few examples that you can use to review the nomenclature rules is given in Figure 9.3.1. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

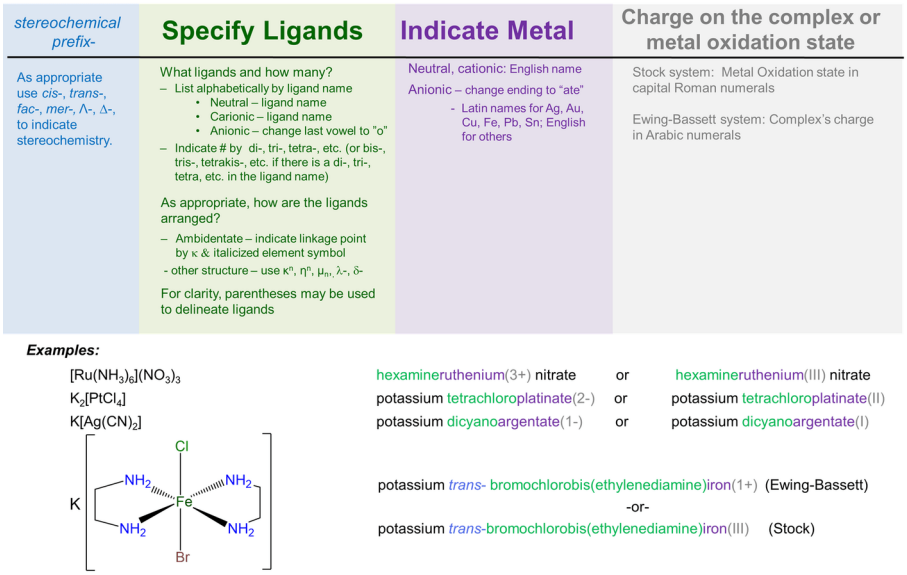


Figure 9.3.1. Summary of nomenclature rules for coordination complexes along with a few examples of their application.

When learning chemical nomenclature, practice makes perfect. The following examples and exercises are provided to give you this practice. Additional examples and exercises on the https://chem.libretexts.org/ site include a set of simple examples with explained solutions, a set of simple exercises with solutions, and a set of more challenging exercises without solutions.

Exercise 9.3.2. Assigning metal oxidation states in a complex

In order to name a complex in the Stock system it is necessary to assign a formal oxidation state to the metal. For this reason it is important to be able to assign the oxidation state of a metal in a complex. Fortunately, this is easy to do if you remember

1. The sum of all atoms' oxidation states will equal the overall charge on the complex
2. When determining the metal's oxidation state the ligands can be treated as having an oxidation state equal to their charge - *i.e.,* the charge they possess in the form in which they coordinate the metal, so if they need to lose a proton to bind, don't forget to account for that.

Given the above, assign the oxidation state of the metal in the following real and hypothetical complexes.

a. $K_3[Fe(CN)_6]$
b. $[CoCl(NH_3)_5](NO_3)_2$
c. $K_2[PtCl_4]$
d. [MnCl(por)]
e. $[Ru(bpy)_3]Cl_2$
f. $[PdCl_2(dppe)]$
g. $[Mn(en)_2(SCN)_2]$

Answer for K3[Fe(CN)6]3-. available at the end of this section.

Exercise 9.3.3: Simple Nomenclature Problems.

Name the following compounds in both the Stock and Ewing-Bassett systems:

a. $[Ru(NH_3)_6](NO_3)_3$
b. $K_2[PtCl_4]$
c. $K[Ag(CN)_2]$

d. $Cs[CuBrCl_2F]$
e. $[Cu(acac)_2]$

Answer available at the end of this section.

Exercise 9.3.4: More simple nomenclature problems.

Name the following compounds and ions in both the Stock and Ewing-Bassett systems.

a. $Cu(OH)_4^-$
b. $[AuXe_4]^{2+}$
c. $AuCl_4^-$
d. $Fe(CN)_6^{3-}$
e. $K_4[Fe(CN)_6]$
f. *trans*-$[Cu(en)_2(NO_2)_2]$ (the N is bound to Cu)
g. cis-$IrCl_2(CO)(PPh_3)$ (ignore stereochemistry)
h. $IrCl(PPh_3)_3$

Answer available at the end of this section.

Exercise 9.3.5: Even more simple nomenclature problems.

Name the following compounds and ions in both the Stock and Ewing-Bassett systems. Ignore prefixes for designating isomers if you haven't learned about those.

a. $Fe(acac)_3$
b. $K_2[CuBr_4]$
c. ReH_9
d. $[Ag(NH_3)_2]BF_4$
e. $[Ag(NH_3)_2][Ag(CN)_2]$
f. $[Ni(CN)_4]^{2-}$
g. $[Co(N_3)(NH_3)_5]SO_4$
h. $[CoBrCl(H_2O)(NH_3)]I$ (ignore stereochemistry)

Sample Answers available at the end of this section.

Exercise 9.3.6: Nomenclature problems, some of which involve consideration of isomerism.

Name the following compounds and ions in both the Stock and Ewing-Bassett systems. Ignore prefixes for designating isomers if you haven't learned about those.

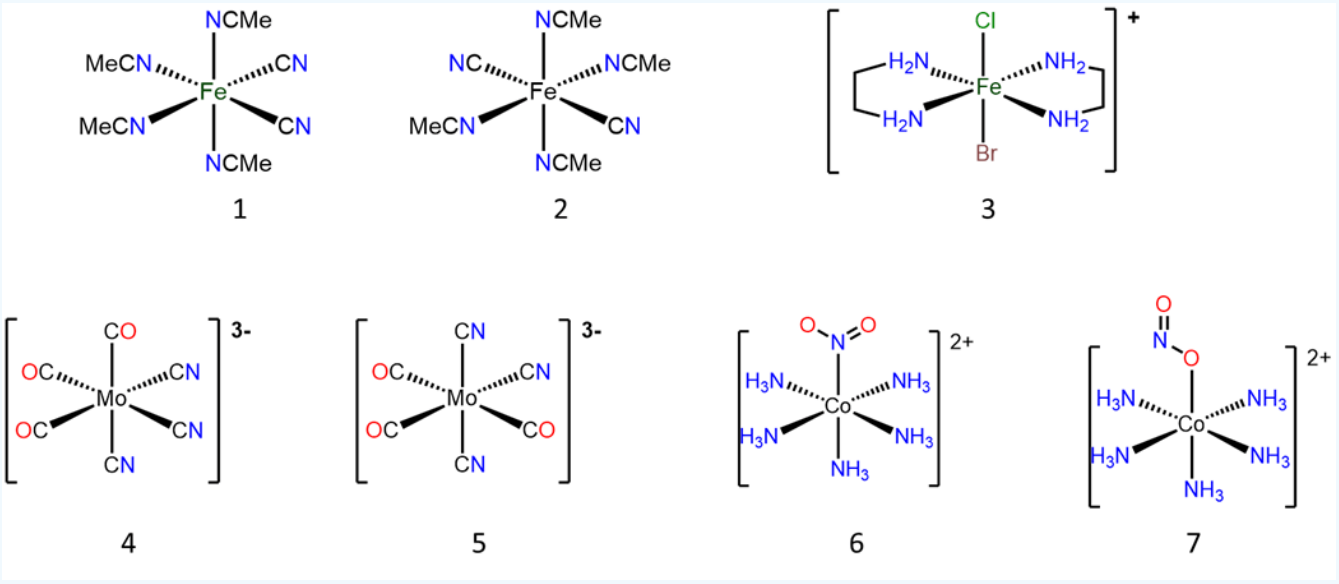
a. *trans*-$[Cu(dppe)_2(NO_2)_2]$ (the N is bound to Cu)
b. $[Pd(en)_2(SCN)_2]$, with the thiocyanates bound Pd-SCN
c. $[Mn(CO)_6]BPh_4$ (BPh_4 = tetraphenylborate)
d. $Rb[AgF_4]$
e. K_2ReH_9
f. K_3CrCl_6
g. $[Ru(H_2O)_6]Cl_2$
h. [*cis*-$Fe(CO)_4I_2$]
i. K_2[*trans*-$Fe(CN)_4(CO)_2$]

j. [*cis*-$MnCl(H_2O)_4(NH_3)](NO_3)$
k. $K_3[$*fac*-$RuCl_3(PMe_3)_3]$

Answer available at the end of this section.

Exercise 9.3.7

Name the compounds and ions below using both the Stock and Ewing-Bassett systems. Ignore prefixes for designating isomers if you haven't learned about those.



Answer available at the end of this section.

Exercise 9.3.8

Draw structural formulae for the following compounds and ions. You may assume that

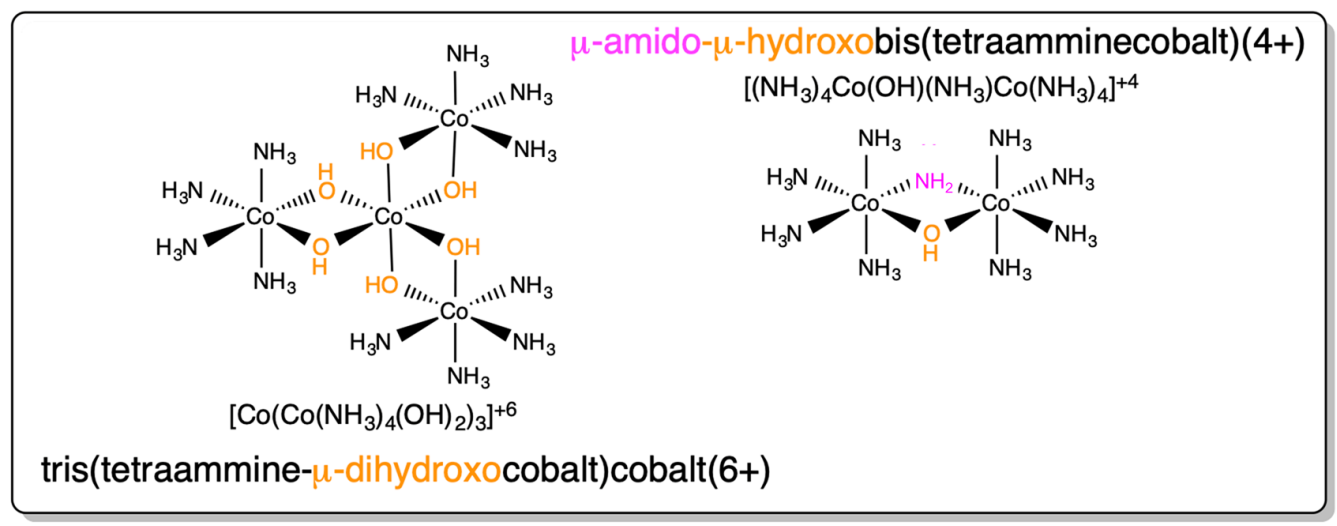
- complexes in which the metal has a coordination number of six are octahedral
- complexes in which the metal has a coordination number of five are trigonal bipyramidal
- complexes in which Pt^{II}, Pd^{II}, or Rh^{I}, or Ir^{I} have a coordination number of four are square planar
- other complexes in which the metal has a coordination number of four will be tetrahedral

a. (2,2'-bipyridine)tetracyanoruthenium(2-)
b. sodium tetrachloroaluminate (note that since Al is a main group metal with a generally fixed oxidation state no oxidation state is given)
c. pentaamminechlorocobalt(2+) sulfate
d. carbonylhydridotris(triphenylphosphine)rhodium(I) (the ligands in this complex occupy sterically preferred positions)
e. bromotrichlorocobaltate(III)
f. hexaaquacopper(2+) sulfate
g. sodium tris(oxalato)cobalt(III)
h. *fac*-(1,10-phenanthroline)tricarbonylchlororhenium(I)
i. *mer*-triaquatrichlorochromium(III)
j. *trans*-dichlorobis(ethylenediamine)platinum(IV)

Answers available at the end of this section.

Exercise 9.3.9.

The name of the structure named tris(tetraammine-μ-dihydroxocobalt)cobalt(6+) in Scheme 9.3.III (reproduced below) is incomplete. Give the complete name of the structure in both the Stock and Ewing-Basset systems.



Answer available at the end of this section.

Note: Rules for Writing the Formulae of Coordination Copounds

Rules for writing the formulae of coordination compounds

As organized predictable formulae can be easier to read and understand than haphazardly written ones, the rules for writing the formulae of coordination compounds have value. To support those who wish to employ them they are given in this section. The rules as given here are adapted from a summary by Robert Lancashire.

The rules for writing the formulae of coordination compounds follow the same convention used to specify their names.

1. If there are multiple ions present list the cations before anions.
2. Enclose all the constituents of each complex ion in square brackets.
3. For each complex ion,
   - Give the **central metal** atom first.
   - Then **ligands** next, listed in alphabetical order, ignoring prefixes according to the first letters in the ligand's symbol as written. This is true regardless of whether the symbol is an element symbol (like C, N, O, etc.) or a symbol for the ligand name (bpy, en, MeCN, etc.). Contrary to widely-circulated myths, the ligand's charge does not matter.[4]
   - The formulae or abbreviations (*e.g.* en) for all polyatomic ligands should be enclosed in ordinary parentheses.
   - As appropriate, use italicized atom symbols to indicate linkage isomerism and prefixes such as *cis*-, *trans*-, *fac*-, *mer*-, Λ-, Δ-, κ^n, η^n , μ_n, λ-, or δ- to indicate stereochemistry.
   - When a ligand is bound to a metal through a particular atom, preferably place that atom closest to the metal - *e.g.,* $[Fe(CN)_6]^{3-}$ not $[Fe(NC)_6]^{3-}$ (Note: this rule is used primarily for ambidentate ligands; although IUPAC recommends that aqua ligands be written as OH_2 when the O would be closest to its coordinated metal, they are still usually written as H_2O).

These rules are graphically summarized in Figure 9.3.2.

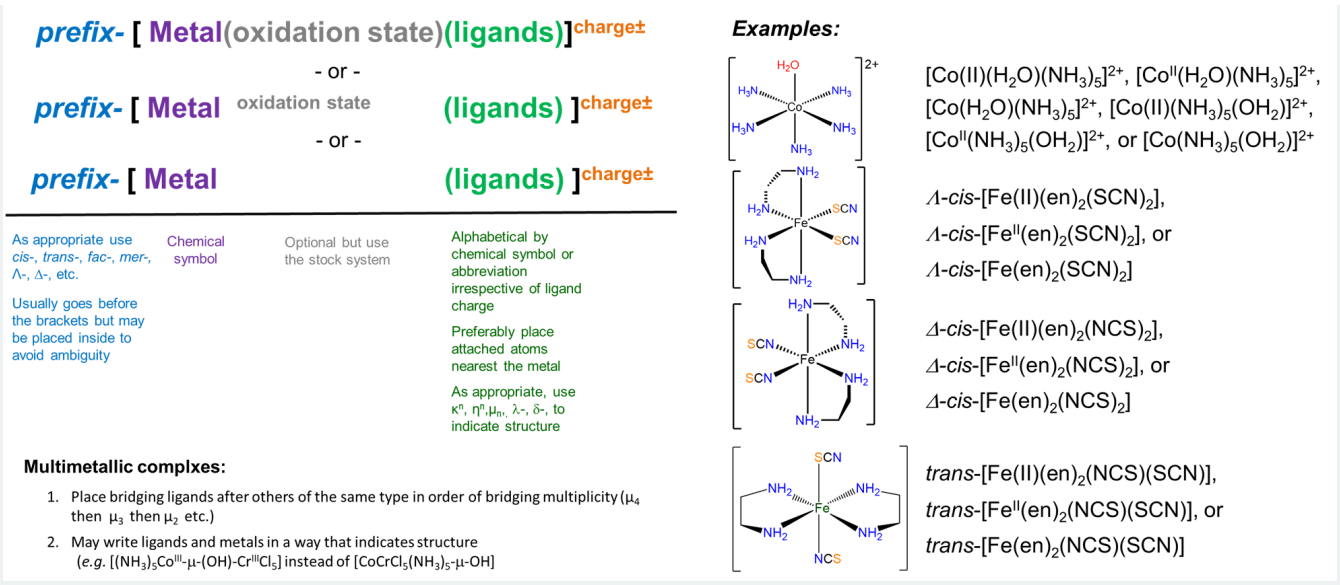
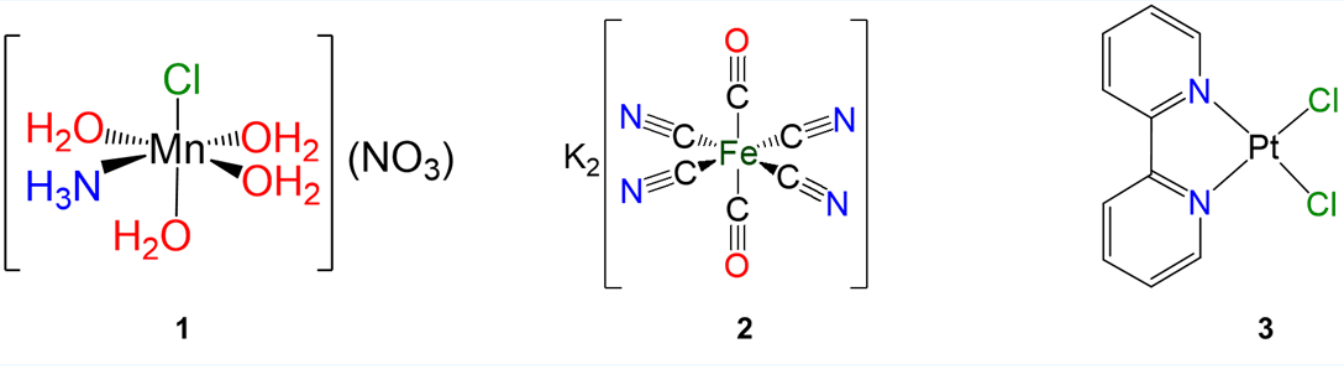


Figure 9.3.2. Summary of the rules for writing the formula of a coordination complexes along with a few examples of their application. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Exercise 9.3.10

Give the formulae of the following complexes.



1 2 3

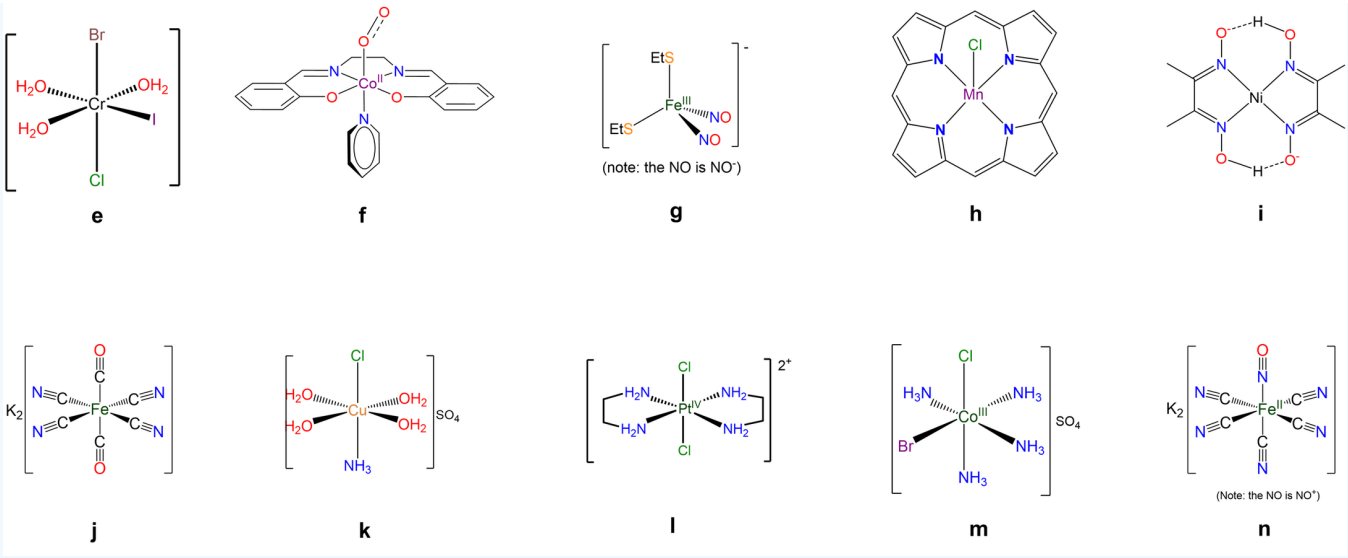
.

Answer available at the end of this section.

Exercise 9.3.11

Write formulae for each of the following compounds and ions. When multidentate ligands are present use suitable abbreviations.

a. pentaamminechlorocobalt(2+) sulfate
b. Δ-diamminebis(oxalato)manganate(III)
c. *trans*-tetraacetonitriledicyanoiron(II)
d. tricarbonyldichlorobis(triphenylphosphine)molybdenum



e f g h i

j k l m n

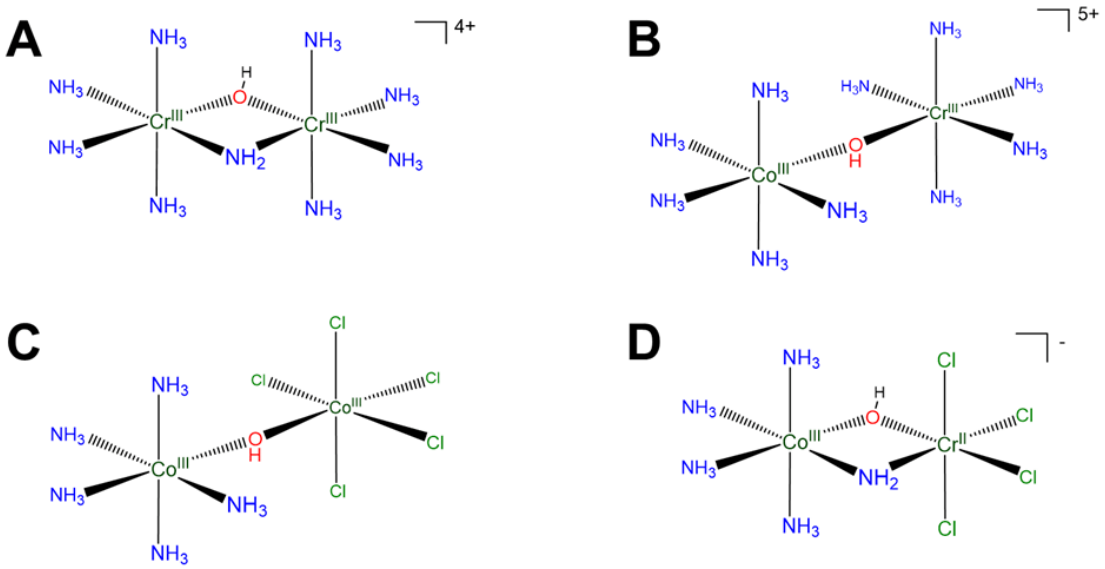
Answers available at the end of this section.

Multinuclear coordination complexes

Multinuclear coordination complexes contain multiple metals connected by one or more bridging ligands. The structures of bridging complexes can usually be inferred from their μ-tagged ligands in their names and formulae. For the benefit of instructors who wish to have their students name multinuclear complexes, the rules are presented below.

Multinuclear complexes are named differently depending on whether the groups on either side of the bridging ligands are identical or different, as shown in Scheme 9.3.VIII.

Scheme 9.3.VIII. Multinuclear coordination complexes may be named differently depending on whether the groups on either side of the bridging ligands are the same or different. The groups are the same if the metal, ligands, and ligand arrangement are identical. This is true in A but in B the metals differ, in C the ligands differ, and in D both the metal and ligands differ.



Naming multinuclear complexes

Let's look at the rules for naming symmetric and asymmetric multinuclear complexes.

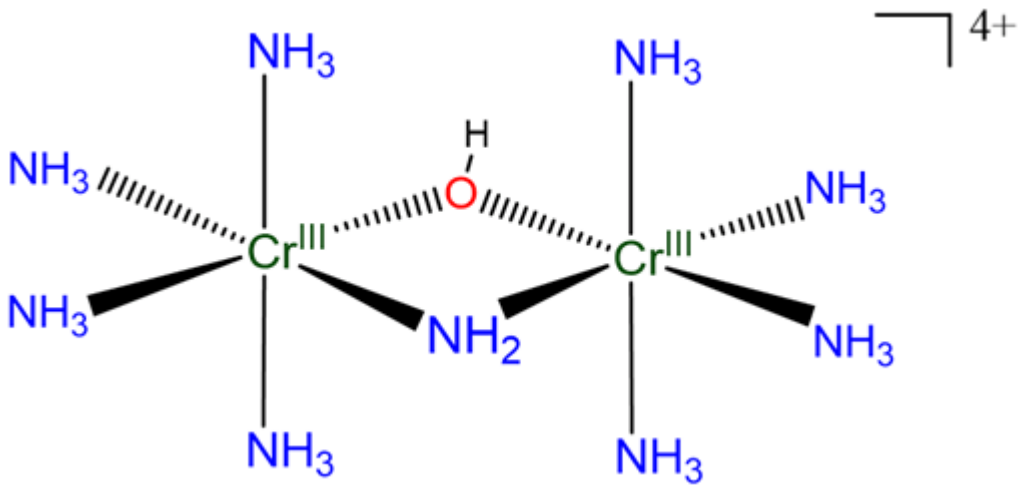
Application of the IUPAC system and variants thereof to symmetric complexes

The IUPAC naming system helpfully avoids the sort of ambiguities and *ad hoc* choices involved in most textbook-level nomenclature systems for multimetallic complexes. Unfortunately, it is correspondingly difficult for beginners to employ. Thus it will only be applied in depth to the case of symmetric complexes. Symmetric complexes are particularly easy to name in the IUPAC system and several of its variants that find common use. In these

1. The ligands are given in alphabetical order. When there are bridging and non-bridging ligands of the same type the bridging ligands are given first. When there are multiple bridging ligands of the same type but which use different bridging modes (*e.g.*, μ_4-, μ_3-, μ_2-), the bridging ligands are specified in decreasing order of bridging multiplicity, *e.g.*, μ_3 -sulfido-di-μ-sulfido.
2. The groups bridged are given afterwards using names that follow the ordinary rules. Generally this involves either
   a. naming all the ligands followed by all the metals, in both cases using prefixes to indicate the number of each, or
   b. naming each group of atoms individually as in the less formal naming system, using prefixes to indicate the number of ligands (this is an unofficial variant of the IUPAC system that some textbook authors seem to prefer).

These two rules are sufficient to describe simple symmetric bridging complexes.

Example: The compound in Scheme 9.3.VIIIA



may be named

[μ-amido-μ-hydroxo-octaamminedichromium(4+)] ion

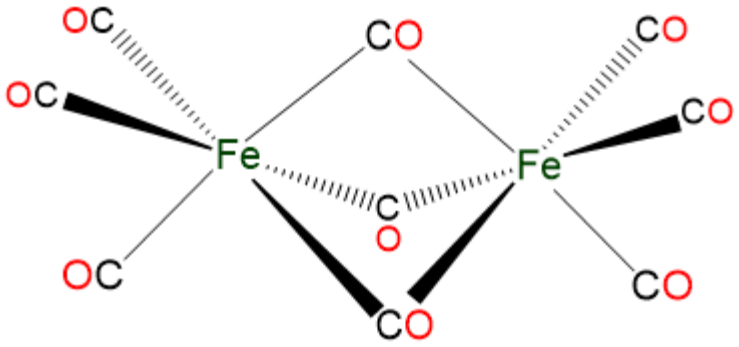
or

[μ-amido-μ-hydroxo-bis(tetraamminechromium(III))] ion

or

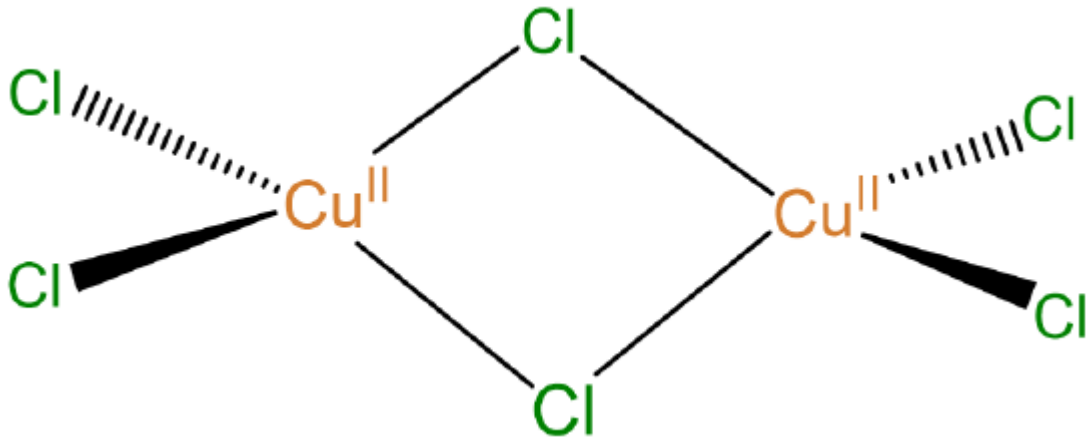
[μ-amido-μ-hydroxo-bis(tetraamminechromium)(4+)] ion

Example: The complex[5]



may be named [tri-μ-carbonyl-bis(tricarbonyliron)(0)], [tri-μ-carbonyl-bis(tricarbonyliron(0))], or [tri-μ-carbonyl-hexacarbonyldiiron)(0)]

Example: The complex



may be named di-μ-chlorido-tetrachloridodicopper(II), di-μ-chlorido-bis(dichlorocopper(II)), or di-μ-chlorido-bis(dichlorocopper)(0)

A note on the application of the IUPAC system and variants thereof to asymmetric complexes

For a symmetrical complex like the $[Cu_2Cl_4(\mu\text{-}Cl)_2]$ considered above it is enough to specify the existence of the two bridging and four terminal chloro ligands; there is no need to number the chloro ligands or to specify exactly which ones are involved in bridging or to clarify that the bridging involves κ^2 coordination of the chloro ligands. In cases where the two metal centers or the chloro ligands differ it is necessary to specify the exact ligands and metals involved and how they are connected.

For example, a more extensive IUPAC name for $[Cu_2Cl_4(\mu\text{-}Cl)_2]$ in which the chloro ligands are individually and more completely specified would read di-μ_2-chlorido-tetrachlorido-1κ^2Cl,2κ^2Cl-dicopper(II).

Even more extensive systems would involve numbering the metals and specifying how they are connected together too. The details of how this is done are typically beyond the level of most undergraduate and graduate courses in inorganic chemistry. Those who want to know the details should consult the red book. In many cases it is sufficient to reserve the use of formal IUPAC names for use in publications and to employ a convenient shorthand naming system for everyday use. An example of one type of system that is sometimes employed is given next.

Unofficial but commonly used methods applicable to complexes in which the groups bridged are identical or different.

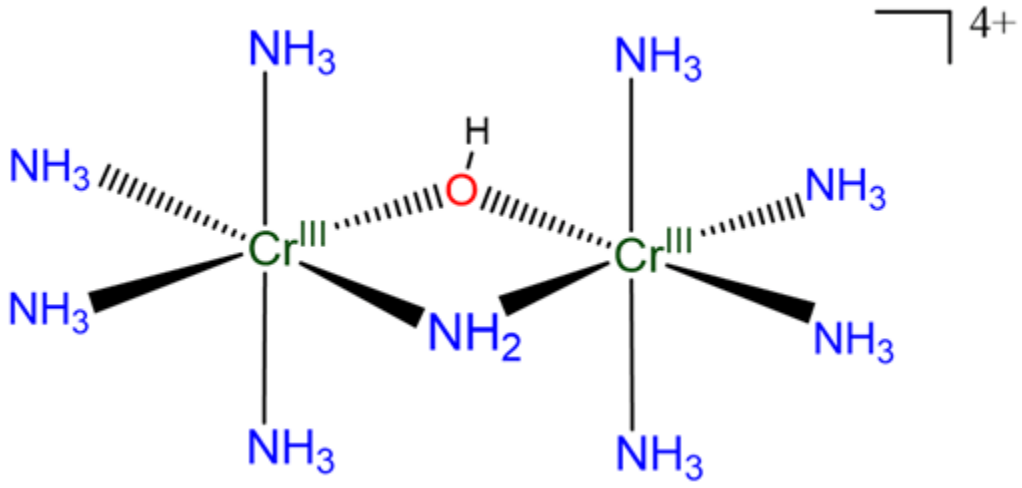
It can be quite complicated to use the IUPAC system to name asymmetric multinuclear coordination complexes. Fortunately it is rarely necessary and there are a variety of simpler somewhat *ad hoc* methods that work well for such cases. Since these methods are commonly used by textbooks and inorganic instructors it is likely worth your while to learn about their general features. In these methods

1. A multinuclear complex is named as a derivative of one of the metal centers and the other metal centers and their ligands are treated as ligands to the prioritized metal center.
2. Unfortunately, most of the time the choice of which metals are part of the ligands and which one is central is made haphazardly. In other words, there is no agreed upon system for assigning which metal center is the central metal and which should be regarded as part of the ligands around it. One way to be more systematic about the selection of the central and ligand-embedded metals is to assign the central metal as the metal of highest priority in the IUPAC priority rules. In the IUPAC priority rules, the central metal is the highest priority metal alphabetically by name; then if there is a tie the ligands on each tied metal center are ranked alphabetically and the tied metal center with the highest priority (or most highest priority) ligands wins.
3. The metal centers not chosen as the primary metal center and all ligands around them, including those bridging to the winning metal center, are then treated as a single ligand that coordinates the winning metal center.
4. When naming the ligands and the overall complex, again there is much that is haphazard. However, in the best systems each coordination sphere is named using the same rules as for mononuclear complexes - *i.e.,* the ligands are given in alphabetical order, etc.

    - This is true of any metal center-containing ligands.
    - When there is a bridging and non-bridging ligand of the same type, the bridging ligands are given first. When there are multiple bridging ligands of the same type but which use different bridging modes (*e.g.* μ_4-, μ_3-, μ_2-), the ligands are specified in decreasing order of bridging multiplicity, *e.g.* μ_3 -sulfido-di-μ-sulfido.

Let's apply these rules to the examples in Scheme 9.3.VIII.

Compound A:



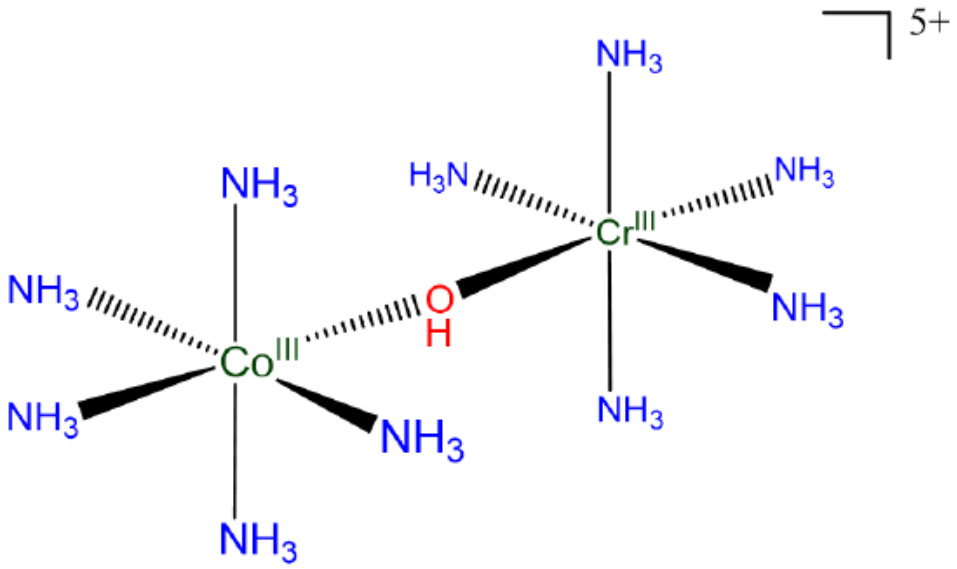
Using hydroxo for the OH^-, it may be named

[(μ-amido-tetraammine-μ-hydroxochromium(III))tetraamminechromium(III)] ion

or

[(μ-amido-tetraammine-μ-hydroxochromium)chromium(4+)] ion

Compound B:



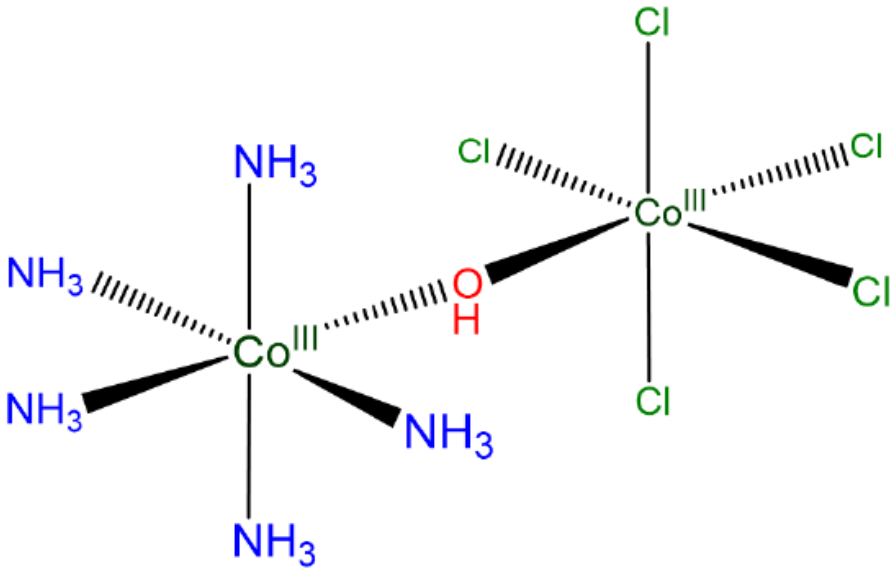
Using hydroxo for the OH^-, it may be named

[(pentaammine-μ-hydroxocobalt(III))tetraamminechromium(III)] ion

or

[(pentaammine-μ-hydroxocobalt)tetraamminechromium(5+)] ion

Compound C:



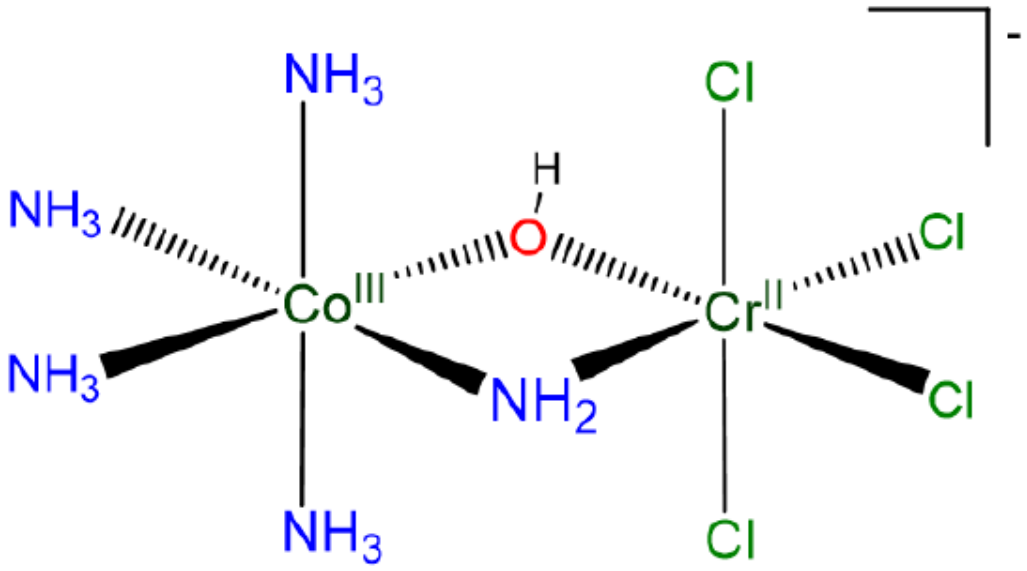
Using hydroxo for OH^-, it may be named

[pentaammine(pentachloro-μ-hydroxocobalt(III))cobalt(III)]

or

[pentaammine(pentachloro-μ-hydroxocobalt)cobalt](9)]

Compound D:



Using hydroxo for OH^- and chloro for Cl^-, it may be named

[pentaammine(pentachloro-μ-hydroxocobalt(III))chromate(III)] ion

or

[(tetrammine-μ-ammine-μ-hydroxocobalt)tetrachlorochromate](1-)] ion

As can be seen from the examples above this system gives serviceable names for multimetallic complexes but those names are not the IUPAC names and so should not be used to describe complexes outside of pedagogical and informal settings.

Writing and interpreting formulae for multinuclear complexes

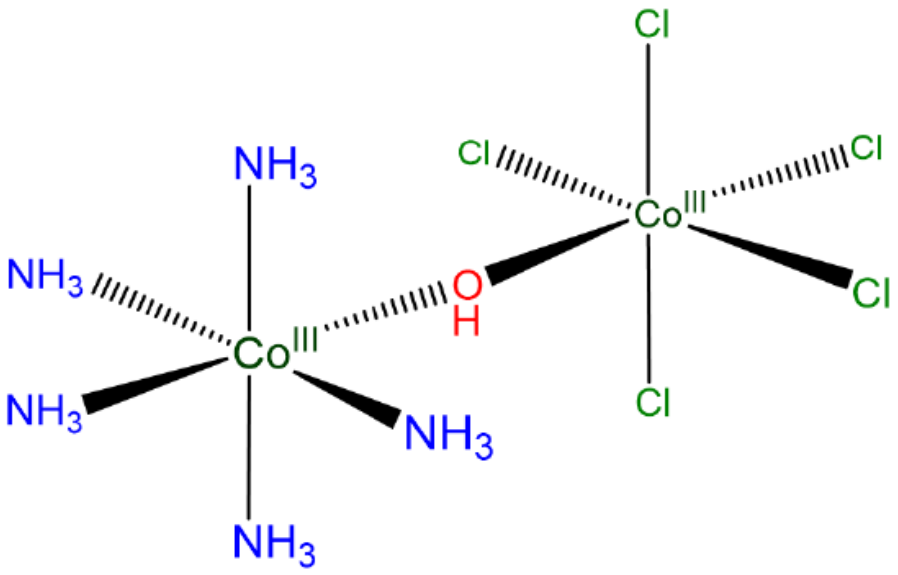
The rules for writing formulae for multinuclear complexes are the same as for mononuclear ones with two added details:

1. Write bridging ligands after nonbridging ligands of the same type. For example, Cu_2Cl_6 should be written as $[Cu_2Cl_4\text{-}(\mu\text{-}Cl)_2]$
2. However, you may ignore that and other rules if you find it helpful to keep groups of metals and ligands together in a way that better conveys how the atoms are connected. Just as the structure of ethane may be more clearly conveyed as H_3CCH_3 instead of CH_3CH_3, the complex $[Cu_2Cl_4(\mu\text{-}Cl)_2]$ may be written as $[(Cl_2Cu)(\mu\text{-}Cl)_2(CuCl_2)]$.

Other Examples:

For dichromate write, $[Cr_2O_6(\mu\text{-}O)]^{2-}$ or $[O_5Cr\text{-}\mu\text{-}O\text{-}CrO_5]^{2-}$

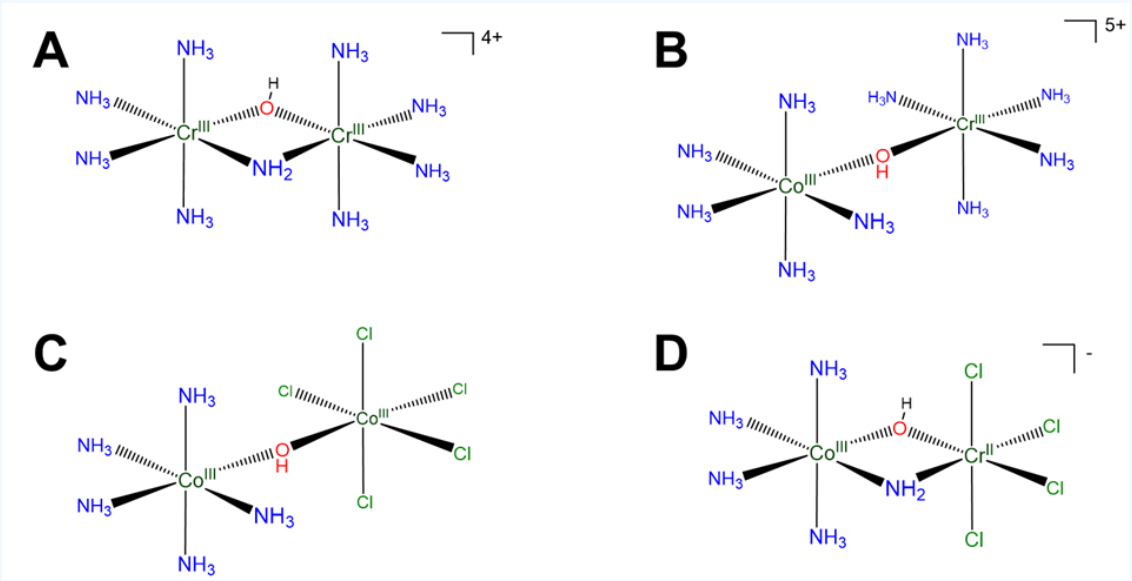
For compound C of Scheme 9.3.VIII.



write $[Co_2Cl_5(NH_3)_5(\mu\text{-}OH)]$ or, even better, $[(H_3N)_5Co(\mu\text{-}OH)CoCl_5]$.

Exercise 9.3.10

Write reasonable formulae for complexes A, B, and D in Scheme 9.3.VIII, which for convenience is reproduced below.



Sample answers for A available at the end of this section.

References

1. International Union of Pure and Applied Chemistry *Nomenclature of Inorganic Chemistry* Cambridge, UK, 2005.

2. The structure and name is taken from Choudhury, S. B.; Allan, C. B.; Maroney, M.; Wodward, A. D.; Lucas, C. R. *Inorg. Synth.* **1998**, *32*, 98-107.

3. Haas, K. Naming Transition Metal Complexes. https://chem.libretexts.org/Courses/

4. There is a widely-circulated myth that anionic ligands should be named before neutral ones. This myth is false. According to the IUPAC red book (bolding mine):

> IR-2.15.3.4: Ordering ligands in formulae and names in formulae of coordination compounds,
>
> The formulae or abbreviations representing the ligands **are cited in alphabetical order as the general rule**. Bridging ligands are cited immediately after terminal ligands of the same kind, if any, and in increasing order of bridging multiplicity. (See also Sections IR-9.2.3 and IR-9.2.5.)
>
> IR-9.2.3.1 Sequence of symbols within the coordination formula
>
> (i) The central atom symbol(s) is (are) listed first.
>
> (ii) The **ligand symbols (line formulae, abbreviations or acronyms) are then listed in alphabetical order** (see Section IR-4.4.2.2).5 Thus, CH_3CN, MeCN and NCMe would be ordered under C, M and N respectively, and CO precedes Cl because single letter symbols precede two letter symbols. **The placement of the ligand in the list does not depend on the charge of the ligand.**
>
> (iii) More information is conveyed by formulae that show ligands with the donor atom nearest the central atom; this procedure is recommended wherever possible, even for coordinated water.

5. Technically organometallic complexes are named according to slightly different rules but the coordination compound naming system works here. Note that this complex was once thought to possess an Fe-Fe bond, in accordance with the predictions of the 18-electron rule. Consequently, older sources often give an [*Fe-Fe*] after the name to reflect the presence of that bond. However, as the complex is no longer thought to possess an Fe-Fe bond it is omitted here.

Contributors and Attributions

Stephen Contakes, Westmont College, to whom comments, corrections, and criticisms should be addressed.

with some examples taken from Naming Transition Metal Complexes by Kathryn Haas.

Consistent with the policy for original artwork made as part of this project, all unlabeled drawings of chemical structures are by Stephen Contakes and licensed under a Creative Commons Attribution 4.0 International License.

Answers

Exercise 9.3.1

(a) bidentate
(b) tridentate
(c) bidentate
(d) tridentate (only the lower N on each ring has a lone pair that can be used to bind the metal)
(e) hexadentate (remember that each carboxylate only counts as one point of attachment)
(f) bidentate
(g) monodentate (through the lone pair on the isocyanide C)
(h) bidentate

Exercise 9.3.2**. Assigning metal oxidation states in a complex**

This contains $[Fe(CN)_6]^{3-}$; so $O.S._{Fe}$ + 6 x (-1) (for CN^-) = -3 (the complex's charge) so $O.S._{Fe}$ = +3 or Fe^{3+}.

This contains $[CoCl(NH_3)_5]^{2+}$; so $O.S._{Co}$ + 1 x (-1) (for Cl^-) + 0 x 5 (for NH_3) = +2 (the complex's charge) so $O.S._{Co}$ = +3 or Co^{3+}.

This contains $2K^+$ and $[PtCl_4]^{2-}$; so $O.S._{Pt}$ + 4 x (-1) (for Cl^-) = -2 (the complex's charge) so $O.S._{Pt}$ = +2 or Pt^{2+}.

$O.S._{Pt}$ + 1 x (-2) (for por; see table 9.2.2) + 1 x (-1) (for Cl^-) = +0 (the complex's charge) so $O.S._{Mn}$ = +3 or Mn^{3+}.

The complex is $[Ru(bpy)3]^{2+}$ so $O.S._{Ru}$ + 0 x 3 (for bpy) = +2 (the complex's charge) so $O.S._{Ru}$ = +2 or Ru^{2+}.

$O.S._{Pd}$ + 2 x (-1) (for Cl^-) + 0 x 3 (for dppe) = +0 (the complex's charge) so $O.S._{Pd}$ = +2 or Pd^{2+}.

O.S.$_{Mn}$ + (2 x 0) (for en) + 2 x (-1) (for SCN^-) = +0 (the complex's charge) so O.S.$_{Mn}$ = +2 or Mn^{2+}.

Exercise 9.3.3: Simple Nomenclature Problems.

	Complex	Stock system name	Ewing-Bassett System name
a	$[Ru(NH_3)_6](NO_3)_3$	hexammineruthenium(III) nitrate	hexammineruthenium(3+) nitrate
b	$K_2[PtCl_4]$	potassium tetrachloroplatinate(II)	potassium tetrachloroplatinate(2-)
c	$K[Ag(CN)_2]$	potassium dicyanoargentate(I)	potassium dicyanoargentate(1-)
d	$Cs_2[CuBrCl_2F]$	cesium bromodichlorofluorocuprate(II)	cesium bromodichlorofluorocuprate(2-)
e	$[Cu(acac)_2]$	bis(acetylacetonato)copper(II)	bis(acetylacetonato)copper(0)

Exercise 9.3.4: More simple nomenclature problems.

	Compound	Stock System Name	Ewing-Bassett System Name
a	$Cu(OH)_4^-$	tetrahydroxidocuprate(III) or tetrahydroxidocuprate(III)	tetrahydroxidocuprate(1-) or tetrahydroxidocuprate(1-)
b	$[AuXe_4]^{2+}$	tetraxenongold(II)	tetraxenongold(2+)
c	$AuCl_4^-$	tetrachloroaurate(III)	tetrachloroaurate(1-)
d	$Fe(CN)_6^{3-}$	hexacyanoferrate(III) or hexacyanidoferrrate(III)	hexacyanoferrate(3-) or hexacyanidoferrate(3-)
e	$K_4[Fe(CN)_6]$	potassium hexacyanoferrate(II) or potassium hexacyanidoferrrate(II)	potassium hexacyanoferrate(4-) or potassium hexacyanidoferrrate(4-)
f	*trans*-$[Cu(en)_2(NO_2)_2]$ (the N is bound to Cu)	bis(ethylenediamine)bisnitrocopper(II) or bis(ethylenediamine)bis(nitrito-κN)copper(II)	bis(ethylenediamine)bisnitrocopper(0) or bis(ethylenediamine)bis(nitrito-κN)copper(0)
g	*cis*-$IrCl_2(CO)(PPh_3)$	*cis*-dichlorocarbonyltriphenylphosphineiridium(I) or *cis*-dichloro(carbonyl)(triphenylphosphine)iridium(I)	*cis*-dichlorocarbonyltriphenylphosphineiridium(0) or *cis*-dichloro(carbonyl)(triphenylphosphine)iridium(0)
h	$IrCl(PPh_3)_3$	chlorotris(triphenylphosphine)iridium(I)	chlorotris(triphenylphosphine)iridium(0)

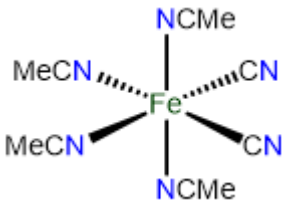
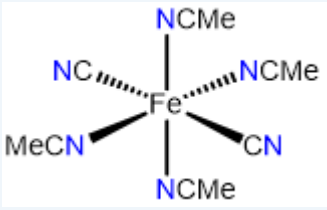
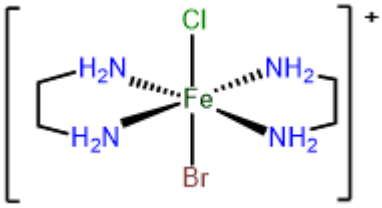
Exercise 9.3.5: Even more simple nomenclature problems.

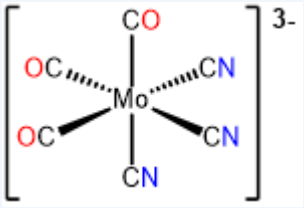
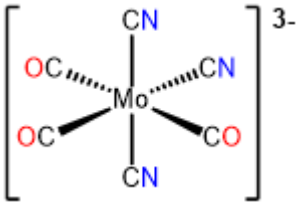
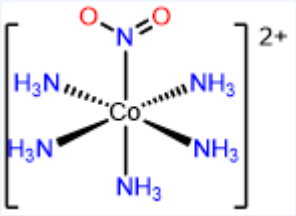
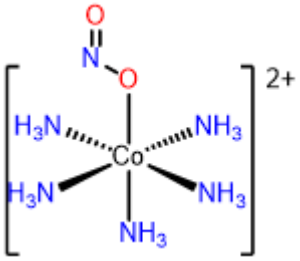
	Complex	Stock system name	Ewing-Bassett System name
a	$Fe(acac)_3$	tris(acetoacetato)iron(III)	tris(acetoacetato)iron(0)
b	$Na_2[CuBr_4]$	sodium tetrabromocuprate(II)	sodium tetrabromocuprate(2-)
c	$[Co(NH_3)_6][Co(ox)_3]$	hexamminecobalt(III) tris(oxalato)cobalt(III)	hexamminecobalt(3+) tris(oxalato)cobalt(3-)
d	$[Ag(NH_3)_2]BF_4$	diamminesilver(I) tetrafluoroborate	diamminesilver(1+) tetrafluoroborate
e	$[Ag(NH_3)_2][Ag(CN)_2]$	diamminesilver(I) dicyanoargentate(I) or diamminesilver(I) dicyanidoargentate(I)	diamminesilver(1+) dicyanoargentate(1-) or diamminesilver(1+) dicyanidoargentate(1-)
f	$[Ni(CN)_4]^{2-}$	tetracyanonickelate(II) or tetracyanonickelate(II) ion	tetracyanonickelate(2-) or tetracyanonickelate(2-) ion
g	$[Co(N_3)(NH_3)_5]SO_4$	pentammineazidocobalt(III) sulfate	pentammineazidocobalt(2+) sulfate
h	$[CoBrCl(H_2O)(NH_3)]I$ (ignore stereochemistry)	ammineaquabromochlorocobalt(III) iodide	ammineaquabromochlorocobalt(1+) iodide

Exercise 9.3.6: Nomenclature problems, some of which involve consideration of isomerism.

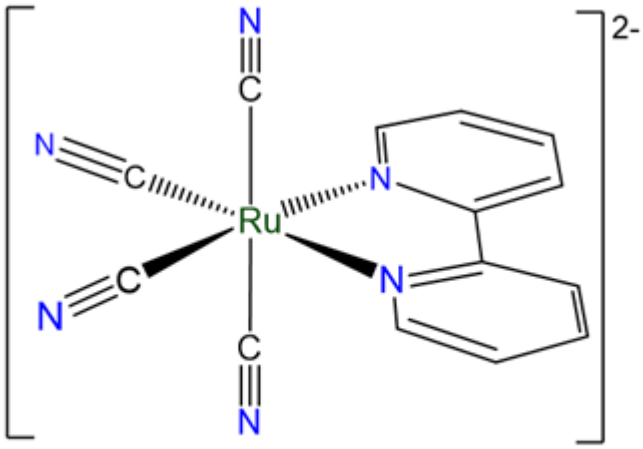
	Complex	Stock system name	Ewing-Bassett System name
a	*trans*-$[Cu(dppe)_2(NO_2)_2]$	*trans*-bis(diphenylphosphinoethane)bisnitrocopper(II) or *trans*-bis(diphenylphosphinoethane)bis(nitrito-κ *N*)copper(II)	*trans*-bis(diphenylphosphinoethane)bisı or *trans*-bis(diphenylphosphino)ethaneb *N*)copper(0)
b	$[Pd(en)_2(SCN)_2]$, with the thiocyanates bound Pd-SCN	bis(ethylenediamine)bisthiocyanatopalladium(II) or bis(ethylenediamine)bis(thiocyanato-S)palladium(II) or bis(ethylenediamine)bis(thiocyanato-κS)palladium(II)	bis(ethylenediamine)bisthiocyanatopalladium(0) or bis(ethylenediamine)bis(thiocyanato-S)palladi or bis(ethylenediamine)bis(thiocyanato-κS)pallad
c	$[Mn(CO)_6]BPh_4$	hexacarbonylmanganese(I) tetraphenylborate	hexacarbonylmanganese(1+) tetrapheny
d	$Rb[AgF_4]$	rubidium tetrafluoroargentate(III)	rubidium tetrafluoroargentate(1-)
e	K_2ReH_9	potassium nonahydridorhenium(VII)	potassium nonahydridorhenium(2-)
f	K_3CrCl_6 or $K_3[CrCl_6]$	potassium hexachlorochromium(III) or potassium hexachloridochromium(III)	potassium hexachlorochromium(3-) or potassium hexachloridochromium(3-)
g	$[Ru(H_2O)_6]Cl_2$	hexaaquaruthenium(II) chloride	hexaaquaruthenium(2+) chloride
h	[*cis*-$Fe(CO)_4I_2$]	*cis*-tetracarbonyldiiodoiron(II)	*cis*-tetracarbonyldiiodoiron(0)
i	K_2[*trans*-$Fe(CN)_4(CO)_2$]	potassium *trans*-dicarbonyltetracyanoferrate(II)	potassium *trans*-dicarbonyltetracyanofe
j	[*cis*-$MnCl(H_2O)_4(NH_3)](NO_3)$	*cis*-ammine tetraaquachloromanganese(0) nitrate	*cis*-ammine tetraaquachloromanganese
k	K[*fac*-$RuCl_3(PMe_3)_3$]	potassium *fac*-trichlorotris(triphenylphosphine)ruthenium(II)	potassium *fac*-trichlorotris(triphenylphosphine)ruth

Exercise 9.3.7

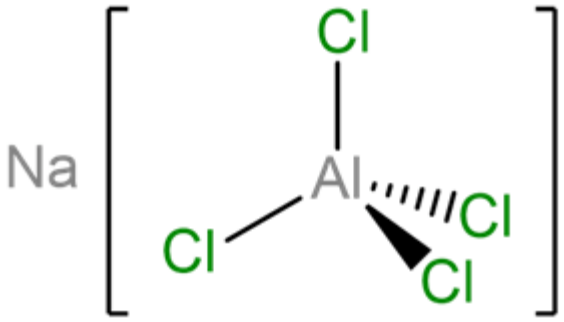
#	Structure	Stock system name	Ewing-Bassett system name
1		*cis*-tetraacetonitriledicyanoiron(II) or *cis*-tetraacetonitriledicyanidoiron(II)	*cis*-tetraacetonitriledicyanoiron(0) or *cis*-tetraacetonitriledicyanidoiron(0)
2		*trans*-tetraacetonitriledicyanoiron(II) or *trans*-tetraacetonitriledicyanidoiron(II)	*trans*-tetraacetonitriledicyanoiron(0) or *trans*-tetraacetonitriledicyanidoiron(0)
3		*trans*-bromochlorobis(ethylenediamine)iron(III) or *trans*-bromidochloridobis(ethylenediamine)iron(III)	*trans*-bromochlorobis(ethylenediamine)iron(1+) or *trans*-bromidochloridobis(ethylenediamine)iron(1+)

#	Structure	Stock system name	Ewing-Bassett system name
4		*fac*-tricarbonyltricyanomolybdate(0) or *fac*-tricarbonyltricyanidomolybdate(0)	*fac*-tricarbonyltricyanomolybdate(3-) or *fac*-tricarbonyltricyanidomolybdate(3-)
5		*mer*-tricarbonyltricyanomolybdate(0) or *mer*-tricarbonyltricyanidomolybdate(0)	*mer*-tricarbonyltricyanomolybdate(3-) or *mer*-tricarbonyltricyanidomolybdate(3-)
6		pentammineitrito-*N*-cobalt(III), pentammineitrito-κ*N*-cobalt(III), or pentammineitrocobalt(III)	pentammineitrito-*N*-cobalt(2+), pentammineitrito-κ*N*-cobalt(2+), or pentammineitrocobalt(2+)
7		pentammineitrito-*O*-cobalt(2+), pentammineitrito-κ*O*-cobalt(2+), or pentammineitritocobalt(2+)	pentammineitrito-*O*-cobalt(2+), pentammineitrito-κ*O*-cobalt(2+), or pentammineitritocobalt(2+)

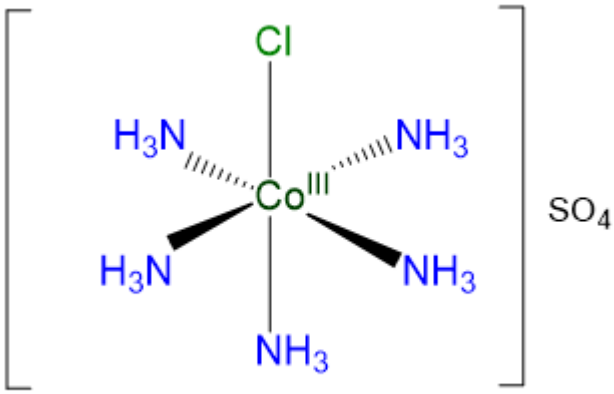
Exercise 9.3.8



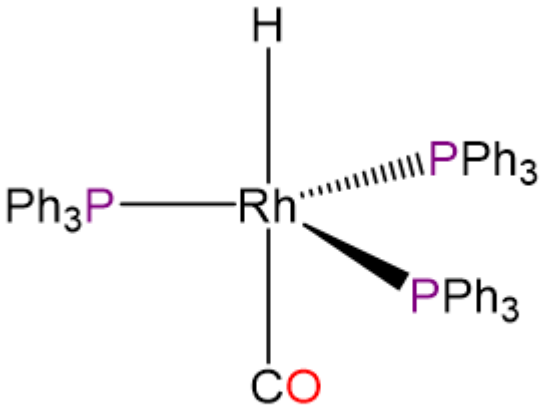
(2,2'-bipyridine)tetracyanoruthenium(2-)



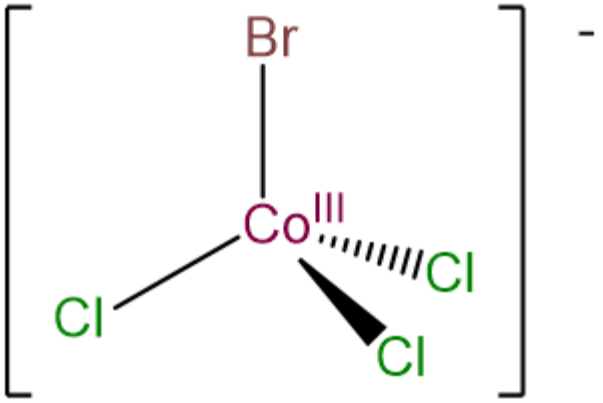
Sodium tetrachloroalumnate



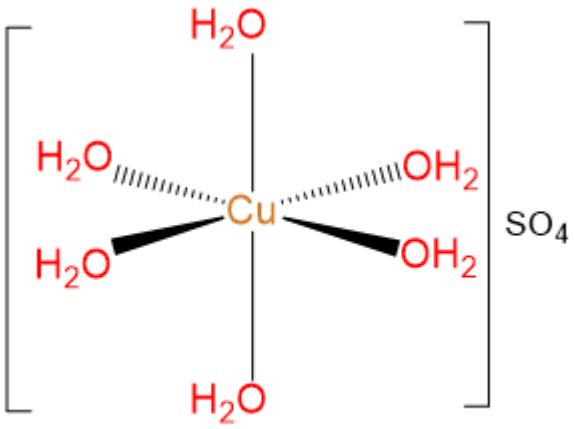
pentaamminechlorocobalt(2+) sulfate



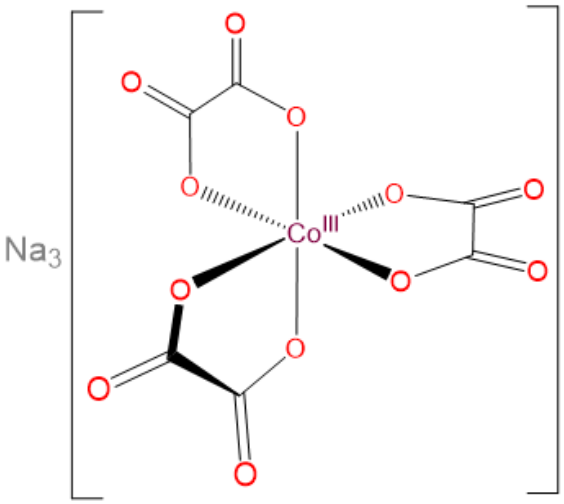
carbonylhydridotris(triphenylphosphine)rhodium(I)



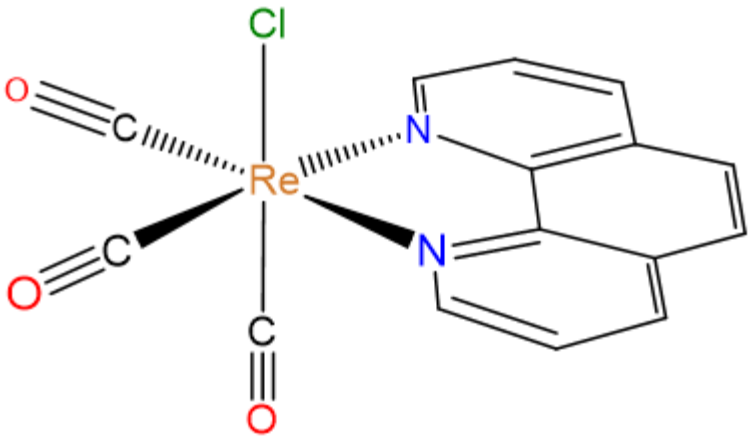
bromotrichlorocobaltate(III)



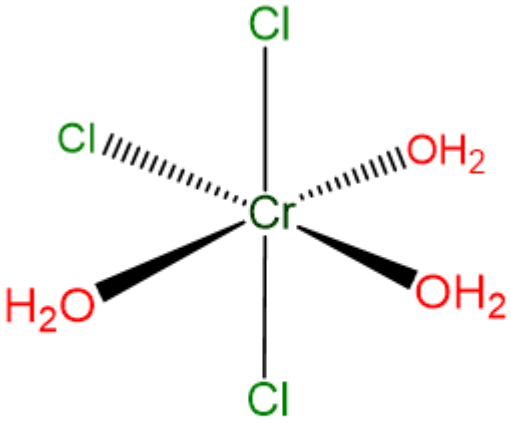
hexaaquacopper(2+) sulfate



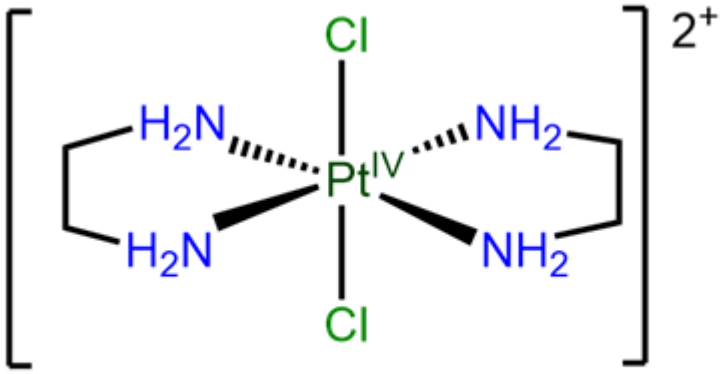
sodium tris(oxalato)cobalt(III)
Λ-enantiomer shown



fac-(1,10-phenanthroline)tricarbonylchlororhenium(I)



mer-triaquatrichlorochromium(III)

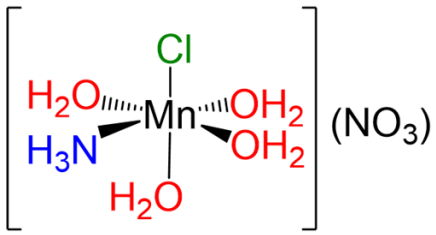


trans-dichlorobis(ethylenediamine)platinum(IV)

Exercise 9.3.9.

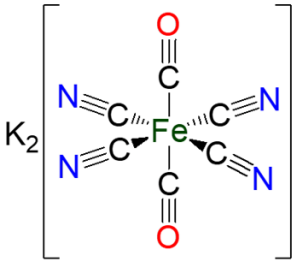
Δ-tris(tetraammine-μ-dihydroxocobalt)cobalt(6+) or Δ-tris(tetraammine-μ-dihydroxocobalt(III)cobalt(III)

Exercise 9.3.10



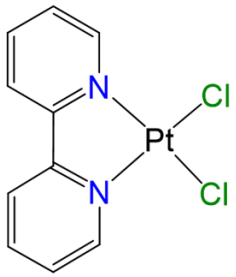
1

[*cis*-MnCl(H_2O)$_4$(NH_3)](NO_3)



2

K_2[*trans*-Fe(CN)$_4$(CO)$_2$]



3

[Pt(bpy)Cl_2]

Exercise 9.3.11

[CoCl(NH_3)$_5$](SO_4)

Δ-[Mn(NH_3)$_2$(ox)$_2$]$^-$

trans-[Fe(CN)$_2$(NCMe)$_4$]

[MoCl$_2$(CO)$_3$(PPh_3)] or MoCl$_2$(CO)$_3$(PPh_3)

mer-[CrBrCl(H_2O)$_3$I]

[Co(O_2)py(salen)]

[Fe(NO)$_2$(SEt)$_2$]$^-$

[MnCl(por)]$^-$ or [MnCl(porphyrin)]$^-$

[Ni(DMG)$_2$] or [Ni(Hdmg)$_2$]

potassium *trans*-[Fe(CN)$_2$(CO)$_4$]

trans-[CuCl(H_2O)$_4$(NH_3)]SO_4

trans-[PtCl$_2$(en)$_2$]$^{2+}$

cis-[CoBrCl(NH_3)$_4$]SO_4

K_2[Fe(CN)$_5$NO]

Exercise 9.3.10

[Cr$_2$(NH_3)$_8$-μ(NH_2)-μ(OH)]$^{4+}$ or [(H_3N)$_4$Cr^{III}-μ(NH_2)-μ(OH)-Cr^{II}(NH_3)$_4$] and variants thereof involving writing the H_3N as NH_3, μ as μ_2, etc.

[CoCr(NH_3)$_{10}$-μ(OH)]$^{5+}$ or, better, [(H_3N)$_5$Co^{III}-μ(OH)-Cr^{III}(NH_3)$_5$]$^{5+}$

This was already done as an example above, [Co$_2$Cl$_5$(NH_3)$_5$-μ(OH)] or, better, [(NH_3)$_5$Co^{III}-μ(OH)-Co^{III}Cl$_5$] and variants thereof

[CoCrCl$_4$(NH_3)$_4$-μ(NH_2)-μ(OH)] or, better, [(H_3N)$_4$Co^{III}-μ(NH_2)-μ(OH)-Cr^{II}Cl$_4$]

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9.4: Isomerism

Metal complexes present a rich, interesting, and diverse structural chemistry. Major points of variation in the structural chemistry of metal complexes include

1. **coordination number** and **coordination geometry**, which involve differences in how many ligands surround a central metal and their overall geometric arrangement. Examples of the latter include the tetrahedral and square planar geometries commonly observed for four-coordinate metal centers. Tetrahedral, square planar, and octahedral coordination serve as a backdrop to the discussion of isomerism on this page. Readers who are unfamiliar with these structures might consider reading the section on coordination geometries before this one.
2. **structural iosmerism** involves differences in how potential ligand atoms are bound to metals in a complex. Possibilities for structural isomerism include
   - linkage or ambidentate isomerism
   - hydrate/solvate isomerism
   - ionization isomerism
   - coordination isomerism.

   Of these, linkage isomerism should always be considered when working with ambidentate ligands. As classifications, the last three forms of structural isomerism are mainly of academic interest since they represent permutations of ordinary structure patterns for solvates, salts, and coordination complexes, respectively.

3. **stereochemistry**, which includes
   - which coordination geometry is adopted for a metal with a given set of ligands in a particular oxidation state. For instance, $[Ni^{II}Cl_4]^{2-}$ is tetrahedral while $[Pt^{II}Cl_4]^{2-}$ is square planar. Since this geometry is usually fixed by the metal and ligands it is typically not a source of stereoisomeric varierty.
   - metal-centric stereoisomerism involving possible variations in where ligands are located relative to one another around the metal. The possibilities depend on the coordination number, geometry, and number of different types of ligands. For instance, square planar complexes can exhibit *cis-/trans-* isomerism while tetrahedral ones cannot. Tetrahedral complexes with four different ligands exhibit *R* and *S* chirality but complexes of that type are relatively rare. The more common cases include *cis* and *trans* isomerism in square planar complexes and *cis* & *trans-*, *mer & fac-*, and Λ & Δ isomerism in octahedral ones, although some multidentate ligands present additional possibilities for stereochemical variation
   - Stereoisomerism centered on the ligands bound to a metal center. Possibilities include
     - stereoisomerism inherent to a ligand. This would include cases where the ligand itself is chiral or, as in the case of amines, exists as a rapidly interconverting mixture of isomers. Thus this sort of stereoisomerism is an extension of the isomerism encountered in ordinary organic and other main group compounds. The main new issues introduced by binding of such ligands to a metal center involve the creation of new possibilities for diastereoisomerism based on the stereochemistry of the metal center and the freezing out of stereocenter inversion on binding to a metal. The latter is particularly important for amines, which as free amines racemize rapidly by nitrogen inversion.
     - or conformational isomerism involving five-membered **chelate rings** created when a multidentate ligand binds to a metal. This isomerism is often called chelate ring twist since individual rings can exhibit one of two conformations depending on how they twist on binding.

A summary of these forms of isomerism is given in Figure 9.4.1.

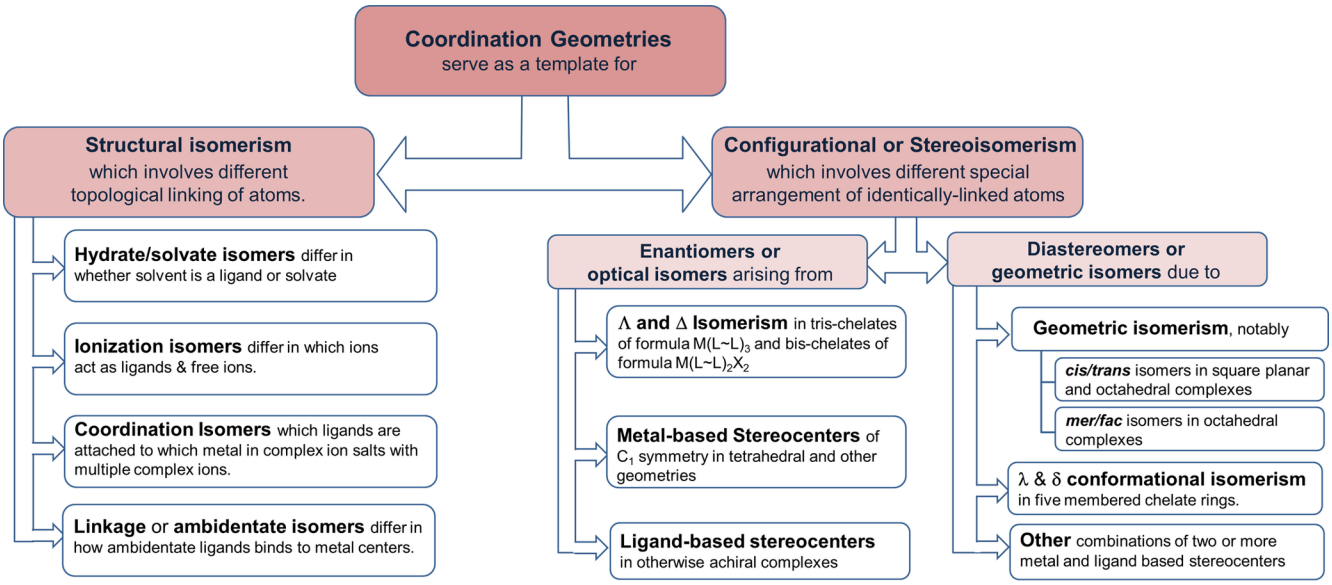


Figure 9.4.1. Relationship among the common types of isomerism in metal complexes. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Structural isomers

Structural isomerism involves different topological linkages of atoms. Differences in atomic linkages distinctive to coordination chemistry involve the linkages between metals and ligands. The main variations are:

1. Hydrate/solvate isomerism

Solvate isomers differ in terms of whether a molecule acts as a ligand or whether it acts as a solvate by occupying a lattice site in the crystal. Among solvate isomers, the case in which water is the ligand or solvate is the best known. The resulting isomers are called **hydrate isomers** after the term for water acting as a solvate, hydrate. A well-known example that illustrates how solvate isomerism works is the series $[CrCl_x(H_2O)_{6-x}]Cl_{3-x}{\cdot}xH_2O$, for which x = 0-2. The structures of the complex ions involved in this series are shown in Figure 9.4.2.[1]

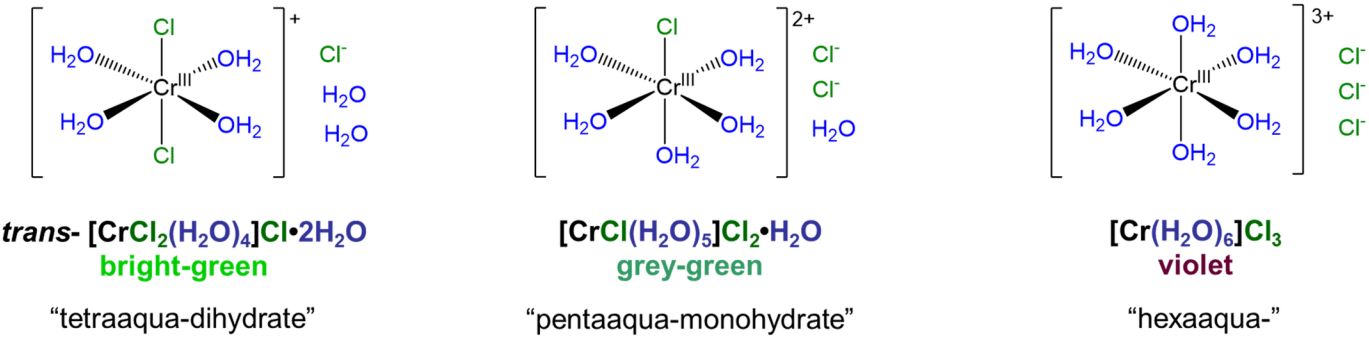


Figure 9.4.2. Complexes of the hydrate isomer series $[CrCl_x(H_2O)_{6-x}]Cl_{3-x}{\cdot}xH_2O$ (x = 0-2). This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

As can be seen from the compounds in Figure 9.4.2, hydrate isomers differ both in terms of whether water acts as a ligand or hydrate *and* in terms of whether a potential counterion acts as a counterion or ligand. Thus, in *trans*-$[CrCl_2(H_2O)_4]Cl{\cdot}2H_2O$ two chlorides act as chloro ligands and four waters as aqua ligands while in $[CrCl(H_2O)_5]Cl_2{\cdot}H_2O$ five water molecules act as aqua ligands while only one chloride acts as a chloro ligand. In this way, solvate isomers simply represent cases in which two or more of the possible permutations for metal ligand binding among a set of solvent and counterion molecules are stable.

2. Ionization isomerism

In **ionization isomerism** there are two or more potential ions that can act as ligands. The ionization isomers differ in terms of which of these ions act as counterions and which act as ligands. Consider, for instance, the complexes shown in Figure 9.4.3. These complexes differ in terms of whether the chloride or sulfate acts as a ligand, with the other acting as a counterion.

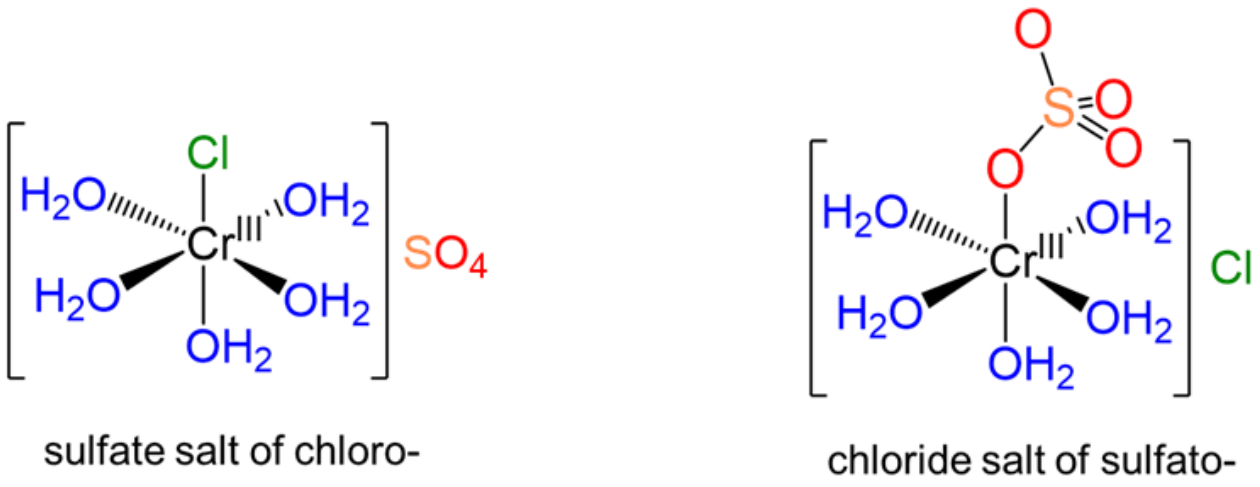


Figure 9.4.3. Ionization isomers comprising a pentaaquachromium(III) fragment and the anions chloride and sulfate. As with all ionization isomers, the isomers differ in terms of which anion acts as a ligand and which a counterion. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

3. Coordination isomerism

Coordination isomers exist in compounds containing two or more complexes, each of which possesses a different set of ligands that can in principle be swapped with a ligand of the other complex. An example involves $[Co^{III}(NH_3)_6][Cr^{III}(ox)_3]$, depicted in Figure 9.4.4A.[1] Coordination isomers of this complex involve swapping the ammine ligands around the Co^{3+} center for oxalato ligands surrounding the Cr^{3+} center. For instance, swapping all the ammine and oxalato ligands between the metal centers gives the coordination isomer $[Cr^{III}(NH_3)_6][Co^{III}(ox)_3]$ shown in Figure 9.4.4B.

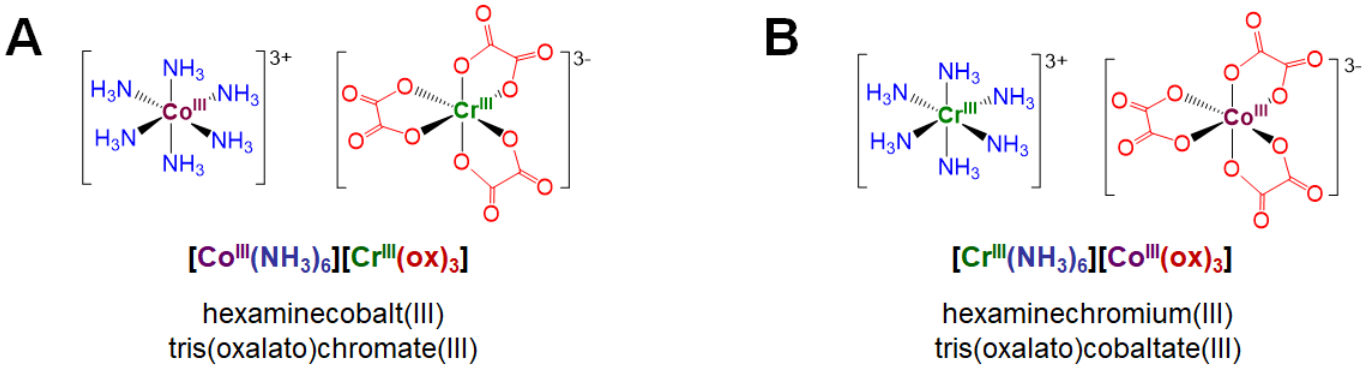
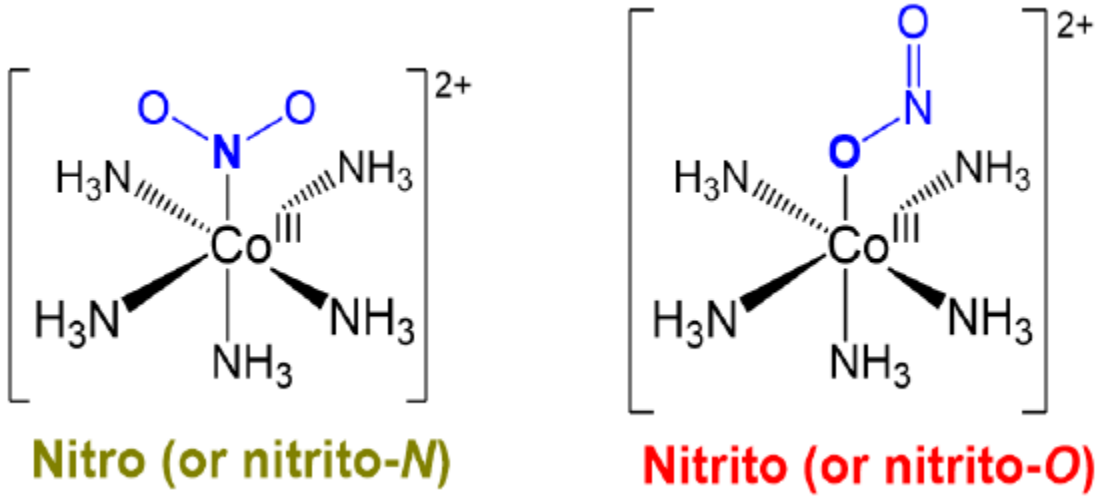


Figure 9.4.4. Two coordination isomers comprising a Co^{3+} ,Cr^{3+}, six NH_3. and three oxalato ligands. The isomers differ in terms of which ligand type is bound to which metal. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

As classifications, hydrate/solvate, ionization, and coordination isomerism represent permutations of ordinary structure patterns for solvates, salts, and coordination complexes, respectively. As a result these forms of isomerism are rarely used as independent conceptual frameworks when thinking and talking about the structure of coordination compounds. Not so the final type of structural isomerism, linkage isomerism. That is because linkage isomerism has to do with the special *capacity* of ambidentate ligands to bind metals in multiple ways.

4. Linkage or ambidentate isomerism

Linkage or ambidentate isomers differ in how one or more ambidentate ligands bind to metal centers in a complex. The classic example dating from the work of Jørgensen and Werner is given in Scheme 9.4.I.



Scheme 9.4.I. Linkage isomers of penaamminenitritocobalt(III) ion. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Just as alkenes exist as *E* and *Z* isomers, compounds possessing ambidentate ligands exist as one among the possible linkage isomers. As such, when working with ambidentate ligands the particular linkage isomer formed should be determined experimentally and considered when interpreting the complex's chemical and physical behavior.

The main ambidentate ligands which give rise to linkage isomerism are

- cyanide, CN^-
- thiocyanate, SCN^-, and the O and Se analogues, OCN^- and $SeCN^-$
- nitrite, NO_2^-
- sulfite, SO_3^-
- nitrosyl, NO

Although ambidentate ligands can bind metals in multiple ways, most exhibit a preferred binding mode (*i.e.,* prefer to bind metal centers in one of the possible ways). For instance, cyanide almost always binds through its carbon atom and thiocyanate almost always binds through its nitrogen (μ-*N*). However, the other binding mode can sometimes be formed kinetically or by using conditions that particularly favor its formation. Thus thiocyanate forms M-SCN^- linkages in the presence of exceptionally soft metal centers or in hard polar solvents (in which Lewis acid groups can stablize the terminal nitrogen of a bound thiocyanate ligand).

Ambidentate ligands are of significant research interest because many don't just bind to metal centers in two ways; the linkage isomers sometimes have significantly different physical properties. In addition, the possibility of two binding modes introduces the possibility of exploiting linkage isomerism to take advantage of some of these ligands:

a. different structural chemistry in different coordination modes. In mononuclear complexes the coordination mode influences which side of the ligand faces away from the complex and might be susceptible to stabilization by interaction with solvent. Additionally, the orientation of the ligand relative to the metal center might differ between one coordination mode and another. For instance, as predicted from the minor contributor to its resonance structure, thiocyanate binds nonlinearly via its S atom and linearly via its N (Figure 9.4.5). Because of this the apparent steric bulk of the ligand around the metal center might differ between forms.

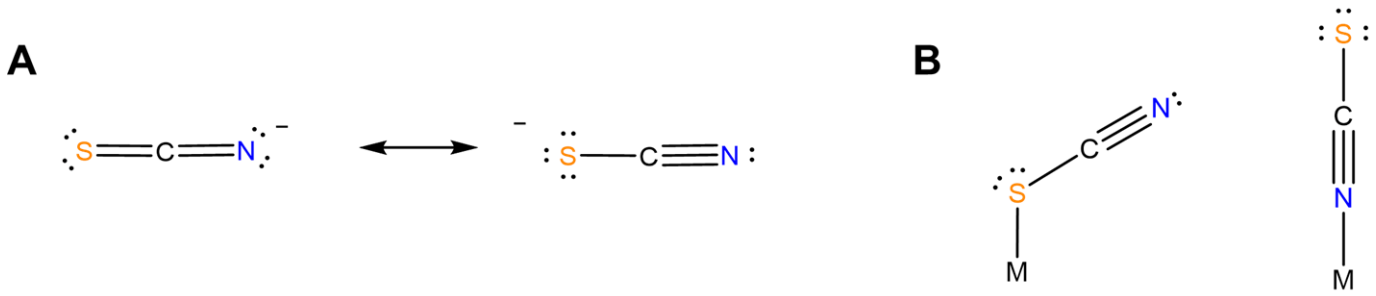


Figure 9.4.5. Thiocyanate generally prefers to bind metals nonlinearly but in some cases forms linear M-SCN bonds. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

b. bind two different metal centers at the same time, linking them together. Perhaps the best-known examples involve thiocyanate and cyanide. The latter forms linkages of the type M-C≡N-M'. In the dye Prussian blue these take the form Fe^{II}-C≡N-Fe^{III}. An example from the author's graduate research involved tetrahedral clusters containing four metal atoms linked by six cyano ligands, as shown in Figure 9.4.6.

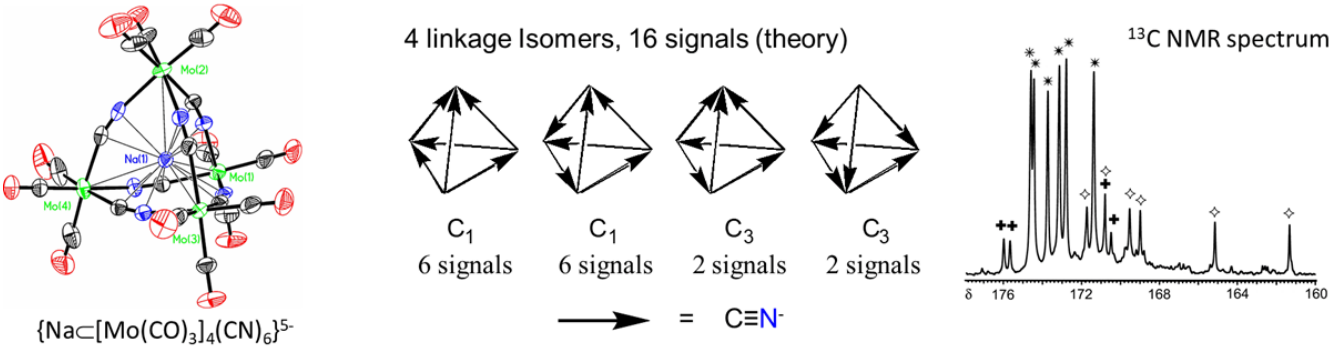


Figure 9.4.6. (A) Structure of $\{Na@[Mo(CO)_3]_4(CN)_6\}$ showing the linking of four Mo centers by six CN ligands. Thermal ellipsoids for the C atoms are shown in black; those of the N atoms in blue. (B) The complex exists as a mixture of four linkage isomers in which the bridging CN^- ligands are oriented in different ways, as may be seen from the presence of the expected sixteen signals in its ^{13}C NMR spectrum. Based on work reported in reference 2.

c. can be induced to change from one binding mode to another in response to a stimulus. The classic example involves the light-driven transformation of the thermodynamically more stable yellow nitro complex of pentamminecobalt(III), $[Co(NH_3)_5NO_2]^{2+}$ to the less stable red *O*-nitrito complex, $[Co(NH_3)_5ONO]^{2+}$. Less stable cyanometallate coordination networks like those in the red $K\{Fe^{II}[Cr^{III}(CN)_6]\}$ transform into the more stable green $K\{Fe^{II}[Cr^{III}(NC)_6]\}$ form on heating, as shown in Figure 9.4.7.[3]

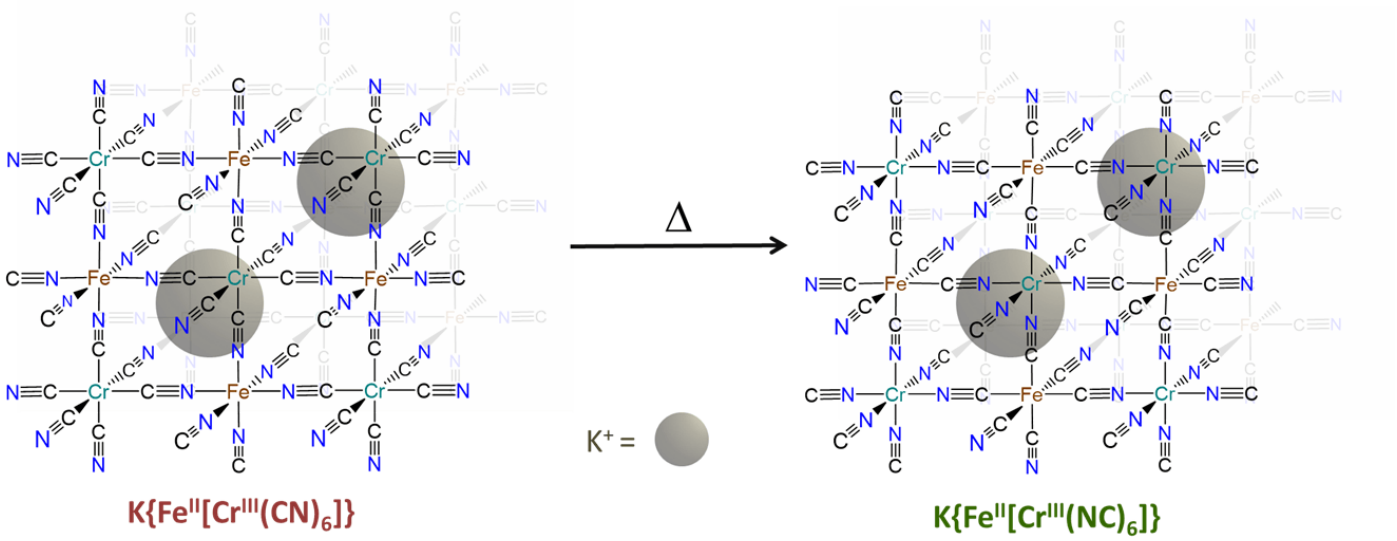


Figure 9.4.7. Thermally-induced transformation of one $K\{Fe^{II}[Cr^{III}(CN)_6]\}$ into its more stable green linkage isomer $K\{Fe^{II}[Cr^{III}(NC)_6]\}$ involves "flipping" the cyano ligands. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Exercise 9.4.1: Bridging ambidentate ligands and the Hard-Soft Acid- Base Principle.

The hard-soft acid-base principle helps explain the preference of bridging ambidentate ligands for particular binding modes. How might the greater stability of the green $K\{Fe^{II}[Cr^{III}(NC)_6]\}$ over red $K\{Fe^{II}[Cr^{III}(CN)_6]\}$ be explained in terms of the hard and soft acid-base concept?

Answer available at the end of this section.

Stereoisomerism

Optical Isomerism/Chirality

Molecules of D_n, C_n, or C_1 symmetry with only proper rotation axes (including $E = C_1$) are chiral and exhibit optical isomerism. As described in Figure 9.4.1, the main sources of such optical isomerism in coordination chemistry are:

1. **Chirality inherent to an organic or main group ligand.**

   This type of isomerism is just an extension of the sort described in undergraduate organic texts and consequently does not merit separate discussion here, other than to note that some forms of optical isomerism which are of little importance in organic chemistry lead to optical activity in coordination compounds. In particular, the nitrogen inversion process which serves to rapidly racemize chiral amines is frozen out on formation of a metal-ligand bond. Because of this chiral amine, ligands bound to a metal form non-interconvertible *R* and *S* enantiomers, as shown in Figure 9.4.8.

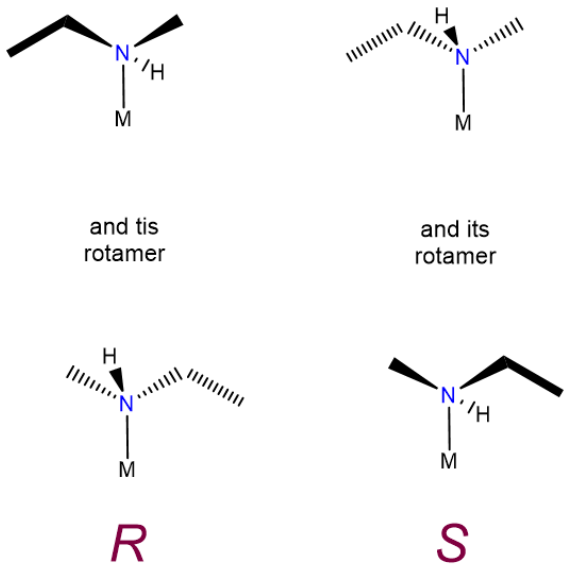


Figure 9.4.8. Two views of *R* and *S* enantiomers formed when the chiral amine ethylmethylamine binds a metal that are commonly used to represent chiral amines in complexes. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

2. Chirality arising from the symmetry of ligands about a metal center.

The two common situations through which such chirality arises involve:

i. Chirality at a tetrahedral metal center surrounded by four different ligand attachment points.

Such cases are often referred to as MABCD or Mabcd where M stands for the metal and a, b, c, and d the four different ligand attachment points. An example of such a complex is given in Figure 9.4.9A. The chirality of such complexes is analogous to the chirality arising from a tetrahedral carbon stereocenter. There are two caveats, though. First, it is not enough to have a four-coordinate complex; the metal must possess tetrahedral symmetry since, as shown in Figure 9.4.9B, square planar M complexes with four different ligands are identical to their mirror images. Second, such chirality is most easily realized using macrocyclic ligands like proteins. Metal ligand bonds involving sterically unhindered monodentate complexes like that in the example of Figure 9.4.9A are in general weaker and more flexible than analogous carbon-carbon bonds. Consequently, in such cases it is likely that the enantiomers would interconvert through a fluxional process, making their resolution difficult if not impossible.

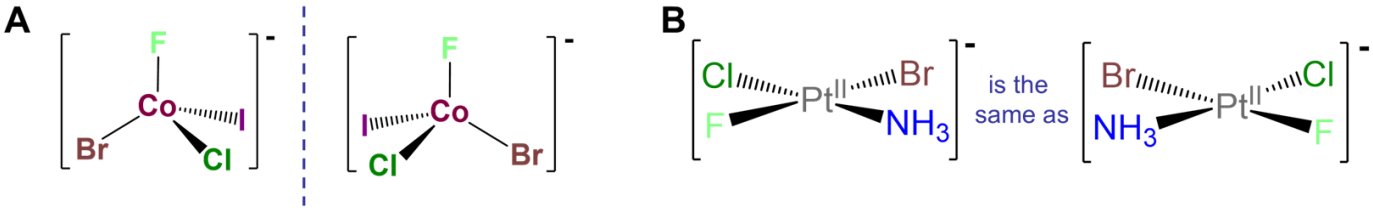


Figure 9.4.9. (A) In principle tetrahedral metal centers surrounded by four different ligands (Mabcd) exhibit chirality analogous to the chirality of tetrahedral carbon stereocenters; (B) in contrast, square planar Macbd complexes like $[PtBrClF(NH_3)]^-$ are not chiral since they are the same as their mirror images. (It is easiest to see this by either working out its point group (C_s) or by rotating the left $[PtBrClF(NH_3)]^-$ structure clockwise 180 degrees to give its mirror image. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

ii. Λ and Δ isomerism at octahedral metal centers surrounded by two or three chelating ligands.

Specifically,

a. Octahedral tris-chelates of formula $M(L\sim L)_3$ exhibit D_3 symmetry.

b. cis-octahedral bis-chelates of formula $M(L\sim L)_2XY$ exhibit C_2 or C_1 symmetry: C_2 if X = Y and C_1 if $X \neq Y$.

As shown in Figure 9.4.10A, octahedral tris-chelates like $[V(ox)_3]^{3-}$ are chiral and can exist as nonsuperimposable Λ and Δ enantiomers. The chirality of these tris-chelates is analogous to that of pinwheels. As shown in Figure 9.4.10B, when looking directly at the head of any individual pinwheel from above, the blades will be angled from back to front going around the pinwheel in either the clockwise or counterclockwise direction. As shown in Figure 9.4.10C, the case for which the blades are angled in the clockwise direction is analogous to the Λ enantiomer and the case when they are angled in the counterclockwise direction the Δ.

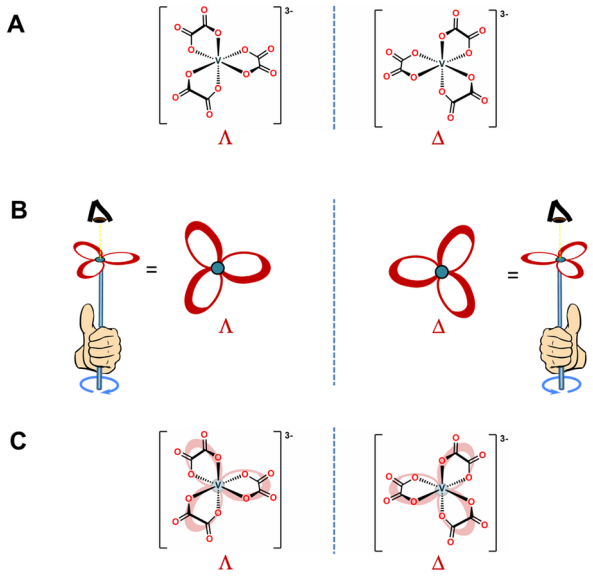


Figure 9.4.10. (A) Octahedral tris-chelates like $[V(ox)_3]^{3-}$ are chiral and can exist as Λ and Δ enantiomers. (B) The chirality in these systems is analogous to that of a pinwheel, with the Λ enantiomer exhibiting the symmetry of a left-handed pinwheel and the Δ enantiomer that of a right handed one. (C) The pinwheel-like nature of Λ and Δ enantiomers is easiest to see by overlaying the structures of $[V(ox)_3]^{3-}$ from A with the pinwheel structures of B. One way to recognize Λ and Δ enantiomers is to draw them in these projections. If a left hand is curled around the Λ enantiomer with the thumb facing up the curl of the fingers will flow from the back of each ligand towards the front. The same will be true if the right hand is curled around the Δ enantiomer. Credits: Although the image is largely an original drawing, the hand images used in part B are adapted from an image by SVGguru / CC BY-SA (https://creativecommons.org/licenses/by-sa/4.0). Otherwise this work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

The Λ and Δ chirality in octahedral bis-chelates is analogous to that in the tris-chelates except this time the third chelating ligand is replaced by an arbitrary pair of ligands. This lowers the symmetry of the complex to either C_2 or C_1, as shown for the C_2 complex $[CoCl_2(en)_2]^+$ in Figure 9.4.11A. In either case the result is that such complexes exist as Λ and Δ enantiomers analogous to those in the metal tris-chelates, as shown in Figure 9.4.11B.

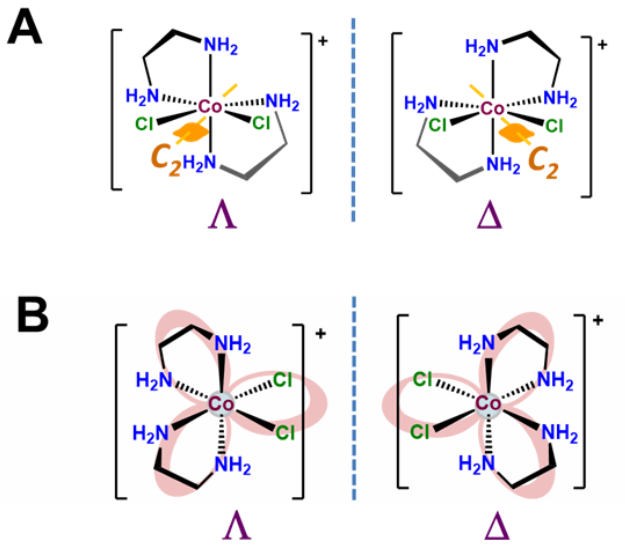


Figure 9.4.9C. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Octahedral complexes containing ligands with denticities of four or more also exhibit Λ and Δ chirality; it is just that in such cases the bound ligand defines multiple rings within the complex that can be defined as existing in either Λ or Δ orientations relative to each other. The procedure for making these assignments is beyond the scope of most introductory inorganic courses but the result is that such complexes are designated as ΛΛ, ΔΔ, ΔΛ, ΔΔΔ, etc., depending on the number of relationships involving the rings defined by the bound ligand. Interested readers should consult reference 4 for more details.

Circular dichroism may be used to characterize optically active metal complexes.

At the present the most definitive way to determine the absolute configuration of an optically active coordination compound is to determine its 3D molecular structure using single crystal X-ray crystallography.[5] However, as that is not always possible or convenient, the optical activity of coordination complexes is also commonly studied using circular dichroism (CD) spectroscopy. CD spectroscopy is used because, unlike most chiral organics, optically active coordination complexes possess low-energy electronic transitions that occur in the far UV and visible range. This means that it is often convenient to use the ability of a complex to refract and absorb different circular polarizations of light to derive information about both the configuration of an optically active complex and its electronic structure. The focus of this section will be to explain how the determination of absolute configuration by circular dichroism and optical rotatory dispersion work, as well as the relationship of these techniques to the more ordinary sort of polarimetry used to measure optical rotation in organic systems. Only brief notes will be made about the instrumental and electronic structure applications of these techniques since the electronic spectra of metal complexes will be discussed in Chapter 11: Coordination Chemistry III - Electronic Spectra and the instrumental aspects of CD are well-treated elsewhere.

Both polarimetry and circular dichroism spectroscopy are grounded in the recognition that plane polarized light is equivalent to a superposition of left and right circularly polarized light, as shown in Figure 9.4.12.

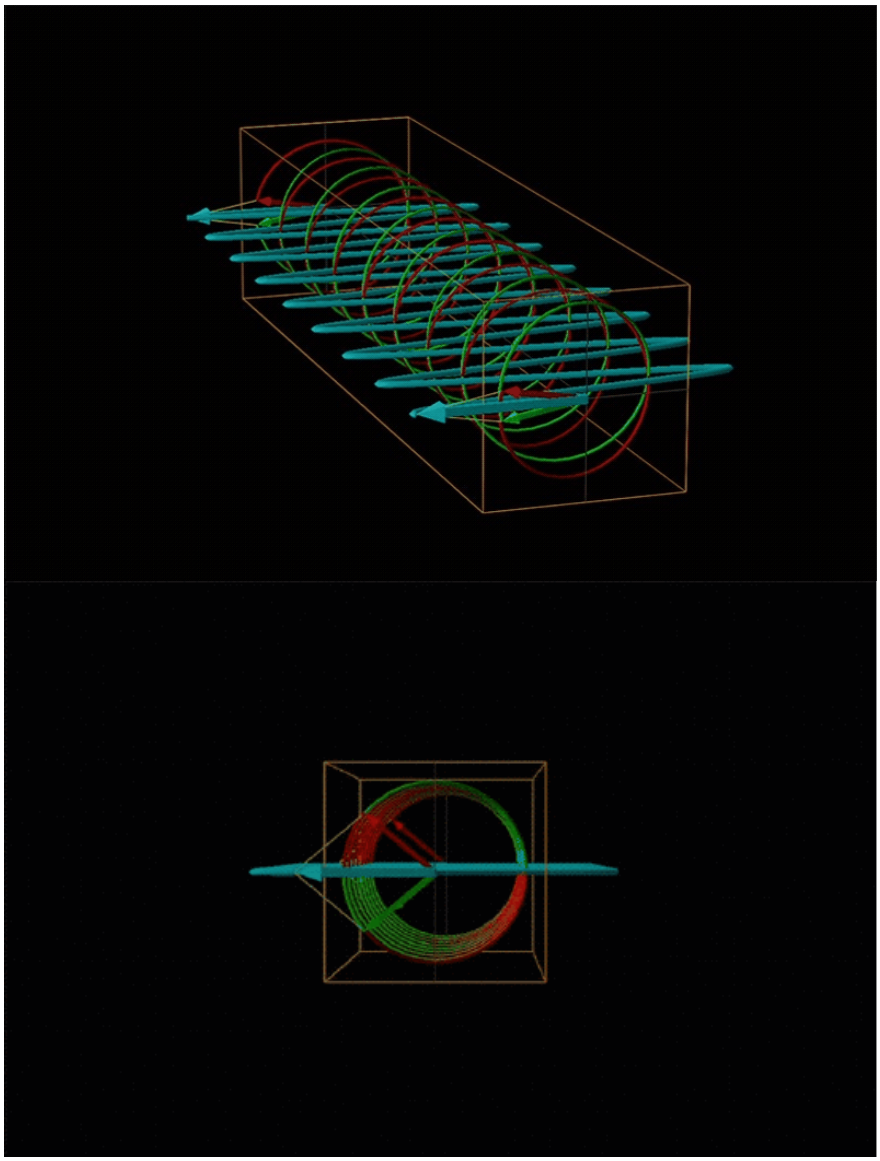


Figure 9.4.12. Angled and front view of plane polarized light (light blue) as the vector sum of left circularly polarized light (red) and right circularly polarized light (green). Created using EMANIM Version 1.2 (2011 July) by Andras Szilagyi (www.enzim.hu/~szia/emanim). This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

When plane polarized light passes through a chiral medium, its left and right circularly polarized components move at different rates (*i.e.,* have different indices of refraction). This causes the plane of polarization to rotate in the direction of the faster component according to the relationship

$$\alpha = \frac{n_l - n_r}{\lambda}$$

where α is the angle of rotation, λ the light's wavelength, and n_l and n_r the refractive indices experienced by left and right circularly polarized light.

An example of such a rotation is shown in Figure 9.4.13.

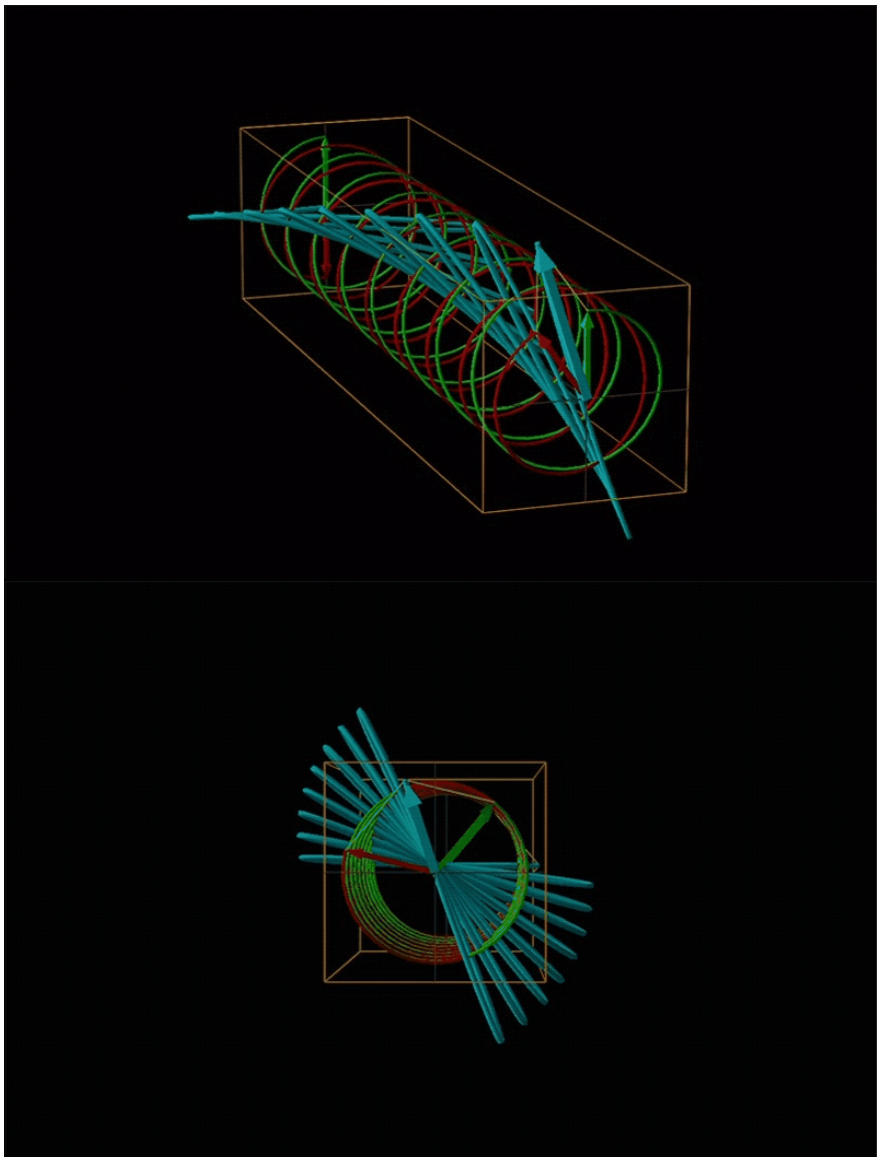


Figure 9.4.13. Angled and front view of plane polarized light (light blue) as it passes through a medium (represented by the orange box) in which left circularly polarized light (red) experiences a higher refractive index (and so moves slower) than right circularly polarized light (green). Created using EMANIM Version 1.2 (2011 July) by Andras Szilagyi (www.enzim.hu/~szia/emanim) with a refractive index of 1.05 for left circularly polarized light and 1.00 for right circularly polarized light. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Chemists typically call this rotation of light by a chiral medium optical rotation. In organic chemistry it is common to measure the optical rotation at the sodium D wavelength of 589.29 nm, a much longer wavelength than most organics are able to absorb. Because of this the optical rotations commonly measured by organic chemists are largely independent of absorption and mainly serve as a characteristic physical property similar to melting points or are used to establish the purity of a mixture of enantiomers. The sort of spectroscopic data used to characterize chiral coordination compounds more commonly makes use of the relationship between absorption and optical rotation.

In coordination chemistry the wavelength-dependence of optical rotation is used to discern information about compounds' electronic spectra. This measurement of the wavelength dependence of optical rotation is called **optical rotatory dispersion (ORD)** and the resulting plots are called optical rotatory dispersion or ORD spectra or curves. Such ORD curves are useful for characterizing the chiral environment in a coordination complex because the ORD curves exhibit a characteristic shape. This characteristic shape is because according to the **Cotton Effect,** the optical rotation changes sign at the absorption maximum of a chromophore in the compound. For one configuration the rotation will go from negative to positive with increasing wavelength and is called a **positive cotton effect**; for the other configuration the rotation will go from positive to negative or exhibit a **negative cotton effect**. This behavior is summarized in the top two curves of Figure 9.4.14.

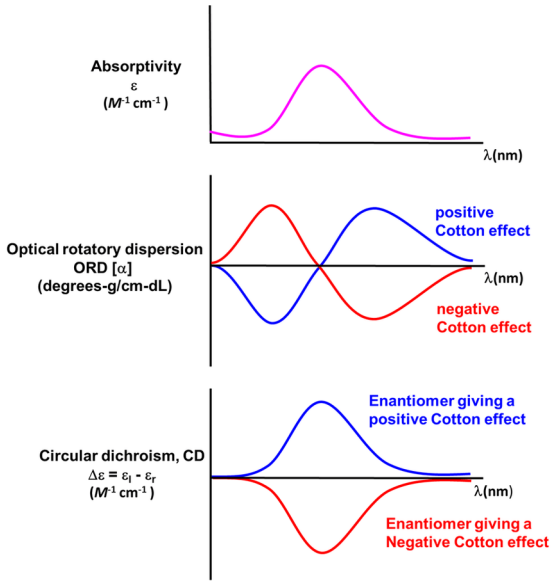


Figure 9.4.14. Idealized relationship between absorbance, ORD, and CD spectra for enantiomers exhibiting a positive and negative Cotton effect. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

A technique used even more often than ORD is **circular dichroism (CD)**, represented by the lowest spectrum in Figure 9.4.14 . Circular dichroism arises from the differential absorption of left and right circularly polarized light by a chiral compound. This gives elliptically polarized light as shown in Figure 9.4.15.

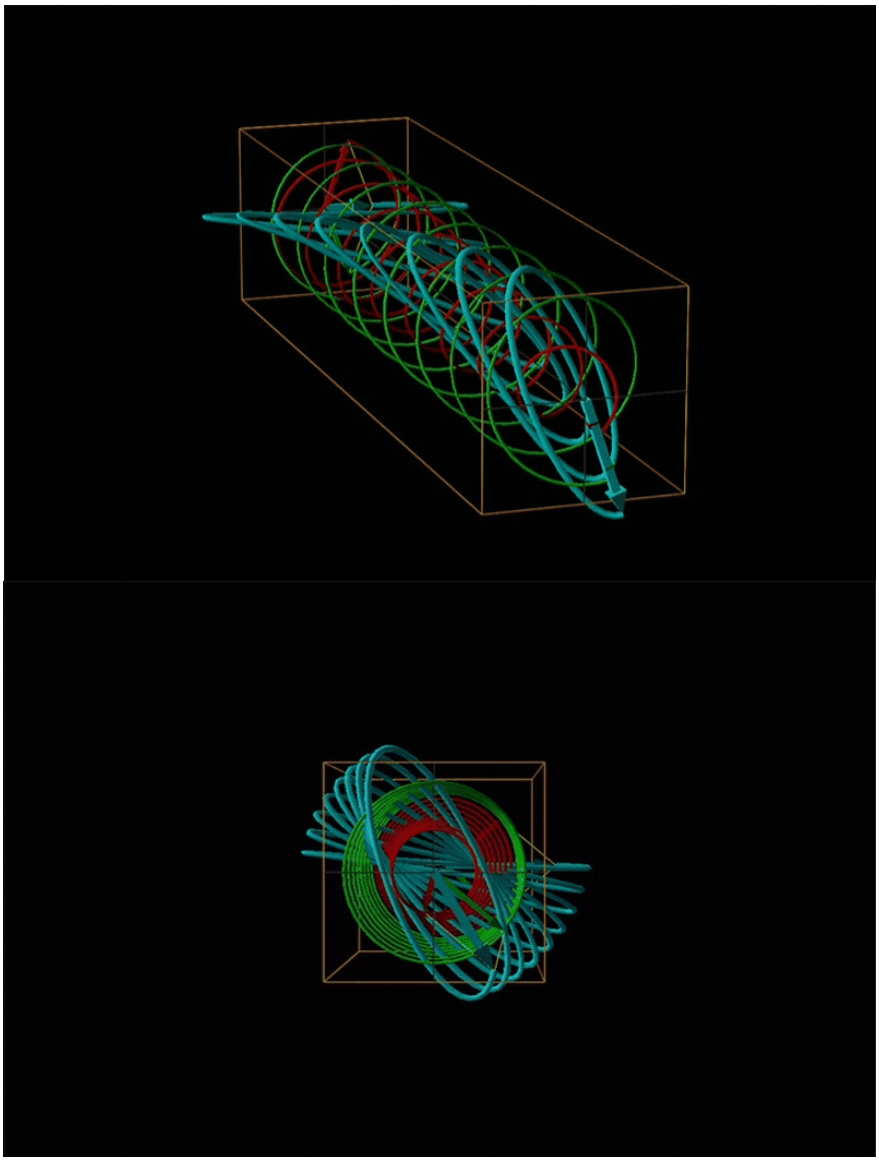


Figure 9.4.15. Angled and front view of plane polarized light (light blue) as it passes through a medium (represented by the orange box) in which left circularly polarized light (red) both experiences a higher refractive index and greater absorption than right circularly polarized light (green). Created using EMANIM Version 1.2 (2011 July) by Andras Szilagyi (www.enzim.hu/~szia/emanim) with a refractive index of 1.05 and an extinction coefficient of 0.05 for left circularly polarized light and a refractive index of 1.00 and extinction coefficient of 0 for right circularly polarized light. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

In circular dichroism (CD) spectroscopy a sample is irradiated with polarized light resulting in the transmission of elliptically polarized light due to differential refraction and absorption of the polarized light's left and right circularly polarized components. For achiral molecules the handedness doesn't affect absorbance, but for chiral molecules, which chiral ground and excited states the handedness of an EM wave affects can determine how readily that wave can distort the chiral ground state into the chiral excited one. For this reason chiral molecules absorb left and right circularly polarized light differently.

In CD spectroscopy the magnitudes of the left and right circularly polarized components of light that is transmitted by the sample are measured and used to determine how much light of each was absorbed (just as in regular absorbance spectroscopy). The difference in absorption between left and right circularly polarized light constitutes the primary signal in CD spectroscopy. More specifically, circular dichroism spectra (CD spectra) show the difference in extinction coefficients for left and right circularly polarized light, $\Delta\epsilon$, as a function of wavelength, where

$$\Delta\epsilon = \epsilon_l - \epsilon_r$$

where Missing open brace for subscript and Missing open brace for subscript are the extinction coefficients

observed with left and right circularly polarized light, respectively.

As with ORD spectra, the signs of the features in CD spectra like that of Δ–[Co(en)$_3$]Cl$_3$ given in Figure 9.4.16 are enantiomer-dependent. As illustrated in the lower spectrum in Figure 9.4.14 , the CD spectra of enantiomers mirror one another. Because of this difference in behavior it is possible in principle to determine the absolute configuration of a complex from its CD spectrum.

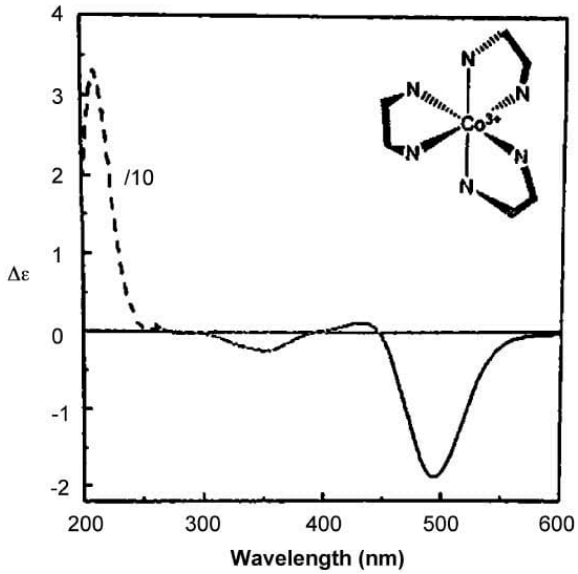


Figure 9.4.16. CD spectrum of Δ–[Co(en)$_3$]Cl$_3$. Taken from reference 6.

There are several ways that ORD and CD spectra can be useful for determining the absolute configuration of a chiral complex.

1. First, the sign of the Cotton effect and peaks in CD spectra exhibited by a given absolute configuration is often consistent across a series of compounds. Thus if a new member of the series is isolated, its configuration can be determined based on which enantiomer has the same Cotton effect. For instance, if both the Λ isomer of a metal diimine complex like [Ru(bpy)$_3$]$^{2+}$ exhibit a positive Cotton effect and a newly resolved metal diimine exhibits a negative Cotton effect it might reasonably be inferred that the newly-resolved complex is in the opposite or Δ configuration.
2. Second, for some systems the expected sign of the Cotton effect and CD peaks for each enantiomer may be predicted semi-empirically based on the spatial locations of substituents relative to the chromophore (the part of the molecule that changes electronic structure during the transition), although the details are beyond the scope of the present discussion.
3. Consideration of interactions between multiple chromophores in a compound can be used to infer absolute configuration. Again, the details are beyond the scope of the present discussion. Interested readers are referred to reference 7 for details.

Common patterns of Diastereomerism

Geometric isomerism

Geometric isomerism involves differences in the geometric placement of atoms in a compound. In coordination chemistry, geometric isomerism involves differences in the relative placement of a set of ligands about a metal center. There are two main types:

cis and *trans* isomerism

This type of isomerism has to do with how two ligands are oriented relative to one another in a square planar or octahedral complex. As shown in Figure 9.4.17, ligands that are next to one another with a L-M-L bond angle of 90° are said to be *cis*; those on opposite sides of the metal with a L-M-L bond angle of 180° are in the *trans* arrangement.

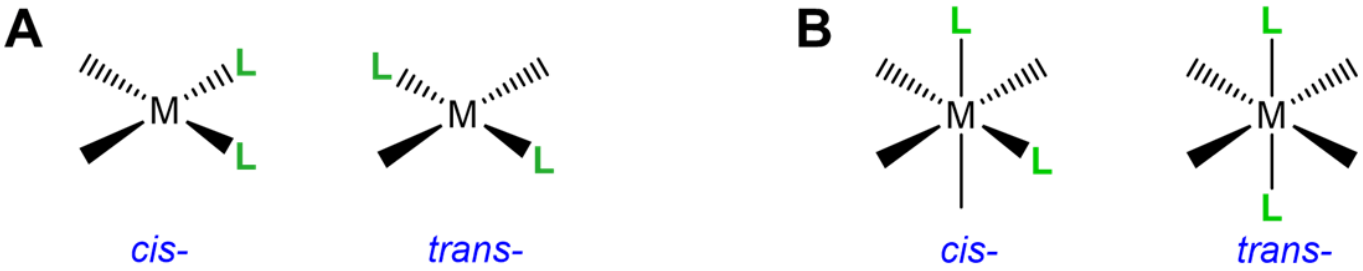


Figure 9.4.17. *cis* and *trans* arrangement of ligands around (A) square planar and (B) octahedral metal centers. Since both types of complexes feature 90° L-M-L bond angles, the arrangements are fundamentally the same in both cases. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Simple *cis* and *trans* geometric isomers can be identified when there are two identical ligands (A) or chelating ligands with distinguishable attachment points (A~B) oriented about either a square planar or octahedral center. Examples are given in Figure 9.4.18. Notice from the example given in Figure 9.4.18C that multidentate ligands have the potential to constrain complexes to adopt a particular geometry.

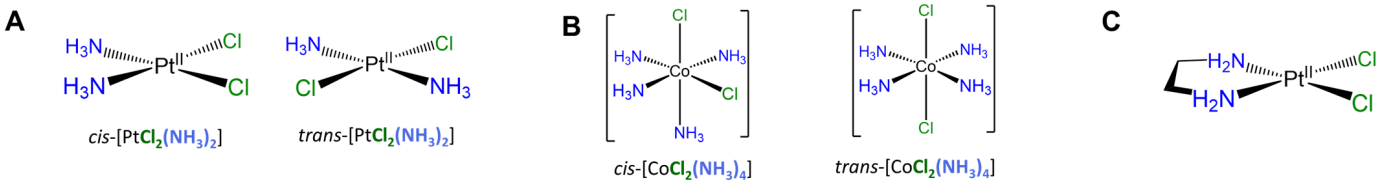


Figure 9.4.18. Examples of square planar and octahedral *cis* and *trans* isomers. (A) *cis* and *trans* isomers of $[PtCl_2(NH_3)_2]$; the former is medicinally important. Sold under the name cisplatin, the *cis* isomer is used as a chemotheraphy against various forms of cancer. (B) *cis* and *trans* isomers of $[CoCl_2(NH_3)_4]$, a compound of more academic interest. (C) $PtCl_2$(en) only exists as the *cis* isomer because the chelating en ligand can only bind in a *cis* arrangement. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Slightly more involved examples involve perturbations of the simple cases above in which there are multiple distinguishable *cis* and/or *trans* relationships. Two square planar examples are given in Figure 9.4.19.

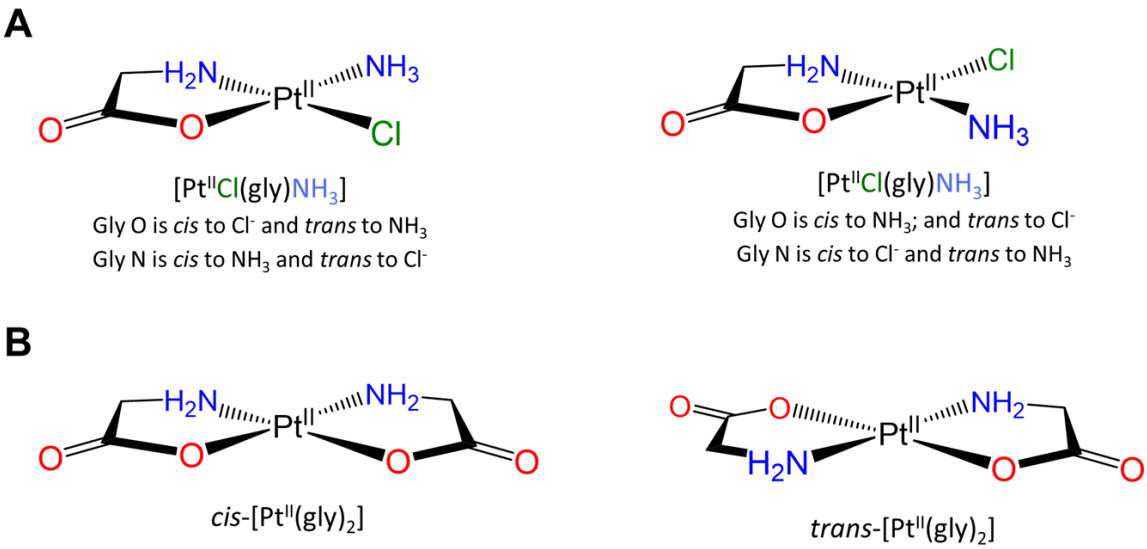


Figure 9.4.19. Examples of more complex square planar systems. (A) Geometric isomers of $[PtCl(gly)NH_3]$, a MA_2BC system for which A = gly^-, B = Cl^-, and C = NH_3. Swapping of the ammine and chloro ligands changes both the *cis* and *trans* relationships involving the Gly ligand. (B) Geometric isomers of $[Pt(gly)_2]$, an $M(A\sim B)_2$ system for which A = the κO glycine carboxy group and B its κN amine. The only possible geometric isomerism involves swapping the orientation of one glycine relative to the other. For this reason the two complexes shown can be designated as *cis* and *trans* isomers based on whether the κO and κN ends of the glycine are *cis* or *trans* to one another. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

More complex examples of *cis* and *trans* relationships between ligands in octahedral complexes are given in the exercises that conclude this page, which also demonstrates how a systematic approach may be used to identify isomers.

mer and *fac* isomerism

This type of isomerism has to do with how three ligands are oriented relative to one another in an octahedral complex. The arrangements are represented in Figure 9.4.20.

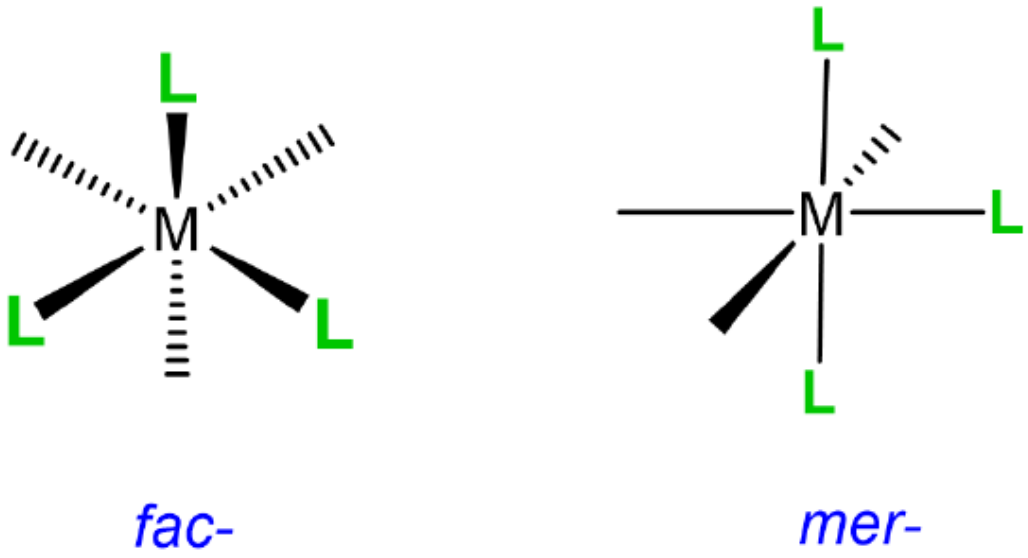


Figure 9.4.20. Simple representation of the *fac* and *mer* arrangements of ligands around an octahedral metal center. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Since it can help to visualize the *mer* and *fac* geometry from multiple points of view, several representations are given in Figure 9.4.21. As shown in Figure 9.4.21, in ***fac*** or **facial arrangements**, the ligands occupy the same "face" of the octahedral coordination sphere, while in the ***mer*** or **meridional geometry** the ligands form a T shape in the same plane or its "meridian."[8]

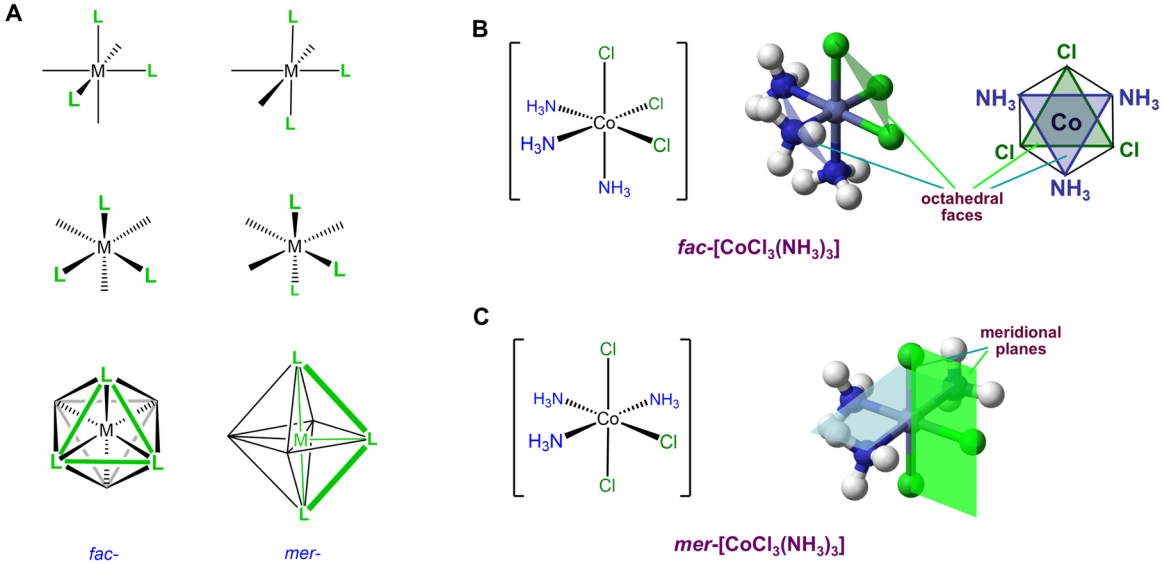
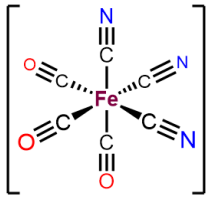
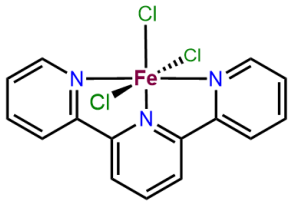


Figure 9.4.21. (A) Three projections of *fac* and *mer* arrangements of ligands around an octahedral metal center emphasizing that in the *fac* arrangement the ligands are oriented along a face of the octahedron while in the *mer* arrangement they are oriented in a plane. (B) Structure of *fac*-$[CoCl_3(NH_3)_3]$ showing the octahedral faces occupied by the chloro and amine ligands. (C) Structure of *mer*-$[CoCl_3(NH_3)_3]$ showing the planar arrangement of the chloro and ammine ligands. The ball and stick models are modified from images by Benjah-bmm27 - Own work, Public Domain, https://commons.wikimedia.org/w/inde...?curid=1874872 and curid=1874873. Otherwise this work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

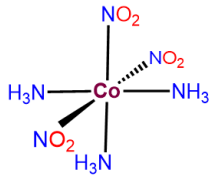
Octahedral complexes with three identical ligands oriented about an octahedral center can only exist in *mer* and *fac* arrangements. Consequently, such complexes can be designated as *mer* and *fac* isomers. Examples are given in Figure 9.4.22.



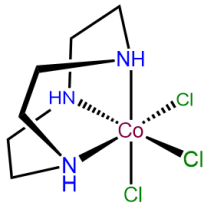
fac-$[Fe(CN)_3(CO)_3]^-$



mer-$[FeCl_3tpy]$



mer-$[Co(NH_3)(NO_2)_3]$



fac-$[FeCl_3(tacn)]$

Figure 9.4.22. Examples of *fac* and *mer* octahedral complexes. Note how some chelating ligands preferentially bind to the metal in a *fac* or *mer* arrangement and, in so doing, force the other ligands to also form a *mer* or *fac* arrangement. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Diastereomerism arising from multiple ligand-associated chiral centers

Diastereomerism can also arise when two or more chiral ligands bind to a metal center. Such cases typically give rise to a complex mixture of isomers, as shown by the example in Figure 9.4.23. As may be seen from Figure 9.4.23, the differences between these isomers can arise from both changes in the stereochemical configuration of the ligand and the relationship of particular ligand centers relative to one another. For instance, the leftmost two structures in Figure 9.4.23 possess one *R* and *S* nitrogen center each but differ in whether the centers are oriented so that the *R* and *S* centers on the two ligands are *trans* or *cis* to one another.

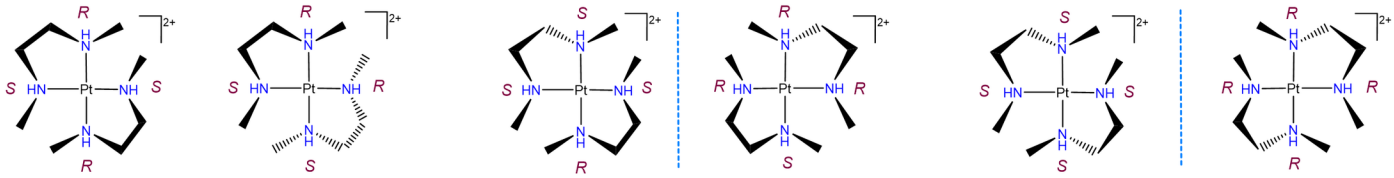


Figure 9.4.23. Diastereomers that can in principle be formed when two *N,N'*-dimethylethylenediamine ligands coordinate a Pt^{2+} center. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Diastereomerism arising from λ and δ ring conformation isomerism.

Chelate rings are formed when a chelating ligand binds a metal

As may also be seen from the structures in Figure 9.4.23, when a multidentate ligand coordinates a metal, the ligand and metal center comprise one or more **chelate rings**. Examples of such chelate rings are shown in Figure 9.4.24.

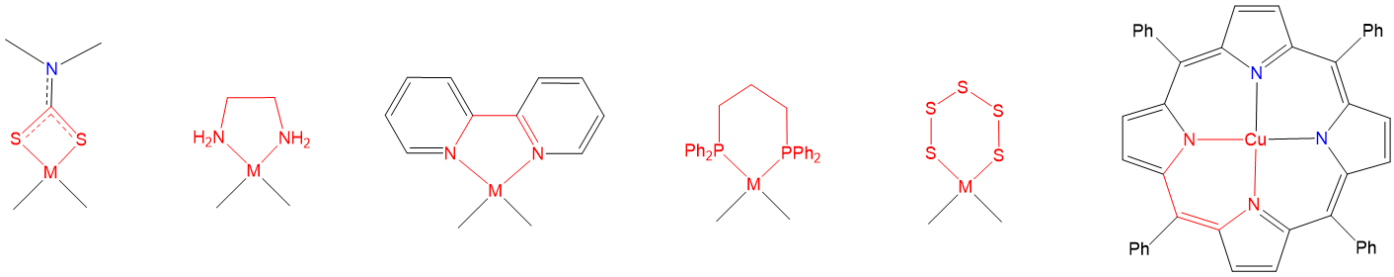


Figure 9.4.24. Four, five, and six-membered chelate rings (shown in red) formed by coordination of selected bidentate ligands to a metal center. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

As may be inferred from the examples in Figure 9.4.24, chelate rings may be of different sizes, although four, six, and especially five-membered rings are particularly common. Exactly which ring sizes will be more stable for a given system depends on the coordination geometry and, due to differences in M-L bond lengths, to a lesser degree on the metal. As a result, for octahedral and square planar complexes with 90° L-M-L bond angles between *cis* ligands, *five-membered rings tend to be especially stable* (Figure 9.4.25).

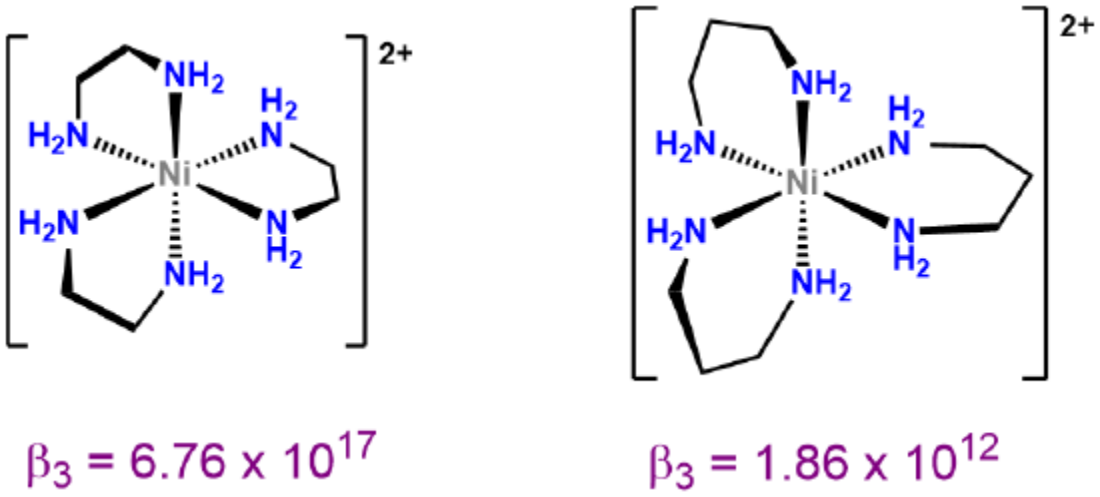


Figure 9.4.25. The greater stability of five-membered chelate rings involving Ni^{2+} and organic ligands is reflected in the higher overall formation constant (β_3) for the five-membered chelate rings contained in $[Ni(en)_3]^{2+}$ compared to that of $[Ni(et)_3]^{2+}$, which has six-membered rings. The data in this figure is taken from Stability of Metal Complexes and Chelation by Robert Lancashire. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Not all metal chelates prefer to form five-membered rings. The steric requirements of chelate rings depend on both the preferred coordination geometry of the metal center and the stereochemistry of the ligand. Both of these effects are typically considered in terms of preferred L-M-L bond angles. From the perspective of the metal center, the preferred bond angle is determined by the coordination geometry. Octahedral and square planar metals prefer 90° L-M-L bond amgles, trigonal bipyramidal systems 90 and 120° L-M-L bond angles, and tetrahedral complexes 109.5° L-M-L angles. The larger preferred bond angles in tetrahedral and trigonal bipyramidal systems often require the formation of larger six or seven-membered chelate rings for maximum stability. The size of the chelate ring actually formed between a metal and ligand is determined by the ligand's structure. As the contributor of all the atoms in the chelate ring but one, the ligand directly determines the chelate ring size. More subtly, ligands naturally prefer to coordinate metals at a particular L-M-L angle, called the **bite angle**, as shown in Figure 9.4.26A. Ligands with bite angles corresponding to the ideal L-M-L angle for a metal's preferred geometry tend to form more stable complexes, although in turn ligand bite angles can cause metals with a weak coordination geometry preference to adopt the ligand's preferred geometry instead.[10] As may be seen from the values in Figure 9.4.26B, bite angles roughly increase with the size of the chelate ring formed but are also influenced by the types of structures used to connect the ligand's Lewis base sites. This facilitates the use of diphosphine ligands to tailor the structure and reactivity of phosphine-containing organometallic catalysts.

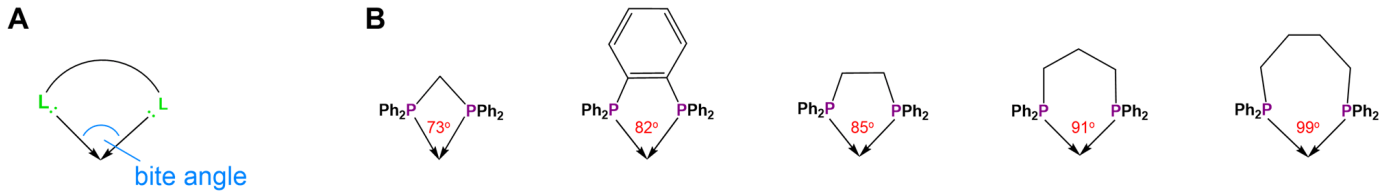


Figure 9.4.26. (A) Definition of the bite angle as the angle at which the ligand's preferred L-M-L angle when coordinating a metal center. (B) Bite angles of selected diphosphines.[9] The bite angles of many such diphosphines have been determined to facilitate the design of phosphine-containing organometallic catalysts. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

λ and δ isomerism involves differences in the conformation of nonplanar five-membered chelate rings

As shown in Figure 9.4.27, some chelate ring systems are planar while others are not.

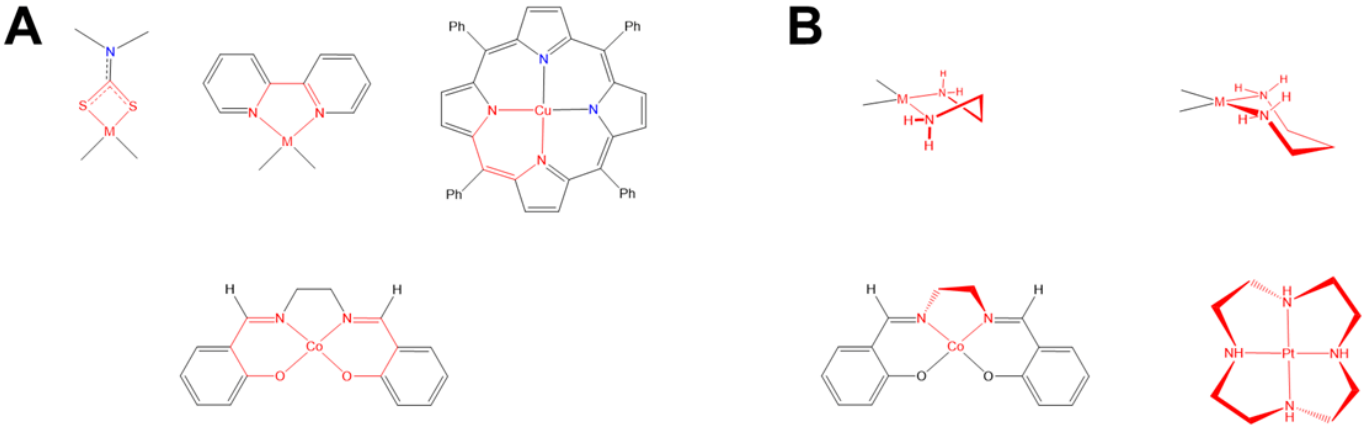


Figure 9.4.27. (A) Planar and (B) Nonplanar chelate rings shown highlighted in red. Notice how [Co(salen)] possesses a nonplanar chelate ring and two planar ones. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Among the nonplanar chelate ring systems are ligands like en and dppe, which contain tetrahedral C, N, O, P, and S atoms. Because these atoms create kinks in the chelate ring they introduce additional opportunities for diastereomerism due to differences in the chelate ring conformation, called **ring twist**. Ring twist in nonplanar systems has been most extensively explored for five-membered chelates like those formed by dppe and by en and other chelating amines. Unlike the more rigid four-membered chelate rings, five-membered chelates tend to be conformationally flexible, but not so conformationally flexible that their conformers are rapidly interconverting at room temperature (at least not when the rings are substituted to introduce additional steric strain). This balance between flexibility and rigidity enables some five-membered chelate rings to exist as mixtures of distinguishable conformational isomers at room temperature.

To understand the two most stable conformers that five-membered chelates rings tend to form, it is helpful to think of five-membered chelate rings as involving two components (Figure 9.4.28):

- a planar L-M-L group, where L are the atoms directly attached to the metal, M, and
- the remaining two ring atoms, E, which form a rigid E-E bar across the back of the chelate ring.

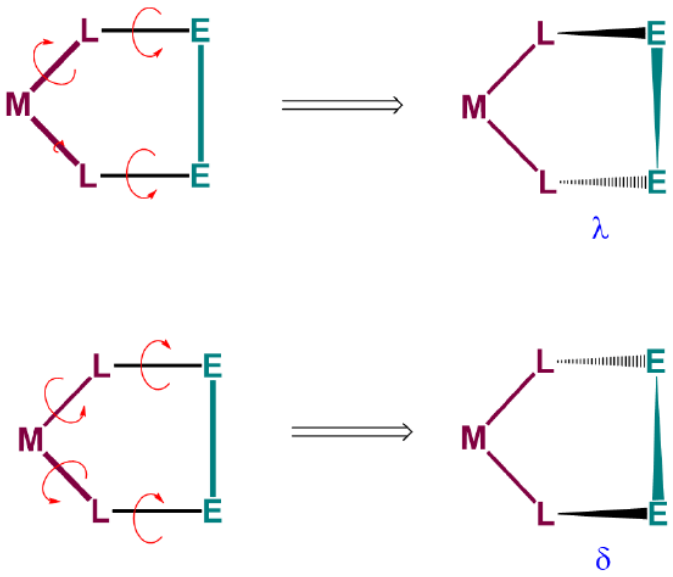


Figure 9.4.28. Five-membered chelate rings consist of a planar L-M-L group connected to a rigid E-E bar. Conformers arise as rotation about the M-L and L-E bonds causes twisting of the E-E bar relative to the L-M-L plane. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

As can be seen from Figure 9.4.28 , rotation about the M-L and L-E bonds causes twisting of the E-E bar relative to the L-M-L plane. The two most stable conformers produced by these motions are the λ or δ conformations as shown in Figures 9.4.29 and 9.4.29.

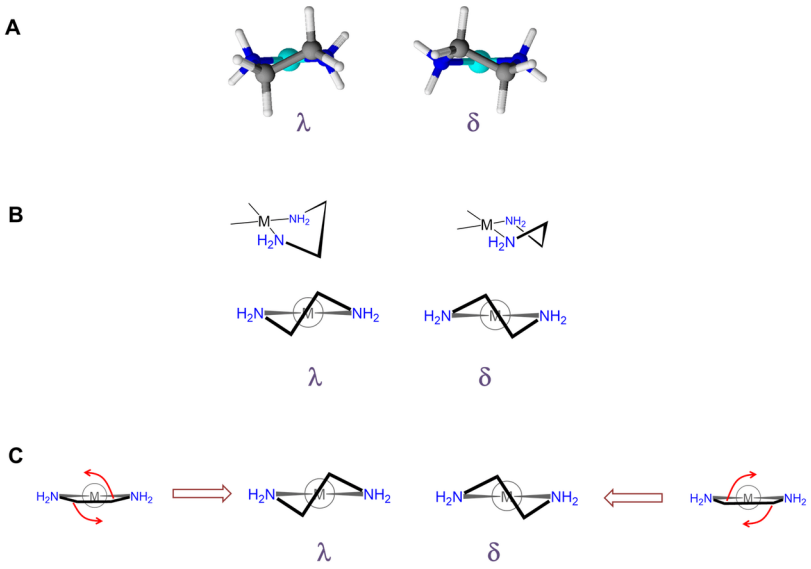


Figure 9.4.29. (A) λ and δ ring twist in a square planar metal ethylenediamine complex (B) along with several ways to represent it in line drawing form. (C) Of these, the projection looking down an axis bisecting the chelate ring makes it easiest to see that, starting with a planar chelate ring the λ conformer corresponds to a counterclockwise twist of the CH_2CH_2 bond relative to the N-M-N plane and the δ conformer a clockwise twist relative to the N-M-N plane. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

The relative stability of the λ and δ conformers will depend on the configuration of any stereocenters present and steric factors. As with organic ring systems, steric effects tend to favor conformers in which bulky groups are placed in the less sterically strained equatorial positions while the configuration of the stereocenters present can serve to restrict the allowable ring twist conformations, as illustrated in Figure 9.4.30. A detailed treatment of such systems is beyond the scope of this page. Interested readers are referred to reference 12 for more details.

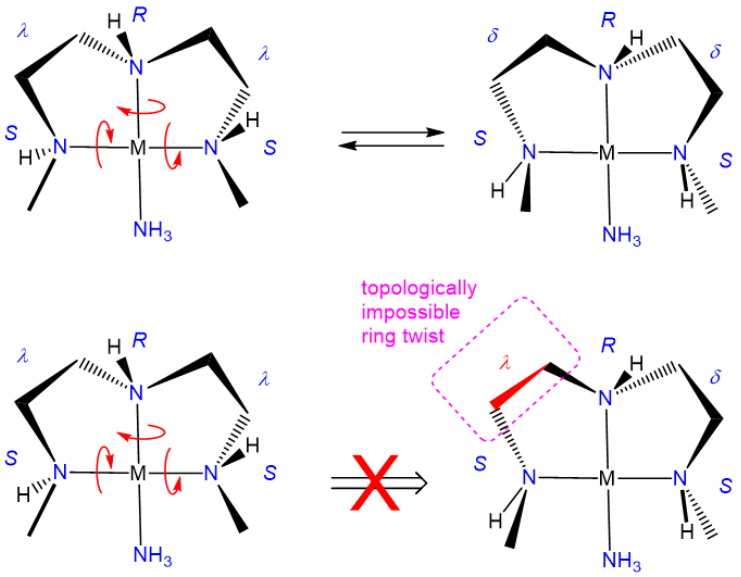


Figure 9.4.30. The configurations at nitrogen in the complex shown restrict the chelate ring conformations to either a $\lambda\lambda$ or $\delta\delta$ conformation because the rotations needed to enable a $\lambda\delta$ configuration are topologically impossible. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

In closing, it should be noted that it might seem to be making much of small effects in pointing out that one source of diastereomerism in metal complexes involves the freezing out of chelate ring conformations. However, that would be to mistake the impacts that ring conformations can have on the steric accessibility of a coordination site and shaping the course of processes that might occur there. As illustrated in Figure 9.4.31, a simple shift in the conformation of one ring in a square planar, pyramidal, or octahedral complex containing coplanar ethylene diamine ligands can exert a significant effect on the steric profile of the complex perpendicular to the MN_4 square plane. Because of effects like these, ring conformation isomerism plays a role in the design of stereoselective transition metal catalysts.

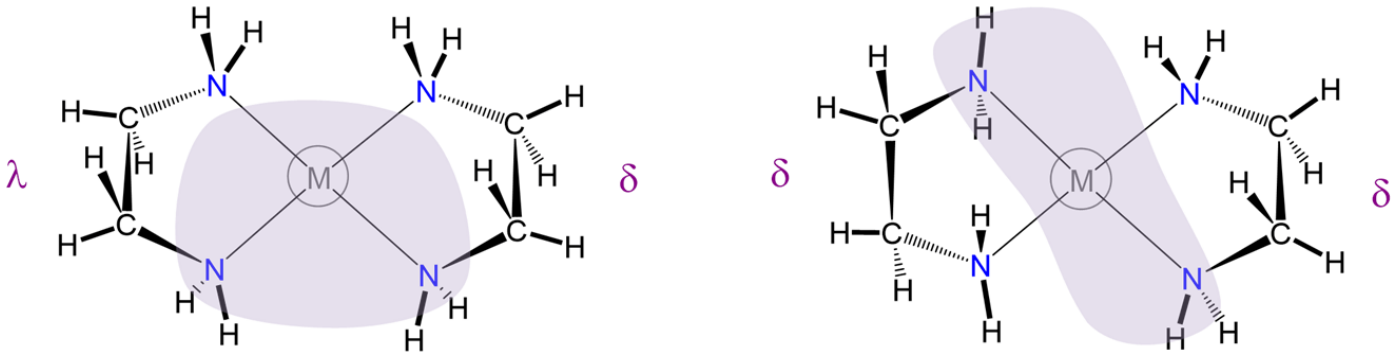


Figure 9.4.31. Schematic illustrating how the conformation of ethlyenediamine ligands bound to a metal center affects the steric accessibility of the metal (shown shaded in violet) to potential ligands attempting to bind from above the MN_4 plane. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Exercises

Exercise 9.4.1. Identify the type of isomerism

What type of isomers are

a. $[CoCl(NH_3)_5](NO_3)$ and $[Co(NH_3)_5(N\text{-}NO_2)]Cl$?
b. $[Co(NH_3)_5\text{-}CN\text{-}Ru(NH_3)_5]^{4+}$ and $[Co(NH_3)_5\text{-}NC\text{-}Ru(NH_3)_5]^{4+}$
c. $[Cr(CN)_5\text{-}CN\text{-}Co(NH_3)_5]$ and $[Co(CN)_5\text{-}CN\text{-}Cr(NH_3)_5]$

d. *cis*-[Mn(en)$_2$(CN)$_2$] and *trans*-[Mn(en)$_2$(CN)$_2$]

Answer a. available at the end of this section.

Exercise 9.4.2. Assigning metal oxidation states in a complex

Many properties of transition metal complexes depend on the metal's oxidation state. For instance,

- octahedral complexes of Co^{II} lose and gain ligands rapidly
- octahedral complexes of Co^{III} lose and gain ligands very slowly
- four-coordinate complexes are generally tetrahedral
- EXCEPT four-coordinate complexes of metals like Pt^{II} , Pd^{II} , Rh^{I}, and Ir^{I}, among others, are square planar

For this reason it is important to be able to estimate the formal oxidation state of a metal in a complex. Fortunately, this is easy to do if you remember

1. The sum of all atoms' oxidation states will equal the overall charge on the complex
2. When determining the metal's oxidation state, the ligands can be treated as having an oxidation state equal to their charge - *i.e.,* the charge they possess in the form in which they coordinate the metal - so if they need to lose a proton to bind, don't forget to account for that.

Given the above, estimate the oxidation state of the metal in the following real and hypothetical complexes.

a. $Na_4[Fe(CN)_6]$
b. $[Cu(phen)_2]BF_4$
c. $[PtF_4(NH_3)_2]$
d. $[Ni(en)_2]SO_4$
e. $Co(acac)_3$
f. [MnCl(O)(salen)]

Answer available at the end of this section.

Exercise 9.4.3. Drawing isomers from descriptions

Draw structures that match the descriptions given, assuming that

- complexes in which the metal has a coordination number of six are octahedral
- complexes in which the metal has a coordination number of five are trigonal bipyramidal
- complexes in which Pt^{II} , Pd^{II} , or Rh^{I}, or Ir^{I} have a coordination number of four are square planar
- other complexes in which the metal has a coordination number of four will be tetrahedral

a. *mer*-triammineaqua-*trans*-dichlorocobalt(III) ion
b. Δ-diaminebis(oxalato)manganate(III)
c. $[CoCl_4]^{2-}$
d. *trans*-diamminebis(ethylenediamine)Nickel(2+) tetracyanopalladate(2-)
e. Λ-bis(ethylenediamine)cobalt(III)- μ-amido μ-hydroxo-Δ-bis(ethylenediamine)cobalt(III)

Answer a. mer-triammineaqua-trans-dichlorocobalt(III) ion. available at the end of this section.

Exercise 9.4.4. Stereoisomers of complexes containing only monodentate ligands.

Draw all the stereoisomers of the following real and hypothetical complexes. You may assume that

- complexes in which the metal has a coordination number of six are octahedral
- complexes in which the metal has a coordination number of five are trigonal bipyramidal
- complexes in which Pt^{II} , Pd^{II} , or Rh^{I}, or Ir^{I} have a coordination number of four are square planar
- other complexes in which the metal has a coordination number of four will be tetrahedral

a. $[IrCl(CO)(PPh_3)_2]$
b. $[CoCl_3(NH_3)_3]$
c. $[CoCl_2(H_2O)_2(NH_3)_2]^+$
d. $[CoBrCl(H_2O)_2(NH_3)_2]^+$
e. $[CoBrClI(NH_3)_3]$

Answer a. [IrCl(CO)(PPh3)2] available at the end of this section.

Exercise 9.4.5. Stereoisomers of complexes with bidentate ligands (ignoring ring twist).

Ignoring ring twist, draw all the stereoisomers of the following real and hypothetical octahedral complexes.

a. $[CoBr_2Cl_2(en)]^-$
b. $[CoBrCl(en)_2]^+$
c. $[CoBrCl(gly)_2]^-$
d. $[Co(en)_3]^{3+}$
e. $[Co(gly)_3]$

Answer a. [CoBr2Cl2(en)]- available at the end of this section.

Exercise 9.4.6. More stereoisomers: Now featuring linkage isomerism

Ignoring ring twist, draw all chemically reasonable stereoisomers for the following real and hypothetical complexes. You may assume that

- complexes in which the metal has a coordination number of six are octahedral
- complexes in which the metal has a coordination number of five are trigonal bipyramidal
- complexes in which Pt^{II} , Pd^{II} , or Rh^{I}, or Ir^{I} have a coordination number of four are square planar
- other complexes in which the metal has a coordination number of four will be tetrahedral

a. $[Pt(en)(SCN)_2]$
b. $[Pt(NH_3)_2(SCN)_2]$
c. $[Co(en)_2(SCN)_2]^+$

Answer a. [Pt(en)(SCN)2] available at the end of this section.

Exercise 9.4.7. Stereoisomer free for all.

Ignoring ring twist, draw all chemically reasonable stereoisomers for the following real and hypothetical complexes. You may assume that

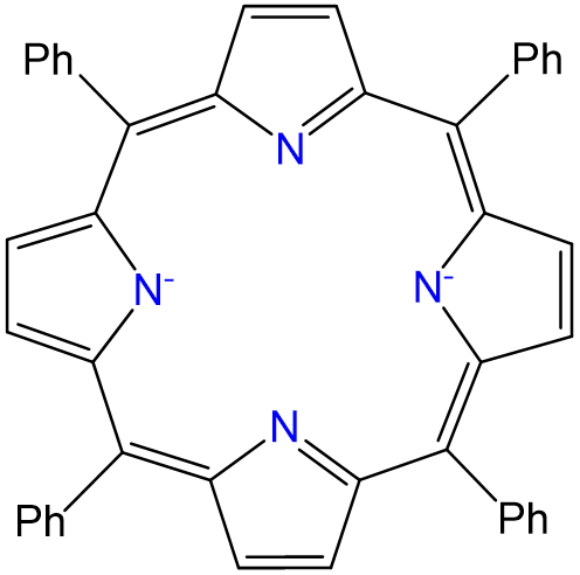
- complexes in which the metal has a coordination number of six are octahedral
- complexes in which the metal has a coordination number of five are trigonal bipyramidal
- complexes in which Pt^{II} , Pd^{II} , or Rh^{I}, or Ir^{I} have a coordination number of four are square planar
- other complexes in which the metal has a coordination number of four will be tetrahedral

a. $[Ru(bpy)(phen)(dppe)]^{2+}$
b. $[CoClF(PPh_3)(py)]^-$
c. $[Ni(en)_2(NO_2)_2]$
d. $[Fe(H_2O)_3(SCN)_3]$
e. $[PtClF(PPh_3)(py)]$
f. $[CoBr_2Cl(NH_3)_3]$

Answer a. [Ru(bpy)(phen)(dppe)]2+ available at the end of this section.

Exercise 9.4.8

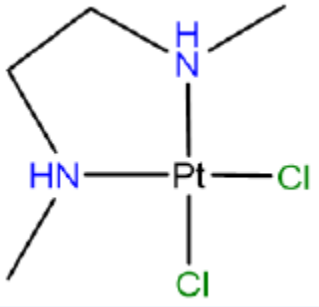
Complexes of formula $Ru(TPP)py_2$ have been prepared, in which TPP is tetraphenylporphyrin, which binds metals in the form given below. Draw all isomers of $Ru(TPP)py_2$.



Answer available at the end of this section.

Exercise 9.4.9

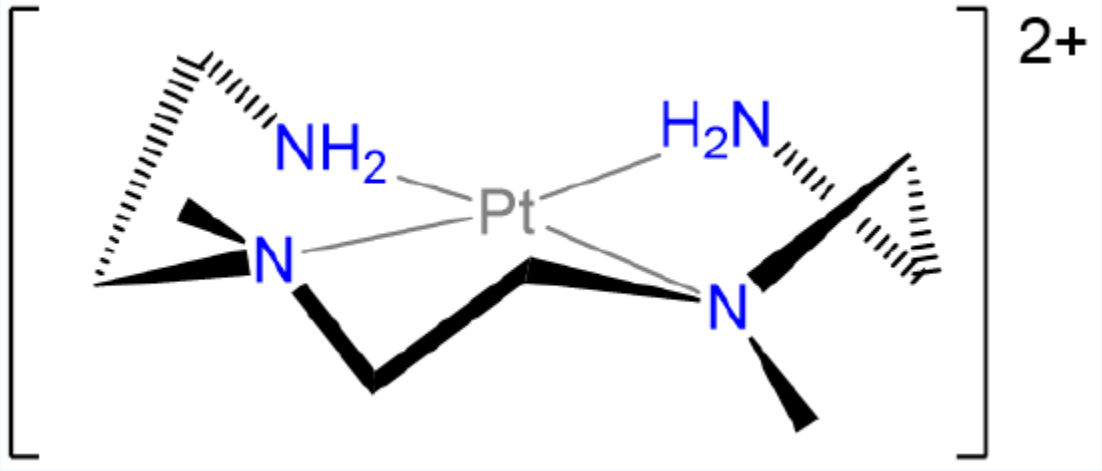
Draw the diastereomers formed due to the chirality of the amine nitrogen atoms in $[PtCl_2(N,N'$-dimethylethane-1,2-diamine)] which has the atomic connectivity represented below



Answer available at the end of this section.

Exercise 9.4.10

Label the conformations of all chelate rings in the structure below.



Answer available at the end of this section.

Answer available at the end of this section.

Appendix: The MABCDEF bookkeeping system for identifying isomers

The Mabcdef or MABCDEF system is one method for identifying the number of isomers in an octahedral complex, although since it is really just a bookkeeping and organizational system it can easily be extended to other geometries as well. The M in Mabcdef stands for metal and the other letters are used to stand in for ligands. The basic approach involves

- classifying the ligands as A, B, C, D, E, or F in order of multiplicity. Thus for

  $[Cr(NH_3)_6]^{3+}$ A = NH_3; there are no B, C, D,E, or F ligands; and the complex is classified as MA_6

  $[CoCl(NH_3)_5]^{2+}$ A = NH_3, B = Cl^-, and the complex is MA_5B

  $[CrCl_2(H_2O)_2(NH_3)_2]^+$ A = Cl^-, B = H_2O, C = NH_3, and the complex is $MA_2B_2C_2$

- in the classification above, multidentate ligands are typically classified before monodentate ones and are designated AA, AB, ABC, ABA, etc. based on the symmetry of the attachment points. Thus

  en has identical attachment amine points and is AA

  gly has a carboxy and amine attachment points and is AB

  trien is ABA

  $CoCl_2(en)_2^+$ is $M(AA)_2B_2$

  $CoCl_2(gly)_2^-$ is $M(AB)_2C_2$

  $CoCl_2(en)(gly)$ is $M(AA)(AB)C_2$

- Systematically list out the possible *trans* arrangements of ligands by
  1. assigning one pair of ligands to be *trans* to one another.

2. Then systematically list out the other possible *trans* pairs by permuting the remaining trans arrangements. It can help to organize the permutations in a table, such as that shown below for an MABCDEF complex where A and B are assigned *trans*. In looking at the table notice how the second set of trans permutations is systematically varied. This helps ensure that no possibility is skipped.
3. Go through the list of isomers and remove any duplicates you generated so far. For instance, notice in the table below that the last three stereoisomers are identical with the first three (*e.g.,* stereoisomer 4 is identical to stereoisomer 3, 5 with 2, and 6 with 1).

Stereoisomer 1	Stereoisomer 2	Stereoisomer 3	Stereoisomer 4 (same as isomer 3)	Stereoisomer 5 (same as isomer 2)	Stereoisomer 6 (same as isomer 1)
trans AB (fixed)	*trans* AB (fixed)	*trans* AB (fixed)	*trans* AB (fixed)	*trans* AB (fixed)	*trans* AB (fixed)
trans CD	*trans* CE	*trans* CF	*trans* DE	*trans* DF	*trans* EF
trans EF	*trans* DF	*trans* DE	*trans* CF	*trans* CE	*trans* CD

4. If the complex possesses multidentate ligands that demand that certain groups exist and *cis* pairs, then also remove any configurations which do not agree with the known binding capability of the ligand (*e.g.,* the two amine groups of ethylenediamine cannot be *trans* to one another, so if you have an en ligand, remove configurations like that from the list).
5. Next, swap or permute the original *trans* pair and repeat the process you just followed. In the case of Mabcdef this gives the following results:

Isomer	"fixed" trans pair	Additional trans pairs	
1	AB	CD	EF
2	AB	CE	DF
3	AB	CF	DE
4	AC	BD	EF
5	AC	BE	BF
6	AC	BF	DE
7	AD	BC	EF
8	AD	BE	CF
9	AD	BF	CE
10	AE	BC	DF
11	AE	BD	CF
12	AE	BF	CD
13	AF	BC	DE
14	AF	BD	CE
15	AF	BE	CD

- Since the procedure explained above only identifies isomers based on unique *trans* pairings, **it does not identify when a configuration is chiral and corresponds to a pair of enantiomers.** Any enantiomers can be identified by drawing out the complexes and either classifying their point groups or by drawing their mirror images and checking if they are superimposable. In the MABCDEF case - *i.e.,* where all the ligands are different - all of the isomers identified have C_1 symmetry so are chiral. This means there will be a pair of enantiomers for each, giving 15 x 2 = 30 different stereoisomers.

References

1. These examples are taken from http://wwwchem.uwimona.edu.jm/courses/inorgnom.html

2. Contakes S. M.; Rauchfuss, T.B. *Chem. Commun.* 2001, 553-554.

3. Shriver, D. F.; Shriver, S. A.; Anderson, S. E., *Inorg. Chem.* 1965, *4(5)*, 725-730.

4. Zelewsky, A. v., *Stereochemistry of Coordination Compounds* Wiley, 1996.

5. In the past it was difficult to determine absolute configurations from X-ray data alone, but recent advances have made it easier to do so.

6. Pavan M. V. Raja & Andrew R. Barron "Circular Dichroism Spectroscopy and its Application for Determination of Secondary Structure of Optically Active Species" in *Physical Methods in Chemistry and Nano Science* https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Book%3A_Physical_Methods_in_Chemistry_and_Nano_Science_(Barron)/07%3A_Molecular_and_Solid_State_Structure/7.07%3A_Circular_Dichroism_Spectroscopy_and_its_Application_for_Determination_of_Secondary_Structure_of_Optically_Active_S

7. Berova, N.; Bari, L. D.; Pescitelli, G., *Chemical Society Reviews* 2007, 36 (6), 914-931.

8. Of course, if one set of ligands occupies a meridional plane, then the other three ligands will be oriented in an equatorial one. The reason they may both be considered meridional is because if the complex were rotated, the equatorial plane would be meridional and vice versa. From that point of view both might be considered meridional planes - albeit not at the same time.

9. Bite angles are taken from Mansell, S. M., Catalytic applications of small bite-angle diphosphorus ligands with single-atom linkers. Dalton Transactions 2017, 46 (44), 15157-15174.

10. Hancock, R. D., The pyridyl group in ligand design for selective metal ion complexation and sensing. Chemical Society Reviews 2013, 42 (4), 1500-1524.

11. Sasi, D.; Ramkumar, V.; Murthy, N. N., Bite-Angle-Regulated Coordination Geometries: Tetrahedral and Trigonal Bipyramidal in Ni(II) with Biphenyl-Appended (2-Pyridyl)alkylamine N,N'-Bidentate Ligands. ACS Omega 2017, 2 (6), 2474-2481.

12. Ehnbom, A.; Ghosh, S. K.; Lewis, K. G.; Gladysz, J. A., Octahedral Werner complexes with substituted ethylenediamine ligands: a stereochemical primer for a historic series of compounds now emerging as a modern family of catalysts. Chemical Society Reviews 2016, 45 (24), 6799-6811.

Answers

Exercise 9.4.1: Bridging ambidentate ligands and the Hard-Soft Acid- Base Principle.

The greater stability of K{$Fe^{II}[Cr^{III}(NC)_6]$} over K{$Fe^{II}[Cr^{III}(CN)_6]$} reflects the greater stability of the Fe^{II}-CN-Cr^{III} linkages in the former over the Fe^{II}-NC-Cr^{III} linkages in the latter. This is consistent with the preference for hard-hard and soft-soft Lewis acid-base interactions of the Hard-Soft Acid-Base Principle.

The Fe^{II}-CN-Cr^{III} linkages are more stable because they possess bonds between

- the softer Lewis acid (Fe^{II}) and Lewis base (the C end of CN^-)
- the harder Lewis acid (Cr^{III}) and Lewis base (the N end of CN^-)

In contrast, the Fe^{II}-NC-Cr^{III} linkages in the less stable linkage isomer involve bonds between

- the softer base (the C end of CN^-) and harder acid (Cr^{III})
- the harder base (the N end of CN^-) and softer acid (Fe^{II})

Exercise 9.4.1. Identify the type of isomerism

Ionization isomers.

Linkage isomers.

Coordination isomers.

Geometric isomers, specifically *cis*/*trans* isomers.

Exercise 9.4.2. Assigning metal oxidation states in a complex

This contains $[Fe(CN)_6]^{4-}$; so $O.S._{Fe}$ + 6 x (-1) (for CN^-) = -4 (the complex's charge) so $O.S._{Fe}$ = +2 or Fe^{2+}.

Since tetrafluoroborate is a monoanion, the complex is $[Cu(phen)_2]^+$ so $O.S._{Cu}$ + 0 x 2 (for phen) = +1 (the complex's charge) so $O.S._{Cu}$ = +1 or Cu^+.

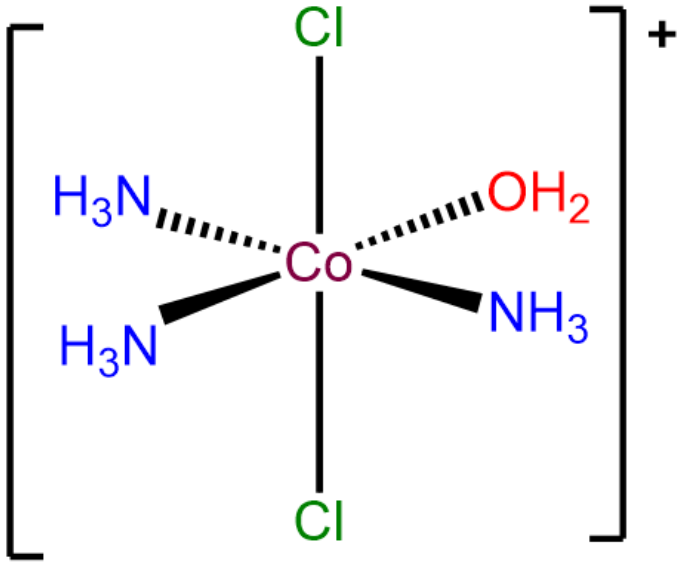
O.S.$_{Pt}$ + 4 x (-1) (for F^-) + 0 x 2 (for NH_3) = +0 (the complex's charge) so O.S.$_{Pt}$ = +4 or Pt^{4+}.

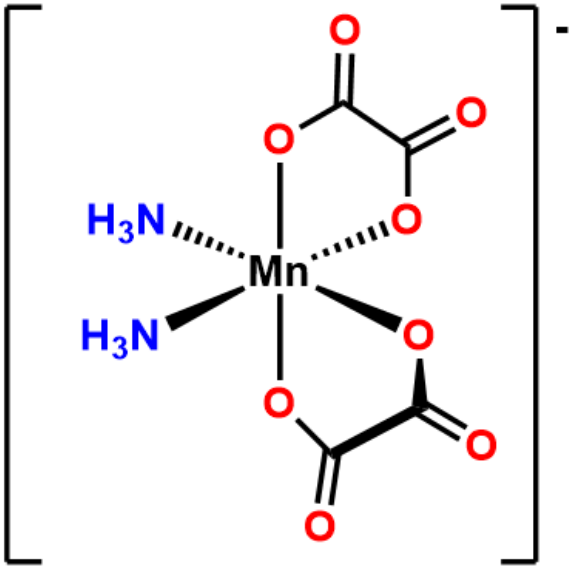
The complex is $[Ni(en)_2]^+$ so O.S.$_{Ni}$ + 0 x 2 (for en) = +2 (the complex's charge) so O.S.$_{Ni}$ = +2 or Ni^{2+}.

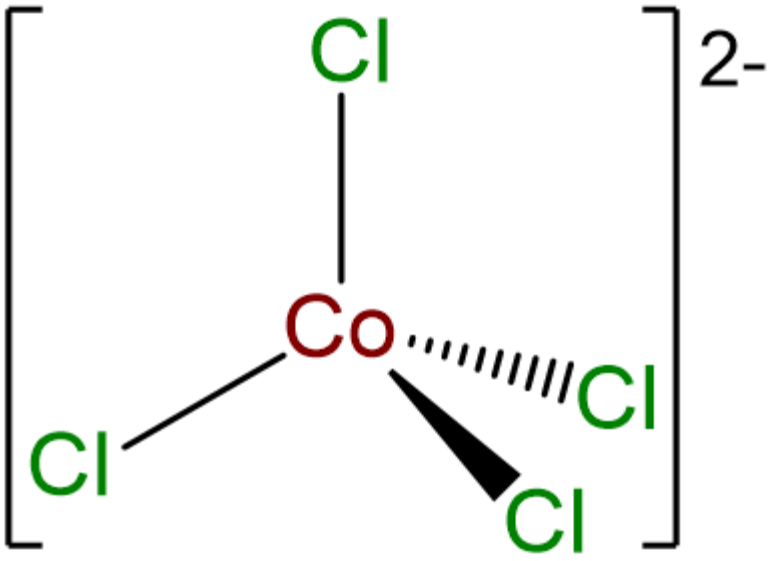
O.S.$_{Co}$ + 3 x (-1) (for acac; see table 9.2.2) = +0 (the complex's charge) so O.S.$_{Co}$ = +3 or Co^{3+}.

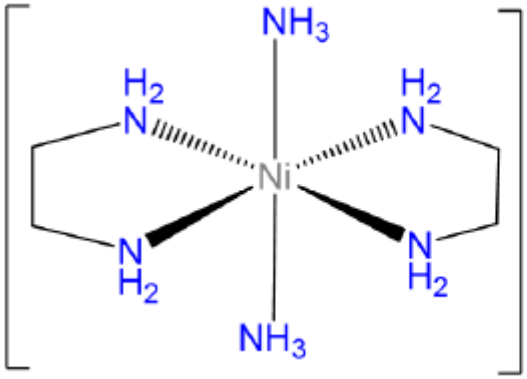
O.S.$_{Mn}$ + 1 x (-1) (for Cl^-) + 1 x (-2)(for oxo) + 1 x (-2) (for salen; see table 9.2.2) = +0 (the complex's charge) so O.S.$_{Mn}$ = +5 or Mn^{5+}.

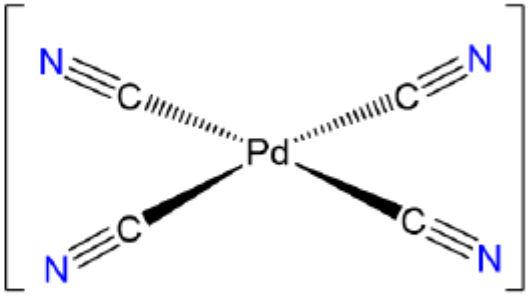
Exercise 9.4.3**. Drawing isomers from descriptions**



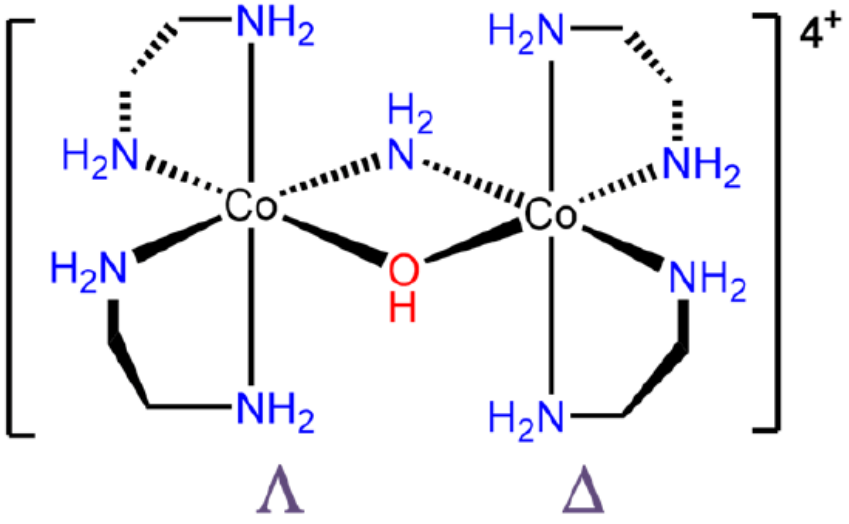






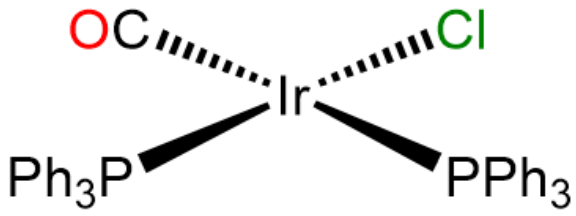


Note that since the Pd in $[Pd(CN)_4]^{2-}$ is Pd^{2+} it will be square planar.

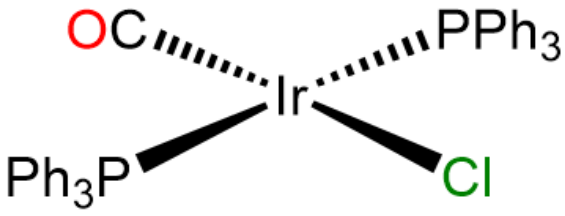


Exercise 9.4.4**. Stereoisomers of complexes containing only monodentate ligands.**

This is a 4-coordinate Ir^{I} complex and, as such will be square planar. Since two of the ligands are identical, it will have *cis* and *trans* isomers. The *trans* isomer is famous for its ability to form adducts and is called Vaska's complex.

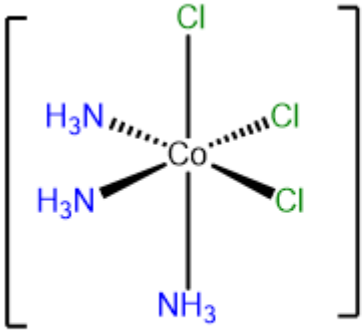


cis-

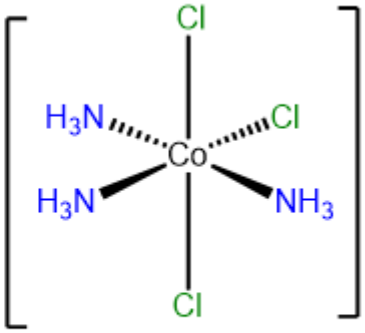


trans-

This complex contains three ammine and three chloro ligands and so will have *fac* and *mer* isomers.

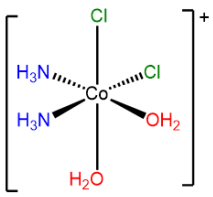


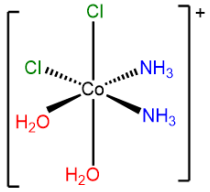
fac-



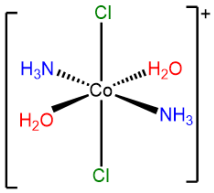
mer-

This is a case of an $MA_2B_2C_2$ system (A = Cl^-, B = H_2O, C = NH_3) involving multiple *cis* and *trans* relationships. The six stereoisomers are shown below.

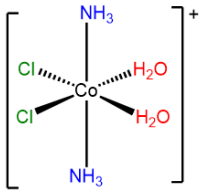




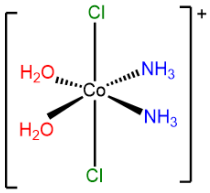
enantiomers of -*cis* NH_3, *cis*-Cl_2, *cis*-H_2O



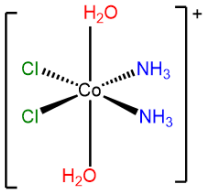
all trans



trans NH_3, *cis*-Cl_2, *cis*-H_2O



cis NH_3, *trans*-Cl_2, *cis*-H_2O

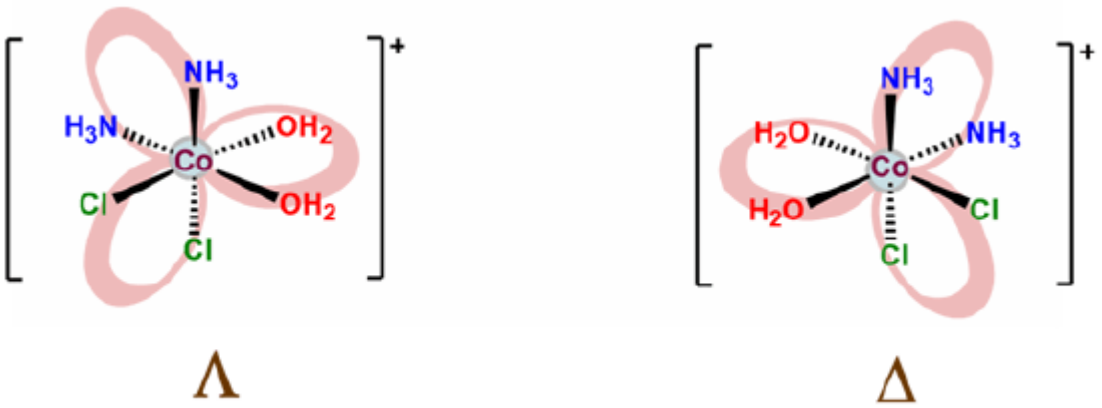


is NH_3, *cis*-Cl_2, *trans*-H_2O

Since it may not be obvious how to arrive at a set of isomers like the ones above, it is worth considering how one might work through the possibilities for a system of ligands like this one. Several systems may be used to systematically identify isomers. Once approach is the Macbdef system described in Note 9.4.1 at the end of these exercises. The solutions presented here and in subsequent problems employ a variant of that approach.

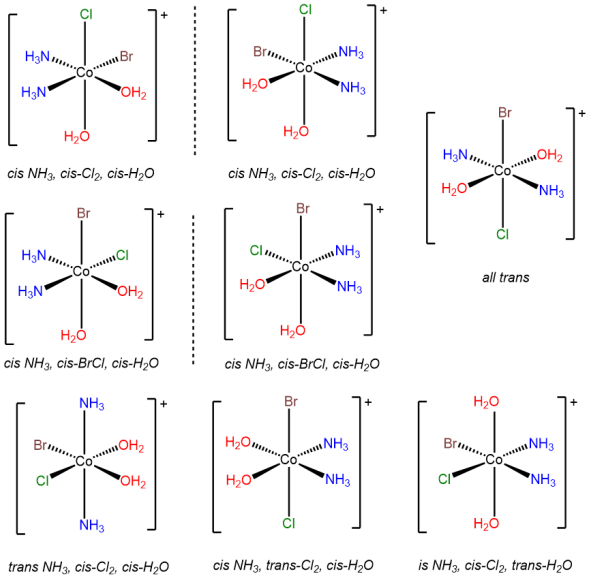
- Start by fixing one set of ligands. In this case the chloro ligands were first fixed as *cis* to one another. Then the remaining ligands might be *cis* or *trans* to one another, although since the *chloro* ligands are already *cis,* the ammine and aqua ligands cannot both be *trans* at the same time. Thus for *cis* chloro ligands the possibilities for the others are:
  - *cis*-H_2O ,*cis*-NH_3,
  - *cis*--H_2O, *trans*-NH_3
  - *trans*-H_2O, *cis*-NH_3
- Swap the configuration of the ligand set you started with. In this case it means placing the chloro ligands *trans* to one another. From that configuration, the possibilities for the ammine and aqua ligands are
  - *cis*-H_2O ,*cis*-NH_3,
  - *trans*-H_2O, *trans*-NH_3
- Check for enantiomers and create mirror images of any chiral complexes you drew. The easiest way to do this is to assign point groups. However, it turns out

that the octahedral all-*cis* case is D_3 and formally equivalent to the symmetry of a tris chelate, as shown below.

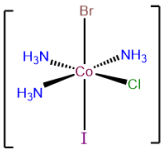


- finally, check to make sure you didn't include the same complex twice. Humans do make mistakes after all.

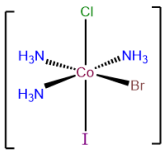
This problem is analogous to the one above except that this complex contains a bromo and chloro ligand in place of the two chloro ligands in $[CoCl_2(H_2O)_2(NH_3)_2]^+$. Consequently, when the bromo and chloro ligands are *cis* to one another, additional possibilities for isomers arise based on whether ammine or aqua ligands are *trans* to the chloro and bromo. The result is eight isomers.



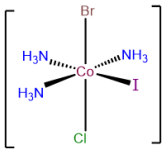
There are two possibilities for this complex - a *fac*-$(NH_3)_3$ and a *mer*-$(NH_3)_3$ arrangement. These may be taken as starting points for examining the possible permutations for the Cl^-, Br^-, and I^- ligands. The top row presents the three possibilities within the *mer*-$(NH_3)_3$ arrangement; each corresponds to a different ligand *trans* to an ammine ligand. The bottom row presents the two possible isomers with a *fac*-$(NH_3)_3$ arrangement. In each, the Cl^-, Br^-, and I^- ligands are *trans* to ammine ligands. However, the complexes possess C_1 symmetry and so are chiral and exist as enantiomers.



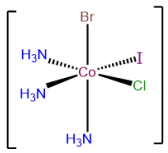
mer with Br *trans* to I

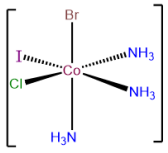


mer with Cl *trans* to I



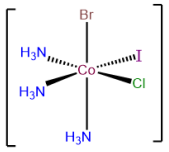
mer with Br *trans* to Cl



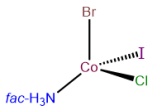


fac enantiomers

(C_1 symmetry or it you think of the *fac*-$(H_3N)_3$ as being "one uniform group" then the symmetry is equivalent to that of a chiral carbon)

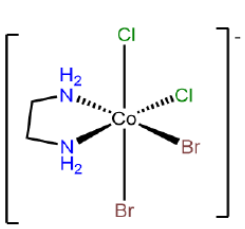


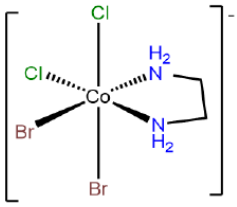
may be thought of as equivalent to



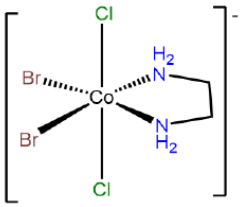
Exercise 9.4.5**. Stereoisomers of complexes with bidentate ligands (ignoring ring twist).**

This complex is analogous to $[CoCl_2(H_2O)_2(NH_3)_2]^+$ in possessing pairs of identical ligating groups. The main difference is that in $[CoBr_2Cl_2(en)]^-$ the two amine ligating group of the en ligand are restricted to a *cis* arrangement. Under the MABCDEF system explained in Note 9.4.1, $[CoCl_2(H_2O)_2(NH_3)_2]^+$ may be $MA_2B_2C_2$, but this complex, $[CoBr_2Cl_2(en)]^-$, is $M(AA)B_2C_2$. The isomers are:

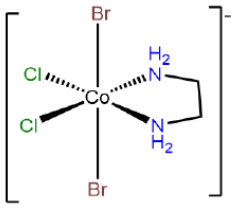




enantiomers of *cis*-Cl_2, *cis*-Br_2

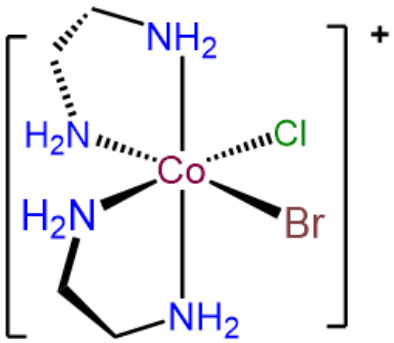


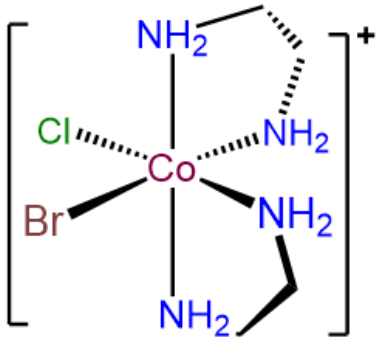
trans-Cl_2, *cis*-Br_2

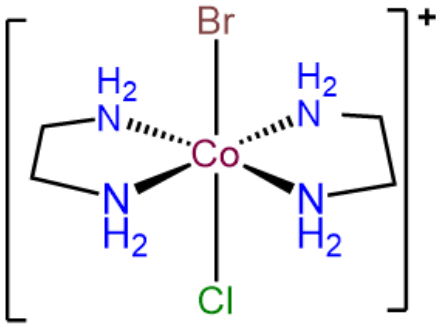


cis-Cl_2, *trans*-Br_2

The key to problems like this is to focus on the unique ligands, in this case Br^- and Cl^-. These can exist in either a *cis* or *trans* arrangement. The *trans* form is achiral, but in the case where Br^- and Cl^- are *cis*, Λ and Δ enantiomers are possible. The result is three isomers.

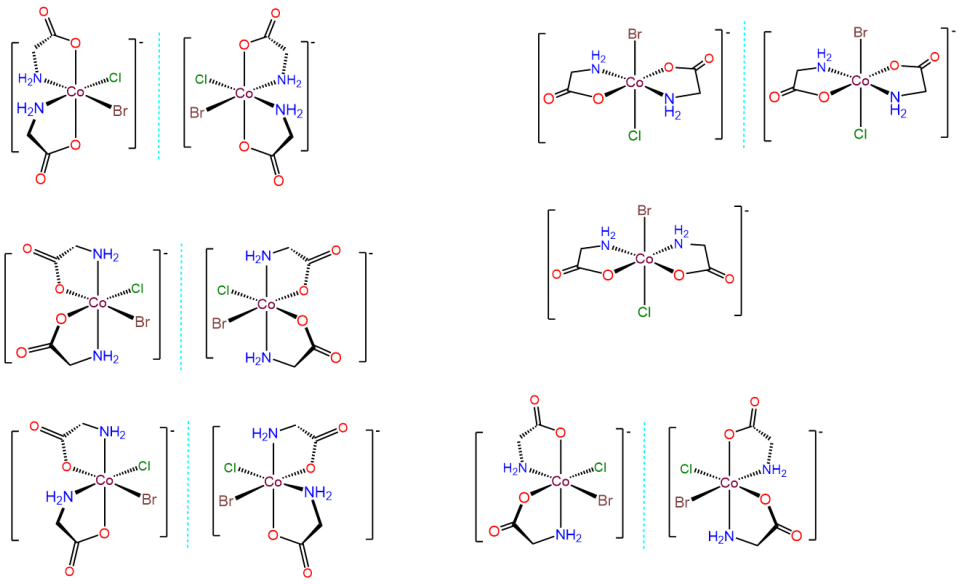




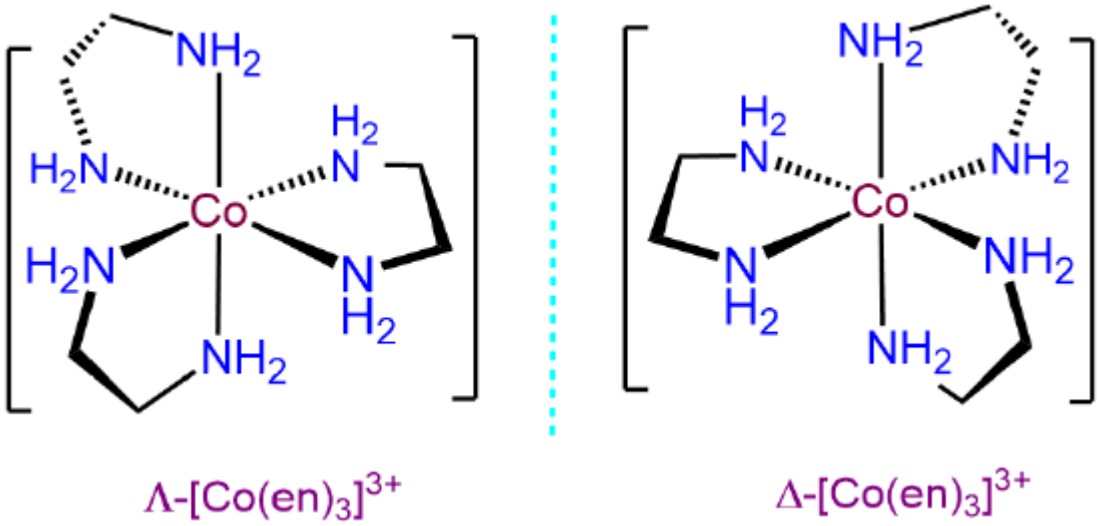


This case is analogous to the one above, but this time the bidentate ligand, gly, possesses distinguishable binding sites. Thus there are additional permutations involving how the gly ligands are bound relative to one another and/or whether the O or N end of the gly is bound *trans* to Br or Cl. The result is 11 different isomers,

which are given below.

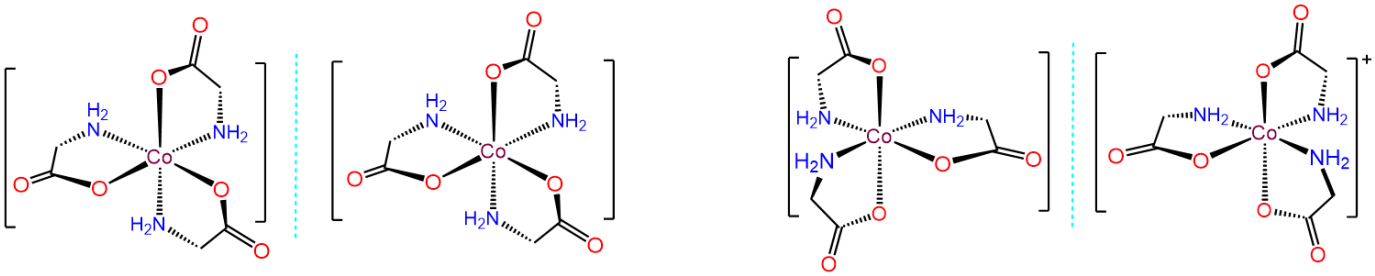


As a tris-chelate of symmetric bidentate ligands, ignoring ring twist, $[Co(en)_3]^{3+}$ will only exhibit Λ and Δ isomerism.



Λ-$[Co(en)_3]^{3+}$ Δ-$[Co(en)_3]^{3+}$

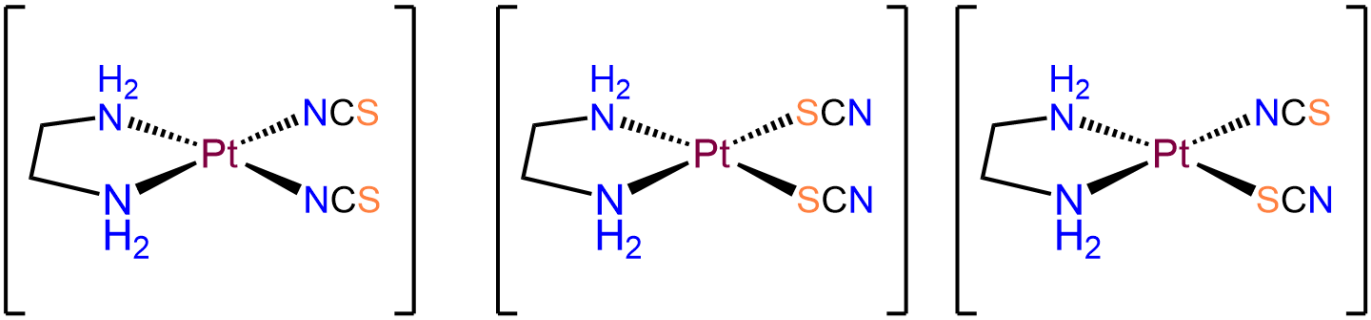
Since there are three gly ligands, each of which have carboxy and amine ends, the allowable arrangements involve whether the resulting three carboxy and three amine ends are oriented in a *mer* or *fac* arrangement. This gives two possibilities, each of which can exist as either the Λ or Δ enantiomer, for a total of four isomers, which are given below.



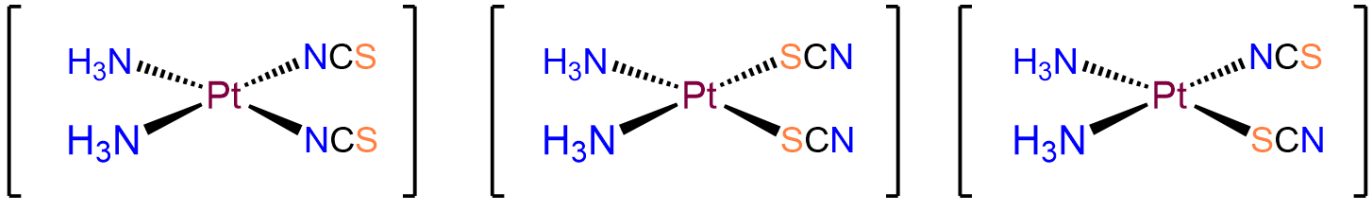
***fac* and Λ** ***fac* and Δ** ***mer* and Λ** ***mer* and Δ**

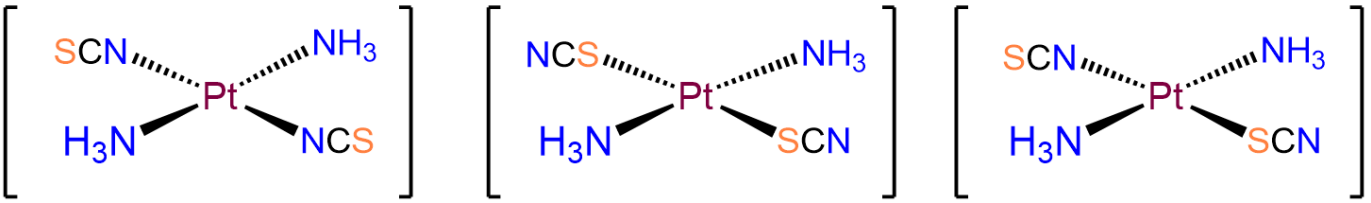
Exercise 9.4.6. More stereoisomers: Now featuring linkage isomerism

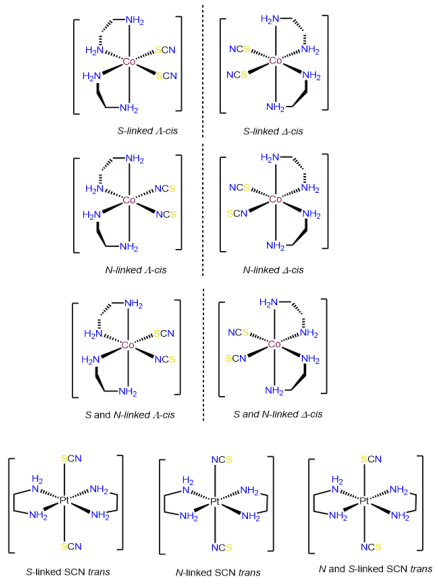
The Pt in this neutral complex must be Pt^{2+} to balance the negative charges of the two SCN^- ligands. Complexes of Pt^{2+} are square planar and four coordinate, consistent with the bidentate en and two thiocyanato ligands. Of the ligands, the en ligand must bind in a *cis* arrangement. Consequently, the two SCN^- ligands will be in a *cis* arrangement as well. The isomers will therefore only differ in whether the two SCN^- bind κN or κS. The possibilities are:



As with the preceding example, this will be a square planar Pt^{2+} complex. The main difference is that this time the coordinated nitrogens are not constrained to adopt a *cis* arrangement so there will be both *cis* and *trans* isomers.

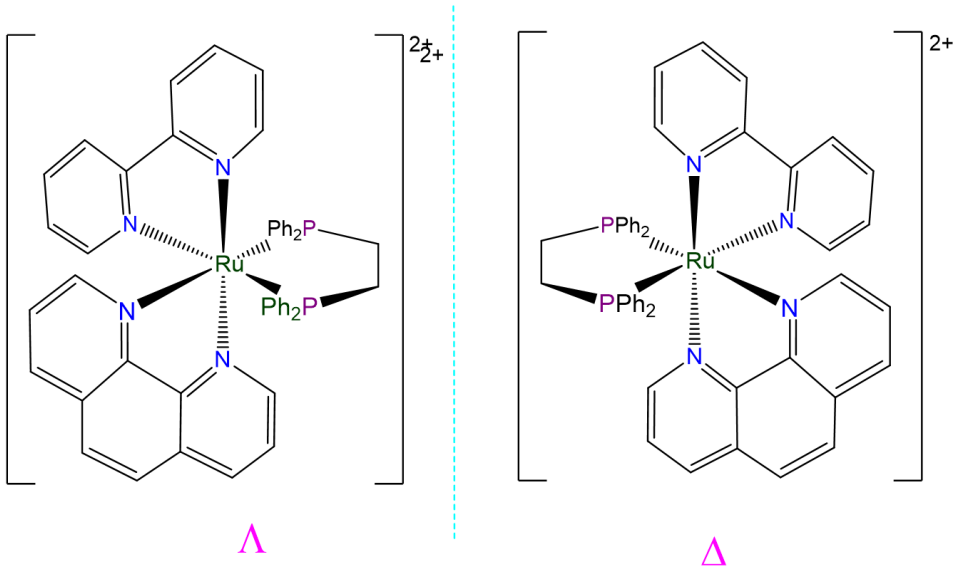




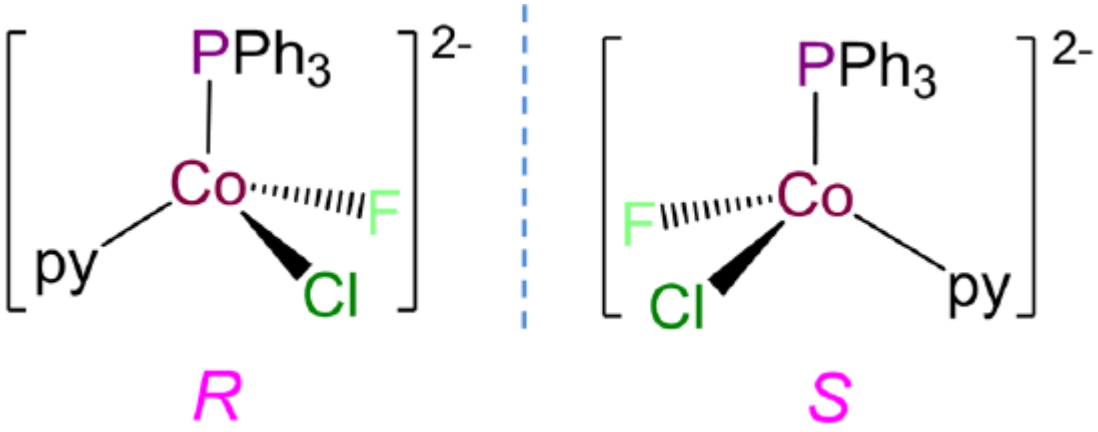


Exercise 9.4.7**. Stereoisomer free for all.**

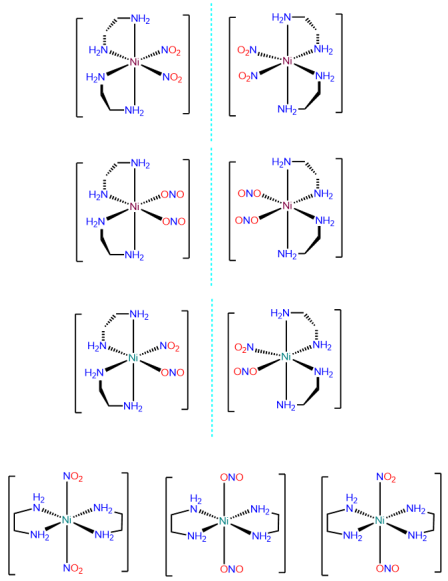
This complex is an octahedral tris-chelate containing symmetric ligands. As such it will exhibit Λ and Δ isomers:



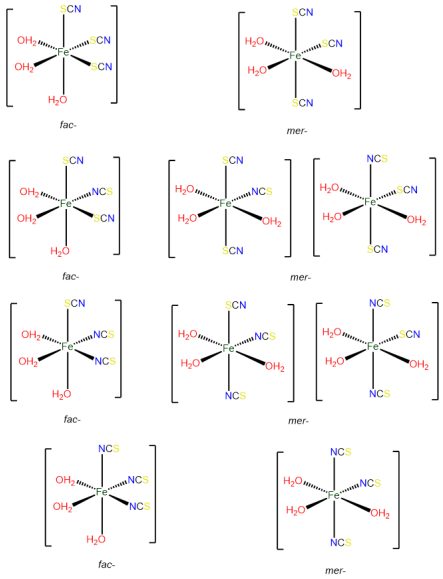
This complex has a coordination number of 4 and contains a Co^{2+} ion with a d^7 electron configuration, so a tetrahedral geometry is expected. Tetrahedral complexes like this one with four different ligands are chiral and can form *R* and S enantiomers.



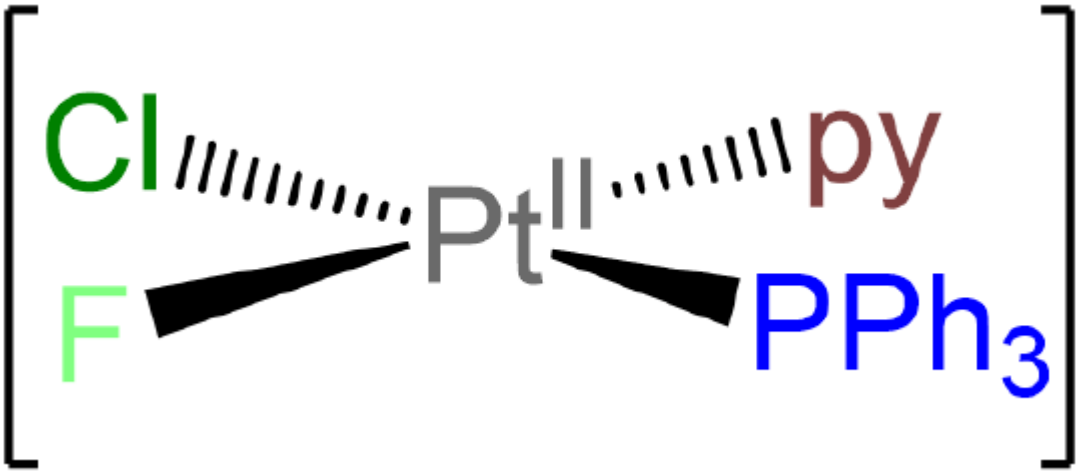
This is an octahedral bis-chelate and will exist in Λ and Δ configurations. Within each configuration the NO_2^- ligands can exist as κN and κO, leading to the following possibilities:



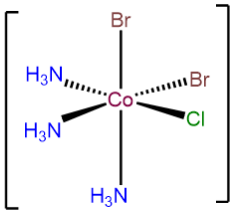
As an octahedral complex with three identical ligands it can exist in *mer* and *fac* configurations, with the ambidentate SCN ligand providing additional possibilities for isomerism.



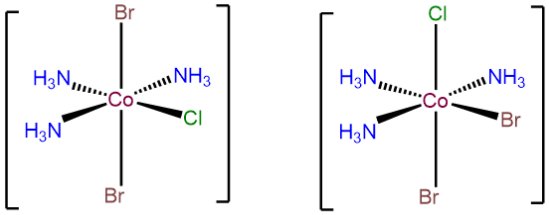
As a square planar complex with four nonidentical ligands, this complex exists as a single isomer.



As an octahedral complex with three identical ligands it will exhibit *mer* and *fac* isomerism. In addition, it will have two *mer* configurations that differ in terms of the cis and trans relationships between the bromo and chloro ligands.



fac

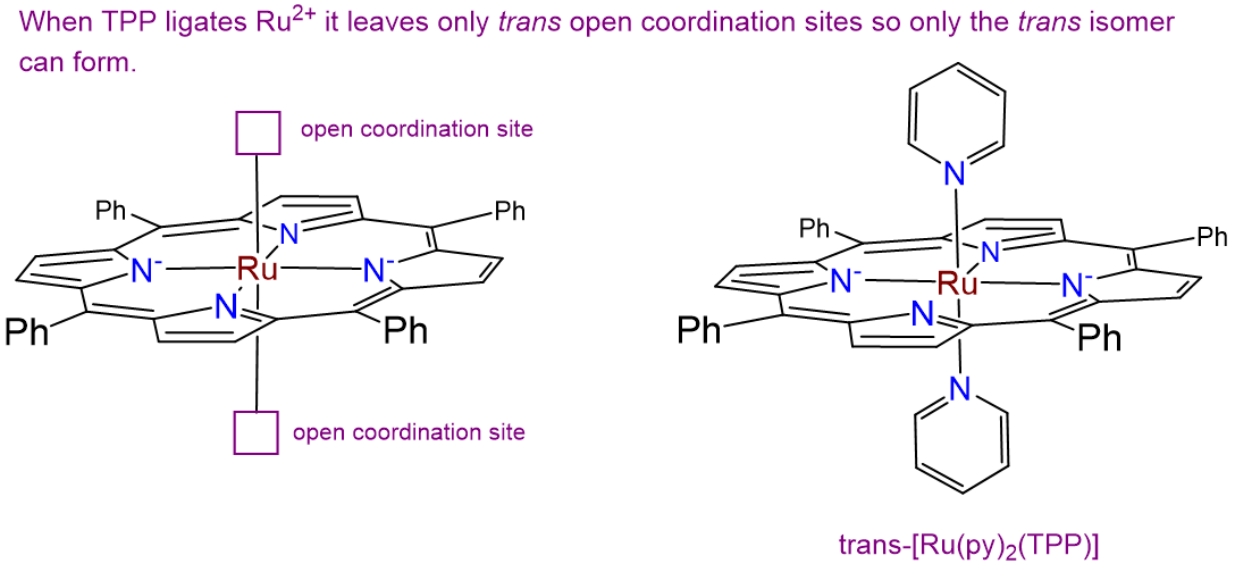


mer with Br *trans* to Br

mer with Cl *trans* to Br

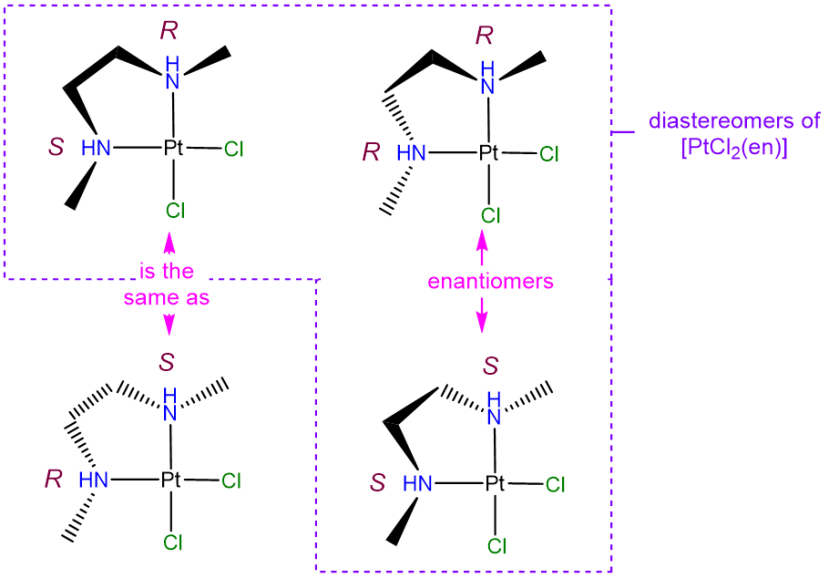
Exercise 9.4.8

There is only one isomer. While normally complexes containing two identical ligands (in this case py) can exhibit *cis* and *trans* isomerism, in this case the planar tetraphenylporphyrin ring ligates the Ru^{2+} ion in a square planar arrangement, as shown at left in the image below. This leaves only a pair of *trans* coordination sites for the chloro ligands to occupy, giving the isomer shown at right below.

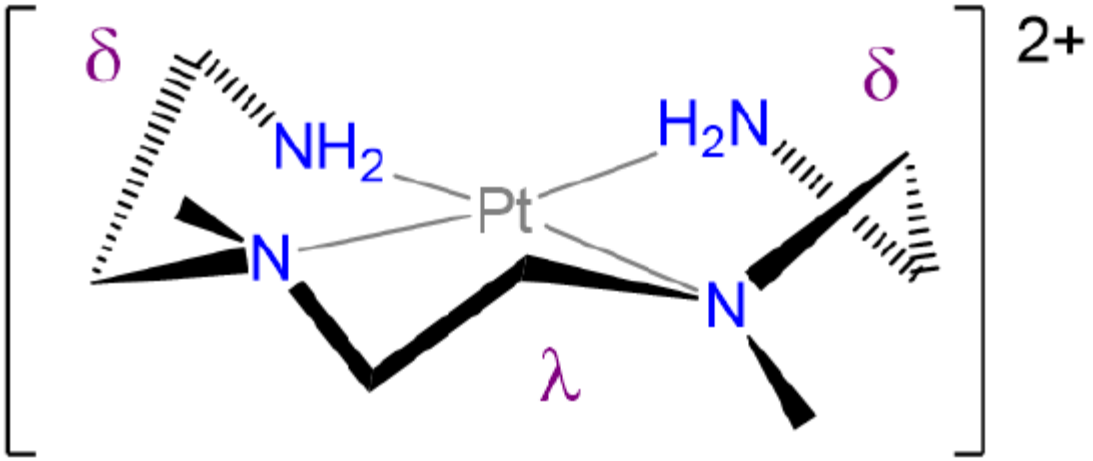


Exercise 9.4.9

The diastereomers will differ in whether the N atoms adopt an *R* or S configuration at the nitrogen atoms. The possible permutations are (*R*,*R*), (S,S), (*R*,S), and (S,*R*). However, as may be seen from the image below, the (*R*,S) and (S,*R*) configurations are identical (the two projections shown can be interconverted through a C_2 rotation along an axis bisecting the Cl-Pt-Cl unit). As a result there are only three unique isomers. Of these, the (*R*,*R*) and (S,S) configurations are enantiomers (they are mirror images by reflection in the $PtCl_2N_2$ plane). Note that in solving problems like this one it can be helpful to keep track of possible isomers by assigning the stereochemistry at each chiral center as *R* or S using the Cahn-Ingold-Prelog-convention, though it is not strictly necessary to do so.



Exercise 9.4.10



Exercise 9.4.10

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9.5: Coordination Numbers and Structures

Why do coordination complexes form the structures they do?

As with all chemical structure, coordination complexes form the structures they do so as to best stabilize the metal center and ligands through the formation of metal-ligand bonds while avoiding destabilizing interactions like steric repulsions. The issue then is how many metal-ligand bonds should be formed and how those bonds should be arranged spatially to give the largest net stabilization possible. This question will eventually be considered in detail in connection with the nature of bonding in coordination compounds. For now, it will be helpful to think about it in terms of seven factors:

The stabilizing effect of metal-ligand bond formation.

The driving force for complex formation is the stabilization of electrons in covalent chemical bonds. In the vast majority of cases, this largely involves stabilization of the ligand lone pair as it experiences the effective nuclear charge of the metal, although a few instances involve stabilization of metal electrons by ligand nuclei (inverse ligand fields). Regardless, metal-ligand bond formation is stabilizing and classified by the way it preferences the addition of ligands to the complex.

Steric effects, specifically steric repulsions between ligands.

One reason coordination numbers do not increase indefinitely is that only so many ligands can fit around a metal. Exactly how many depends on

- *the size of the metal center*. This is one of the more important factors. Many metals tend to exhibit preferred coordination numbers, which depend on their oxidation state and size as shown in Figure 9.5.1. Larger inner transition metals like the Lanthanides and Actinides can accommodate 9-12 sterically undemanding ligands, while the smaller transition metals tend to accommodate up to six, although larger coordination numbers are more common for low valent metals and as size increases on moving from right to left across the transition metal block of the periodic table. Thus, the early transition metal molybdenum forms seven- and eight-coordinate $[Mo^{III}(CN)_7]^{4-}$ and $[Mo^{IV}(CN)_8]^{4-}$ with the sterically undemanding cyano ligand.
- *the size of the ligands*. As long as ligands are not excessively rigid and bulky, their size is less important than the size of the metal in determining the number of ligands that coordinate. Ligands' ability to donate electrons to the metal center also tends to influence coordination number more than ligand size. However, all other things being equal for a given metal and ligand donor ability, small ligands allow higher coordination numbers while fewer bulky ligands will fit around the metal center.
- *how the ligand bonds to the metal*. Again, all other things being equal, ligands that are more sterically demanding in the vicinity of the metal center tend to limit the ability of other ligands to bind more than those which bind through a small extended group. For example, a bulky isocyanide like t-BuCN will sterically crowd the metal less than a bulky phosphine like t-BuH_2P would. For this reason the effective size of a ligand is sometimes rated in terms of either a cone angle of space they are estimated to occupy around the metal (called the Tolman cone angle, it is commonly used to evaluate phosphines' steric bulk) or in terms of the percentage of the metal's coordination sphere the ligand occupies (called the percent buried volume, it is used to estimate the steric impact of *N*-heterocyclic carbenes).

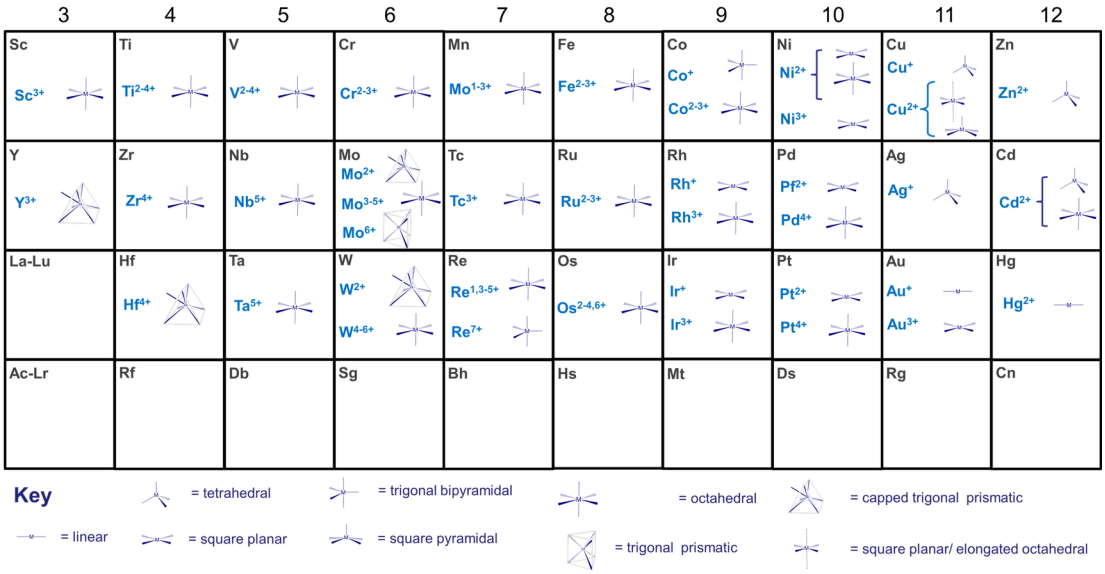


Figure 9.5.1. Preferred coordination geometries of the transition elements. Assignments are as reported in reference 1 except for Cu^{2+}, which is assigned above as square planar/elongated octahedral instead of the square planar assignment given in that work. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Repulsion between M-L bonding electrons on different ligands.

For many complexes, steric effects are neither the only effects nor the most important. Among the additional factors that should be considered are the repulsions that occur between the electrons that different ligands donate to the metal-ligand bonding. These electron-electron repulsions affect the

a. **Coordination number.** When a ligand donates its electrons to a metal center to form a new metal-ligand bond, the electron density around the metal increases, raising the overall energy of the other M-L bonding electrons. This increased repulsion often limits the number of coordinated ligands. As more ligands are added, the electron-electron repulsions keep increasing until the lowering of energy of the ligand electrons in the new bond is insufficient to compensate for the raising of energy of the existing M-L bonding electrons. Based on this effect alone,
   - larger metals tend to achieve higher coordination numbers than smaller ones because the electron-electron repulsions are spread across a larger coordination sphere.
   - With a given metal, ligands that are more electron donating have a greater tendency to form complexes with lower coordination numbers with a given metal than similar neutral ones do. This is why anionic ligands (which tend to be better electron donors) tend to give lower coordination numbers than comparable neutral ligands (which tend to be weaker donors). Thus Co^{2+} forms $CoCl_4^{2-}$ with chloro ligands but $[Co(H_2O)_6]^{2+}$ with aqua ligands.

b. **Coordination geometry.** In the **Kepert model** for the shapes of coordination complexes, this intraligand repulsion determines the most stable coordination geometry by causing the ligands to move as far apart from one another on the metal's coordination sphere as possible.

Formally, according to the **Kepert model**

- any of the metal's valence electrons not involved in metal-ligand bonds occupy (n-1)*d* orbitals and function as core electrons. As core electrons they do not influence the molecular shape.
- electrons involved in bonding to a given ligand constitute an electron group that repels all other electron groups around the metal.
- all other things being equal, the complex will form the geometry that maximizes the intra-electron group repulsions.

Notice the similarities of these postulates to those of VSEPR theory. In predicting coordination geometries in terms of electron-electron repulsions, the Kepert model is just an extension of VSEPR theory to coordination compounds. The difference between VSEPR theory and the Kepert model is that in the Kepert model, only electrons involved in metal-ligand bonds count.

Coordination geometries predicted by the Kepert model for coordination numbers two through nine are given in Figure 9.5.2. As may be seen from the geometries listed in Figure 9.5.2, these are just equivalent to VSEPR geometries for cases in which the

number of electron groups is equal to the coordination number.

The difference between optimal and suboptimal coordination geometries is greater with few ligands, and becomes smaller as ligands become increasingly dispersed across the metal's coordination sphere. In complexes containing five, seven, eight, or higher coordinate metals, there are a number of geometries that are similar in energy to the preferred geometry. These geometries, which should be regarded as accessible, are also listed in Figure 9.5.2.

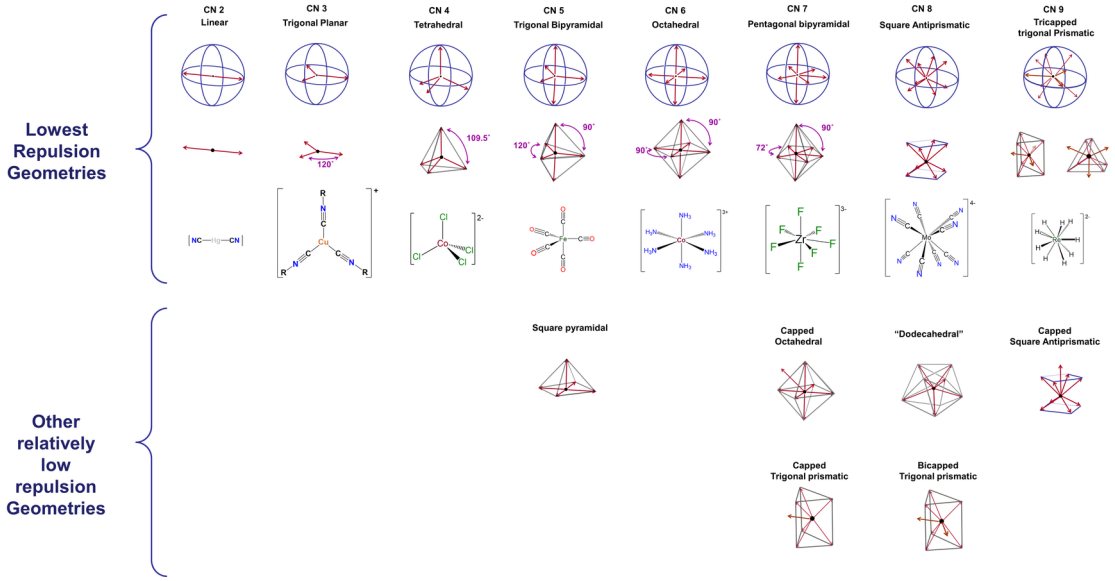


Figure 9.5.2. Coordination geometries predicted by the Kepert model for coordination numbers two through nine along with other coordination geometries similar in energy to the lowest repulsion geometry. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

d-electron effects

A few coordination geometries are noticeably absent from the Kepert-preferred and Kepert-accessible geometries in Figure 9.5.1. These include the trigonal prismatic geometries formed by compounds like $W(CH_3)_6$ and the very common square planar geometry illustrated by complexes like $[PtCl_4]^{2-}$ and $[IrClH(PPh_3)_2]$. One of the reasons the Kepert model fails to predict the existence of such structures is its neglect of directional interactions involving *d* electrons on the metal center. Metal *d* electrons exert a profound influence on almost all properties of transition metal complexes, including their structures. The way in which this occurs will be explored at length in the next chapter. For now, it is enough to note that both the ligand-donated electrons surrounding a metal center and the electrons occupying particular *d* orbitals on that metal are oriented in specific directions relative to one another. Because of this, the strength of the interactions between the ligand and metal *d* electrons depends on the number of *d* electrons present, how strongly metal-ligand binding affects their energy, and how the ligands are arranged about the metal center. The impact of these effects, here termed ligand field effects, differs from case to case and can include

- distortions of the complex's geometry. For instance, an ideal octahedral coordination geoemtry might be tetragonally distorted by flattening or elongating it.
- imparting a strong preference for non-Kepert coordination geometries. This is why, for example, 2nd and 3rd row complexes in which the metal has a d^8 electron configuration are almost always square planar.
- stabilizing non-Kepert geometries enough to permit complexes to adopt them in the presence of a rigid or semirigid ligand that prefers to coordinate the metal in that geometry.[3]

Because of these effects, square planar and trigonal prismatic geometries are also observed, and the list of coordination geometries given in Figure 9.5.2 may be extended to that shown in Figure 9.5.3.

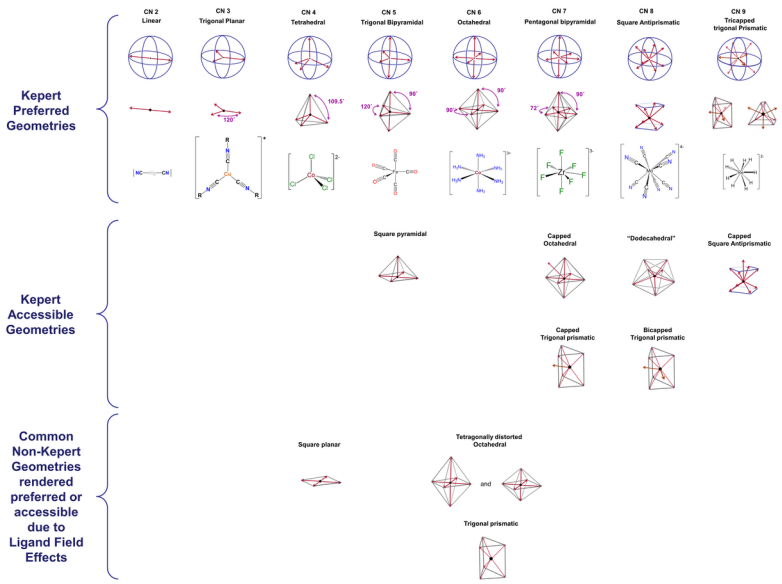


Figure 9.5.3. Coordination geometries accessible for 2-9 coordinate complexes even without constraint by rigid or semirigid ligands. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Ligand constraints imposed by rigid or semirigid ligands

Rigid or semirigid ligands influence the coordination geometry of metal complexes in two main ways:

a. Bulky rigid ligands that crowd the metal center prevent other ligands from binding. Thus such ligands are useful for preparing low-coordinate complexes.
b. Rigid and semirigid ligands can impose their preferred coordination geometry on a metal center. This is because these ligands energetically prefer to adopt a particular conformation when they bind a metal center. In doing so they shift the coordination geometry energy landscape toward that preferred geometry. If the shift is large enough relative to the native preference due to ligand repulsion and ligand field effects, the complex will either adopt the ligand-preferred geometry or be distorted in the direction of the ligand-preferred geometry. Examples are given in Figure 9.5.4.

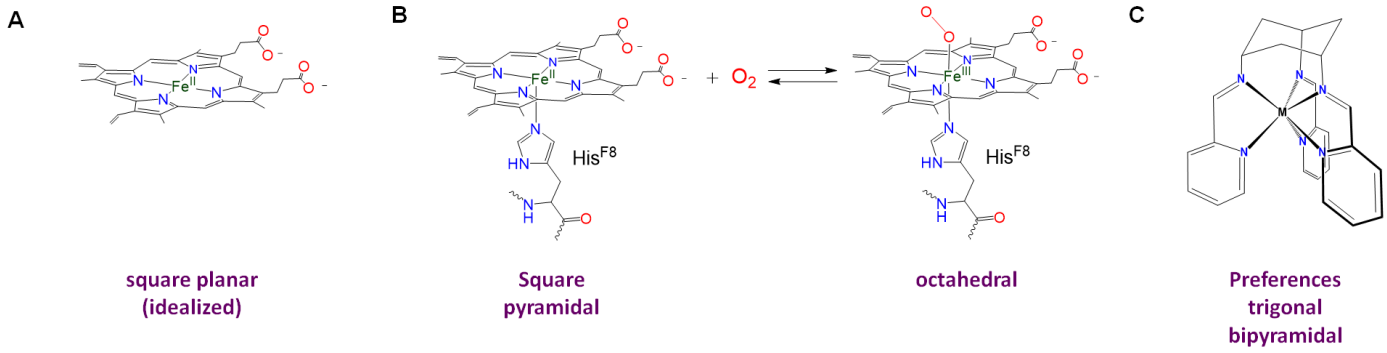


Figure 9.5.4. Examples of rigid/semirigid ligands that can impose their preferred coordination geometry on a metal center. Porphyrins, phyhalocyanines and related macrocycles tend to impose a slightly bent square planar coordination geometry, although (B) many such complexes, including the iron of myoglobin's heme cofactor, coordinate additional ligands to give square planar or octahedral complexes. (C) Synthetic multidentate ligands have been developed to preference trigonal prismatic coordination geometries, including the one shown here. It forms roughly trigonal prismatic complexes with Co^{II} and Zn^{II}, albeit imperfect ones.[3] This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

The influence of ligands on coordination geometry is important in living systems, in which proteins and nucleic acids can act as rigid or semirigid ligands. The ability of these ligands to distort the coordination geometries of metal atoms in ways that enable them to perform specific functions is so common that the resulting distorted geometries are termed entactic states. A particularly spectacular case of an entactic state involves the blue copper proteins azurin and plastocyanin, the structure of which is given in Figure 9.5.5.

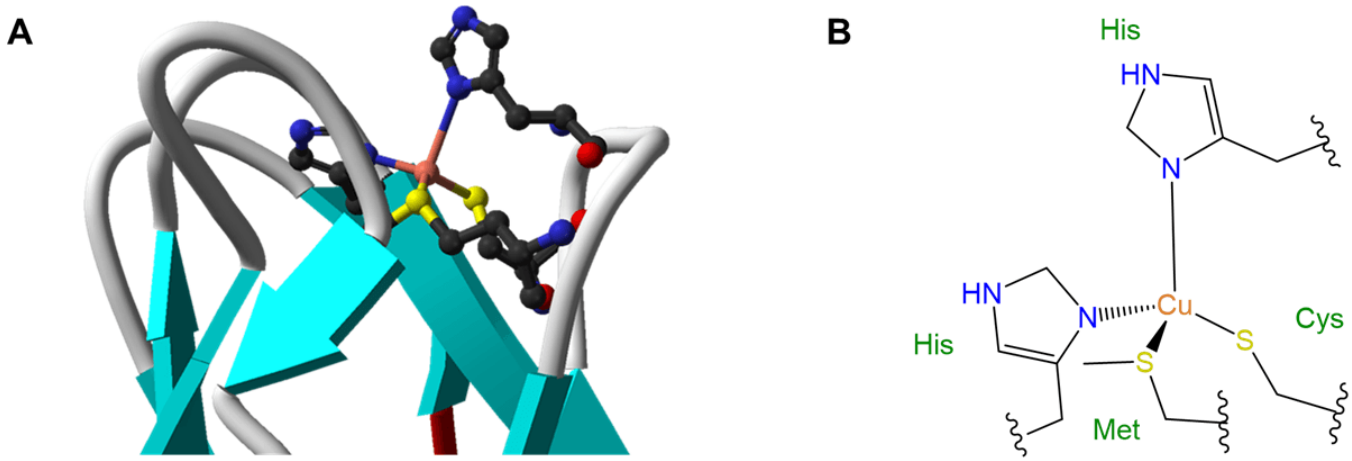


Figure 9.5.5. (A) Structure and (B) schematic of the plastocyanin active site showing the distorted tetrahedral coordination environment that the protein imposes on the copper center (tan), which is most evident from the long vertically oriented Cu-Histidine bond. The image in part A is cropped from an original image by Ben Mills - Own work, Public Domain, https://commons.wikimedia.org/w/inde...?curid=62020620. The image in part B is by Stephen Contakes and licensed under a Creative Commons Attribution 4.0 International License.

As may be seen from the structure in Figure 9.5.5, the copper in plastocyanin exibits a distorted tetrahedral coordination geometry. The protein is said to act like a medieval torture device called a rack in stretching the metal into its distorted geometry. This distortion makes it easier for the copper center to undergo facile redox reactions, enabling it to better function as an electron carrier.

Crystal packing effects, in which the energy-lowering packing of molecules and ions in a crystal drives the distortion of a complex's structure away from what it would adopt in the gas phase or solution

This effect is similar to that of ligand constraints except that in this case it arises not from the structure internal to a ligand but out of the forces involves in maximizing the stabilization energy of a crystal. With lower coordination number complexes, packing effects can shift the conformations of flexible ligands but only give rise to very small distortions of the overall coordination geometry. Packing effects can drive a shift in the overall coordination geometry of higher coordination number complexes, for which packing effects are significant relative to the small difference in energy between geometries. Thus while $[Mo(CN)_8]^{4-}$ has a square antiprismatic coordination geometry, in solution it exhibits a dodecahedral coordination geometry in the crystals of many of its salts.

Relativistic effects on orbital energies

The proximity of fast moving electrons to massive nuclei in the heavier transition elements results in relativistic expansion and contraction of orbitals. The net results are that

- heavier elements tend to be smaller than expected. This effect preferences lower coordination numbers.
- the relative energies of orbitals shift. Orbitals which become contracted are lowered in energy while those which are expanded increase in energy, as shown for the case of gold in Figure 9.5.6A.

The combination of smaller sizes and altered orbital energies affects coordination preferences. Relativistic effects contribute to the greater tendency of Au^{I} relative to other group 11 metals to form linear two-coordinate complexes. As shown in Figure 9.5.6B , the relative closeness in energy of the 6s and 5*d* orbitals of gold makes mixing of these orbitals more favorable, facilitating the ability of gold to form two-coordinate complexes with strong sigma bonds oriented 180/(^{\circ}\) from one another.

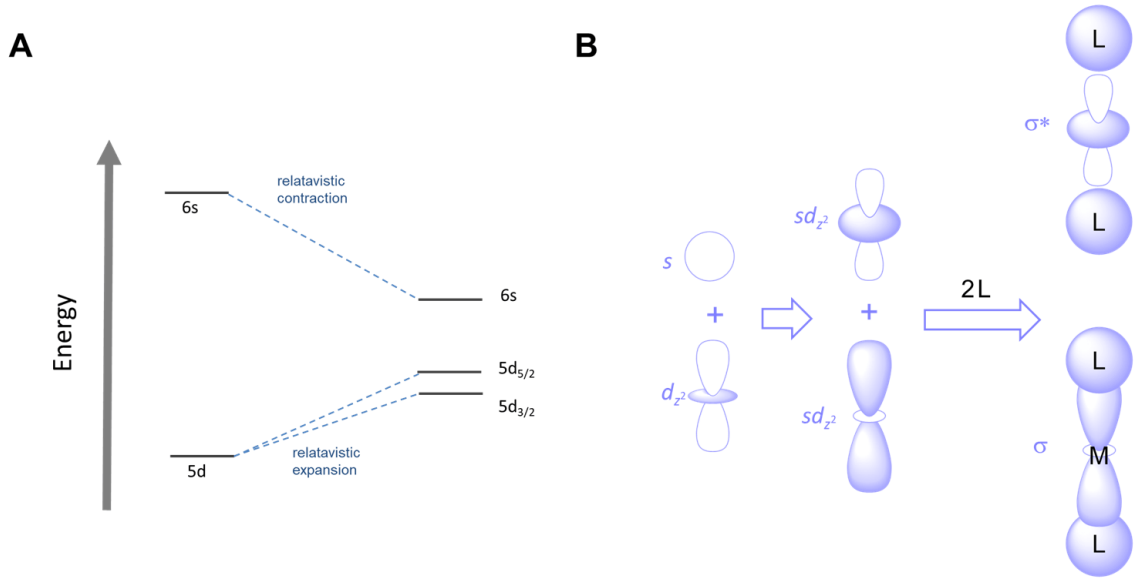


Figure 9.5.6. (A) Gold experiences relativistic expansion and contraction of its 5*d* and 6s orbitals, resulting in shifts to their relative energies. (B) This makes mixing of these orbitals more favorable, facilitating the ability of gold to form two-coordinate complexes with strong sigma bonds that involve considerable sd_{z^2} character. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

What structures do coordination complexes form?

Metal complexes with coordination numbers ranging from one to 16 are known, although values greater than seven are rare for the transition metals. In this section, examples of common coordination geometries will be presented in order of coordination number.

Coordination Number 1.

Condensed phase monocoordinate complexes are unknown for the transition metals, although the post-transition metals Tl and In form monocoordinate complexes with the bulky ligands triazapentadienyl and 2,6-tris(2,4,6-triisopropylphenyl)benzene as shown in Figure 9.5.7.

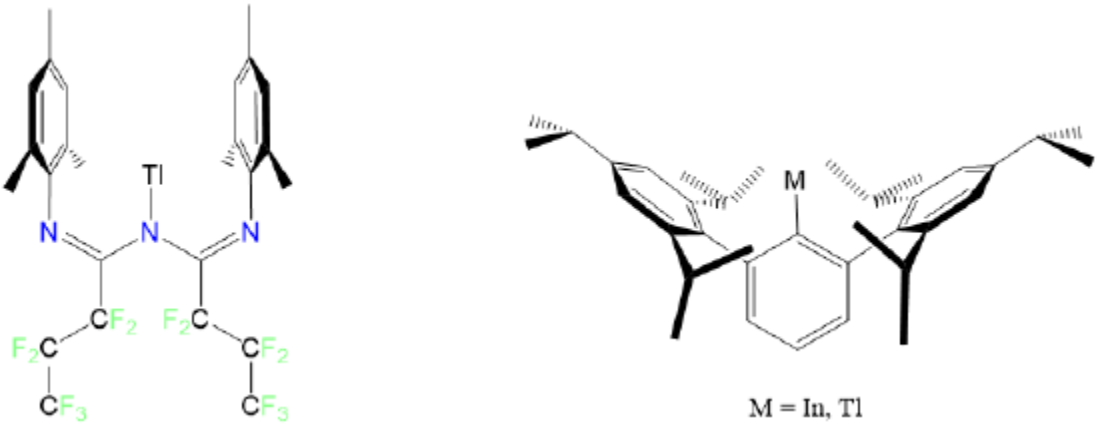


Figure 9.5.7. No monocoordinate transition metal complexes are known, but Tl^+ and In^+ form monocoordinate complexes with extremely bulky ligands. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Coordination Number 2.

A coordination number of 2 is rare outside of ***d*^{10} complexes of the group 11 metals and mercury**, specifically, Cu^+, Ag^+, Au^+,

and Hg^{2+}. In accordance with the predictions of the Kepert model these give **linear complexes.**



Among these,

- Cu^{+} more commonly gives tetrahedral complexes but can be coaxed to give linear ones. The most prominent example is $[CuCl_2]^-$, which forms when CuCl is treated with concentrated HCl under anerobic conditions.
- Ag^{+} also commonly forms tetrahedral or trigonal planar complexes but can give linear ones. The most prominent example is $[Ag(NH_3)_2]^+$, which can be formed by treating silver slats with concentrated aqueous or liquid ammonia.
- Au^{+} almost always forms linear complexes, but many of these formally two-coordinate complexes associate as depicted in Figure 9.5.8. The ability of Au^{+} to form linear complexes with cyanide is even used to selectively extract metallic gold from low grade ores. The stability of $[Au(CN)_2]^-$ means that the dissolution of metallic gold in aqueous cyanide is thermodynamically favorable under aerobic conditions.

$$4\ Au + 8\ CN^- + O_2 + 2\ H_2O \longrightarrow 4\ [Au(CN)_2]^- + 4\ OH^-$$

- Hg^{2+}, like Au^{+}, benefits from relativistic effects and more commonly forms two-coordinate complexes with a linear geometry. Among these is $[Hg(CN)_2]$. However, its preference for linearity is not as rigid as for Au^{+}, and so complexes with a variety of coordination geometries are known.

And by means of honorary mention, the mercury(I) ion, Hg_2^{2+}, forms linear complexes of the type L-Hg-Hg-L, although since Hg_2^{2+} is often considered as a single unit, these aren't always considered to be two-coordinate complexes.

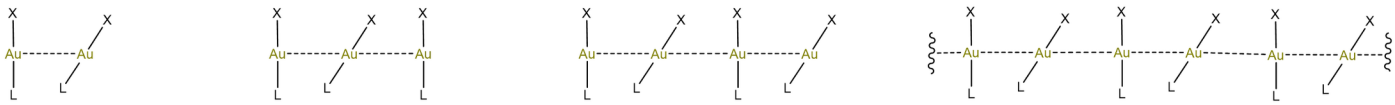


Figure 9.5.8. Many "linear" gold complexes associate side-on to form dimers, trimers, tetramers, and chains. Although in this chapter L is usually taken to represent a generic ligand, in this scheme L represents a neutral ligand that donates two electrons to the metal (py, PR_3, CO, etc.) and X an anionic one (*e.g.*, Cl^-, CN^-, etc.). Exactly which structure forms depends on the identity of L and X. Redrawn from reference 5. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Two-coordinate complexes may also be formed through the use of bulky ligands that only allow for the binding of two to the metal center. The classic examples are given in Figure 9.5.9.

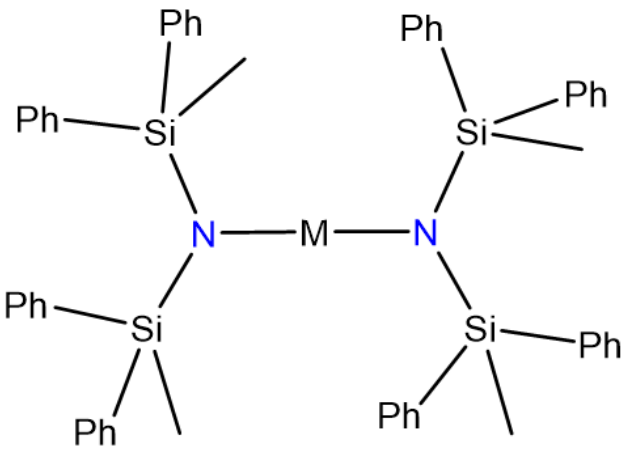


Figure 9.5.9. Two-coordinate complexes form between Mn^{2+}, Fe^{2+}, and Co^{2+} with $N(SiMePh_2)_2$.[6] This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Coordination Number 3

Three-coordinate complexes are similar to two-coordinate ones in that they are rare and, aside from the constraining influence of ligands, usually limited to d^{10} metal ions such as Cu^+ , Ag^+, Au^+, Hg^{2+}, and Pt(0). As expected from the Kepert model, in the absence of constraining ligands, three-coordinate complexes are trigonal planar.

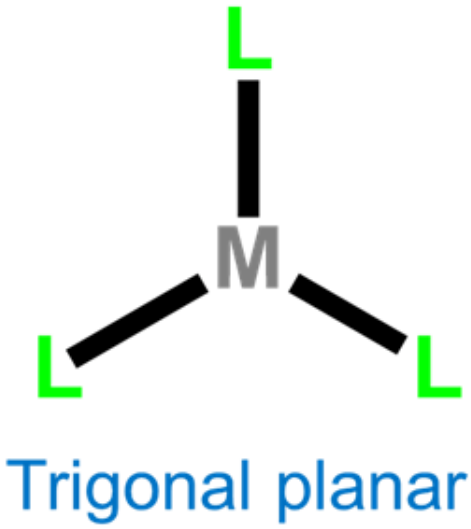


Figure 9.5.10.



Figure 9.5.10. Three-coordinate complexes prepared using bulky and semirigid ligands. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Coordination Number 4

The two common four-coordinate geometries are tetrahedral and square planar.



Tetrahedral complexes are commonly formed by metals possessing either a d^0 or d^{10} electron configuration. Monometallic examples of d^0 configurations include $TiCl_4$, VO_4^{3-}, WS_4^{2-}, MnO_4^-, CrO_4^{2-}, and OsO_4, while d^{10} examples are $[Ni(CO)_4]$, $[HgBr_4]^{2-}$, $[ZnCl_4]^{2-}$, and $[CdI_4]^{2-}$. For other electron configurations, tetrahedral complexes are known but much less common. Examples usually involve good donor ligands and include $[FeCl_4]^-$ (d^5), $[CoCl_4^{2-}]$ (d^6), and $[NiCl_4]^{2-}$ (d^7).

Second and third row transition metal centers with d^8 electron configurations like Rh^+, Ir^+, Pd^{2+}, Pt^{2+}, and Au^{3+} almost exclusively exhibit **square planar geometries**. Beyond this, square planar geometries are often formed by Ni^{2+} (d^8), Ni^{3+} (d^7), and Cu^{2+} (d^9). Examples of square planar complexes include $[Cu(acac)_2]$; $[PtCl_4]^{2-}$;Wilkinson's catalyst, $[RhCl(PPh_3)_3]$; and Vaska's complex, *trans*-$[Ir(CO)Cl(PPh_3)_2]$.



Coordination Number 5

The two common coordination geometries for five-coordinate complexes are trigonal bipyramidal and square pyramidal.



Figure 9.5.11.

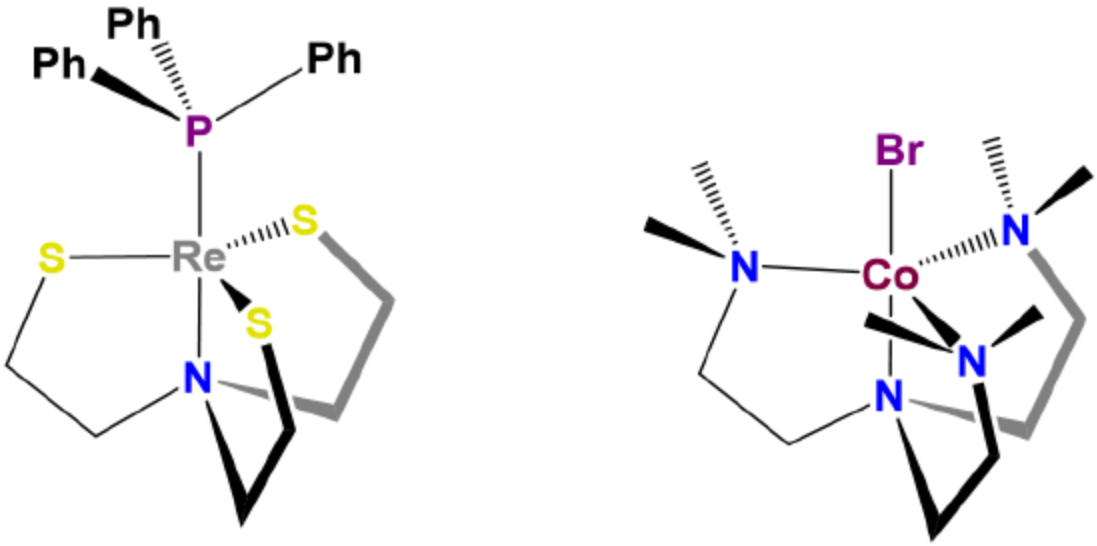


Figure 9.5.11. Some tripodal ligands preference the formation of trigonal bipyramidal complexes. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Homoleptic $[Ni(CN)_5]^{3-}$ possesses a square pyramidal structure, although the geometry is more common for macrocyclic complexes like the iron protoporphyrin of deoxymyoglobin shown in figure 9.5.4 and for complexes containing oxo and nitrido ligands, examples of which are shown in Figure 9.5.12.

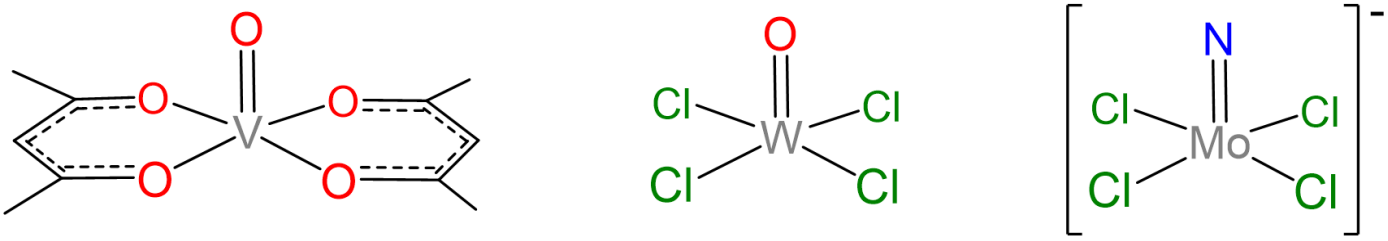


Figure 9.5.12. Some square pyramidal oxo and nitrido complexes. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

In the absence of rigid constraining ligands, the relatively low energy difference between the trigonal bipyramidal and square pyramidal coordination geometries provides a mechanism for interconversion of the axial and equatorial ligands in a trigonal planar complex. For example, pentacarbonyliron(0) exhibits fluxionality involving a square pyramidal intermediate via a Berry pseudorotation mechanism, as shown in Figure 9.5.13.

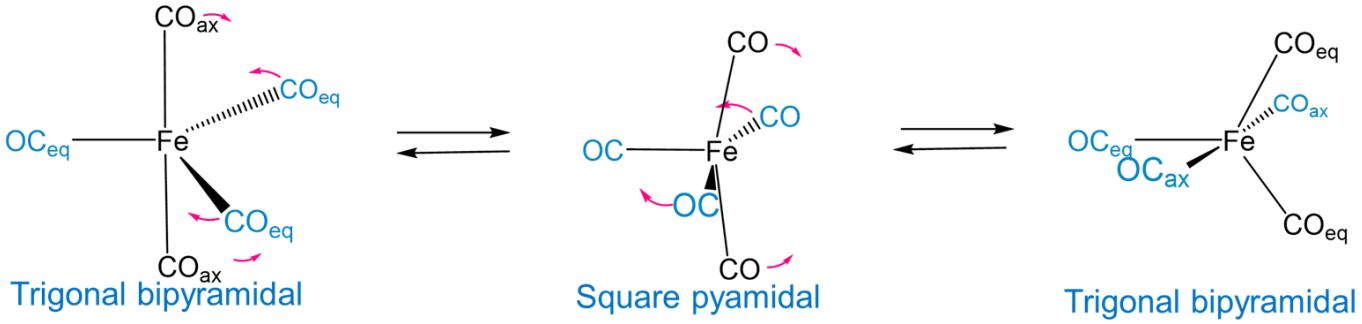


Figure 9.5.13. Fluxionality in pentacarbonyliron(0) involves exchange of axial and equatorial carbonyl ligands via Berry pseudorotation. Interconversion of the axial and equatorial carbonyl groups occurs faster than the NMR timescale at room temperature. As a result the ^{13}C NMR spectrum of $Fe(CO)_5$ exhibits a single signal rather than two separate signals for the axial and equatorial carbonyl carbons. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Coordination Number 6

The two common coordination geometries for coordination number 8 are octahedral and trigonal prismatic.

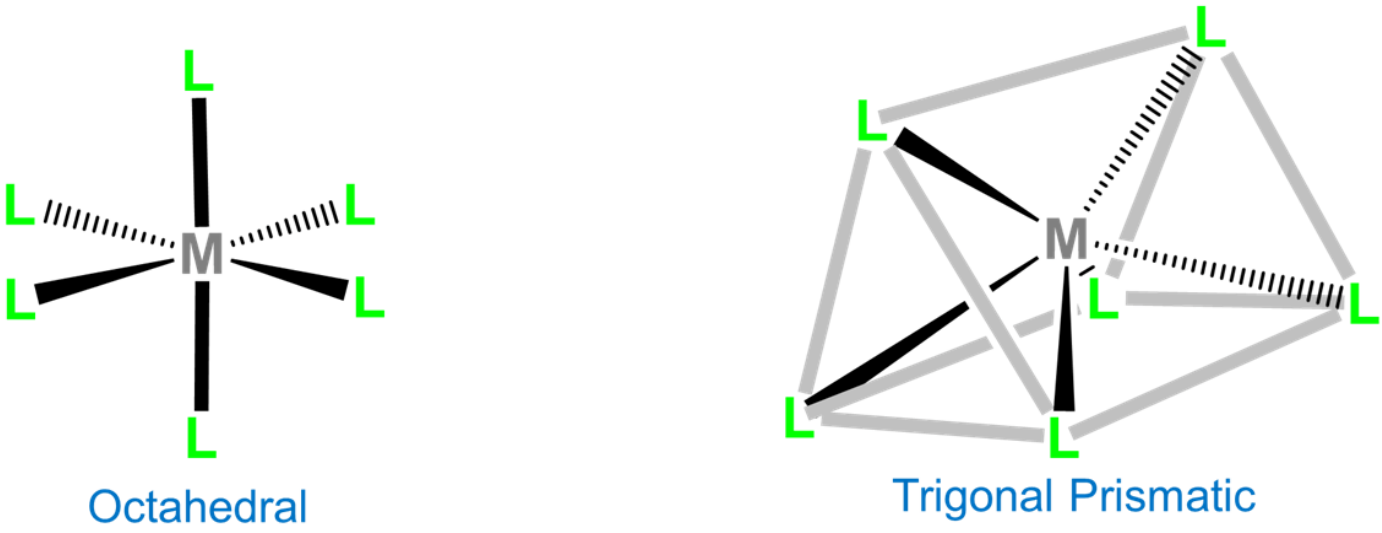


Figure 9.5.14.

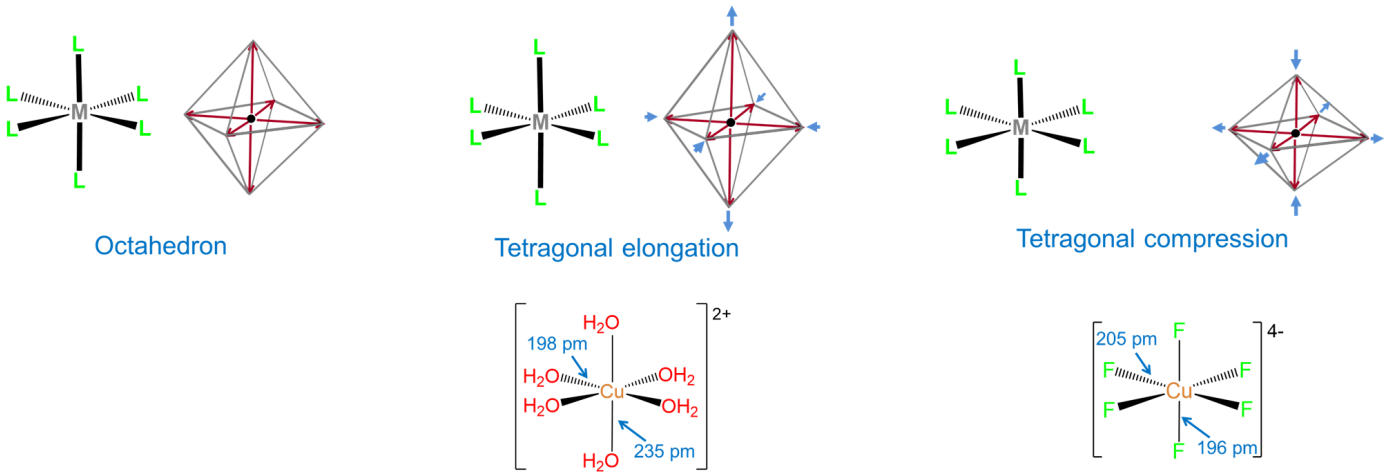


Figure 9.5.14. Tetragonal distortions commonly occur for d^4, d^7 , and d^9 octahedral complexes. The most common type involves axial elongation in which the octahedron is stretched along a single *trans*-L-M-L axis, but axial compressions in which the octahedron is compressed along such an axis instead are sometimes observed. An example of an axial elongated complex is $[Cu(H_2O)_6]^{2+}$ in solution, while $[CuF_6]^{4-}$ is axially compressed when doped into a Ba_2ZrF_6 lattice (it is elongated when doped into a -----. Bond distances are taken from references 7 and 8. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Trigonal prismatic coordination is related to octahedral coordination as shown in Figure 9.5.15. As may be seen in Figure 9.5.15 , an octahedral coordination sphere is just a trigonal antiprism in which all edge lengths are identical. Rotation of one triangular face relative to its opposite until the two are eclipsed gives a trigonal prismatic geometry. In fact, since continuation of this rotation gives another octahedral complex, the trigonal prismatic geometry is an intermediate in isomerization reactions involving octahedral complexes.

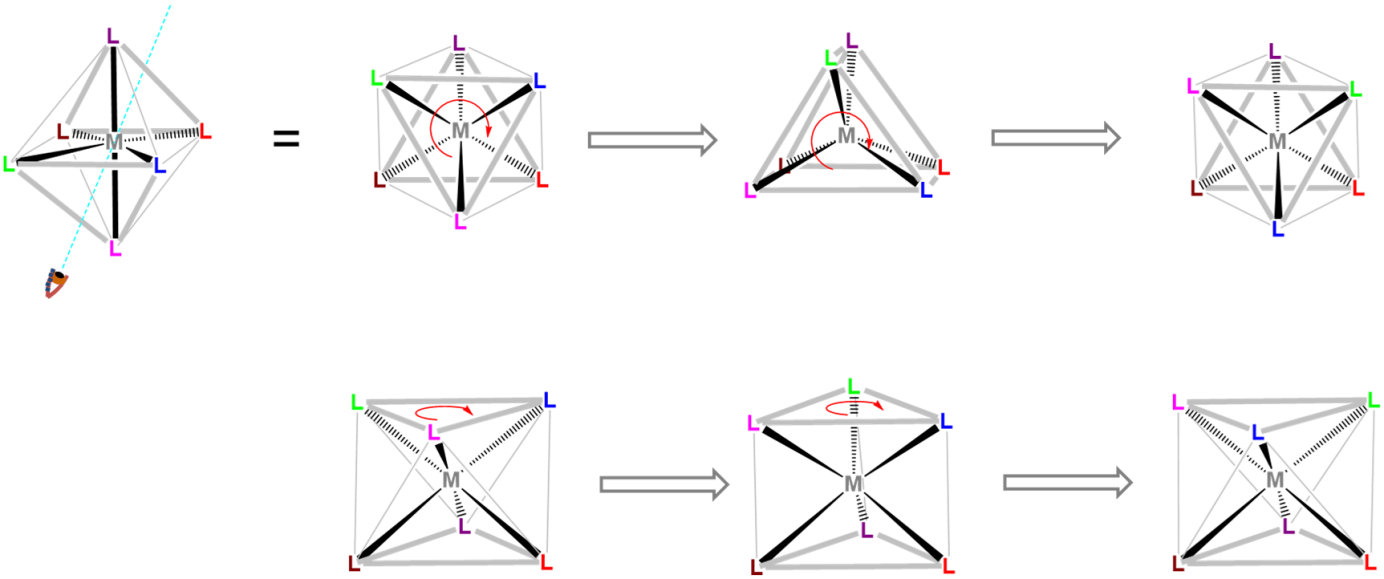


Figure 9.5.15. Since an octahedron is a trigonal antiprism, a trigonal prism may be produced by rotating or "twisting" one face of the octahedron relative to its opposite. Since continuation of the rotation gives an isomer of the original octahedron, when the energy landscape for twists like these is thermally or photochemically accessible, such twists provide one pathway for isomerization reactions involving octahedral complexes. In tris- and bis-chelates, such isomerizations are said to occur by Bailar and Ray-Dutt twists, which differ only in the relationship between the chelate rings and the faces twisted. Top: View looking down an axis bisecting a pair of opposing faces. Bottom: View perpendicular to that shown at top. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

In contrast to octahedral coordination geometries, trigonal prismatic coordination (and distorted versions thereof) are rare and occur mostly for d^0, d^1, and d^2 configurations. Examples of trigonal prismatic metal centers include the d^2 Mo^{4+} centers in MoS_2, d^1 $[Re(S_2C_2Ph_2)_3]^-$, and d^0 $[Ta(CH_3)_6]^-$, of which the latter two structures are given in Figure 9.5.16. Semirigid ligands like that shown in Figure 9.5.4C may be used to encourage the adoption of a trigonal prismatic geometry, although once the number of *d* electrons present exceeds two, the preference for octahedral coordination is too great for a trigonal prismatic geometry to occur.

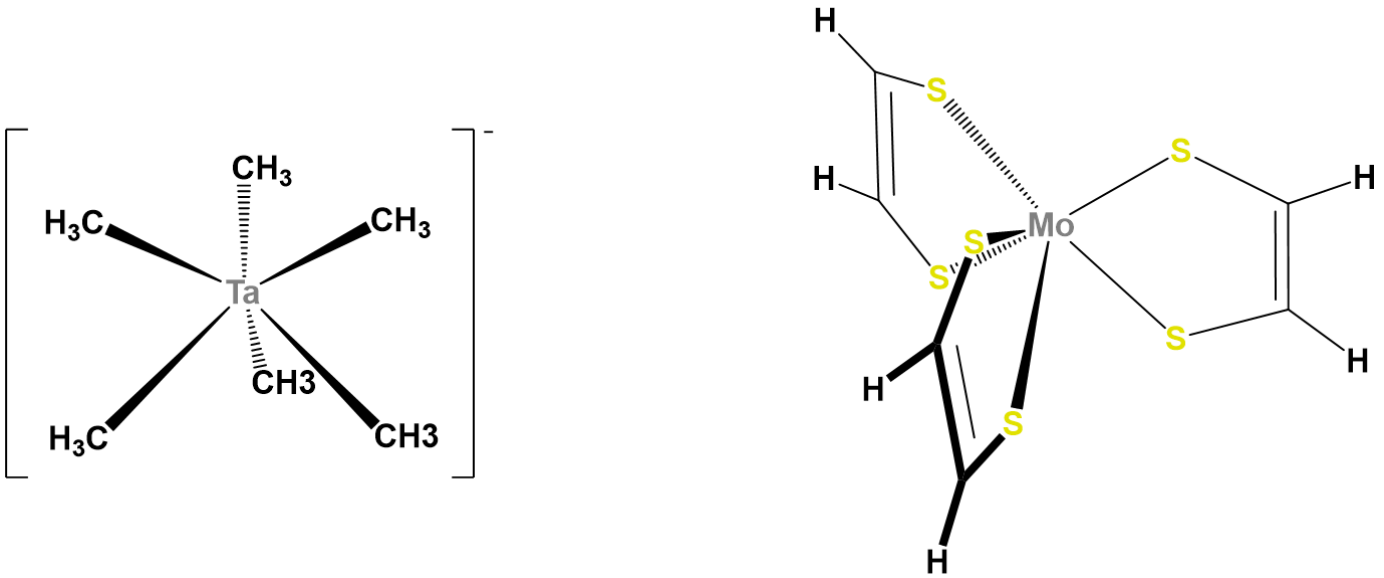
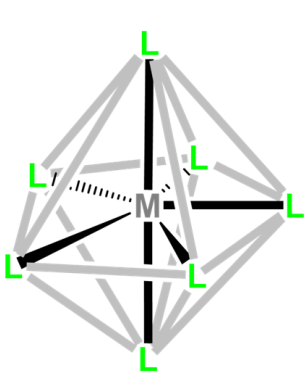


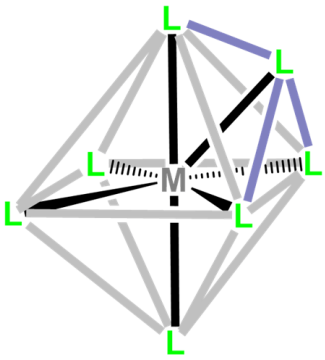
Figure 9.5.16. The complexes $[Ta(CH_3)_6]^-$ and $[Mo(S_2C_2H_2)_3]$ adopt a trigonal prismatic geometry. Trigonal prismatic coordination is common for d^0 and d^1 complexes with alkyl and dithiolene ligands. It is also typical for the dithiolene ligands to coordinate along the rectangular edges of the trigonal prism instead of the triangular ones. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Coordination Number 7

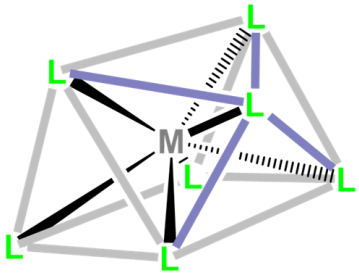
Seven-coordinate complexes are rare outside of the relatively large early transition metals, lanthanides, and actinides. The three common seven-coordinate geometries are pentagonal bipyramidal, monocapped octahedral, and monocapped trigonal prismatic. The latter two are often called capped octahedral and capped trigonal prismatic, with the mono- prefix being understood.



Pentagonal bipyramidal



Capped octahedral



Monocapped trigonal prismatic

Although intraligand repulsions are smaller in the pentagonal bipyramidal coordination geometry than the capped octahedral and capped trigonal prismatic geometries, the difference is small, and the three structures are often close in energy. As a result the structure observed is often dependent on ligand-based constraints, crystal packing, and solvent effects that preference one geometry over the others.

Heptacyano complexes are often pentagonal bipyramidal. Examples include $[Mo(CN)_7]^{3-}$, $[W(CN)_7]^{3-}$, and $[Os(CN)_7]^{3-}$. Seven-coordinate complexes containing oxo ligands commonly are pentagonal bipyramidal with the oxo ligand(s) in the less sterically hindered axial position. Examples include $[NbOF_6]^{3-}$ and, for the inner transition metals, $[UO_2F_5]^{3-}$. Ligands that have been used to promote formation of seven-coordinate species include 15-crown-5 and 2,2':6',2":6",2"'-quaterpyridine. Representative complexes are given in Figure 9.5.17.

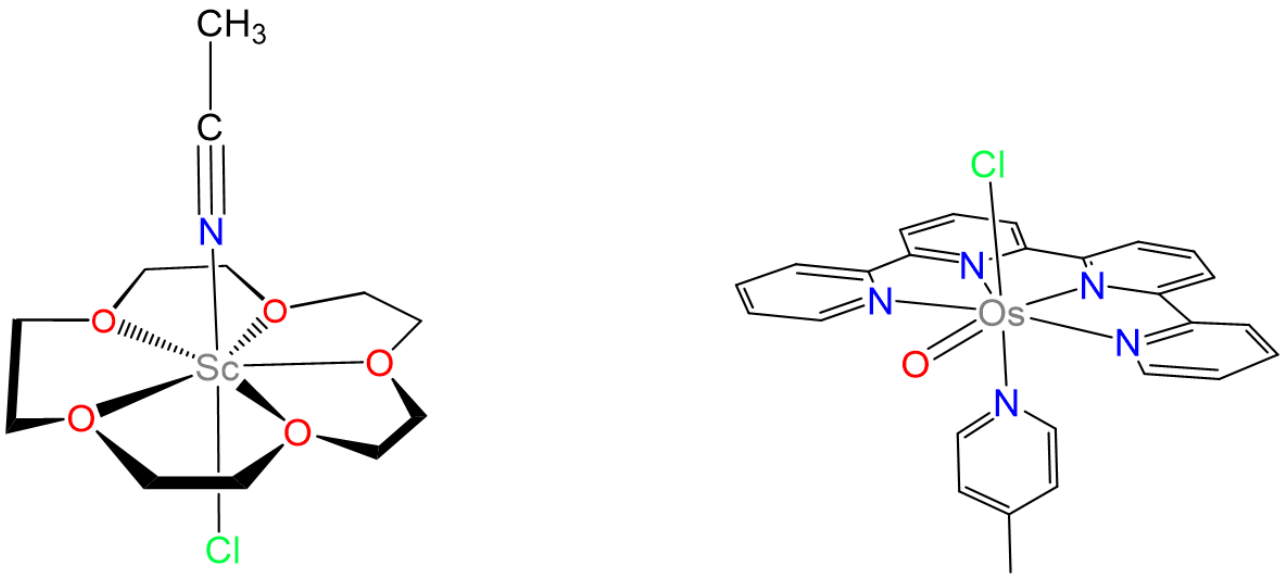


Figure 9.5.17. Seven-coordinate complexes containing ligands that encourage the formation of seven-coordinate geometries. Note that while in $[NbOF_6]^{3-}$ and $[UO_2F_5]^{3-}$ the oxo ligands occupy axial positions, the Osmium complex shown possesses an oxo ligand in an equatorial position. This is likely because the parent octahedral complex, in which the oxo ligand is not present, possesses an expanded outer N-Os-N angle of 121.655° that opens to 154.161° to accommodate the oxo group. Drawn based on the structures reported in references 9 and 10. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Capped trigonal prismatic geometries are common for complexes of the early transition metals. Examples include $[NbF_7]^{2-}$,$[TaF_7]^{2-}$, and $[ZrF_7]^{3-}$ in $(NH_4)_3[ZrF_7]$.

Capped octahedral geometries are found in $[MoMe_7]^-$, $[WMe_7]^-$, and $[WBr_3(CO)_4]$, which contains three pairs of *trans*-Br and CO with the final CO capping the octahedron's $(CO)_3$ face, as shown in Figure 9.5.18.

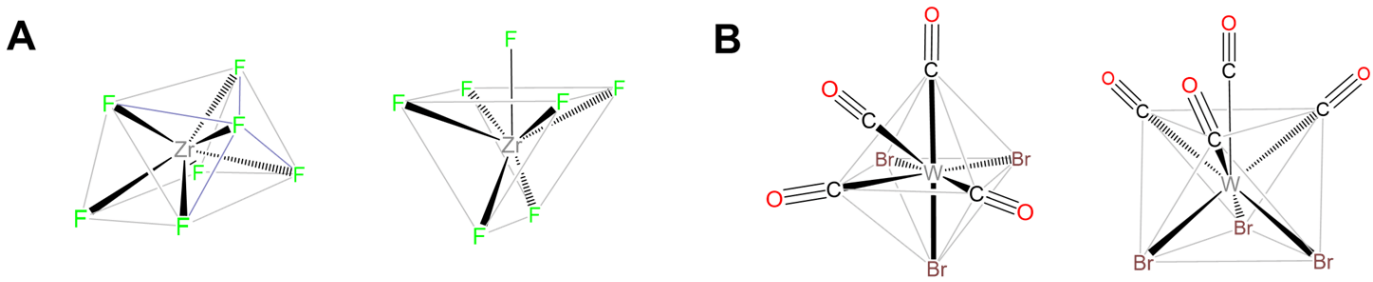


Figure 9.5.18. Examples of complexes that adopt monocapped triconal prismatic and monocapped octahedral geometries.(A) Two views of the structure of (A) capped trigonalprismatic $[ZrF_7]^{3-}$ and (B) capped octahedral $[WBr_3(CO)_4]$. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

In seven- and higher-coordinate complexes, ligand and crystal packing effects frequently give distorted coordination geometries. These geometries are intermediate between two or more of the idealized seven coordinate geometries, making it difficult to tell exactly which structure they are a distortion of (Figure 9.5.19).

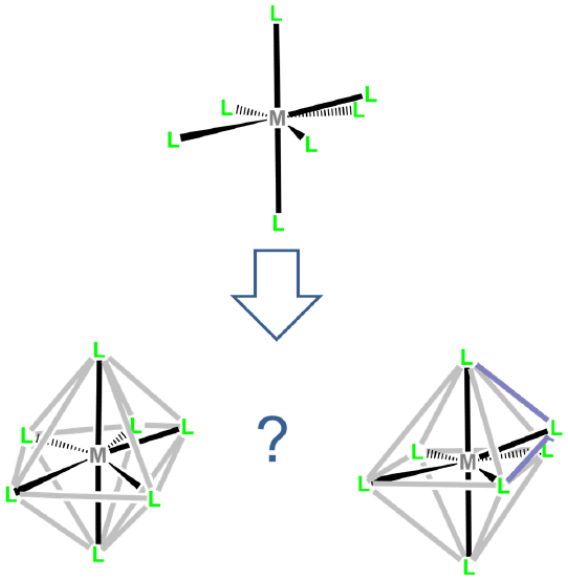


Figure 9.5.19. Many seven-coordinate structures are distorted and can be difficult to classify. For example, how should the geometry of this complex be described - as distorted trigonal bipyramidal or distorted monocapped octahedral? This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Coordination Number 8

Eight-coordinate complexes are rare and occurs in discrete molecules and ions only for the relatively large early transition metals, lanthanides, and actinides. The three common eight-coordinate geometries are square antiprismatic, dodecahedral, and bicapped trigonal prismatic. In contrast, the cubic coordination geometry is only found in ionic lattices like that of CsCl and in complexes of the inner transition metals such as $Na_3[UF_8]$.

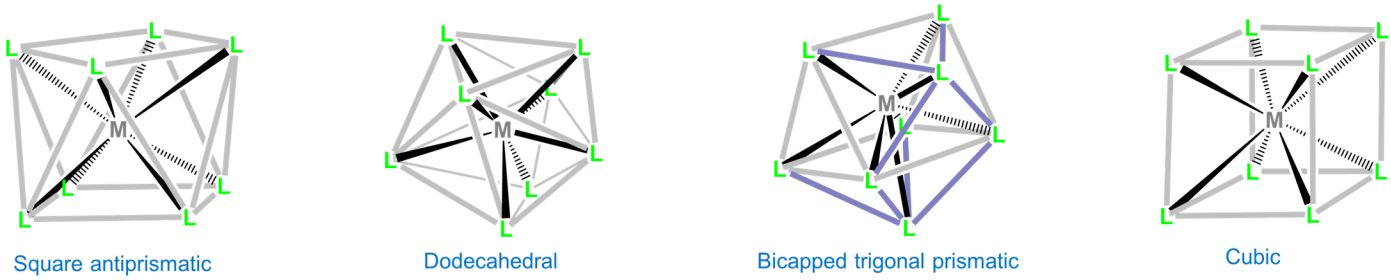


Figure 9.5.20. The square antiprism may be made by twisting one face of a cube relative to another, and the dodecahedron by folding opposing faces towards one another.

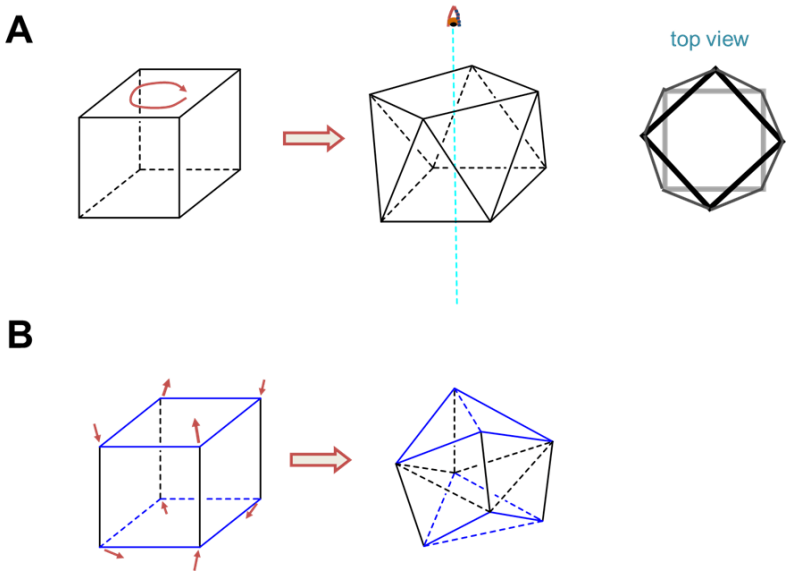


Figure 9.5.20. The (A) square antiprismatic and (B) dodecahedral coordination geometries are distorted cubic geometries. (A) The square antiprismatic coordination geometry is just a cubic coordination geometry in which one face has been rotated 45° relative to its opposite (and for which the distance between those faces need not be equal to the distance between adjacent atoms within a face) (B) The dodecahedral geometry may be thought of as a cube in which opposing faces are folded up and down relative to one another as shown. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

As with other high-coordinate structures, the energy difference between these eightfold coordination geometries is small enough that packing effects can significantly influence the observed structure. For example, octacyanomolybdates commonly adopt a square antiprismatic coordination geometry but depending on the counterions present can give dodecahedral or bicapped trigonal prismatic complexes. Examples are given in Figure 9.5.21.

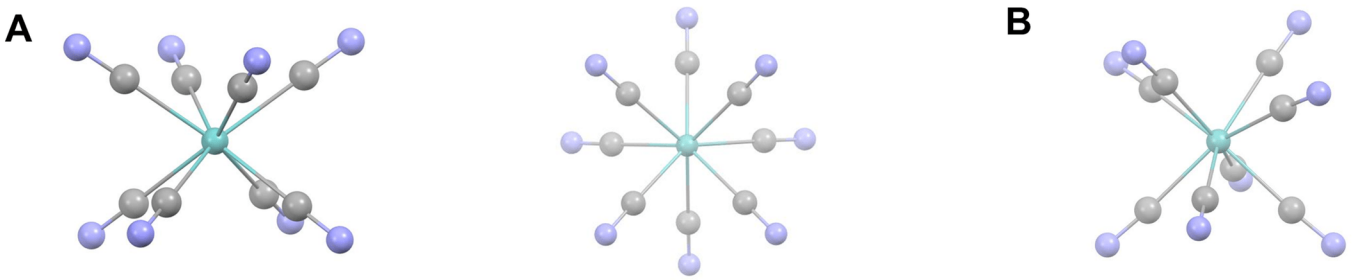


Figure 9.5.21: Structures reported for (A) square antiprismatic $[Mo(CN)_8]^{3-}$ as a solid 4,4'-Diazenediyldipyridinium salt and (B) dodecahedral $[Mo(CN)_8]^{4-}$ as a solid tetra-n-butylammonium salt.

Coordination Number 9

Again, nine-coordinate complexes typically require larger transition metals, lanthanides, and actinides. Coordination geometries

are typically either tricapped trigonal prismatic or idiosyncratically determined by the ligands. Simple examples include the aqua complexes $[Sc(H_2O)_9]^{3+}$, $[Y(H_2O)_9]^{3+}$, and $[La(H_2O)_9]^{3+}$, as well as $[TcH_9]^{2-}$ and $[ReH_9]^{2-}$.

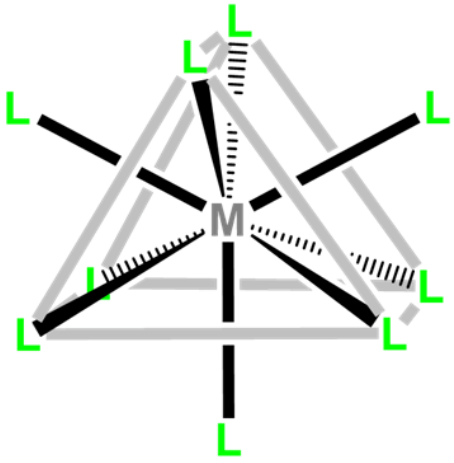


Figure 9.5.22.

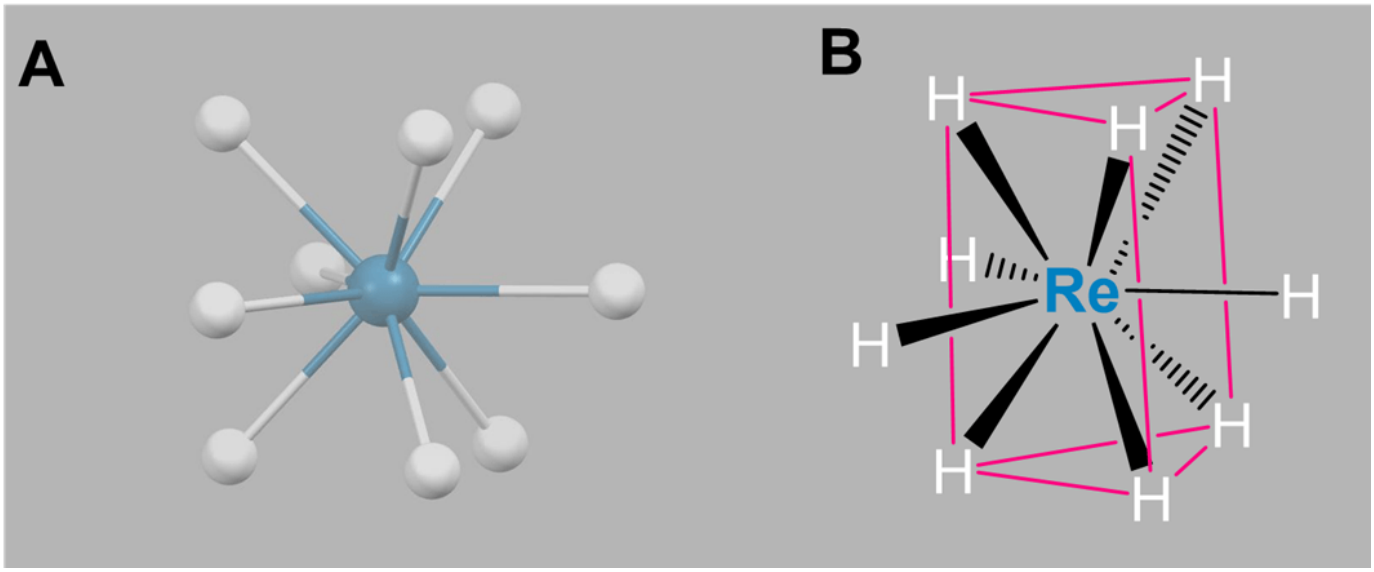


Figure 9.5.22. (A) Structure of $[ReH_9]^{2-}$ in $K_2[ReH_9]$ and (B) schematic showing how the structure maps onto a tricapped trigonal pyramidal coordination geometry. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Coordination Numbers 10-16

Coordination numbers higher than nine are extremely rare for compounds that bind in κ fashion (form conventional metal-ligand bonds)[14] and usually involve some combination of large metals, sterically undemanding ligands, and special ligand structures that promote higher coordination. Noteworthy examples include

1. Twelve-coordinate $[Hf(BH_4)_4]$, which illustrates how small multidentate ligands promote higher coordination numbers. As shown in Figure 9.5.23, $[Hf(BH_4)_4]$ has a cubooctahedral structure in which BH_4^- acts as a tridentate ligand, with BH_3 units occupying triangular faces of the cubooctahedron to give a tetrahedron of BH_4^- ligands around the Hf.

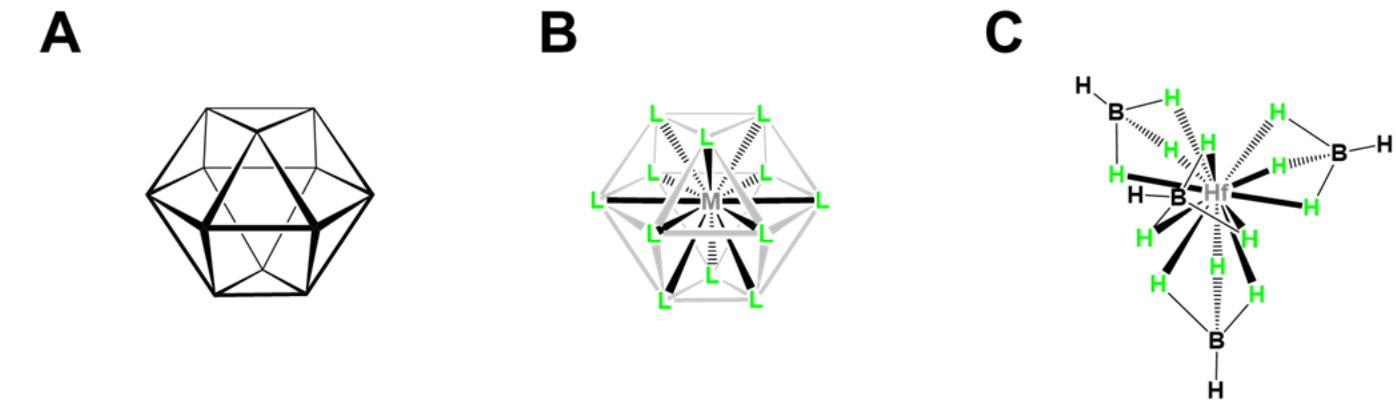


Figure 9.5.23. The anticubooctahedral coordination geometry is observed for $[Hf(BH_4)_4]$. (A) An anticubooctahedron consists of a hexagonal ring capped with antiparallel triangles above and below the ring. (B) Idealized anticubooctahedral complex. (C) Structure of $[Hf(BH_4)_4]$. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

2. Twelve-coordinate $[Ce(NO_3)_6]^{2-}$, in which the nitrate oxygens define an icosahedral coordination geometry as shown in Figure 9.5.24. The nitrates in the structure bind the Ce center in bidentate fashion in an octahedral array.

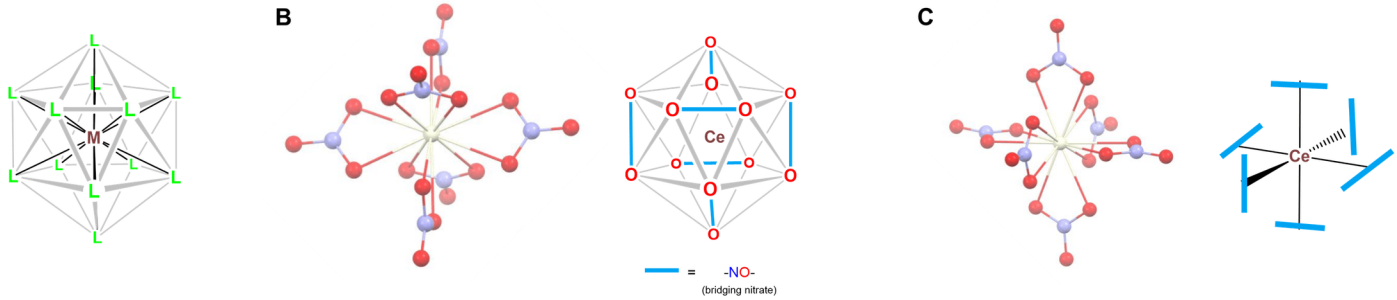


Figure 9.5.24. Coordination geometry of $[Ce(NO_3)_6]^{2-}$ in $[Mg(H_2O)_6][Ce(NO_3)_6]\cdot H_2O$. (A) Idealized icosahedral coordination. (B) View of the structure of $[Ce(NO_3)_6]^{2-}$ showing how it maps onto the icosahedral coordination geometry. (C) The structure may also be thought of as comprising an octahedral geometry in which each vertex of the octahedron is occupied by a κ^2-NO_3^-. The structure of $[Ce(NO_3)_6]^{2-}$ is rendered in Mercury from the cif data in reference 15. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

3. Fifteen-coordinate $[Th(H_3BNMe_2BH_3)_4]$, which also uses bridging H-B-H units that occupy little of the coordination sphere. In $[Th(H_3BNMe_2BH_3)_4]$, three of the four $H_3BNMe_2BH_3$ ligands bind in κ^4 fashion and one binds κ^3, giving the fifteen fold coordination.[16]

4. Sixteen-coordinate $[CoB_{16}]^-$, which possesses the highest coordination number yet observed. Its structure is given in Figure 9.5.25. The coordination geometry is an octahedral antiprism, and the complex should be considered to involve a Co center in the midst of a B_{16}^- "molecular drum" held together by cluster bonds.

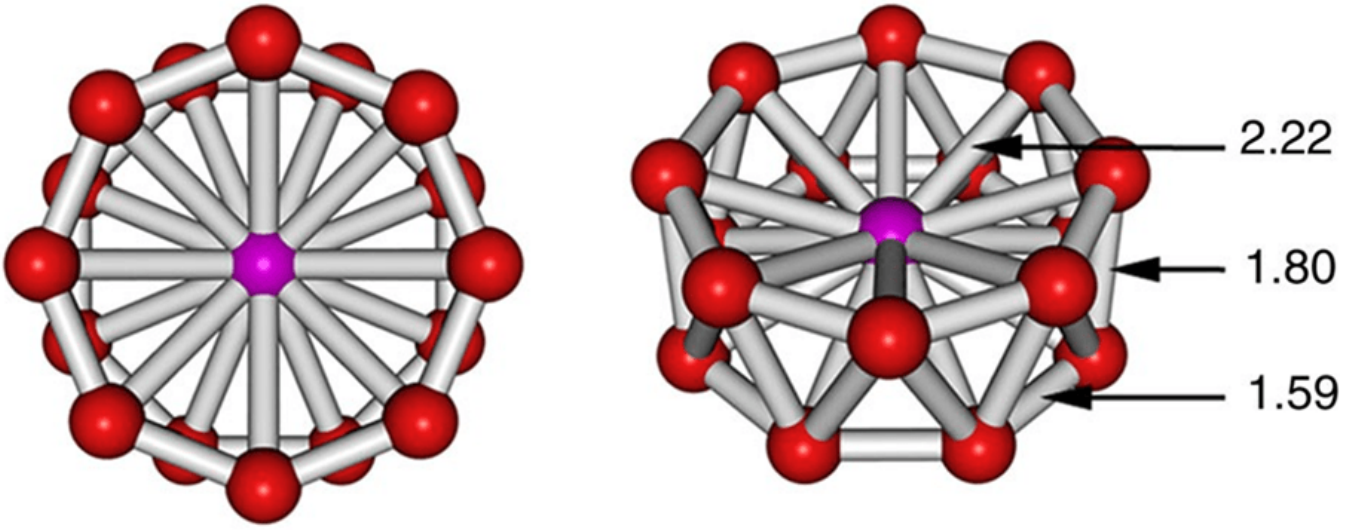


Figure 2A from Popov, I., Jian, T., Lopez, G. *et al.* Cobalt-centered boron molecular drums with the highest coordination number in the CoB_{16}^- cluster. *Nat Commun* **6,** 8654 (2015). https://doi.org/10.1038/ncomms9654, which is is licensed in that publication under a Creative Commons Attribution 4.0 International License.

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12. The structures are rendered from cif data reported in the following publications: (A) square antiprismatic $[Mo(CN)_8]^{3-}$: Wen-Yan Liu, Hu Zhou, Ai-Hua Yuan, *Acta Crystallographica Section E: Structure Reports Online*, 2008, 64, m1151, (B) dodecahedral $[Mo(CN)_8]^{4-}$: B.J.Corden, J.A.Cunningham, R.Eisenberg, *Inorganic Chemistry*, 1970, 9, 356.
13. The structure of ReH_9^{2-} is rendered from the structure reported in Abrahams, S.C.; Ginsberg, A.P.; Knox, K. Transition metal-hydrogen compounds. II. The crystal and molecular structure of potassium rhenium hydride, K_2ReH_9 *Inorganic Chemistry*,

1964, *3*, 558-567.
14. There are other complexes in which a metal may be said to interact with more than sixteen "ligand atoms", but these are not usually considered to possess a higher coordination number. For example, in some π complexes like η^5-Cp_4U, technically there are 20 C atoms fastened to the U, but these complexes are better considered as 12-coordinate than twenty (since each cyclopentadienyl ring is isolobal with a *fac*-coordinated set of 3 L ligands), while the metal centers in endohedral fullerene species like $La@C_{60}$ do not interact with all sixty carbon atoms at once, and so are better thought of as a metal trapped in a spacious sixty-carbon cage.
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9.6: Coordination Frameworks

Bridging ligands link metals in multicenter coordination complexes

Some ambidentate and multidentate ligands have the capacity to bridge two metal centers. For instance, the cyano ligands can bridge two metal centers by forming linear links of the type

$$\mathrm{M{-}CN{-}M'}$$

Linkages like these can be used to bridge multiple metal centers in a cluster or network solid, the latter of which is sometimes called a coordination framework. When the cyano ligand is combined with octahedral metal centers possessing 90° L-M-L bond angles, a cubic coordination network results. An example is the Prussian Blue coordination framework, which possesses the unit cell depicted in Figure 9.6.1A.

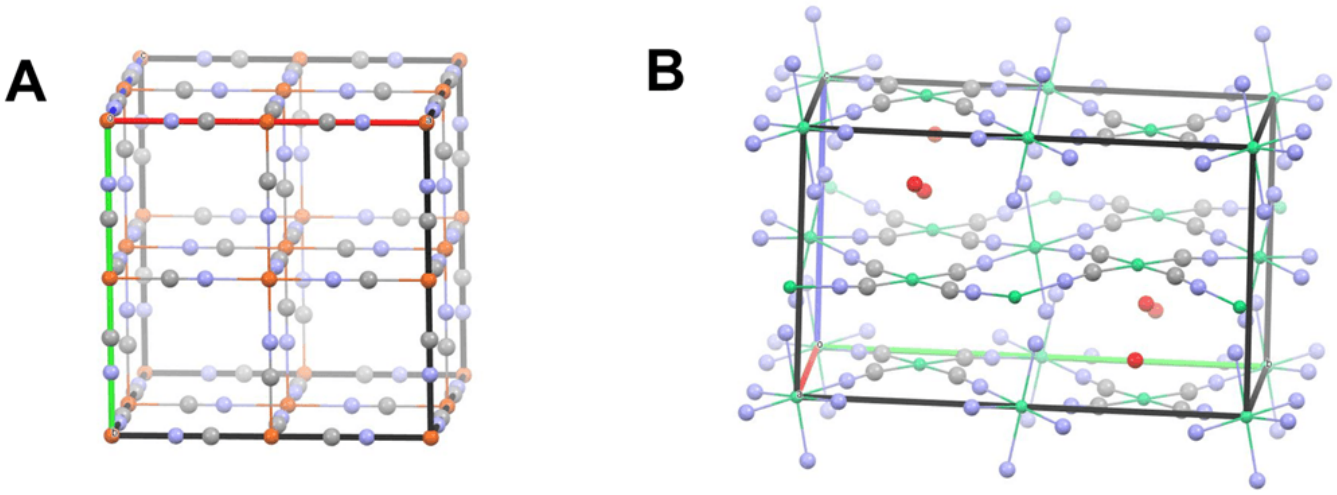


Figure 9.6.1. (A) Idealized unit cell of Prussian Blue showing the cubic coordination framework of interconnected $[Fe^{II}(CN)_6]^{4-}$ and Fe^{3+} units. Because the ratio of Fe^{3+} to $[Fe^{II}(CN)_6]^{4-}$ is 4:3, some of the $[Fe^{II}(CN)_6]^{4-}$ sites are occupied by aqua ligands. (B) Structure of a Hofmann-type clathrate consisting of layers of square planar $[Ni(CN)_4]^{2-}$ units linked by $Ni(NH_3)_2^{2+}$ units. In this structure water occupies the sites between the layers, but structures like these can adjust to accommodate a variety of organic molecules. Hydrogen atoms are omitted for clarity. Rendered from the structures reported in references 1. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

The cubic network shown in Figure 9.6.1A reflects the 3D structure of the octahedron, in which the M-L bonds point along the x, y, and z axes. If a square planar metal center is used, a 2D coordination network comprising interlinked squares is produced instead. An example is the Hofmann clathrate shown in Figure 9.6.1B, which depicts a Hofmann clathrate in which square planar $[Ni(CN)_4]^{2-}$ units are linked by *trans*-$Ni(NH_3)_2^{2+}$ units (which are octahedral but have a square plane of open coordination sites perpendicular to the NH_3-Ni-NH_3 axis).

The structures of coordination polyhedra and frameworks reflect ligand and metal coordination geometries

As illustrated by the Prussian Blue and Hofmann clathrate coordination networks shown in Figure 9.6.1, the structures formed when a bridging ligand links multiple metal centers depends on the geometry of the centers, the ligand, and the metal-ligand bonds formed. Because the directionality of metal-ligand bonding in many types of complexes is well-characterized and predictable, it is possible to design metal complexes and linkers that can serve as building blocks for clusters and networks. In particular

- metal complexes with combinations of labile (substitutable) ligands in particular topologies. These insure that the linking

ligand will be arranged around the metal center in those defined directions.
- Ligands that possess binding sites oriented in defined directions so that they link the metal centers together in particular topologies.

Examples of the sort of metal centers that can be used and examples of linking ligands are given in Figure 9.6.2.

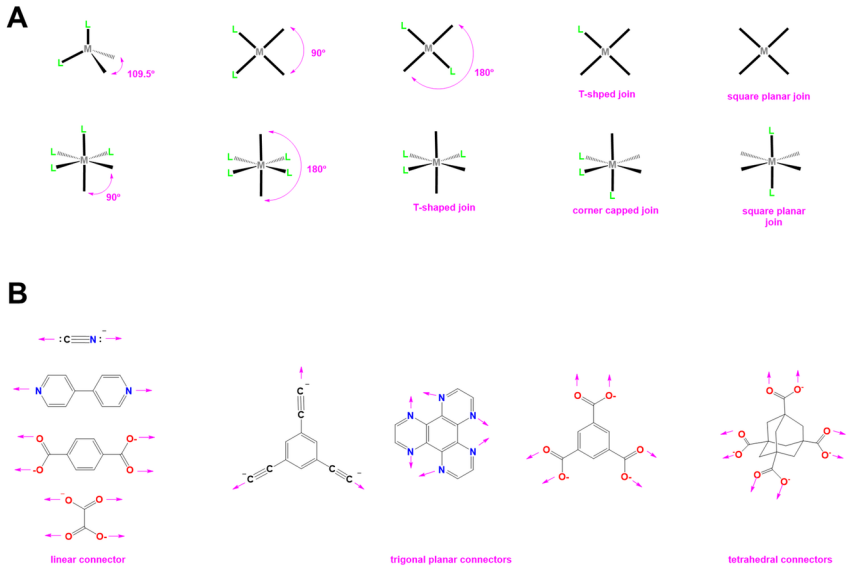


Figure 9.6.2. The directionality of M-L bonding permits the rational construction of structures using metal and ligand "building blocks". For example, (A) Tetrahedral, octahedral, and square planar metal centers alone can be used to connect sets of ligands at 90°, 109.5°, and 180° bond angles in a variety of arrangements while (B) the selection of organic linkers shown can be used as linear, trigonal planar, and tetrahedral linkers.

Examples of how the building blocks shown in Figure 9.6.2 might be used to prepare molecular polyhedra and coordination networks are depicted schematically as shown in Figure 9.6.3. Among the examples shown in Figure 9.6.3, those depicted on the right schematize the Hofmann clathrate (top) and Prussian Blue (bottom) coordination networks of Figure 9.6.1.

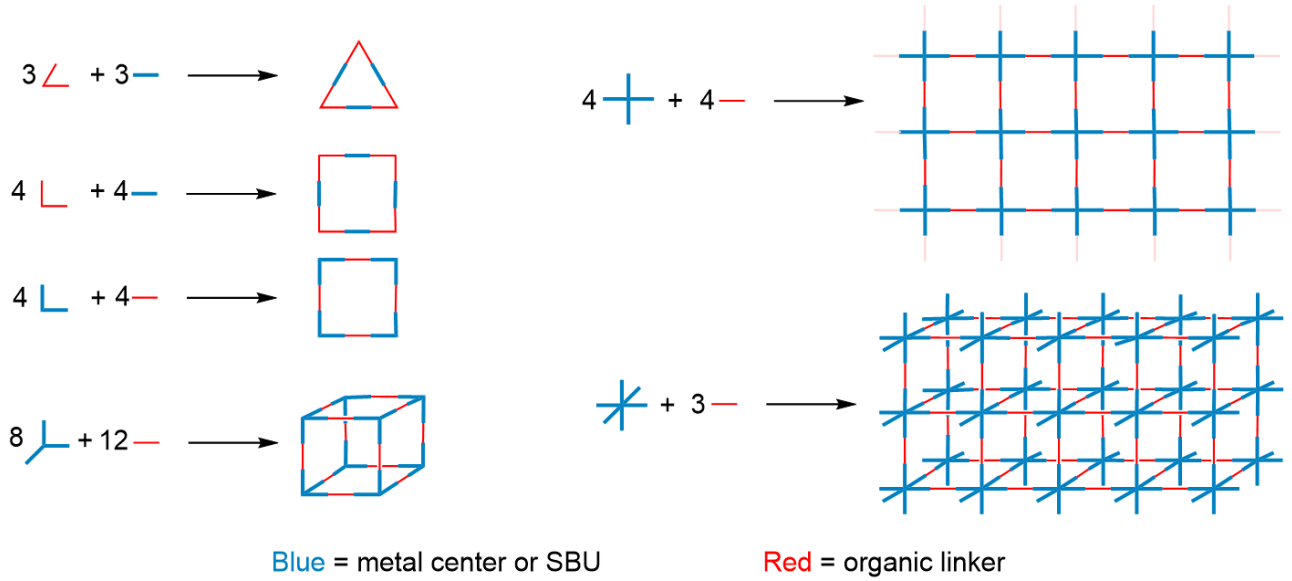


Figure 9.6.3. Examples illustrating how the combination of metal and organic linker units gives rise to polyhedral and network structures that reflect the geometry of the building blocks used.

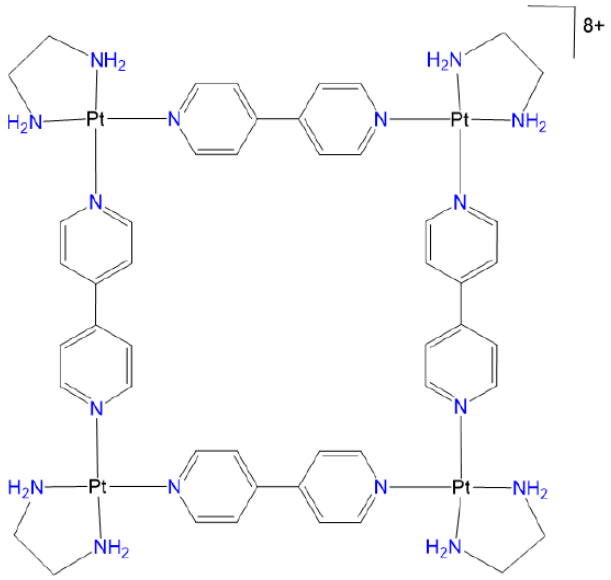


Figure 9.6.4. In its structure, the $Pt(en)^{2+}$ centers possess *cis*-90° coordination sites linked by the linear linker 4,4'-bipyridine.

A wider variety of structures are possible than those hinted at by the building blocks and structures shown in Figures 9.6.2 and 9.6.3. More may be obtained using the principles of molecular structure outlined in the sections on coordination geometry, ligands, and isomerism. In fact, one of the first coordination polyhedra prepared involved Jean-Marie Lehn's recognition that planar bidentate ligands in a tetrahedral bis-chelate are oriented perpendicular to one another, as shown in Figures 9.6.5A. This enabled him to prepare a molecular trigonal prism by combining a source of Cu^{2+} with the trigonal planar and linear-capable organic linkers that bind the Cu^{2+} in bidentate fashion, as shown in Figure 9.6.5B.

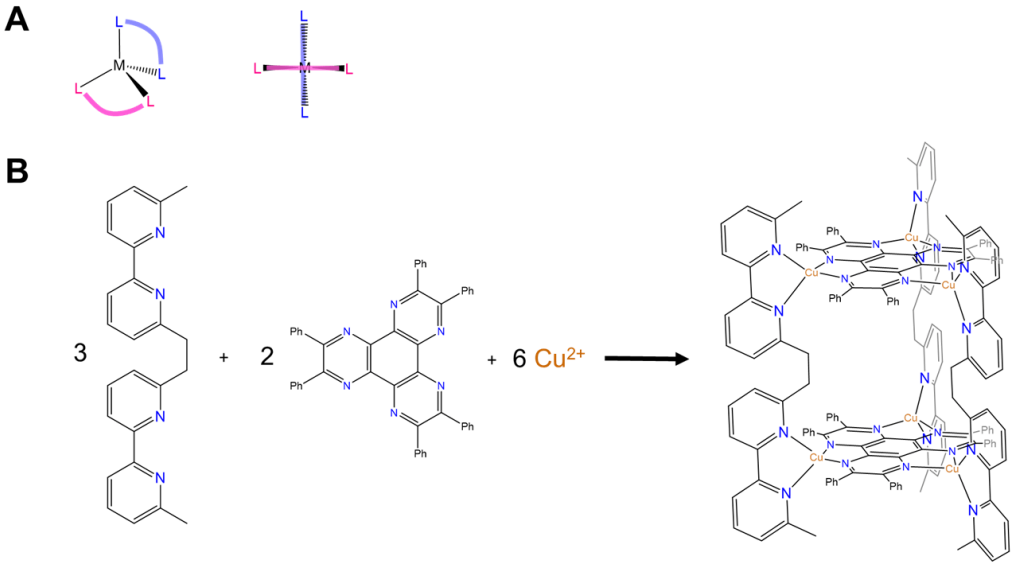


Figure 9.6.5. (A) When a tetrahedral metal center is coordinated by two planar bidentate ligands, the ligands are oriented at 90° to one another. (B) This permitted Jean Marie-Lehn and his cowokers to prepare a molecular trigonal prism consisting of six Cu^{2+} ions linked by the rigid and semirigid nitrogen-containing ligands on the prism's trigonal faces and rectangular edges as shown. Redrawn from structures given in reference 3.

Metal Organic Frameworks (MOFs) are porous coordination polymers in which metal "building units" are connected by rigid organic ligand "struts"

One class of coordination frameworks that has received much attention over the past 25 years is the metal organic frameworks (MOFs). These consist of metal centers linked by rigid organic ligands to give a porous structure similar to those of the aluminosilicate-based zeolites. The structure of one MOF, called MIL-53, is given in Figure 9.6.6A.

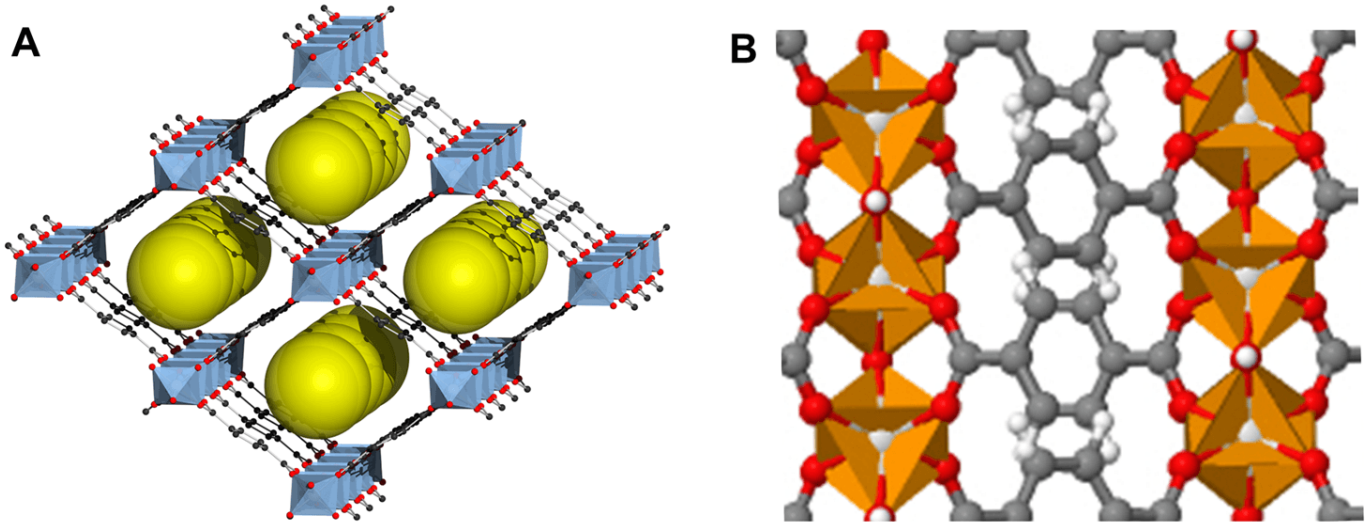


Figure 9.6.6. In metal organic frameworks containing carboxylate ligands, the two oxygens in each carboxylate usually bind to different metal centers. A simple example involves the structure of MIL-53, in which linear *p*-terephthalato (1,4'-benzenedicarboxylato or BDC) ligands bridge chains of linked MO_6 octahedra. (A) Structure of MIL-53 showing the open structure of the MOF, indicated by the yellow spheres. (B) Top-down image of an MIL-53 structure showing how the carboxylic acid oxygens in the BDC ligands coordinate two different metals. The image in part A is by Tony Boehle - Tony Boehle, Public Domain, https://commons.wikimedia.org/w/inde...curid=10328580 The image in part B is rendered from the jmol structure of MIL-53(Sc) at https://www.chemtube3d.com/mof-mil53sc-2/

As can be seen from the overall structure of MIL-53 depicted in Figure 9.6.6A, the structure possesses large rhombic prismatic voids, represented by the yellow spheres. These voids can in principle be occupied by small molecule substrates. Because of MOF's potential to bind and store substrates, there is considerable interest in developing MOFs that are useful for storing and separating particular gases.

A closer look at the structure of MIL-53 reveals that the carboxylate oxygens in the benzenedicarboxylato (BDU) linkers span two different metal centers rather than binding to only one. As explained in Figure 9.6.7, this binding mode enables the formation of rigid stable networks, although it requires the use of metal building blocks in which two or more metal centers are held in close proximity.

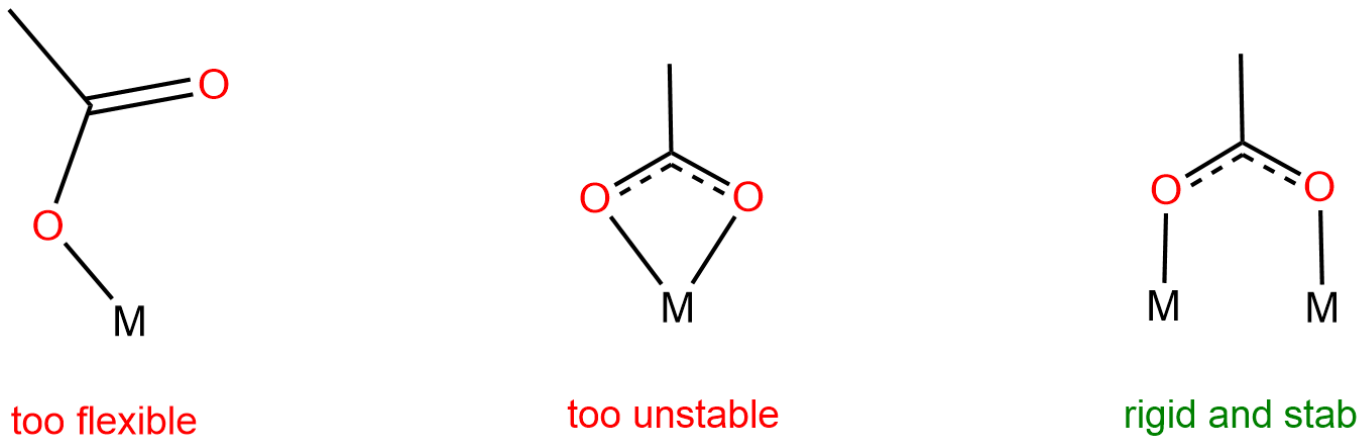


Figure 9.6.7. The carboxylate groups in the ligands of metal organic frameworks commonly bind κ^1 to two different metal centers rather than κ^1 or κ^2 to a single center because the single metal κ^1 binding mode is too flexible to give rigid networks while the small chelate rings and narrow bite angles of the κ^2 chelate rings make them less stable.

In MIL-53, the metal centers that the DBU ligands coordinate are chains of octahedral metal centers bridged by μ_2 hydroxo ligands. These chains form spontaneously as the network forms under the high temperature conditions of its synthesis. In other cases, metal secondary building units (SBUs) containing the necessary bridging dicarboxylate ligands are used. One common class of metal SBUs used is the paddlewheel carboxylates shown in Figure 9.6.8A. These consist of two metals spanned by a square plane of four carboxylates in a paddlewheel arrangment.

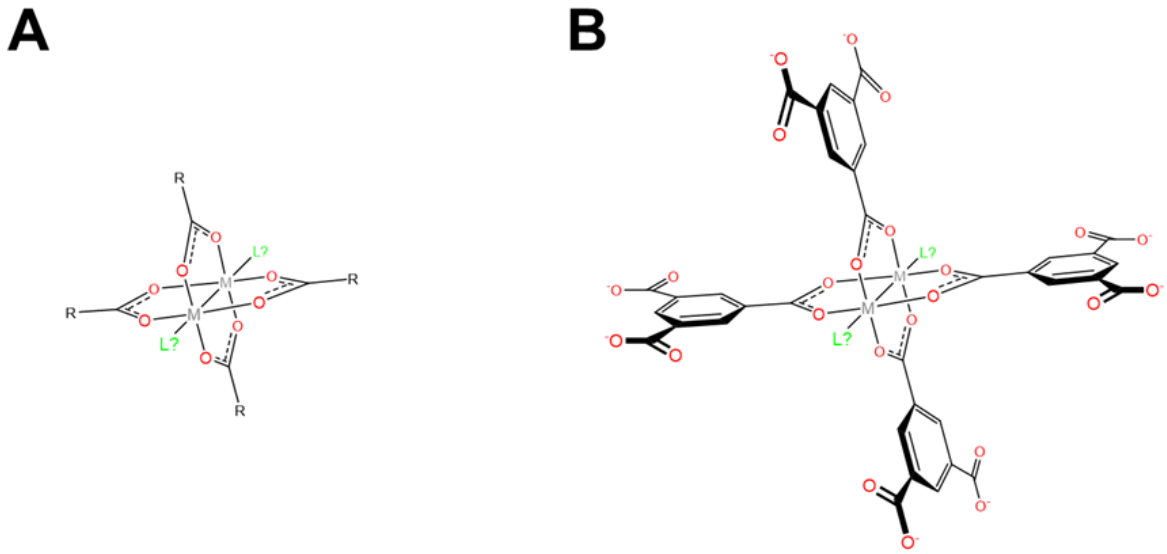


Figure 9.6.8. Metal organic frameworks do not use a metal center directly but instead employ a metal cluster as a secondary building unit (SBU). (A) Paddlewheel carboxylates are a common SBU. They consist of two metals surrounded by four carboxylato ligands in a square planar "paddlewheel" arrangement. (B) In complexes where the ligands contain additional carboxylates, they function as a planar center in a MOF. An example is the paddlewheel carboxylate present in the HKUST class of MOFs, in which each carboxylato ligand is capable of bridging to three dimetal units. Note that in the structures shown, the axial ligands shown in green may be present or absent depending on the specific metal carboxylate used and/or whether the ligand was removed during processing of the MOF.

The use of paddlewheel carboxylate metal SBUs and bridging organic carboxylate ligands enables the construction of coordination frameworks like that of HKUST-1 shown in Figure 9.6.9. The structure of these networks depends on the geometry of the linking ligand. For instance, in HKUST-1 the 1,3,5-benzenetricarboxylato bridging ligands each link three paddlewheel SBUs to give the cubic network shown in Figure 9.6.9. Other organic carboxylate ligands give different network topologies. In addition, the ability of some paddlewheel carboxylates to coordinate ligands perpendicular to the carboxylates, represented by the ligands marked L? in Figure 9.6.8, affords additional opportunities to use these networks to bind substrates that can coordinate those sites.

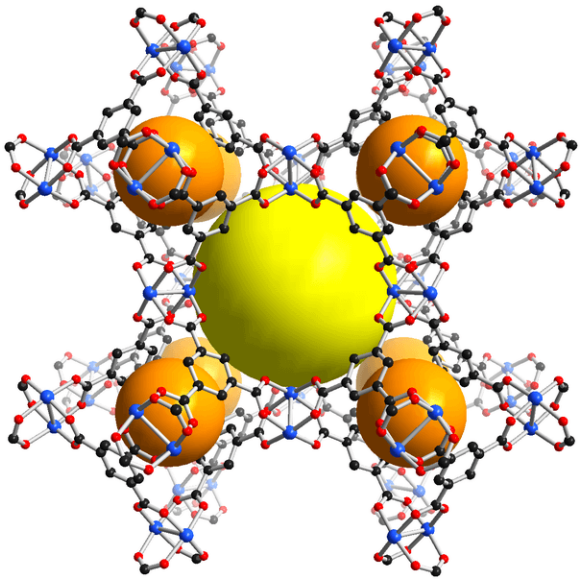


Figure 9.6.9. Desolvated HKUST-1 member of the HKUST class of MOFs showing open regions in the structure. The structure consists of paddlewheel carboxylates linked by trigonal planar tricarboxylate organic SBUs. The image is by Tony Boehle - Own work, CC BY-SA 3.0, https://commons.wikimedia.org/w/inde...curid=27424501

Another common metal SBU is the basic zinc acetate structure shown in Figure 9.6.10. As shown in Figure 9.6.10A, the structure is analogous to those of the basic beryllium acetates and involves an OZn_4 tetrahedron in which the tetrahedrally arranged Zn^{2+} are connected by carboxylate ligands spanning the tetrahedron's six edges. When these carboxylate ligands are replaced by rigid dicarboxylates (Figure 9.6.10B), the result is that the Zn_4O core is surrounded by an octahedral coordination sphere of carboxylate ligands (Figure 9.6.10C).

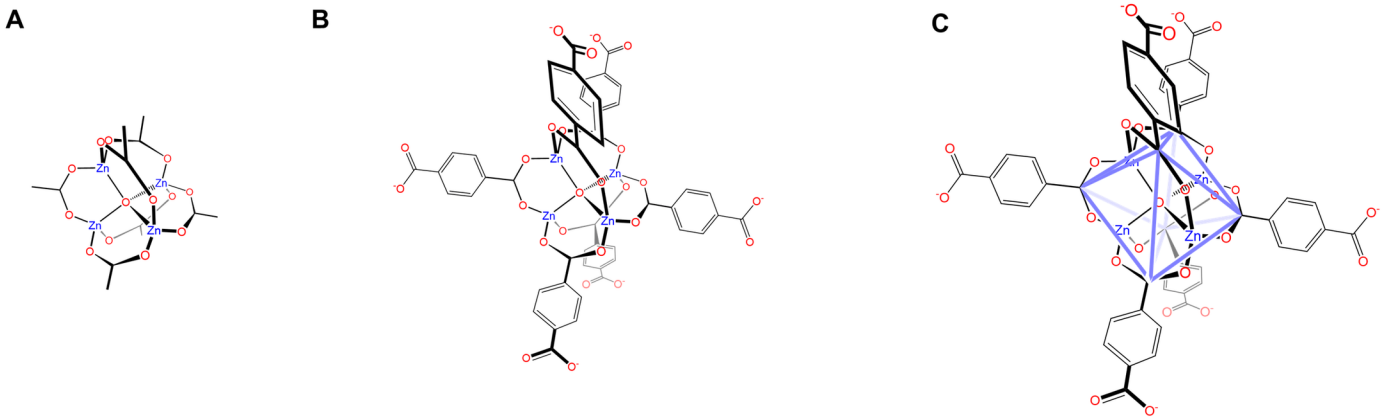


Figure 9.6.10. (A) Basic zinc acetate is a common SBU used as a pseudooctahedral center in MOFs. (B) Exchange of its acetate ligands with *p*-terephthalate (1,4-benzenedicarboxylate) linkers gives a complex in which the free dicarboxylates are oriented towards the vertices of an octahedron (C).

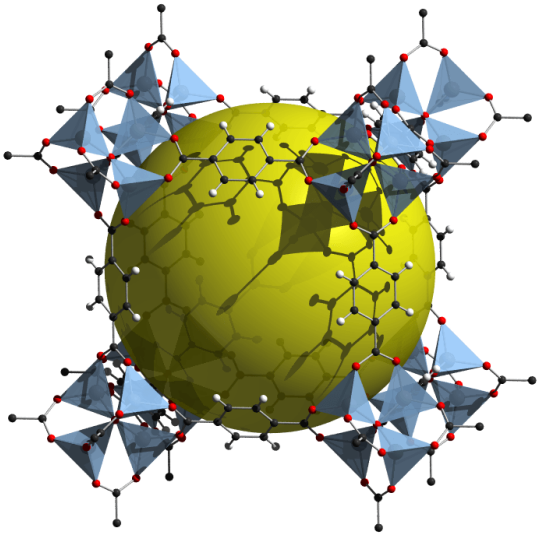


Figure 9.6.11. A cubic metal organic framework derived from the basic zinc acetate SBU. The structure is called MOF-5 and consists of Zn_4O^{6+} pseudooctahedra linked by linear *p*-terephthalate (1,4-benzenedicarboxylate) ligands. The large golden sphere inside the unit cell has a radius of 12 Angstroms (defined with the aromatic rings oriented as shown) and represents the space available for the framework to accommodate guest molecules. By Tony Boehle - Own work, Public Domain, https://commons.wikimedia.org/w/inde...curid=10319204.

The structure of MOF-5 also illustrates how the size of the pores in an MOF structure may be tailored by lengthening or shortening the organic linker. In particular, from Figure 9.6.11 it can be seen that the size of the MOF-5's cubic unit cell depends on the length of the organic portion of the carboxylate linker. In MOF-5 this linker consists of a single benzene unit and gives 9-Angstrom pores, while the use of two and three benzene rings increases the pore size to 13 and 16 Angstroms, respectively, as shown in 9.6.12.

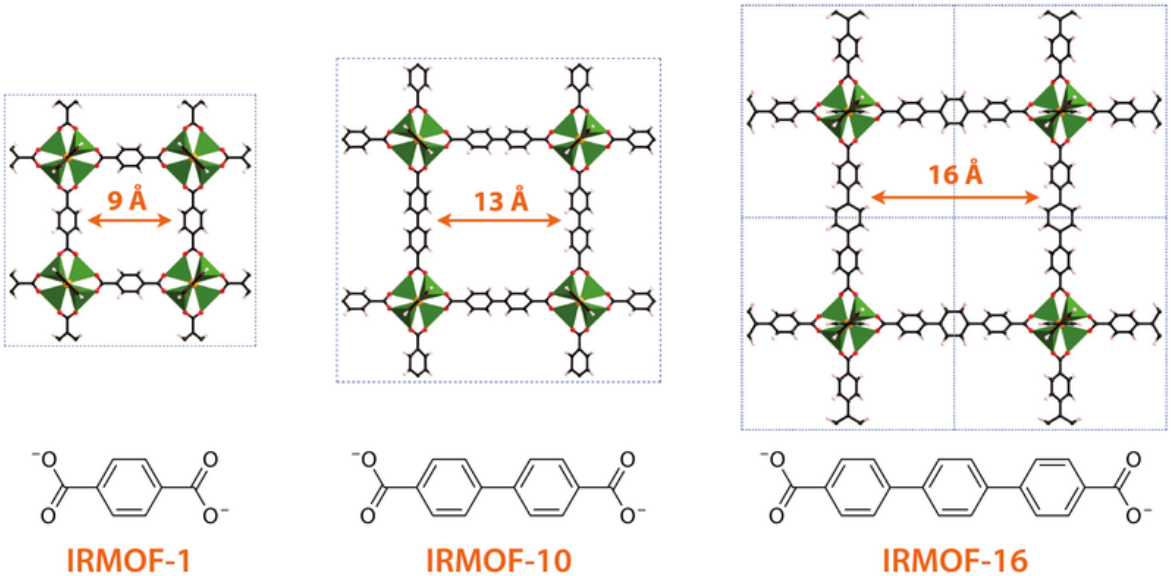


Figure 9.6.12. The spacing between metal centers in a coordination network may be tailored by the use of organic linkers of differing lengths. By François-Xavier Coudert - Own work, CC BY 4.0, https://commons.wikimedia.org/w/inde...curid=89656071

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9.P: Problems

19.1: Occurrence, Preparation, and Properties of Transition Metals and Their Compounds

Q19.1.1

Write the electron configurations for each of the following elements:

a. Sc
b. Ti
c. Cr
d. Fe
e. Ru

S19.1.1

The electron configuration of an atom is the representation of the arrangement of electrons distributed among the orbital shells and sub-shells. The electron configuration of each element is unique to its position on the periodic table where the energy level is determined by the period and the number of electrons is given by the atomic number of the element. There are four different types of orbitals (s, p, d, and f) which have different shapes and each orbital can hold a maximum of 2 electrons, but the p, d and f orbitals have different sub-levels, meaning that they are able to hold more electrons.

The periodic table is broken up into groups which we can use to determine orbitals and thus, write electron configurations:

Group 1 & 2: S orbital

Group 13 - 18: P orbital

Group 3 - 12: D orbital

Lanthanide & Actinides: F orbital

Each orbital (s, p, d, f) has a maximum number of electrons it can hold. An easy way to remember the electron maximum of each is to look at the periodic table and count the number of periods in each collection of groups.

Group 1 & 2: 2 (2 electrons total = 1 orbital x max of 2 electrons = 2 electrons)

Group 13 - 18: 6 (6 electrons total = 3 orbitals x 2 electrons max = 6 electrons)

Group 3 - 12: 10 (10 electrons total = 5 orbitals x 2 electrons max = 10 electrons)

Lanthanide & Actinides: 14 (14 electrons total = 7 orbitals x 2 electrons max = 14 electrons)

Electron fills the orbitals in a specific pattern that affects the order in which the long-hand versions are written:

Electron filling pattern: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f

An easier and faster way to write electron configurations is to use noble gas configurations as short-cuts. We are able to do this because the electron configurations of the noble gases always have all filled orbitals.

$$\text{He: } 1s^2 2s^2$$

$$\text{Ne: } 1s^2 2s^2 2p^6$$

Ar: $1s^2 2s^2 2p^6 3s^2 3p^6$

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

Xe: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6$

Rn: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6$

The most common noble gas configuration used is Ar. When you want to use the noble gas configuration short-cut, you place the noble gas's symbol inside of brackets:

[Ar]

and then write it preceding the rest of the configuration, which is solely the orbitals the proceed after that of the noble gas.

a. Sc

Let's start off by identifying where Scandium sits on the periodic table: row 4, group 3. This identification is the critical basis we need to write its electron configuration.

By looking at Scandium's atomic number, 21, it gives us both the number of protons and the number of electrons. At the end of writing its electron configuration, the electrons should add up to 21.

At row 4, group 3 Sc, is a transition metal; meaning that its electron configuration will include the D orbital.

Now, we can begin to assign the 21 electrons of Sc to orbitals. As you assign electrons to their orbitals, you move right across the periodic table.

Its first 2 electrons are in the 1s orbital which is denoted as

$1s^2$

where the "1" preceding the s denotes the fact that it is of row one, and it has an exponent of 2 because it fulfills the s orbital's maximum electron number. Now we have 21-2=19 more electrons to assign.

Its next 2 electrons are in the 2s orbital which is denoted as

$2s^2$

where the "2" preceding the s indicates that it is of row two, and it has an exponent of 2 because it fulfills the s orbital's maximum electron number. Now we have 19-2=17 more electrons to assign.

Its next 6 electrons are in the 2p orbital which is denoted as

$2p^6$

where the "2" preceding the p indicates that it is of row two, and it has an exponent of 6 because it fulfills the p orbital's maximum electron number. Now we have 17-6=11 more electrons to assign.

Its next 2 electrons are in the 3s orbital which is denoted as

$3s^2$

where the "3" preceding the s indicates that it is of row three, and it has an exponent of 2 because it fulfills the s orbital's maximum electron number. Now we have 11-2=9 more electrons to assign.

Its next 6 electrons are in the 3p orbital which is denoted as

$$3p^6$$

where the "3" preceding the p indicates that it is of row three, and it has an exponent of 6 because it fulfills the p orbital's maximum electron number. Now we have 9-6=3 more electrons to assign.

Its next 2 electrons are in the 4s orbital which is denoted as

$$4s^2$$

where the "4" preceding the s indicates that it is of row four, and it has an exponent of 2 because it fulfills the s orbital's maximum electron number. Now we have 3-2=1 more electron to assign.

Its last electron would be alone in the 3 d orbital which is denoted as

$$3d^1$$

where the "3" preceding the d indicates that, even though it is technically of row 4, by disregarding the first row of H and He, this is the third row and it has an exponent of 1 because there is only 1 electron to be placed in the d orbital. Now we have assigned all of the electrons to the appropriate orbitals and sub-orbitals, so that the final, entire electron configuration is written as:

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

This is the long-hand version of its electron configuration.

So for Sc, its short-hand version of its electron configuration would therefore be:

$$[Ar]\ 4s^2 3d^1$$

b. Ti

Start off by identifying where Titanium sits on the periodic table: row 4, group 4, meaning it has 22 electrons total. Titanium is one element to the right of the previous problem's Sc, so we will basically use the same method except, in the end, there will be 2 electrons remaining, so therefore the final orbital will be denoted as:

$$3d^2$$

If needed, look above to the exact steps for how to do it in detail again; the long-hand electron configuration for Titanium will be:

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

So for Ti, its short-hand version of its electron configuration would therefore be:

$$[Ar]\ 4s^2 3d^2$$

c. Cr

Start off by identifying where Chromium sits on the periodic table: row 4, group 6, that means it has a total of 24 electrons. But first, Cr, along with Mo, Nb, Ru, Rh, Pd, Cu, Sg, Pt and Au, is a special case. You would think that since it has 24 electrons that its configuration would look like:

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

which is how we learned it earlier. However, this electron configuration is very unstable because of the fact that there are 4 electrons in its 3 d orbital. The most stable configurations are half-filled (d^5) and full orbitals (d^{10}), so the elements with electrons resulting in ending with the d^4 or d^9 are so unstable that we write its stable form instead, where an electron from the preceding s orbital will be moved to fill the d orbital, resulting in a stable orbital.

If needed, look above to the exact steps for how to do the beginning of the configuration in detail again. However we have to apple the new rule to attain stability so that the long-hand electron configuration for Chromium will be:

$$1s^2 2s^2 2p^6 3s^2 3p^6 \mathbf{4s^1 3d^5}$$

So for Cr, its short-hand version of its electron configuration would therefore be:

$$[Ar]\ 4s^1 3d^5$$

d. Fe

Start off by identifying where Iron sits on the periodic table: row 4, group 8, meaning it has 26 electrons total. This is 5 elements to the right of the previous problem's Sc, so we will basically use the same method except, in the end, there will be 6 electrons remaining, so therefore the final orbital will be denoted as:

$$3d^6$$

If needed, look above to the exact steps for how to do it in detail again; the long-hand electron configuration for Iron will be:

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

So for Fe, its short-hand version of its electron configuration would therefore be:

$$[Ar]\ 4s^2 3d^6$$

e. Ru

Start off by identifying where Ruthenium sits on the periodic table: row 5, group 8, that means it has a total of 44 electrons. But first, as stated earlier, Ru, along with Cr, Mo, Nb, Rh, Pd, Cu, Sg, Pt and Au, is a special case. You would think that since it has 44 electrons that its configuration would look like:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 \mathbf{5s^2\ 4d^6}$$

which is how we learned it earlier. However, this electron configuration is very unstable because of the fact that, even though there are 4 paired electrons, there are also 4 electrons unpaired. This results in a very unstable configuration, so to restore stability, we have to use a configuration that has the most paired electrons, which would be to take an electron from the s orbital and place it in the d orbital to create:

$$5s^1 4d^7$$

If needed, look above to the exact steps for how to do the beginning of the configuration in detail again. However we have to apple the new rule to attain stability so that the long-hand electron configuration for Ru will be:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 \mathbf{5s^1 4d^7}$$

So for Cr, its short-hand version of its electron configuration would therefore be:

$$[Kr]\ 5s^1 4d^7$$

A19.1.1

a. Sc: $[Ar]4s^2 3d^1$
b. Ti: $[Ar]4s^2 3d^2$
c. Cr: $[Ar]4s^1 3d^5$
d. Fe: $[Ar]4s^2 3d^6$

e. Ru: [Kr]$5s^1 4d^7$ (anomalous configuration)

Q19.1.2

Write the electron configurations for each of the following elements and its ions:

a. Ti
b. Ti^{2+}
c. Ti^{3+}
d. Ti^{4+}

S19.1.2

Electrons are distributed into molecular orbitals, the $s, p, d, and f$ blocks. An orbital will have a number in front of it and a letter that corresponds to the block. The s block holds two electrons, the p block holds six, the d block holds ten, and the f block holds fourteen. So, based on the number of electrons an atom has, the molecular orbitals are filled up in a certain way. The order of the orbitals is $1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p$. An exponent will be put after the letter for each orbital to signify how many electrons are in that orbital. Noble gas notation can also be used by putting the noble gas prior to the element you are writing the configuration for, and then proceed by writing the orbitals filled after the noble gas. Metal ions of the d-block will have the two electrons removed from the s block prior to any electrons being removed from the proceeding d-block.

Solutions:

1. Ti

Titanium has an atomic number of 22, meaning it has 22 electrons. The noble gas prior to Titanium is Argon. Looking at row 4 of the periodic table, Titanium still has 4 electrons to be placed in orbitals since Argon has 18 electrons that are already placed. The remaining electrons will fill the $4s$ orbital and the remaining two electrons will go into the $3d$ orbital. [Ar]$4s^2 3d^2$

2. Ti^{+2}

This is an ion with a plus 2 charge, meaning 2 electrons have been removed. The electrons will be removed from the $4s$ orbital and the 2 remaining electrons will be placed in the $3d$ orbital. Like number 1, the prior noble gas is Argon. [Ar]$3d^2$

3. Ti^{+3}

This is an ion with a plus 3 charge, meaning 3 electrons have been removed. The first 2 electrons will be removed from the $4s$ orbital, and the third will be taken from the $3d$ orbital, and the 1 remaining electron will be placed in the 3d orbital. Like number 1, the prior noble gas is Argon. [Ar]$3d^1$

4. Ti^{+4}

This is an ion with a plus 4 charge, meaning 4 electrons have been removed. The first 2 electrons will be removed from the $4s$ orbital and the second 2 will be removed from the $3d$ orbital. This results in the ion having the same electron configuration as Argon. [Ar]

Answers:

1. $[Ar]4s^2 3d^2$
2. $[Ar]3d^2$
3. $[Ar]3d^1$
4. $[Ar]$

A19.1.2

a. $[Ar]4s^2 3d^2$

b. $[Ar]3d^2$
c. $[Ar]3d^1$
d. $[Ar]$

Q19.1.3

Write the electron configurations for each of the following elements and its 3+ ions:

a. La
b. Sm
c. Lu

S19.1.3

In order to write the electron configuration, we begin by finding the element on the periodic table. Since La, Sm, and Lu are all a period below the noble gas Xenon, we can abbreviate $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$ as [Xe] when writing the orbital configurations. We then find the remaining of the orbital configurations using the Aufbau Principle. For other elements not just those in period 6, the shorthand notation using noble gases would be the noble gas in the period above the given element.

1. La has three additional electrons. Two of them fill the 6s shell and the other single electron is placed on the 5d shell.

La : [Xe] $6s^2 5d^1$

2. Sm has eight more electrons. The 6s orbital is filled as previously and the 4f orbital receives 6 electrons because pairing electrons requires lower energy on the 4f shell than on the 5d shell.

Sm : [Xe] $6s^2 4f^6$

3. Lu has seventeen more electrons. Two electrons fill the 6s orbital, 14 electrons fill the 4f orbital, and extra single electron goes to the 5d orbital .

Lu : [Xe] $6s^2 4f^{14} 5d^1$

To find the 3+ ion electron configuration, we remove 3 electrons from the neutral configuration, starting with the 6s orbital.

1. The ionization of La^{3+} removes the three extra electrons. So it reverts back to the stable Xenon configuration.

La^{3+} : [Xe]

2. The ionization of Sm^{3+} removes two electrons from the 6s shell and one from the outermost (4f) shell

Sm^{3+} : [Xe] $4f^5$

3. The ionization of Lu^{3+} removes its two 6s shell and one from the outermost (5d) shell, leaving only a full 4f shell

Lu^{3+} : [Xe] $4f^{14}$

A19.1.3

La: [Xe]6s ^{2}5*d* ^{1}, La^{3+}: [Xe]; Sm: [Xe]6s ^{2}4*f* ^{6}, Sm^{3+}: [Xe]4*f* ^{5}; Lu: [Xe]6s ^{2}4*f* ^{14}5*d* ^{1}, Lu^{3+}: [Xe]4*f* ^{14}

Q19.1.4

Why are the lanthanoid elements not found in nature in their elemental forms?

A19.1.4

Lanthanides are rarely found in their elemental forms because they readily give their electrons to other more electronegative elements, forming compounds instead of staying in a pure elemental form. They have very similar chemical properties with one another, are often found deep within the earth, and difficult to extract. They are the inner transition elements and have partially filled d orbitals that can donate electrons. Because of this, they are very reactive and electropositive.

Q19.1.5

Which of the following elements is most likely to be used to prepare La by the reduction of La_2O_3: Al, C, or Fe? Why?

S19.1.5

An **activity series** is a list of elements in decreasing order of their reactivity. Elements on the top of the list are good **reducing agents** because they easily give up an electron, and elements on the bottom of the series are good **oxidizing agents** because they are highly electronegative would really want to accept an electron.

Step 1: Compare Aluminum, Carbon, and Iron on an activity series. Many activity series include carbon and hydrogen as references. An activity series can be found here

The activity series goes in the order (from top to bottom): Aluminum, Carbon, and Iron.

Step 2: Identify which element is the best reducing agent.

Elements on the top of the list are the best reducing agents, because they give up electrons the best.

Aluminum is the best reducing agent of the options available.

Therefore aluminum will be the best reducing agent to prepare La by the reduction of La_2O_3 because it is the most reactive in the series amongst the three elements.

A19.1.5

Al is used because it is the strongest reducing agent and the only option listed that can provide sufficient driving force to convert La(III) into La.

Q19.1.6

Which of the following is the strongest oxidizing agent: $\mathrm{VO_4}^{3-}$, $\mathrm{CrO_4}^{2-}$, or $\mathrm{MnO_4}^{-}$?

S19.1.6

Oxidizing agents oxidize other substances. In other words, they gain electrons or become reduced. These agents should be in their highest oxidation state. In order to determine, the strength of the compounds above as oxidizing agents, determine the oxidation numbers of each constituent elements.

$$\mathrm{VO_4^{3-}}$$

We know that O has a -2 oxidation state and the overall charge of the ion is -3. We just need to determine Vanadate's oxidation number in this compound.

$$\mathrm{V} + -2(4) = -3$$

$$\mathrm{V} = +5$$

Vanadate has an oxidation number of +5, which is its highest possible oxidation state.

$\mathrm{CrO_4^{2-}}$

Like in the previous calculation, O has a -2 oxidation state. The overall charge is -2. So calculate for chromium.

$$\mathrm{Cr} + -2(4) = -2$$

$$\mathrm{Cr} = +6$$

Chromium is in its highest possible oxidation state of +6 in this compound.

$\mathrm{MnO_4^-}$

O has a -2 oxidation state and the overall charge is -1.

$$\mathrm{Mn} + -2(4) = -1$$

$$\mathrm{Mn} = +7$$

Manganese is also in its highest oxidation state, +7.

An oxidizing agent has to be able to gain electrons which, in turn, reduces its oxidation state. Here manganese has the greatest oxidation state which allows it to experience a greater decrease in its oxidation state if needed, meaning it can gain the most electrons. So among the three compounds, $\mathrm{MnO_4^-}$ is the strongest oxidizing agent. This method assumes the metals have similar electronegativities.

Alternatively, check a redox table.

A19.1.6

MnO_4^-

Q19.1.7

Which of the following elements is most likely to form an oxide with the formula MO_3: Zr, Nb, or Mo?

S19.1.7

Mo because Zr has an oxidation state of +4 and Nb has a oxidation state of +5 and those would not balance out the charge of 3 oxygens in the state of -2 which creates a charge of -6. Mo however has multiple oxidation states, the most common being +6 which balances out the -6 charge created by 3 oxygen ions. This is why its most likely to form an oxide with the formula MO_3 or $\mathrm{MoO_3}$.

A19.1.7

Mo

Q19.1.8

The following reactions all occur in a blast furnace. Which of these are redox reactions?

a. $3\,\mathrm{Fe_2O_3}(s) + \mathrm{CO}(g) \longrightarrow 2\,\mathrm{Fe_3O_4}(s) + \mathrm{CO_2}(g)$
b. $\mathrm{Fe_3O_4}(s) + \mathrm{CO}(g) \longrightarrow 3\,\mathrm{FeO}(s) + \mathrm{CO_2}(g)$
c. $\mathrm{FeO}(s) + \mathrm{CO}(g) \longrightarrow \mathrm{Fe}(l) + \mathrm{CO_2}(g)$
d. $\mathrm{C}(s) + \mathrm{O_2}(g) \longrightarrow \mathrm{CO_2}(g)$
e. $\mathrm{C}(s) + \mathrm{CO_2}(g) \longrightarrow 2\,\mathrm{CO}(g)$
f. $\mathrm{CaCO_3}(s) \longrightarrow \mathrm{CaO}(s) + \mathrm{CO_2}(g)$

g. $\mathrm{CaO}(s) + \mathrm{SiO_2}(s) \longrightarrow \mathrm{CaSiO_3}(l)$

S19.1.8

o identify redox reaction, we have to determine if have to see if the equation is an oxidation-reduction reaction-meaning that the species are changing oxidation states during the reaction, which involves the transfer of electrons between two species. If a species is losing electrons, then that species is being oxidized. If a species is gaining electrons, then that species is being reduced. A way to remember this is using the acronyms OIL RIG. **O**xidation **I**s **L**oss, and **R**eduction **I**s **G**ain, referring to electrons. Both of these must occur for an equation to be a redox reaction. Let's see if these equations are redox reactions or not:

a. In the reactants side $\mathrm{Fe_2O_3}$, Fe is has an oxidation number of +3. In the product $\mathrm{Fe_3O_4}$, Fe has an oxidation number of +2.67. Since Fe changed from +3 to +2.67, we can say that Fe had gained electrons and therefore reduced. In the reactant, CO, carbon has an oxidation number of +2, and in $\mathrm{CO_2}$ (product) carbon has an oxidation number of +4. Therefore, carbon has lost electrons and it has been oxidized. Since there is oxidation and reduction of species- we can conclude that this **is a redox reaction**.

b. In the reactant, $\mathrm{Fe_3O_4}$, Fe has an oxidation number of +2.67. In the product, FeO, Fe has an oxidation number of +2. Since the oxidation of Fe has changed from +2.67 to +2, electrons have been added therefore Fe has been reduced. In the reactant, CO, carbon has an oxidation number of +2, and in $\mathrm{CO_2}$ (product) carbon has an oxidation number of +4. Therefore, carbon has lost electrons and it has been oxidized. Since there is oxidation and reduction of species- we can conclude that this **is a redox reaction**.

c. In the reactant side, in FeO, Fe has an oxidation number of +2 and in the products side Fe has an oxidation number of 0. Since the oxidation number of Fe changed from +2 to 0, electrons have been gained and therefore Fe has been reduced. In the reactant, CO, carbon has an oxidation number of +2, and in $\mathrm{CO_2}$ (product) carbon has an oxidation number of +4. Therefore, carbon has lost electrons and it has been oxidized. Since there is oxidation and reduction of species- we can conclude that this **is a redox reaction**.

d. In the reactants C has an oxidation number of 0, and in the products side in $\mathrm{CO_2}$, C has an oxidation number of +4. Since the oxidation number of C has changed from 0 to +4, we can say that C has been oxidized. In the reactants, in $\mathrm{O_2}$ oxygen has an oxidation number of 0, and in the products CO2, oxygen has an oxidation number of -2. Since the oxidation number of oxygen has changed from 0 to -2, oxygen has been reduced. Since there is oxidation and reduction of species- we can conclude that this **is a redox reaction**.

e. In the reactants $\mathrm{CO_2}$ has an oxidation number of +4, and in the products side in CO, C has an oxidation number of +2. Since carbon went from +4 to +2, carbon has been reduced. In the reactants, in $\mathrm{CO_2}$ oxygen has an oxidation number of -4 and in the products CO carbon has an oxidation number of -2. Since oxygen went from -4 to -2, it has been oxidized. Since there is oxidation and reduction of species- we can conclude that this **is a redox reaction**.

f. In the reactants, $\mathrm{CaCO_3}$ Ca has an oxidation number of +2, and in products CaO Ca has an oxidation number of +2. Since the oxidization number doesn't change- we can conclude that this equation **is not a redox reaction.**

g. In the products CaO Ca has an oxidation number of +2, and in the products $\mathrm{CaSiO_3}$ Ca has an oxidation number of +2. Since the oxidization number doesn't change- we can conclude that this equation **is not a redox reaction.**

A19.1.8

a, b, c, d, e

Q19.1.9

Why is the formation of slag useful during the smelting of iron?

S19.1.9

Slag is a substance formed as a byproduct of iron ore or iron pellets melting together in a blast furnace. Slag is also the byproduct that is formed when a desired metal has been separated from its raw ore. It is important to note that slag from steel mills is created in a manner that reduces the loss of the desired iron ore. The $\mathrm{CaSiO_3}$slag is less dense than the molten iron, so it can

easily be separated. Also, the floating slag layer creates a barrier that prevents the molten iron from exposure to O_2, which would oxidize the Fe back to Fe_2O_3. Since Fe has a low reduction potential of -0.440 this means it has a high oxidation potential so it would easily oxidize in the presence of O2. Creating a barrier between iron and oxygen allows the maximum product of iron to be obtained in the end of smelting.

A19.1.9

The $CaSiO_3$ slag is less dense than the molten iron, so it can easily be separated. Also, the floating slag layer creates a barrier that prevents the molten iron from exposure to O_2, which would oxidize the Fe back to Fe_2O_3.

Q19.1.10

Would you expect an aqueous manganese(VII) oxide solution to have a pH greater or less than 7.0? Justify your answer.

S19.1.10

Manganese(VII) oxide, can be written as Mn_2O_7.

In relation to the Lewis acid-base theory, a Lewis acid accepts lone pair electrons, and is also known as the electron pair acceptor. Based on this theory, acidity can be measured by the element's ability to accept electron pairs. By doing the math, we find that Manganese has an oxidation state of +7 (Oxygen has an oxidation state of -2, and 2x-7=-14 **or this can be shown as** $-7(2) + 2(x) = 0$ **and** $x = 7$ **since the whole compound has a charge of zero**, in order to balance the ion's charge, Mn must be +7). Therefore Mn has high capability of accepting electrons due to its high positive charge. For most metals, as the oxidation number increases, so does its acidity, because of its increased ability to accept electrons.

A19.1.10

In relation to the Lewis acid-base theory, the Lewis acid accepts lone pair electrons; thus, it is also known as the electron pair acceptor. This may be any chemical species. Acids are substances that must be lower than 7. Therefore, oxides of manganese is most likely going to become more acidic in (aq) solutions if the oxidation number increases.

Q19.1.11

Iron(II) can be oxidized to iron(III) by dichromate ion, which is reduced to chromium(III) in acid solution. A 2.5000-g sample of iron ore is dissolved and the iron converted into iron(II). Exactly 19.17 mL of 0.0100 *M* $Na_2Cr_2O_7$ is required in the titration. What percentage of the ore sample was iron?

S19.1.11

To answer this question, we must first identify the net ionic equation from the given half-reactions. We can write the oxidation and reduction half-reactions:

$$\text{oxidation: } \mathrm{Fe}^{2+} \rightarrow \mathrm{Fe}^{3+} \tag{9.P.1}$$

$$\text{reduction: } \mathrm{Cr_2O_7}^{2-} \rightarrow \mathrm{Cr}^{3+} \tag{9.P.2}$$

We can quickly balance the oxidation half-reaction by adding the appropriate number of electrons to get

$$\mathrm{Fe}^{2+} \rightarrow \mathrm{Fe}^{3+} + \mathrm{e}^- \tag{9.P.3}$$

The first step in balancing the reduction half-reaction is to balance elements in the equation other than O and H. In doing so, we get

$$\mathrm{Cr_2O_7}^{2-} \rightarrow 2\ \mathrm{Cr}^{3+} \tag{9.P.4}$$

The second step would be to add enough water molecules to balance the oxygen.

$$\mathrm{Cr_2O_7}^{2-} \rightarrow 2\ \mathrm{Cr}^{3+} + 7\,\mathrm{H_2O} \tag{9.P.5}$$

Next, we add the correct amount of H^+ to balance the hydrogen atoms.

$$\mathrm{Cr_2O_7}^{2-} + 14\ \mathrm{H}^+ \rightarrow 2\ \mathrm{Cr}^{3+} + 7\,\mathrm{H_2O} \tag{9.P.6}$$

Finally, we add enough electrons to balance charge.

$$\mathrm{Cr_2O_7}^{2-} + 14\ \mathrm{H}^+ + 6\ \mathrm{e}^- \rightarrow 2\ \mathrm{Cr}^{3+} + 7\,\mathrm{H_2O} \tag{9.P.7}$$

The electrons involved in both half-reactions must be equal in order for us to combine the two to get the net ionic equation. This can be done by multiplying each equation by the appropriate coefficient. Scaling the oxidation half-reaction by 6, we get

$$6\ \mathrm{Fe}^{2+} \rightarrow 6\ \mathrm{Fe}^{3+} + 6\ \mathrm{e}^- \tag{9.P.8}$$

Now we can combine both half-reactions to get

$$6\ \mathrm{Fe}^{2+} + \mathrm{Cr_2O_7}^{2-} + 14\ \mathrm{H}^+ + 6\ \mathrm{e}^- \rightarrow 6\ \mathrm{Fe}^{3+} + 6\ \mathrm{e}^- + 2\ \mathrm{Cr}^{3+} + 7\,\mathrm{H_2O} \tag{9.P.9}$$

The electrons cancel out, so you get:

$$6\ \mathrm{Fe}^{2+} + \mathrm{Cr_2O_7}^{2-} + 14\ \mathrm{H}^+ \rightarrow 6\ \mathrm{Fe}^{3+} + 2\ \mathrm{Cr}^{3+} + 7\,\mathrm{H_2O} \tag{9.P.10}$$

From this we can see that the mole ratio of $Cr_2O_7^{2-}$ to Fe^{2+} is 1:6. Given that 19.17 mL (or 0.01917 L) of 0.01 M $Na_2Cr_2O_7$ was needed for titration we know that

$$0.01917\ \mathrm{L} \times 0.01\ \mathrm{M} = 1.917 \times 10^{-4}\ \mathrm{mol} \tag{9.P.11}$$

of $Na_2Cr_2O_7$ reacted. Also, since any number of moles of $Na_2Cr_2O_7$ produces the same number of moles of $Cr_2O_7^{2-}$ in solution

$$1.917 \times 10^{-4}\ \mathrm{mol\ of\ Na_2Cr_2O_7} = 1.917 \times 10^{-4}\ \mathrm{mol\ of\ Cr_2O_7}^{2-} \tag{9.P.12}$$

We can use the mole ratio of $Cr_2O_7^{2-}$ to Fe^{2+} to determine how many moles of iron (ii) was in the solution. The number of moles of iron (ii) is the same as the number of moles of pure iron in the sample since all of the iron was converted into iron (ii).

$$1.917 \times 10^{-4}\ \mathrm{mol\ of\ Cr_2O_7}^{2-} \times \frac{6\ \mathrm{mol\ of\ Fe}^{2+}}{1\ \mathrm{mol\ of\ Cr_2O_7}^{2-}} = 0.0011502\ \mathrm{mol\ of\ Fe}^{2+} \tag{9.P.13}$$

$$0.0011502\ \mathrm{mol\ of\ Fe}^{2+} = 0.0011502\ \mathrm{mol\ of\ Fe} \tag{9.P.14}$$

Now we can find the number of grams of iron that were present in the 2.5 g iron ore sample.

$$0.0011502\ \mathrm{mol\ of\ Fe} \times \frac{55.847\ \mathrm{g}}{1\ \mathrm{mol}} = 0.0642352194\ \mathrm{g\ of\ Fe} \tag{9.P.15}$$

Finally, we can answer the question and find what percentage of the ore sample was iron.

$$\frac{0.0642352194\ \mathrm{g}}{2.5\ \mathrm{g}} \times 100 \approx 2.57 \tag{9.P.16}$$

So 2.57% of the ore sample was iron.

A19.1.11

2.57%

Q19.1.12

How many cubic feet of air at a pressure of 760 torr and 0 °C is required per ton of Fe_2O_3 to convert that Fe_2O_3 into iron in a blast furnace? For this exercise, assume air is 19% oxygen by volume.

S19.1.12

This question uses a series of unit conversions and the $PV = nRT$ equation.

The first step is to write out the balanced chemical equation for the conversion of Fe_2O_3 to pure iron.

$$2\ Fe_2O_3(s) \rightarrow 4\ Fe(s) + 3\ O_2(g) \tag{9.P.17}$$

Next, we need to analyze the original question to determine the value that we need to solve for. Because the question asks for a value of cubic feet, we know we need to solve for volume. We can manipulate $PV = nRT$ to solve for volume.

$$V = nRT/P \tag{9.P.18}$$

Now determine the known variables and convert into units that will be easy to deal with.

$$n = 2000\ lbs\ Fe_2O_3 \frac{453.592\ grams\ Fe_2O_3}{1\ lb\ Fe_2O_3} \frac{1\ mole\ Fe_2O_3}{159.69\ grams\ Fe_2O_3} \frac{3\ moles\ O_2}{2\ moles\ Fe_2O_3} \tag{9.P.19}$$

$$n = 8521\ moles\ of\ O_2 \tag{9.P.20}$$

Convert to atm for easier calculations

$$R = \frac{.0821\ L\ atm}{mol\ K} \tag{9.P.21}$$

$$T = 0^{\circ}C = 273\ K \tag{9.P.22}$$

$$P = 760\ torr = 1\ atm \tag{9.P.23}$$

Now plug the numbers into the manipulated gas law to get to an answer for V.

$$V = 190991.8\ liters\ of\ O_2 \tag{9.P.24}$$

From here we convert liters to cubic feet.

use the conversion

$$1\ L = .0353 ft^3 \tag{9.P.25}$$

thus we have 6744.811 ft^3 of O_2

We then refer back to the initial question and remember that this value is only 19% of the volume of the total air. So use a simple equation to determine the total volume of air in cubic feet.

$$6744.811 ft^3 = .19x \tag{9.P.26}$$

x=35499 ft^3 of air

A19.1.12

35499 ft^3 of air

Q19.1.13

Find the potentials of the following electrochemical cell:

Cd | Cd^{2+} (*M* = 0.10) ‖ Ni^{2+} (*M* = 0.50) | Ni

S19.1.13

Step 1 Write out your two half reactions and identify which is oxidation and which is reduction using the acronym OIL RIG to remember that oxidation is loss of electrons and reduction is gain of electrons

$Cd(s) \diamond Cd^{2+}(aq)+2e^-$ (oxidation)

$Ni^{2+}(aq)+2e^- \diamond Ni(s)$ (reduction)

Step 2 Write out complete balanced equation

$Cd(s)+ Ni^{2+}(aq) \diamond Cd^{2+}(aq)+Ni(s)$

Step 3 Find E^o_{cell}

Image result for reduction potential table

$E^o_{cell} = E_{cathode}-E_{anode}$

oxidation: $Cd(s) \diamond Cd^{2+}(aq)+2e^-$ $E^o=-0.40V$

reduction: $Ni^{2+}(aq)+2e^- \diamond Ni(s)$ $E^o=-0.26V$

* E values come from standard reduction potentials table given above. Also, remember anode is where oxidation happens, and cathode is where reduction happens.

$E^o cell=-0.26-(-.40)$

$E^o_{cell}=0.14V$

Step 4 Find Q

Q=[products]/[reactants] (look at complete balanced equation) (remember that [x] means the concentration of x typically given in molarity and that we ignore solids or liquids)

$Q=[Cd^{2+}]/[Ni^{2+}]$

Q=0.10/0.50

Q=0.2

Step 5 Calculate E using $E= E^o_{cell}-(.0592/n)\log Q$ (n is number of moles of electrons transferred and in our case the balanced reaction transfers 2 electrons)

$E= 0.14-(.0592/2)\log(0.2)$

E= 0.14-(-.207)

E=0.16 V

A19.1.13

0.16 V

Q19.1.14

A 2.5624-g sample of a pure solid alkali metal chloride is dissolved in water and treated with excess silver nitrate. The resulting precipitate, filtered and dried, weighs 3.03707 g. What was the percent by mass of chloride ion in the original compound? What is the identity of the salt?

S19.1.14

A 2.5624-g sample of a pure solid alkali metal chloride is dissolved in water and treated with excess silver nitrate. The resulting precipitate, filtered and dried, weighs 3.03707 g. What was the percent by mass of chloride ion in the original compound? What is the identity of the salt?

Assuming that metal chloride is XCl

The balance equation for the reaction would be:

$$XCl(aq) + AgNO_3(aq) \rightarrow XNO_3(aq) + AgCl(s) \tag{9.P.27}$$

The mass of AgCl = 3.03707g

To find the moles of AgCl present:

Next, we can determine the moles of AgCl present in the reaction since 1) the mass of the precipitate is given to us and 2) this value can help us determine the moles of alkali metal chloride compound present. Given the mass of AgCl is 3.03707g in the problem and the molecular mass of AgCl per mole is 143.32g, we can solve for how many moles of AgCl is in the reaction:

$$molesofAgcl = \frac{3.03707g}{143.32g/mol} = 0.0211mol \tag{9.P.28}$$

Since the molar ratio of the compounds are 1:1 so the number of moles of XCl used = 0.0211 mol

We can calculate the weight of Cl^- with the equation:

$$0.0211mol \times 35.5g/mol = 0.7490g \tag{9.P.29}$$

the amount of metal present in the original compound is the weight of the compound subtracted by weight of the Cl ion:

$$(2.5624 - 0.7490)g = 1.8134g \tag{9.P.30}$$

And the percentage can be calculate by

$$\frac{0.7490}{2.5624} \times 100 = 29.23\% \tag{9.P.31}$$

the molar ratio of XCl is 1:1 so then

Atomic mass of metal = $= \frac{1.8134\ g\ metal}{0.0211\ mol\ RbCl} = 85.943g/mol$

So the atomic mass is 85.943 g/mol which is of Rb hence the identity of the salt is RbCl

Q19.1.15

The standard reduction potential for the reaction $[Co(H_2O)_6]^{3+}(aq)\ + e^- \longrightarrow [Co(H_2O)_6]^{2+}(aq)$ is about 1.8 V. The reduction potential for the reaction $[Co(NH_3)_6]^{3+}(aq)\ + e^- \longrightarrow [Co(NH_3)_6]^{2+}(aq)$ is +0.1 V. Calculate the cell potentials to show whether the complex ions, $[Co(H_2O)_6]^{2+}$ and/or $[Co(NH_3)_6]^{2+}$, can be oxidized to the corresponding cobalt(III) complex by oxygen.

S19.1.15

To calculate the cell potential, we need to know the potentials for each half reaction. After doing so, we need to determine which

one is being oxidized and which one is being reduced. The one that is oxidized is the anode and the one that is reduced is the cathode. To find the cell potential, you use this formula and the reduction potential values found in a reduction potential table. If E°cell is positive, ΔG is negative and the reaction is spontaneous.

E°cell= E°cathode - E°anode

Because it states that $[Co(H_2O)_6]^{3+}$ will be oxidized, this means it is the anode.

$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O$ +1.229 V

O_2 is being reduced, so it is the cathode.

1.229V - 1.8V= -.571 V, or -0.6 V using significant figures. This cannot happen spontaneously because E°cell is negative.

For $[Co(NH_3)_6]^{3+}$, it is again being oxidized, meaning it's the anode.

1.229-.1= 1.129 V or 1.1 V using significant figures. This reaction is spontaneous because E°cell is positive.

A19.1.15

a) E ° = −0.6 V, *E* ° is negative so this reduction is not spontaneous.

b) E ° = +1.1 V, *E* ° is positive so this reduction is spontaneous.

Q19.1.16

Predict the products of each of the following reactions. (Note: In addition to using the information in this chapter, also use the knowledge you have accumulated at this stage of your study, including information on the prediction of reaction products.)

a. $\mathrm{MnCO_3}(s) + \mathrm{HI}(aq) \longrightarrow$
b. $\mathrm{CoO}(s) + \mathrm{O_2}(g) \longrightarrow$
c. $\mathrm{La}(s) + \mathrm{O_2}(g) \longrightarrow$
d. $\mathrm{V}(s) + \mathrm{VCl_4}(s) \longrightarrow$
e. $\mathrm{Co}(s) + xs\mathrm{F_2}(g) \longrightarrow$
f. $\mathrm{CrO_3}(s) + \mathrm{CsOH}(aq) \longrightarrow$

S19.1.16

There is a myriad of reactions that can occur, which include: single replacement, double replacement, combustion, acid-base/neutralization, decomposition or synthesis. The first step to determine the products of a reaction is to identify the type of reaction. From then on, the next steps you take to predict the products will vary based on the reaction type.

1. This reaction is a **double displacement reaction**, in which the cations and anions of the reactants switch places to form new compounds. Writing out the equation in terms of it's aqueous ions will help you visualize what exactly is getting moved around:

$$2H^+(aq) + 2I^-(aq) \rightarrow 2H^+(aq) + CO_3^{2-}(aq) + Mn^{2+}(aq) + 2I^-(aq) \tag{9.P.32}$$

   In this case, the hydrogen cations will recombine with carbonate anions whilst manganese cations will recombine with iodide anions giving us the following equation:

$$\mathrm{MnCO_3}(s) + 2\,\mathrm{HI}(aq) \longrightarrow \mathrm{MnI_2}(aq) + \mathrm{H_2CO_3}(aq) \tag{9.P.33}$$

   This is still not the final answer however, as carbonic acid is unstable and decomposes to carbon dioxide and water under standard conditions. Taking this into account, our final equation is:

$$\mathrm{MnCO_3}(s) + 2\,\mathrm{HI}(aq) \longrightarrow \mathrm{MnI_2}(aq) + \mathrm{CO_2}(g) + \mathrm{H_2O}(l) \tag{9.P.34}$$

2. This reaction is a **synthesis reaction**, in which two or more reactants combine to form a more complex compound. In this

case we are also reacting a metal oxide with oxygen which would result in another metal oxide as the product. The resulting product would be the mixed valence oxide Co_3O_4 in which one cobalt atom has a +2 oxidation state whilst the other two have a +3 oxidation state. Now all is left is to balance the equation:

$$6\,\mathrm{CoO}(s)+\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{Co_3O_4}(s) \tag{9.P.35}$$

3. Like equation 2, this reaction is also a **synthesis reaction** involving a metal and oxygen which should result in the formation of a metal oxide. It is a matter now of balancing the oxidation states to attain a neutral compound. Oxygen will always hold a -2 oxidation state in compounds whilst lanthanum will always exhibit a +3 oxidation state. As such, a combination of 2 lanthanum atoms with a +3 oxidation state and 3 oxygen atoms with a -2 oxidation state will give us a molecule with an overall charge of 0 (3(-2)+2(+3)=0). We know our product now, La_2O_3, and now just need to balance the overall equation, giving us:

$$4\,\mathrm{La}(s)+3\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{La_2O_3}(s) \tag{9.P.36}$$

4. This reaction is slightly harder to define as it encapsulates both the properties of synthesis and decomposition reactions, wherein vanadium reacts with vanadium tetrachloride to produce vanadium trichloride. This reaction however is primarily a **synthesis reaction** since we are combining two reactants to produce one complex compound. With vanadium trichloride as our product, we can balance the equation:

$$\mathrm{V}(s)+3\,\mathrm{VCl_4}(s) \longrightarrow 4\,\mathrm{VCl_3}(s) \tag{9.P.37}$$

5. This is another **synthesis reaction** combining cobalt and fluorine. This equation includes the "xs" notation in front of fluorine which is short for 'excess', meaning more fluorine than actually required is present in the reactants, ensuring the reaction goes to completion. Finding the products if a simple matter of combining the cobalt and fluorine into one molecule, which already leaves us with a balanced equation:

$$\mathrm{Co}(s) + xs\mathrm{F_2}(g) \longrightarrow \mathrm{CoF_2}(s) \tag{9.P.38}$$

6. It may not be obvious here, but the reaction we've been given here is actually an **acid-base/neutralization reaction**, with chromium trioxide acting as the acid and cesium hydroxide as the base. Chromium trioxide is referred to as an acidic oxide which means that it will react with water to form an acid. Note that this reaction can still proceed even if the reactants aren't in the same phases. The basic rule for acid-base/neutralization reactions is they form a salt (salt being the general term for any ionic compound formed from acid-base reactions) and water. Since we know water is one of our products, our other product must be a salt composed of cesium, chromium and oxygen. Thus, our other product should be cesium chromate, and you can now balance the equation accordingly:

$$\mathrm{CrO_3}(s) + 2\,\mathrm{CsOH}(aq) \longrightarrow \mathrm{Cs_2CrO_4}(aq) + \mathrm{H_2O} \tag{9.P.39}$$

A19.1.16

1. $\mathrm{MnCO_3}(s) + 2\,\mathrm{HI}(aq) \longrightarrow \mathrm{MnI_2}(aq) + \mathrm{CO_2}(g) + \mathrm{H_2O}(l)$
2. $6\,\mathrm{CoO}(s) + \mathrm{O_2}(g) \longrightarrow 2\,\mathrm{Co_3O_4}(s)$
3. $4\,\mathrm{La}(s) + 3\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{La_2O_3}(s)$
4. $\mathrm{V}(s) + 3\,\mathrm{VCl_4}(s) \longrightarrow 4\,\mathrm{VCl_3}(s)$
5. $\mathrm{Co}(s) + xs\mathrm{F_2}(g) \longrightarrow \mathrm{CoF_2}(s)$
6. $\mathrm{CrO_3}(s) + 2\,\mathrm{CsOH}(aq) \longrightarrow \mathrm{Cs_2CrO_4}(aq) + \mathrm{H_2O}$

Q19.1.17

Predict the products of each of the following reactions. (Note: In addition to using the information in this chapter, also use the knowledge you have accumulated at this stage of your study, including information on the prediction of reaction products.)

a. $\mathrm{Fe}(s) + \mathrm{H_2SO_4}(aq) \longrightarrow$
b. $\mathrm{FeCl_3}(aq) + \mathrm{NaOH}(aq) \longrightarrow$
c. $\mathrm{Mn(OH)_2}(s) + \mathrm{HBr}(aq) \longrightarrow$
d. $\mathrm{Cr}(s) + \mathrm{O_2}(g) \longrightarrow$
e. $\mathrm{Mn_2O_3}(s) + \mathrm{HCl}(aq) \longrightarrow$
f. $\mathrm{Ti}(s) + xs\mathrm{F_2}(g) \longrightarrow$

S19.1.17

Predict the products of each of the following reactions.

- $Fe(s)+H_2SO_4(aq)$?

  Whenever a metal reacts with an acid, the products are salt and hydrogen. Because Fe is lower on the activity series, we know that when it reacts with an acid it will result in the formation of Hydrogen gas. To simplify the equation is:

  $$Metal + Acid \longrightarrow Salt + Hydrogen \tag{9.P.40}$$

  The salt produced will depend on the metal and in this case, the metal is iron (Fe) so the resulting equation would be:

  $$\mathrm{Fe}(s)+\mathrm{H_2SO_4}(aq) \longrightarrow \mathrm{FeSO_4}(aq) + \mathrm{H_2}(g) \tag{9.P.41}$$

  This equation works out as the H2 is removed from H_2SO_2, resulting in a SO_4^{2-} ion where Fe will take on an oxidation state of Fe^{+2} to form $FeSO_4$ which will be the salt in this example.

  But since $FeSO_4$ and $H2SO_4$ are aqueous, the reactants and products can also be written as its ions where the overall equation can be:

  $$\mathrm{Fe}(s) + 2\,\mathrm{H_3O^+}(aq) + \mathrm{SO_2}^{-4}(aq) \longrightarrow \mathrm{Fe_2}^{+}(aq) + \mathrm{SO_2}^{-4}(aq) + \mathrm{H_2}(g) + 2\,\mathrm{H_2O}(l) \tag{9.P.42}$$

- $FeCl_3(aq)+NaOH(aq)$?

  In this case, adding a metal hydroxide (NaOH) to a solution with a transition metal ion (Fe) will form a transition metal hydroxide (XOH). As iron is bonded to three chlorine atoms in the reactants side, it has the oxidation state of +3 where three hydroxide ions (OH^-) are needed to balance out the charges when they are bonded in the products. The remaining ions are Na^+ and Cl^- where they bond together in a 1:1 ratio where there are 3 molecules of NaCl once the reaction is balanced.

  The overall reaction will be:

  $$\mathrm{FeCl_3}(aq) + \mathrm{NaOH}(aq) \longrightarrow \mathrm{Fe(OH)_3}(s) + 3\,\mathrm{NaCl}(aq) \tag{9.P.43}$$

  NOTE: $Fe(OH)_3(s)$ is a solid as it is a rule that all all transition metal hydroxides are insoluble and a precipitate is formed.

  Since NaOH(aq) and NaCl(aq) are aqueous, we can write them out in their ion forms:

  $$\mathrm{FeCl_3}(aq) + 3\,\mathrm{Na^+}(aq) + 3\,\mathrm{OH^-}(aq) + \mathrm{Fe(OH)_3}(s) + 3\,\mathrm{Na^+}(aq) + 3\,\mathrm{Cl^+}(aq) \tag{9.P.44}$$

- Mn(OH)2(s)+HBr(aq) ?

  This is an example of a metal hydroxide reacting with an acid where a metal salt and water will always be formed:

  $$MetalHydroxide + Acid \longrightarrow MetalSalt + Water \tag{9.P.45}$$

  When this rule is applied to this equation, we will get the following:

  $$\mathrm{Mn(OH)_2}(s) + \mathrm{HBr}(aq) \longrightarrow \mathrm{MnBr_2}(aq) + 2\,\mathrm{H_2O}(l) \tag{9.P.46}$$

  But to follow through with this question, the aqueous solutions such as HBr(aq) and $MnBr_2$(aq) can be re-written as:

  $$\mathrm{Mn(OH)_2}(s) + 2\,\mathrm{H_3O^+}(aq) + 2\,\mathrm{Br^-}(aq) \longrightarrow \mathrm{Mn_2}^{+}(aq) + 2\,\mathrm{Br^-}(aq) + 4\,\mathrm{H_2O}(l) \tag{9.P.47}$$

- $Cr(s)+O_2(g)$?

  This is the general reaction of a metal reacting with oxygen which will always result in a metal oxide. However, the metal oxide is determined by the oxidation state of the metal so there may be several outcomes of this reaction such as:

  $$4\,\mathrm{Cr}(s) + 3\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{Cr_2O_3}(s) \tag{9.P.48}$$

$$\mathrm{Cr}(s)+\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{CrO}(s) \tag{9.P.49}$$

$$\mathrm{Cr}(s)+\mathrm{O_2}(g) \longrightarrow \mathrm{CrO_2}(s) \tag{9.P.50}$$

$$2\,\mathrm{Cr}(s)+3\,\mathrm{O_2}(g) \longrightarrow \mathrm{CrO_3}(s) \tag{9.P.51}$$

However, Cr_2O_3 is the main oxide of chromium so it can be assumed that this is the general product of this reaction.

- $Mn_2O_3(s)+HCl(aq)$⟐?

  This follows the general reaction of a metal oxide and an acid will always result in a salt and water

  $$MetalOxide + Acid \longrightarrow Salt + Water \tag{9.P.52}$$

  Using this general reaction, similar to the general reactions above, the reaction will result in:

  $$\mathrm{Mn_2O_3}(s) + \mathrm{HCl}(aq) \longrightarrow 2\,\mathrm{MnCl_3}(s) + 9\,\mathrm{H_2O}(l) \tag{9.P.53}$$

  However, since HCl is an aqueous solution, the overall equation can also be re-written as:

  $$\mathrm{Mn_2O_3}(s) + 6\,\mathrm{H_3O^+}(aq) + 6\,\mathrm{Cl^-}(aq) \longrightarrow 2\,\mathrm{MnCl_3}(s) + 9\,\mathrm{H_2O}(l) \tag{9.P.54}$$

- $Ti(s)+xsF_2(g)$⟐?

  Titanium is able to react with the halogens where there are two oxidation state that titanium can be: +3 and +4. The following reactions follow each oxidation state accordingly:

  $$2\,\mathrm{Ti}(s) + 3\,\mathrm{F_2}(g) \longrightarrow 2\,\mathrm{TiF_3}(s) \tag{9.P.55}$$

  $$\mathrm{Ti}(s) + 2\,\mathrm{F_2}(g) \longrightarrow \mathrm{TiF_4}(s) \tag{9.P.56}$$

  However, since there is the symbol "xs", this indicates that F_2 is added in excess so the second reaction is favored more as it drives the reaction to completion.

  OVERALL:

  \[\ce{Ti}(s)+\ce{xsF2}(g)⟐\ce{TiF4}(g)\]

A19.1.17

a. $\mathrm{Fe}(s) + 2\,\mathrm{H_3O^+}(aq) + \mathrm{SO_4}^{2-}(aq) \longrightarrow \mathrm{Fe}^{2+}(aq) + \mathrm{SO_4}^{2-}(aq) + \mathrm{H_2}(g) + 2\,\mathrm{H_2O}(l)$;
b. $\mathrm{FeCl_3}(aq) + 3\,\mathrm{Na^+}(aq) + 3\,\mathrm{OH^-}(aq) + \mathrm{Fe(OH)_3}(s) + 3\,\mathrm{Na^+}(aq) + 3\,\mathrm{Cl^+}(aq)$;
c. $\mathrm{Mn(OH)_2}(s) + 2\,\mathrm{H_3O^+}(aq) + 2\,\mathrm{Br^-}(aq) \longrightarrow \mathrm{Mn^{2+}}(aq) + 2\,\mathrm{Br^-}(aq) + 4\,\mathrm{H_2O}(l)$;
d. $4\,\mathrm{Cr}(s) + 3\,\mathrm{O_2}(g) \longrightarrow 2\,\mathrm{Cr_2O_3}(s)$;
e. $\mathrm{Mn_2O_3}(s) + 6\,\mathrm{H_3O^+}(aq) + 6\,\mathrm{Cl^-}(aq) \longrightarrow 2\,\mathrm{MnCl_3}(s) + 9\,\mathrm{H_2O}(l)$;
f. $\mathrm{Ti}(s) + xs\mathrm{F_2}(g) \longrightarrow \mathrm{TiF_4}(g)$

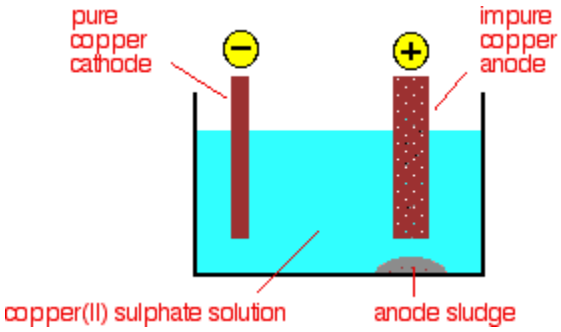
Q19.1.18

Describe the electrolytic process for refining copper.

S19.1.18

By electrolysis, copper can be refined and purely made. The reason why copper needs to remove the impurities is because it helps increase the electrical conductivity in electrical wire. You can refine copper and remove the impurities through electrolysis. Pure copper is important in making electrical wire, because it creates better electrical conductivity when transferring electricity. In order for better electrical conductivity, the impurities needs to be removed and this can be done by firing the impure copper to remove the impurities, such as sulfur, oxygen, etc. and shaping them into electrical anodes that can be used in electrolysis. Then the copper electrodes are placed into an electrical cell (into separate beakers) where electrical current can pass through the

beakers and onto the electrodes. Through this process, the copper is stripped off of the anode and deposited onto the cathode. This process helps remove the impurities and refine copper because all the copper has been deposited onto the cathode all in one electrode. This process increases the weight of the cathode due to copper being deposited onto the cathode. This is a prime example of how to tell if an electrode is a cathode or an anode, as stated in Q17.2.9 above.



Q19.1.19

Predict the products of the following reactions and balance the equations.

a. Zn is added to a solution of $Cr_2(SO_4)_3$ in acid.
b. $FeCl_2$ is added to a solution containing an excess of $Cr_2O_7^{2-}$ in hydrochloric acid.
c. Cr^{2+} is added to $Cr_2O_7^{2-}$ in acid solution.
d. Mn is heated with CrO_3.
e. CrO is added to $2HNO_3$ in water.
f. $FeCl_3$ is added to an aqueous solution of NaOH.

S19.1.19

1. Zn is added to a solution of $Cr_2(SO_4)_3$ in acid.
   - Oxidized half-reaction: $3Zn(s) \rightarrow 3Zn^{2+}(aq) + 6e^-$
   - Reduction half reaction:
   - Overall reaction:
   - Chromium will precipitate out of the solution because it has a higher reduction potential than Zinc; the reaction is a single replacement.
2. $FeCl_2$ is added to a solution containing an excess of $Cr_2O_7^{2-}$ in hydrochloric acid.
   - Dissociation reaction: $6FeCl_2(s) \rightarrow 6Fe^{2+}(aq) + 12Cl^-(aq)$
   - Oxidation half-reaction: $6Fe^{2+}(aq) \rightarrow 6Fe^{3+}(aq) + 6e^-$
   - Reduction half-reaction: $Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
   - Overall reaction:
   - The reduction potential for permanganate is larger so the reaction is still favorable even when the oxidation of Fe^{2+} is negative.
3. Cr^{2+} is added to $Cr_2O_7^{2-}$ in acid solution.
   - Reduction half-reaction:
   - Oxidation half-reaction:
   - Overall reaction: $6Cr^{2+}(aq) + Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 8Cr^{3+}(aq) + 7H_2O(l)$
   - The reaction is favorable with a high positive E°
4. Mn is heated with CrO_3.
   - Reduction half-reaction: $8CrO_3(aq) + 24H^+ + 24e^- \rightarrow 4Cr_2O_3(aq) + 12H_2O(l)$

- Oxidation half-reaction: $9Mn(s) + 12H_2O(l) \rightarrow 3Mn_3O_4(aq) + 24H^+(aq) + 24e^-$
- Overall reaction: $8CrO_3(aq) + 9Mn(s) \rightarrow^{\Delta} 4Cr_2O_3(aq) + 3Mn_3O_4(aq)$
- Heat creates a product with higher energy than both previous reactants.

5. CrO is added to HNO_3 in water.
   - Strong acid dissociation: $2HNO_3(aq) + 2H_2O(l) \rightarrow 2H_3O^+(aq) + 2NO_3^-(aq)$
   - Overall reaction: $2HNO_3(aq) + CrO(aq) \rightarrow Cr^{2+}(aq) + 2NO_3^-(aq) + H_2O(l)$
   - This reaction works by exchange of electrons to yield Chromium ions.
6. $FeCl_3$ is added to an aqueous solution of $NaOH$.
   - Overall reaction: $3NaOH(aq) + FeCl_3(s) \rightarrow 3Na^+(aq) + FeOH_3^-(s) + 3Cl^-(aq)$
   - Iron hydroxide will precipitate because the two metals will exchange anions.

A19.1.19

a. $\mathrm{Cr_2(SO_4)_3}(aq) + 2\,\mathrm{Zn}(s) + 2\,\mathrm{H_3O^+}(aq) \longrightarrow 2\,\mathrm{Zn^{2+}}(aq) + \mathrm{H_2}(g) + 2\,\mathrm{H_2O}(l) + 2\,\mathrm{Cr^{2+}}(aq) + 3\,\mathrm{SO_4^{2-}}(aq)$;
b. $4\,\mathrm{TiCl_3}(s) + \mathrm{CrO_4^{2-}}(aq) + 8\,\mathrm{H^+}(aq) \longrightarrow 4\,\mathrm{Ti^{4+}}(aq) + \mathrm{Cr}(s) + 4\,\mathrm{H_2O}(l) + 12\,\mathrm{Cl^-}(aq)$;
c. In acid solution between pH 2 and pH 6, $\mathrm{CrO_4^{2-}}$ forms $\mathrm{HrCO_4^-}$, which is in equilibrium with dichromate ion. The reaction is $2\,\mathrm{HCrO_4^-}(aq) \longrightarrow \mathrm{Cr_2O_7^{2-}}(aq) + \mathrm{H_2O}(l)$. At other acidic pHs, the reaction is $3\,\mathrm{Cr^{2+}}(aq) + \mathrm{CrO_4^{2-}}(aq) + 8\,\mathrm{H_3O^+}(aq) \longrightarrow 4\,\mathrm{Cr^{3+}}(aq) + 12\,\mathrm{H_2O}(l)$;
d. $8\,\mathrm{CrO_3}(s) + 9\,\mathrm{Mn}(s) \xrightarrow{\Delta} 4\,\mathrm{Cr_2O_3}(s) + 3\,\mathrm{Mn_3O_4}(s)$;
e. $\mathrm{CrO}(s) + 2\,\mathrm{H_3O^+}(aq) + 2\,\mathrm{NO_3^-}(aq) \longrightarrow$ [redacted]$(aq) + 2\,\mathrm{NO_3^-}(aq) + 3\,\mathrm{H_2O}(l)$;
f. $\mathrm{CrCl_3}(s) + 3\,\mathrm{NaOH}(aq) \longrightarrow \mathrm{Cr(OH)_3}(s) + 3\,\mathrm{Na^+}(aq) + 3\,\mathrm{Cl^-}(aq)$

Q19.1.20

What is the gas produced when iron(II) sulfide is treated with a nonoxidizing acid?

S19.1.20

Formula for iron(II) sulfide:

$$FeS \tag{9.P.57}$$

Definition of non-oxidizing acid: A non-oxidizing acid is an acid that doesn't act the oxidizing agent. Its anion is a weaker oxidizing agent than H+, thus it can't be reduced. Examples of non-oxidizing acids:

$$HCl, HI, HBr, H_3PO_4, H_2SO_4 \tag{9.P.58}$$

Step 2: Choose one of the non-oxidizing acid, in this case HCl, and write the chemical reaction:

$$FeS(s) + 2HCl(aq) \rightarrow FeCl_2(s) + H_2S(g) \tag{9.P.59}$$

The gas produced when iron (II) sulfide treated with a non-oxidizing acid, HCl, is H_2S (dihydrogen sulfide) gas.

Q19.1.21

Predict the products of each of the following reactions and then balance the chemical equations.

a. Fe is heated in an atmosphere of steam.
b. NaOH is added to a solution of $Fe(NO_3)_3$.
c. $FeSO_4$ is added to an acidic solution of $KMnO_4$.
d. Fe is added to a dilute solution of H_2SO_4.
e. A solution of $Fe(NO_3)_2$ and HNO_3 is allowed to stand in air.
f. $FeCO_3$ is added to a solution of $HClO_4$.
g. Fe is heated in air.

S19.1.21

a. Steam is water (H_2O)

We can write out the reaction as:

$$Fe + H_2O \rightarrow ?$$

This is a single replacement reaction, so Fe replaces H_2. So, one of the products is Fe_3O_4 since it is a combination of iron(II) oxide, FeO, and iron(III) oxide, Fe_2O_3.

The Fe is heated in an atmosphere of steam. H_2 becomes neutrally charged and becomes another product.

After balancing the coefficients, the final reaction is:

$$3\,Fe(s) + 4\,H_2O(g) \rightarrow Fe_3O_4(s) + 4\,H_2(g)$$

b. $NaOH$ added to a solution of $Fe(NO_3)_3$ is a double replacement and precipitation reaction.

We can write out the reaction as:

$$NaOH + Fe(NO_3)_3 \rightarrow ?$$

The Na and Fe switch to form $Fe(OH)_3(s)$ and $NaNO_3(aq)$.

$Fe(OH)_3$ is solid because it is insoluble according to solubility rules.

After balancing the coefficients in the reaction, the final reaction is:

$$Fe(NO_3)_3(aq) + 3\,NaOH(aq) \rightarrow Fe(OH)_3(s) + NaNO_3(aq)$$

c. For instance, the acid used to make the acidic solution is H_2SO_4, then the reaction is:

$$FeSO_4 + KMnO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + MnSO_4 + H_2O + K_2SO_4$$

Next, the net ionic reaction has to be written to get rid of the spectator ions in the reaction, this is written as:

$$Fe^{2+} + MnO_4{}^- + H^+ \rightarrow Fe^{3+} + Mn^{2+} + H_2O$$

As seen in the net ionic equation above, Fe^{2+} is oxidized to Fe^{3+} and $MnO_4{}^-$ is reduced to Mn^{2+}. These can be written as two half reactions:

$$Fe^{2+} \rightarrow Fe^{3+}$$

$$MnO_4{}^- \rightarrow Mn^{2+}$$

To balance the oxidation half reaction, one electron as to be added to the Fe^{3+}, this is shown as:

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

The reduction half reaction also has to be balanced, but with H^+ ions and H_2O, this is shown as:

$$MnO_4{}^- + 8\,H^+ \rightarrow Mn^{2+} + 4\,H_2O$$

After the charge of the Mn atoms are balanced, the overall charge has to be balanced on both sides because on the reactants side, the charge is $7+$, and the charge on the products side is $2+$. The overall charge can be balanced by adding electrons, this is shown as:

$$MnO_4{}^- + 8\,H^+ + 5\,e^- \rightarrow Mn^{2+} + 4\,H_2O$$

Now since both half reactions are balanced, the electrons in both half reactions have to be equal, and then the half reactions are added together. After this is done, the reaction looks like this:

$$\mathrm{MnO_4^-} + 8\,\mathrm{H^+} + 5\,\mathrm{Fe^{2+}} + 5\,\mathrm{e^-} \rightarrow \mathrm{Mn^{2+}} + 4\,\mathrm{H_2O} + 5\,\mathrm{Fe^{3+}} + 5\,\mathrm{e^-}$$

The $5\,\mathrm{e^-}$ on both sides cancel out and the final balanced reaction is:

$$\mathrm{MnO_4^-} + 8\,\mathrm{H^+} + 5\,\mathrm{Fe^{2+}} \rightarrow \mathrm{Mn^{2+}} + 4\,\mathrm{H_2O} + 5\,\mathrm{Fe^{3+}}$$

d. Fe added to a dilute solution of $\mathrm{H_2SO_4}$ is a single replacement reaction.

The Fe is added to a dilute solution so the $\mathrm{H_2SO_4}$ is written as separate ions.

We can write out the reaction as:

$$\mathrm{Fe}(s) + 2\,\mathrm{H^+}(aq) + (\mathrm{SO_4})^{2-}(aq) \rightarrow \ ?$$

The Fe replaces the $\mathrm{H^+}$ ion, and becomes an $\mathrm{Fe^{2+}}$ ion.

$\mathrm{H_2O}$ is also a product because the solution is dilute.

Furthermore, the $\mathrm{FeSO_4}$ also has to be separated into ions as a result of the Fe being added to a dilute solution.

After balancing all of the coefficients, the final reaction is:

$$\mathrm{Fe}(s) + (2\,\mathrm{H_3O})^{+}(aq) + (\mathrm{SO_4})^{2-}(aq) \rightarrow \blacksquare(aq) + {\mathrm{SO_4}}^{2-}(aq) + \mathrm{H_2}(g) + 2\,\mathrm{H_2O}(l)$$

Note: $\mathrm{H^+}$ can also be written as the the hydronium ion, $(\mathrm{H_3O})^{+}$.

e. We initially can initially write out:

$$4\,\mathrm{Fe(NO_3)_2} + 4\,\mathrm{HNO_3} + \mathrm{O_2} \rightarrow \ ?$$

We write the oxygen term in the reactants because it is stated that the solution is allowed to stand in air.

We just have to analyze the possible products that can be formed and we can see that the hydrogen from nitric acid can combine with oxygen gas to form water and then combining everything together, we get the final reaction to be:

$$4\,\mathrm{Fe(NO_3)_2}(aq) + 4\,\mathrm{HNO_3}(aq) + \mathrm{O_2}(g) \rightarrow 2\,\mathrm{H_2O}(l) + 4\,\mathrm{Fe(NO_3)_3}(aq)$$

f. When $\mathrm{FeCO_3}$ is added to $\mathrm{HClO_4}$, a double replacement reaction occurs.

The $\mathrm{Fe^{2+}}$ ion switches spots with the $\mathrm{H^+}$ ion to form $\mathrm{Fe(ClO_4)_2}$ as a product.

When the $\mathrm{H^+}$ ion is added to the $(\mathrm{CO_3})^{2-}$ ion, $\mathrm{H_2CO_3}$ is formed.

After balancing the coefficients, the final reaction is:

$$\mathrm{FeCO_3}(s) + \mathrm{HClO_4}(aq) \rightarrow \mathrm{Fe(ClO_4)_2}(aq) + \mathrm{H_2O}(l) + \mathrm{CO_2}(g)$$

g. Air is composed of oxygen gas, which is a diatomic molecule, so it is $\mathrm{O_2}$.

Adding Fe to $\mathrm{O_2}$ will cause a synthesis reaction to occur forming $\mathrm{Fe_2O_3}$.

After balancing coefficients, the final reaction is:

$$3\,\mathrm{Fe}(s) + 2\,\mathrm{O_2}(g) \rightarrow \mathrm{Fe_2O_3}(s)$$

A19.1.21

a. $3\,Fe(s) + 4\,H_2O(g) \longrightarrow Fe_3O_4(s) + 4\,H_2(g)$;
b. $3\,NaOH(aq) + Fe(NO_3)_3(aq) \xrightarrow{H_2O} Fe(OH)_3(s) + 3\,Na^+(aq) + 3\,NO_3{}^-(aq)$;
c. $MnO_4{}^- + 8\,H^+ + 5\,Fe^{2+} \rightarrow Mn^{2+} + 4\,H_2O + 5\,Fe^{3+}$
d. $Fe(s) + (2\,H_3O)^+(aq) + (SO_4)^{2-}(aq) \rightarrow$ [redacted]$(aq) + SO_4{}^{2-}(aq) + H_2(g) + 2\,H_2O(l)$
e. $4\,Fe(NO_3)_2(aq) + 4\,HNO_3(aq) + O_2(g) \rightarrow 2\,H_2O(l) + 4\,Fe(NO_3)_3(aq)$
f. $FeCO_3(s) + HClO_4(aq) \rightarrow Fe(ClO_4)_2(aq) + H_2O(l) + CO_2(g)$
g. $3\,Fe(s) + 2\,O_2(g) \rightarrow Fe_2O_3(s)$

Q19.1.22

Balance the following equations by oxidation-reduction methods; note that *three* elements change oxidation state.

$$Co(NO_3)_2(s) \longrightarrow Co_2O_3(s) + NO_2(g) + O_2(g) \tag{9.P.60}$$

S19.1.22

Balance the following equations by oxidation-reduction methods; note that three elements change oxidation state.

$$Co(NO_3)_2(s) \longrightarrow Co_2O_3(s) + NO_2(g) + O_2(g) \tag{9.P.61}$$

In this reaction, N changes oxidation states from +5 to +4 (reduced), Co changes oxidation states from +2 to +3 (oxidized), and O changes oxidation states from -2 to 0 (also oxidized).

First, split this reaction into an oxidation and reduction half reaction set, and balance all of the elements that are not hydrogen or oxygen (we will deal with these later):

$$Reduction: 2Co(NO_3)_2 \rightarrow Co_2O_3 + 4NO_2 \tag{9.P.62}$$

Now, for the oxidation reaction, we are only dealing with O_2 on the products side. In order to balance this, we will need to add water and hydrogen to both sides:

$$Oxidation: 2H_2O \rightarrow O_2 + 4H^+ \tag{9.P.63}$$

Balance the amount of oxygens on each side by adding the correct number of water molecules (H_2O), and balance the amount of hydrogen by adding the correct number of H^+ atoms:

$$Reduction: 2H^+ + 2Co(NO_3)_2 \rightarrow Co_2O_3 + 4NO_2 + H_2O \tag{9.P.64}$$

$$Oxidation: 2H_2O \rightarrow O_2 + 4H^+ \tag{9.P.65}$$

Finally, balance the charges by adding electrons to each side of the equation. For the reduction reaction, we will add 2 electrons to balance out the $2H^+$, and to the oxidation reaction, we will add 4 electrons to balance out the $4H^+$. Remember, the goal of this step is to make sure that the charges are balanced, so we can cancel them out in the end.

$$Reduction: 2e^- + 2H^+ + 2Co(NO_3)_2 \rightarrow Co_2O_3 + 4NO_2 + H_2O \tag{9.P.66}$$

$$Oxidation: 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{9.P.67}$$

Multiply the reduction reaction by two, in order to balance the charges so there are 4 electrons on each side of the reaction.

$$Reduction: 2(2e^- + 2H^+ + 2Co(NO_3)_2 \rightarrow Co_2O_3 + 4NO_2 + H_2O) \tag{9.P.68}$$

and combine both reactions which comes out to:

$$2H_2O + 4Co(NO_3)_2 + 4H^+ \rightarrow 2CO_2O_3 + 8NO_2 + 2H_2O + O_2 + 4H^+ \tag{9.P.69}$$

Cancel out like terms:

$$4Co(NO_3)_2(s) \rightarrow 2CO_2O_3(s) + 8NO_2(g) + O_2(g) \tag{9.P.70}$$

Both sides have overall charges of 0 and can be checked to see if they are balanced.

A19.1.22

$$4Co(NO_3)_2(s) \rightarrow 2CO_2O_3(s) + 8NO_2(g) + O_2(g) \tag{9.P.71}$$

Q19.1.23

Dilute sodium cyanide solution is slowly dripped into a slowly stirred silver nitrate solution. A white precipitate forms temporarily but dissolves as the addition of sodium cyanide continues. Use chemical equations to explain this observation. Silver cyanide is similar to silver chloride in its solubility.

S19.1.23

Dilute sodium cyanide solution is slowly dripped into a slowly stirred silver nitrate solution. A white precipitate forms temporarily but dissolves as the addition of sodium cyanide continues. Use chemical equations to explain this observation. Silver cyanide is similar to silver chloride in its solubility.

A: Step 1: look at the question and begin to write out a general product to reactant formula for this reaction.

Step 2: try to reason out why a precipitate will form but only for a finite period of time before reforming in an aqueous substance.

Step 3: With step 2 you should have noticed that the reaction is a multiple step reaction and using the rough formula that you derived in step 1, you should try and see what the series of steps are that lead to the overall product of liquid $AgCN_2$

In this reaction we see how NaCN is added to $AgNO_3$ .A precipitate forms but then disappears with the addition of even more NaCN, this must mean that its an intermediate reaction which will not appear as the final product. The silver and the cyanide temporarily bond, but the bond is too weak to hold them together so they are pulled apart again when NaCN is added because a new, more stronger and stable compound is formed: $[Ag(CN)_2]^-$ (aq).

The actual reaction equation when it is first taking place is

$$AgCl(aq) + NaCN(aq) \rightarrow AgCN(s) + NaCl(aq) \tag{9.P.72}$$

This can be written out in the following way: as CN^- is added, the silver and the cyanide combine : $Ag^+(aq)+CN^-(aq) \rightarrow AgCN(s)$

As more CN^- is added the silver and two cyanide combine to create a more stable compound: $Ag^+(aq)+2CN^-(aq) \rightarrow [Ag(CN)_2]^-$ (aq)

$AgCN(s) + CN^-(aq) \rightarrow [Ag(CN)_2]^-(aq)$

A19.1.23

As CN^- is added,

$$\mathrm{Ag^+}(aq) + \mathrm{CN^-}(aq) \longrightarrow \mathrm{AgCN}(s) \tag{9.P.73}$$

As more CN^- is added,

$$\mathrm{Ag^+}(aq) + 2\,\mathrm{CN^-}(aq) \longrightarrow [\mathrm{Ag(CN)_2}]^-(aq) \tag{9.P.74}$$

$$\mathrm{AgCN}(s) + \mathrm{CN^-}(aq) \longrightarrow [\mathrm{Ag(CN)_2}]^-(aq) \tag{9.P.75}$$

Q19.1.24

Predict which will be more stable, $[CrO_4]^{2-}$ or $[WO_4]^{2-}$, and explain.

S19.1.24

According to the rules associated with Crystal Field Stabilizing Energies, stable molecules contain more electrons in the lower-energy molecular orbitals than in the high-energy molecular orbitals. In this case, both complexes have O_4 as ligands, and both have a -2 charge. Therefore, you determine stability by comparing the metals. Chromium is in the 3d orbital, according to the periodic table. Tungsten (W) is in the 5d orbital. 3d is a lower energy level than 5d.Higher-level orbitals are more easily ionized, and make their base elemental form more stable. If the elemental form is more stable the oxidized form is less stable. Therefore, $[CrO_4]^{2-}$ is more stable than $[WO_4]^{2-}$.

A19.1.24

$[CrO_4]^{2-}$ is more stable because Chromium is in the 3d orbital while Tungsten is in the 4d orbital, which has a higher energy level and makes it less stable.

Q19.1.25

Give the oxidation state of the metal for each of the following oxides of the first transition series. (Hint: Oxides of formula M_3O_4 are examples of *mixed valence compounds* in which the metal ion is present in more than one oxidation state. It is possible to write these compound formulas in the equivalent format $MO{\cdot}M_2O_3$, to permit estimation of the metal's two oxidation states.)

a. Sc_2O_3
b. TiO_2
c. V_2O_5
d. CrO_3
e. MnO_2
f. Fe_3O_4
g. Co_3O_4
h. NiO
i. Cu_2O

S19.1.25

The first step to solving this problem is looking at the rules of Oxidizing states for various elements:

chem.libretexts.org/Core/Analytical_Chemistry/Electrochemistry/Redox_Chemistry/Oxidation_State

The main rules that will be used in these problems will be the oxidation state rule 6 which states that oxidation state for Oxygen is (-2) and rule 2 which is that the total sum of the oxidation state of all atoms in any given species is equal to the net charge on that species. Solving these problems requires simple algebra. The oxidation states of both elements in the compound is equal to zero, so set the unknown oxidation of the element that is not oxygen to a variable x, and the oxidation state of Oxygen equal to -2. Then multiply both oxygen states by the number of atoms of the element present. Add the values together, set the equation equal to zero and solve for x.

1. $\mathrm{Sc_2O_3} = 3(-2) + 2x = 0 \longrightarrow -6 + 2x = 0 \longrightarrow x = Sc = +3\ Sc^{3+}$
2. $\mathrm{TiO_2} = 2(-2) + x = 0 \longrightarrow -4 + x = 0 \longrightarrow x = Ti = +4\ Ti^{4+}$
3. $\mathrm{V_2O_5} = 5(-2) + 2x = 0 \longrightarrow -10 + 2x = 0 \longrightarrow x = V = +5\ V^{5+}$
4. $\mathrm{CrO_3} = 3(-2) + x = 0 \longrightarrow -6 + x = 0 \longrightarrow x = Cr = +6\ Cr^{6+}$
5. $\mathrm{MnO_2} = 2(-2) + x = 0 \longrightarrow -4 + x = 0 \longrightarrow x = Mn = +4\ Mn^{4+}$
6. $\mathrm{Fe_3O_4} = \mathrm{FeO} \cdot \mathrm{Fe_2O_3} =$

$\mathrm{FeO} = -2 + x = 0 \longrightarrow x = Fe = +2\ Fe^{2+}$

$\mathrm{Fe_2O_3} = 3(-2) + 2x = 0 \longrightarrow -6 + 2x = 0 \longrightarrow x = Fe = +3\ Fe^{3=}$

(One Fe Atom has an oxidation state of +2 and the other 2 Fe atoms have an oxidation state of +3)

7. $\mathrm{Co_3O_4} = \mathrm{CoO} \cdot \mathrm{Co_2O_3} =$

$\mathrm{CoO} = -2 + x = 0 \longrightarrow x = Co = +2\ Co^{2+}$

$\mathrm{Co_2O_3} = 3(-2) + 2x = 0 \longrightarrow -6 + 2x = 0 \longrightarrow x = Co = +3\ Co^{3+}$

(One Co Atom has an oxidation state of +2 and the other 2 Co atoms have an oxidation state of +3)

8. $\mathrm{NiO} = -2 + x = 0 \longrightarrow x = Ni = +2\ Ni^{2+}$

9. $\mathrm{Cu_2O} = -2 + 2x = 0 \longrightarrow -2 + 2x = 0 \longrightarrow x = Cu = +1\ Cu^{1+}$

A19.1.25

Sc^{3+}; Ti^{4+}; V^{5+}; Cr^{6+}; Mn^{4+}; Fe^{2+} and Fe^{3+}; Co^{2+} and Co^{3+}; Ni^{2+}; Cu^{+}

19.2: Coordination Chemistry of Transition Metals

Q19.2.1

Indicate the coordination number for the central metal atom in each of the following coordination compounds:

a. $[Pt(H_2O)_2Br_2]$
b. $[Pt(NH_3)(py)(Cl)(Br)]$ (py = pyridine, C_5H_5N)
c. $[Zn(NH_3)_2Cl_2]$
d. $[Zn(NH_3)(py)(Cl)(Br)]$
e. $[Ni(H_2O)_4Cl_2]$
f. $[Fe(en)_2(CN)_2]^+$ (en = ethylenediamine, $C_2H_8N_2$)

S19.2.1

First we must identify whether or not the ligand has more than one bonded atom (bidentate/polydentate). Using the table below we are able to do this.

Ligand	Number of bonded atoms
Ammine (NH_3)	monodentate
Aqua (H_2O)	monodentate
Bromo (Br)	monodentate
Chloro (Cl)	monodentate
Cyano (CN)	monodentate
Pyridine (C_5H_5N)	monodentate
Ethylenediamine ($C_2H_8N_2$)	bidentate

Now that we have identified the number of bonded atoms from each ligand, we can find the total number of atoms bonded to the central metal ion, giving us the coordination number.

a. $[Pt(H_2O)_2Br_2]$: We can identify the metal ion in the complex as Pt, platinum, as the other two are listed as ligands above and are nonmetallic. We can now use the number of ligands and their bonding atoms to find its coordination number. From the table above we see that H_2O has only one bonding atom and Br as well. So for each Br atom we have one bonding atom, and we have two of these, yielding 2 bonding atoms; this is the same for H_2O, giving us a total number of 4 bonding atoms, and therefore a coordination number of 4.
b. $[Pt(NH_3)(py)(Cl)(Br)]$ (py = pyridine, C_5H_5N): The metal ion in this complex, similarly to the first one, can be identified as Pt, platinum. The ligands can be identified as NH_3, pyridine, Cl, and Br, which are all monodentate ligands and have one bonding atom each. Since we have four ligands, each with one bonding atom, the total number of bonding atoms on the metal ion is 4, therefore the complex has a coordination number of 4.
c. $[Zn(NH_3)_2Cl_2]$: The metal ion in this complex can be identified as Zn, zinc, and the ligands can be identified as NH_3 and Cl. Since these two are both monodentate ligands they have one bonding atom each. Since we have a total of two NH_3 and two Cl ligands, we get a total of four monodentate ligands, giving us 4 bonding atoms and a coordination number of 4.
d. $[Zn(NH_3)(py)(Cl)(Br)]$: The metal ion in this complex can be identified as Zn, zinc, and the ligands can be identified as NH_3, pyridine, Cl, and Br, which are all monodentate ligands and have one bonding atom each. Since we have four ligands, each with one bonding atom, the total number of bonding atoms on the metal ion is 4, therefore the complex has a coordination number of 4.
e. $[Ni(H_2O)_4Cl_2]$: The metal ion in this complex can be identified as Ni, nickel, and we can now use the number of ligands and their bonding atoms to find its coordination number. From the table above we see that H_2O has only one bonding atom and Cl as well. So for each Cl atom we have one bonding atom, and we have two of these, yielding 2 bonding atoms. H_2O is the same, having only one bonding atom, but there are four of these. So this gives us a total number of 6 bonding atoms, and therefore a coordination number of 6.
f. $[Fe(en)_2(CN)_2]^+$ (en = ethylenediamine, $C_2H_8N_2$): The metal ion in this complex can be identified as Fe, iron, and the ligands can be identified as (en) and CN. Since (en) is bidentate, meaning it has 2 bonding atoms, and there are two of these, the total number of bonding atoms from (en) is four. Since CN is monodentate, meaning it has one bonding atom, and there are two of these, the total number of bonding atoms from CN ligand is two. So, the total number of bonding atoms is 6, therefore the complex has a coordination number of 6.

A19.2.1

a. The 2 aqua and the 2 bromo ligands form a total of 4 coordinate covalent bonds and as a result the coordination number is 4.
b. The ammine, pyridine, chloro and bromo each form one coordinate covalent bond that gives a total of 4 and hence CN=4.
c. Two ammine and two chloro ligands give a total of 4 coordinate covalent bonds and a CN = 4.
d. One ammine, a pyrimidine, a chloro and a bromo ligand give a total of 4 covalent bonds, resulting in CN = 4.
e. Four aqua ligands and two chloro ligands form a total of 6 coordinate covalent bonds and a CN =6.
f. Ethylenediamine is a bidentate ligand that forms two coordinate covalent bonds; along with two cyano ligands, it forms a total of 6 bonds, and hence has a CN=6.

Q19.2.2

Give the coordination numbers and write the formulas for each of the following, including all isomers where appropriate:

a. tetrahydroxozincate(II) ion (tetrahedral)
b. hexacyanopalladate(IV) ion
c. dichloroaurate ion (note that *aurum* is Latin for "gold")
d. diamminedichloroplatinum(II)
e. potassium diamminetetrachlorochromate(III)
f. hexaamminecobalt(III) hexacyanochromate(III)
g. dibromobis(ethylenediamine) cobalt(III) nitrate

S19.2.2

To determine coordination numbers we must count the total number of ligands bonded to the central metal and distinguish monodentate and polydentate ligands. To determine the formulas, we use the nomenclature rules and work backwards.

1. "tetrahydroxo" = 4 hydroxide ligands; since hydroxide is a monodentate ligand, we have a total of 4 bonds to the central

metal.
Coordination Number: 4

We review the basics of nomenclature and see that "tetra" = 4 and "hydroxo" = OH^-. Since the charge on zinc is 2+, which is given in the nomenclature by the Roman numerals, we can calculate the total charge on the complex to be 2-.

Formula: $[Zn(OH)_4]^{2-}$

2. "hexacyano" = 6 cyanide ligands; since cyanide is a monodentate ligand, we have a total of 6 bonds to the central metal.
Coordination Number: 6

We review the basics of nomenclature and see that "hexa" = 6 and "cyano" = CN^-. Since the charge on Pd is 4+, which is given in the nomenclature by the Roman numerals, we can calculate the total charge on the complex to be 2-.

Formula: $[Pd(CN)_6]^{2-}$

3. "dichloro" = 2 chloride ligands; since chloride is a monodentate ligand, we have a total of 2 bonds to the central metal.
Coordination Number: 2

We review the basics of nomenclature and see that "di" = 2 and "chloro" = Cl^-. Since the charge on Au is always 1+, we can calculate the total charge on the complex to be 1-.

Formula: $[AuCl_2]^-$

4. "diammine" = 2 ammonia ligands and "dichloro" = 2 chloride ligands; since both ammonia and chloride ligands are monodentate, we have a total of 4 bonds to the central metal.
Coordination Number: 4

We review the basics of nomenclature and see that "di" = 2, "chloro" = Cl^- and "ammine" = NH_3. Since the charge on Pt is 2+, which is given in the nomenclature by the Roman numerals, we can calculate that the total charge is 0, so the complex is neutral.

Formula: $[Pt(NH_3)_2Cl_2]$

5. "diammine" = 2 ammonia ligands and "tetrachloro" = 4 chloride ligands; since both ammonia and chloride ligands are monodentate, we have a total of 6 bonds to the central metal.
Coordination Number: 6

We review the basics of nomenclature and see that "di" = 2, "ammine" = NH_3, "tetra" = 4 and "chloro" = Cl^-. Since the charge on the central metal, Cr, is 3+, which is given in the nomenclature by the Roman numerals, we can calculate that the total charge of the complex is 1-. The "potassium" at the front of the nomenclature indicates that it is the corresponding cation to this anionic complex.

Formula: $K[Cr(NH_3)_2Cl_4]$

6. Both of the metal complexes have "hexa" monodentate ligands, which means both have coordination numbers of 6.
Coordination Number: 6

We review the basics of nomenclature and see that "hexa" = 6, "ammine" = NH_3, and "cyano" = CN^-. Since the charge on Cr is 3+ and Co is 3+, which is given in the nomenclature by the Roman numerals, we find that these complexes' charges balance out.

Formula: $[Co(NH_3)_6][Cr(CN)_6]$

7. "dibromo" = 2 bromide ligands "bis(ethylenediamine)" = 2 (en) ligands; bromide is a monodentate ligand while (en) is a bidentate ligand. Therefore, we have a coordination number of 6.
Coordination Number: 6

We review the basics of nomenclature and see that "di" = 2, "bromo" = Br^-, "bis" = 2, and "ethylenediamine" = en. Since the charge on Co is 3+, which is given in the nomenclature by the Roman numerals, we find that the total charge of the complex is 1+. Nitrate is the corresponding anion to this cationic complex.

Formula: $[Co(en)_2Br_2]NO_3$

A19.2.2

a. 4, $[Zn(OH)_4]^{2-}$;
b. 6, $[Pd(CN)_6]^{2-}$;
c. 2, $[AuCl_2]^-$;
d. 4, $[Pt(NH_3)_2Cl_2]$;
e. 6, $K[Cr(NH_3)_2Cl_4]$;
f. 6, $[Co(NH_3)_6][Cr(CN)_6]$;
g. 6, $[Co(en)_2Br_2]NO_3$

Q19.2.3

Give the coordination number for each metal ion in the following compounds:

a. $[Co(CO_3)_3]^{3-}$ (note that CO_3^{2-} is bidentate in this complex)
b. $[Cu(NH_3)_4]^{2+}$
c. $[Co(NH_3)_4Br_2]_2(SO_4)_3$
d. $[Pt(NH_3)_4][PtCl_4]$
e. $[Cr(en)_3](NO_3)_3$
f. $[Pd(NH_3)_2Br_2]$ (square planar)
g. $K_3[Cu(Cl)_5]$
h. $[Zn(NH_3)_2Cl_2]$

S19.2.3

You can determine a compound's coordination number based on how many ligands are bound to the central atom.

1) In this compound, Cobalt is the central atom, and it has 3 CO_3^{2-} molecules attached to it. However, CO_3^{2-} is a bidentate ligand, which means it binds to the central atom in two places rather than one. This means that the coordination number of $[Co(CO_3)_3]^{3-}$ is 6. A coordination number of 6 means that the structure is most likely octahedral.

2) In this compound, Copper is the central atom. 4 ammonia molecules are attached to it. This means the coordination number is 4, and the structure is likely tetrahedral.

3) For this compound, we can ignore the $(SO_4)_3$ because it is not bound to the central atom. The central atom is cobalt, and it has 4 ammonia molecules and 2 bromine molecules bound to it. The coordination number is 6.

4) There are two compounds here, indicated by the brackets. The central atom for both is platinum. One of them has 4 ammonia molecules attached, and the other has 4 chlorine atoms attached. Both complexes have a coordination number of 4.

5) We can ignore $(NO_3)_3$ for this compound. The central atom is Chromium. There are 3 ethylenediamine molecules attached to the chromium. Ethylenediamine is a bidentate ligand, so the coordination number is 6.

6) Palladium is the central atom. 2 ammonia molecules and 2 bromine atoms are bound to the palladium atom. The coordination number is 4.

7) We can ignore the K_3 structure. Copper is the central atom, and there are 5 chlorine molecules attached to it. The coordination number is 5, so the structure is either trigonal bipyramidal or square pyramidal.

8) In this compound, zinc is the central atom. There are 2 ammonia molecules and 2 chlorine atoms attached. This means that the coordination number is 4.

Q19.2.4

Sketch the structures of the following complexes. Indicate any *cis*, *trans*, and optical isomers.

a. $[Pt(H_2O)_2Br_2]$ (square planar)
b. $[Pt(NH_3)(py)(Cl)(Br)]$ (square planar, py = pyridine, C_5H_5N)
c. $[Zn(NH_3)_3Cl]^+$ (tetrahedral)
d. $[Pt(NH_3)_3Cl]^+$ (square planar)
e. $[Ni(H_2O)_4Cl_2]$
f. $[Co(C_2O_4)_2Cl_2]^{3-}$ (note that $C_2O_4^{2-}$ is the bidentate oxalate ion, $-O_2CCO_2-$)

S19.2.4

Cis and trans are a type of geometric isomer, meaning there is a difference in the orientation in which the ligands are attached to the central metal. In cis, two of the same ligands are adjacent to one another and in trans, two of the same ligands are directly across from one another.

Optical isomers → have the ability to rotate light, optical isomers are also chiral. Only chiral complexes have optical isomers

Chiral → asymmetric, structure of its mirror image is not superimposable

Enantiomers: chiral optical isomers (compound can have multiple enantiomers)

Tetrahedral complex with 4 distinct ligands → always chiral

- For tetrahedral, if 2 ligands are the same, then it cannot be chiral, has a plane of symmetry

Solutions:

a. $[Pt(H_2O)_2Br_2]$ (square planar)

This complex has 2 kinds of ligands. The matching ligands can either be adjacent to each other and be cis, or they can be across from each other and be trans.

b. $[Pt(NH_3)(py)(Cl)(Br)]$ (square planar, py = pyridine, C_5H_5N)

This complex has 4 different ligands. There is no plane of symmetry in any of the enantiomers, making the structures chiral and therefore has optical isomers.

c. $[Zn(NH_3)_3Cl]^+$ (tetrahedral)

There is a plane of symmetry from NH_3 through Zn to the other NH_3, therefore it is not chiral.

d. $[Pt(NH_3)_3Cl]^+$ (square planar)

There is a plane of symmetry from NH_3 through Pt to the other NH_3, therefore it is not chiral.

e. $[Ni(H_2O)_2Cl_2]$

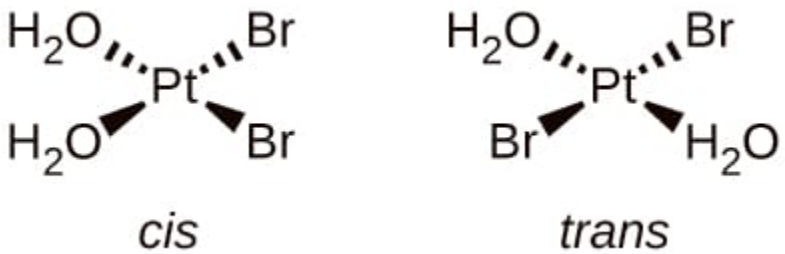
The Cl ligands can either be right next to each other, or directly across from one another allowing for both cis and trans geometries.

f. $[Co(C_2O_4)_2Cl_2]^-3$ (note that $C_2O_4^-2$ is the bidentate oxalate ion, $^-O_2CCO_2^-$

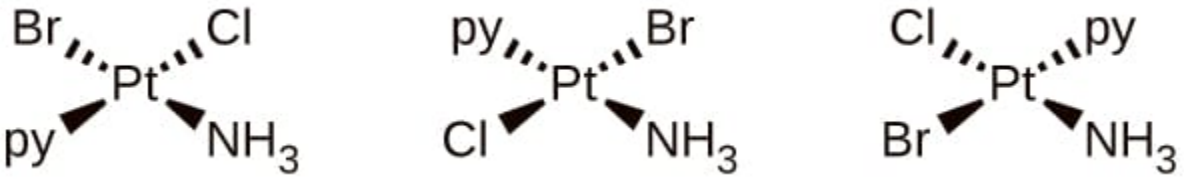
There is a plane of symmetry from Cl through Co to the other Cl in a "trans" chlorine configuration, therefore it is not chiral in a chlorine "trans" configuration. However, there is no symmetry in the chlorine "cis" configuration, indicating multiple "cis" isomers.

A19.2.4

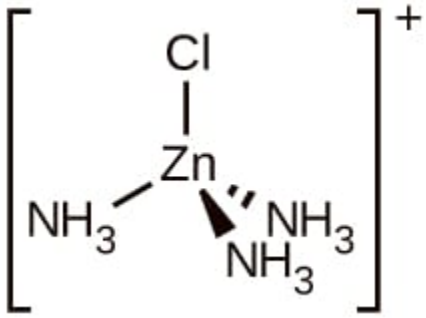
a. [Pt(H$_2$O)$_2$Br$_2$]:



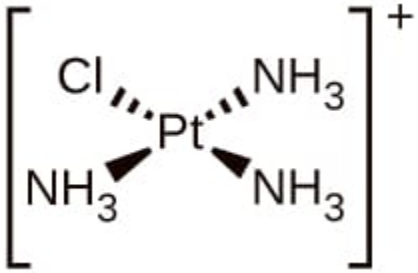
b. $[Pt(NH_3)(py)(Cl)(Br)]$:



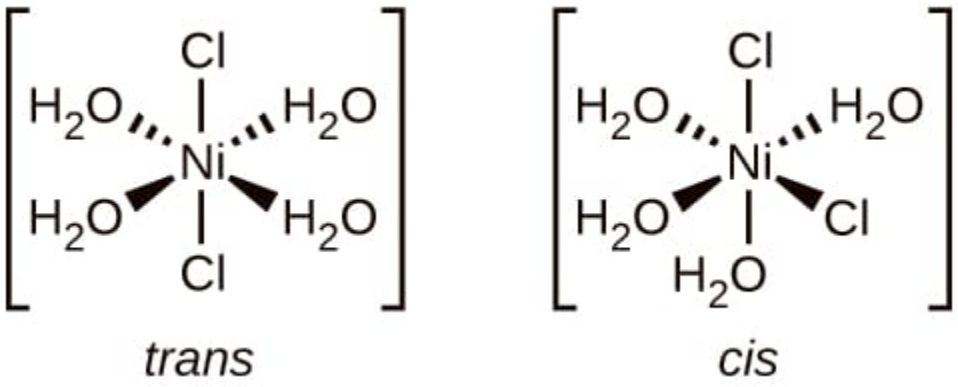
c. $[Zn(NH_3)_3Cl]^+$:



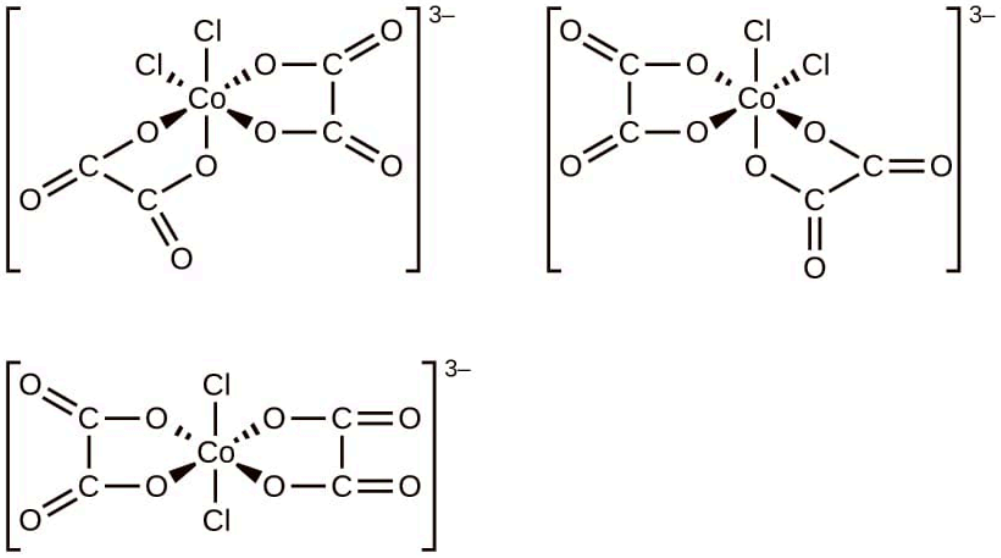
d. $[Pt(NH_3)_3Cl]^+$:



e. $[Ni(H_2O)_4Cl_2]$:



f. $[Co(C_2O_4)_2Cl_2]^{3-}$:



Q19.2.5

Draw diagrams for any *cis*, *trans*, and optical isomers that could exist for the following (en is ethylenediamine):

a. $[Co(en)_2(NO_2)Cl]^+$
b. $[Co(en)_2Cl_2]^+$
c. $[Pt(NH_3)_2Cl_4]$
d. $[Cr(en)_3]^{3+}$
e. $[Pt(NH_3)_2Cl_2]$

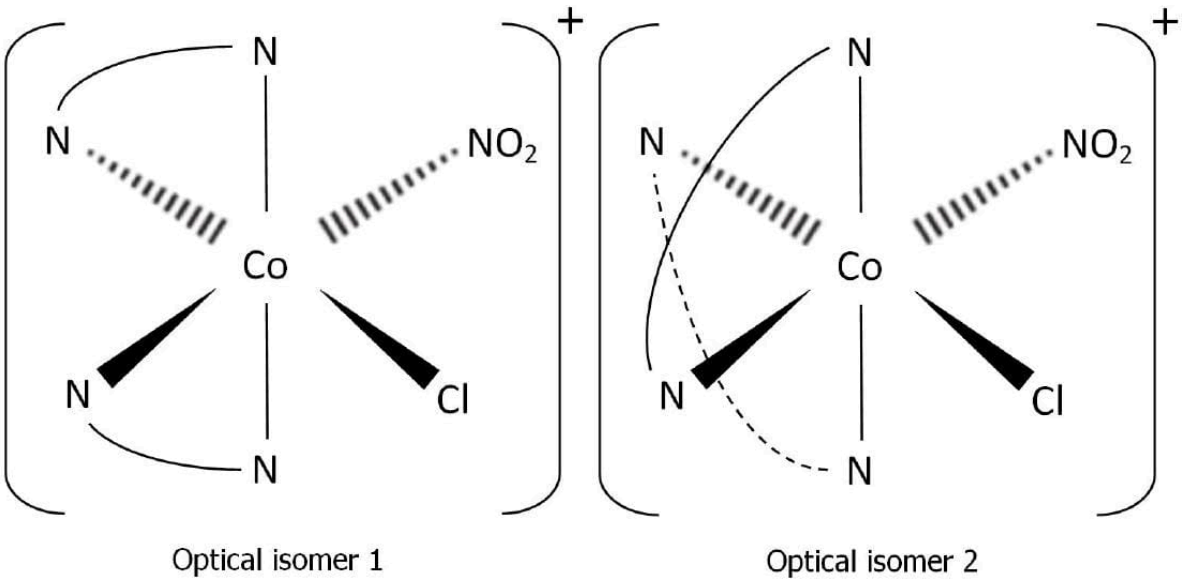
S19.2.5

We are instructed to draw all geometric isomers and optical isomers for the specified compound. Optical isomers exist when an isomer configuration is not superimposable on its mirror image. This means there are two distinct molecular shapes. Often a left and right hand are cited as an example; if you were to take your right hand and place it upon your left, you cannot make the major parts of your hand align on top of one another. The basic idea when deciding whether something is optically active is to look for a plane of symmetry--if you are able to bisect a compound in a manner that establishes symmetry, then the compound does not have an optical isomer.

Cis isomers exist when there are 2 ligands of the same species placed at 90 degree angles from each other. Trans isomers exist when there are 2 ligands of the same species placed at 180 degree angles from each other.

Problem 1

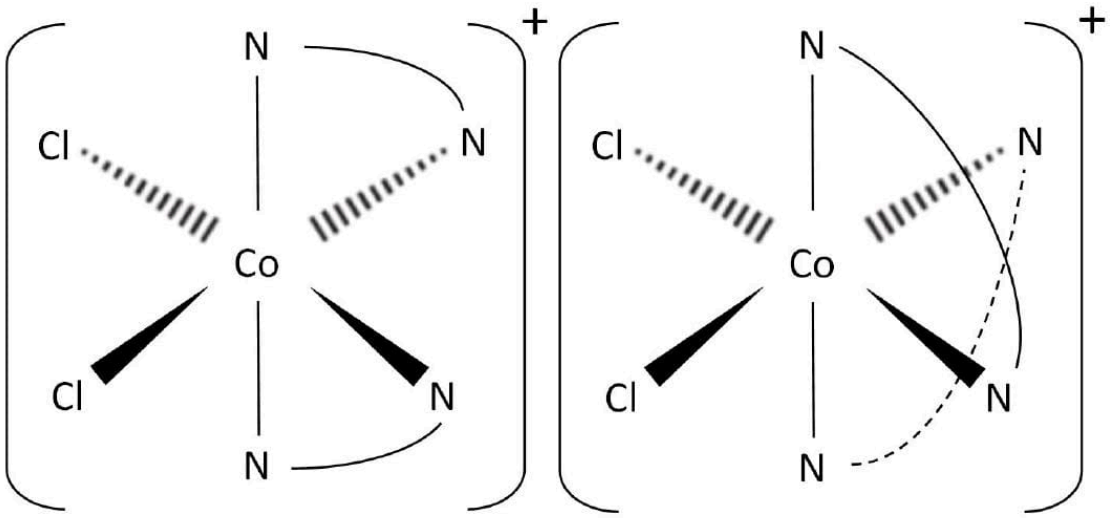
This compound is an octahedral molecule, so the six ligands (atoms in the complex that are not the central transition metal) are placed around the central atom at 90 degree angles. Two optical isomers exist for $[Co(en)_2(NO_2)Cl]^+$. The second isomer is drawn by taking the mirror image of the first.



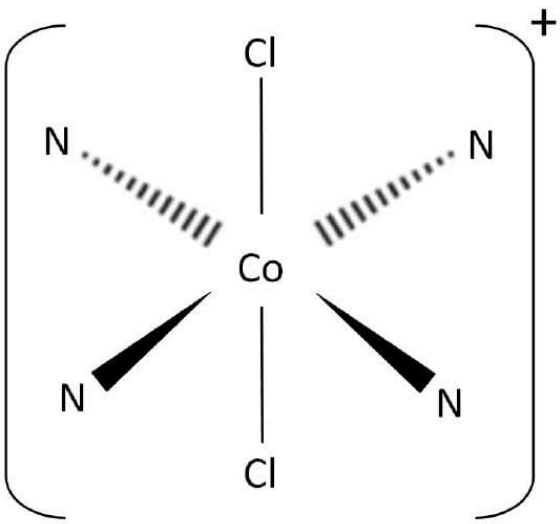
Optical isomer 1 Optical isomer 2

Problem 2

This compound is also an octahedral molecule. Two cis (optical) isomers and one trans isomer exist for $[Co(en)_2Cl_2]^+$. The trans isomer can be drawn by placing the chlorine ligands in positions where they form a 180 degree angle with the central atom. The first cis isomer can be drawn by placing the chlorine ligands in positions where they form a 90 degree angle with the central atom. The second cis isomer can be found by mirroring the first cis isomer, like we did in problem 1.



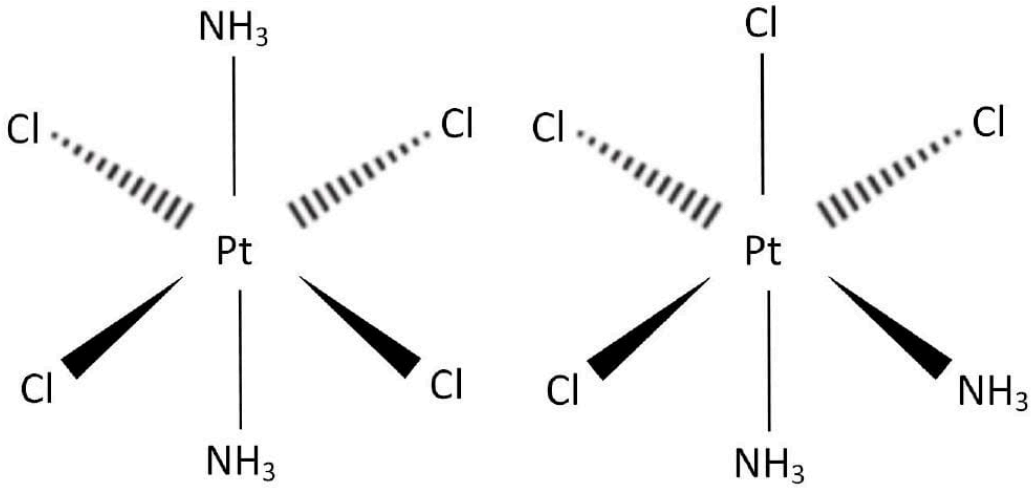
Cis isomer (Optical 1) Cis isomer (Optical 2)



Trans isomer

Problem 3

This compound is also an octahedral molecule. One trans isomer and one cis isomer of $[Pt(NH_3)_2Cl_4]$ exist. The trans isomer can be drawn by placing the ammonia ligands in positions where they form a 180 degree angle with the central atom. The cis isomer can be drawn by placing the ammonia ligands in positions where they form a 90 degree angle with the central atom.

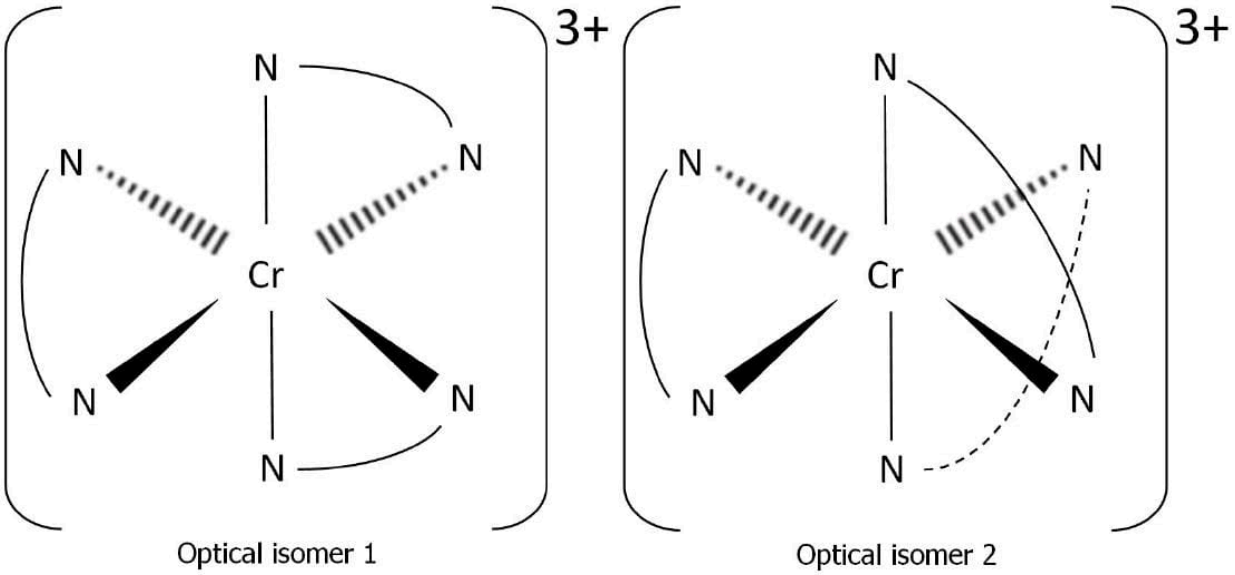


Trans isomer

Cis isomer

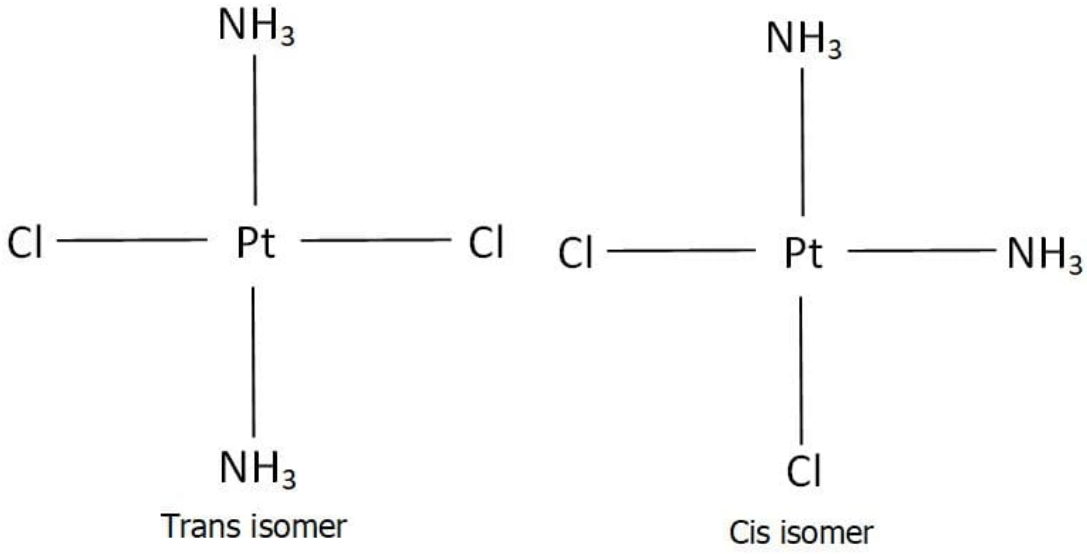
Problem 4

This compound is also an octahedral molecule. Two optical isomers for $[Cr(en)_3]^{3+}$ exist. The second optical isomer can be drawn by taking the mirror image of the first optical isomer.



Problem 5

This compound is a square planar complex, so the ligands are placed around the central atom in a plane, at 90 angles. A trans isomer and a cis isomer exist for the complex $[Pt(NH_3)_2Cl_2]$. The trans isomer can be drawn by placing the ammonia ligands in positions where they form a 180 degree angle in the plane with the central atom. The cis isomer can be drawn by placing the ammonia ligands in positions where they form a 90 degree angle in the plane with the central atom.



Q19.2.6

Name each of the compounds or ions given in Exercise Q19.2.3, including the oxidation state of the metal.

S19.2.6

Rules to follow for coordination complexes

1. Cations are always named before the anions.

2. Ligands are named before the metal atom or ion.

3. Ligand names are modified with an -o added to the root name of an anion. For neutral ligands the name of the molecule is used, with the exception of OH2, NH3, CO and NO.

4. The prefixes mono-, di-, tri-, tetra-, penta-, and hexa- are used to denote the number of simple ligands.

5. The prefixes bis-, tris-, tetrakis-, etc., are used for more complicated ligands or ones that already contain di-, tri-, etc.

6. The oxidation state of the central metal ion is designated by a Roman numeral in parentheses.

7. When more than one type of ligand is present, they are named alphabetically. Prefixes do not affect the order.

8. If the complex ion has a negative charge, the suffix –ate is added to the name of the metal.

9. In the case of complex-ion isomerism the names cis, trans, fac, or mer may precede the formula of the complex-ion name to indicate the spatial arrangement of the ligands. Cis means the ligands occupy adjacent coordination positions, and trans means opposite positions just as they do for organic compounds. The complexity of octahedral complexes allows for two additional geometric isomers that are peculiar to coordination complexes. Fac means facial, or that the three like ligands occupy the vertices of one face of the octahedron. Mer means meridional, or that the three like ligands occupy the vertices of a triangle one side of which includes the central metal atom or ion.

A19.2.6

a. tricarbonatocobaltate(III) ion;
b. tetraaminecopper(II) ion;
c. tetraaminedibromocobalt(III) sulfate;
d. tetraamineplatinum(II) tetrachloroplatinate(II);
e. *tris*-(ethylenediamine)chromium(III) nitrate;
f. diaminedibromopalladium(II);
g. potassium pentachlorocuprate(II);
h. diaminedichlorozinc(II)

Q19.2.7

Name each of the compounds or ions given in Exercise Q19.2.5.

S19.2.7

Given:

1. $[Co(en)_2(NO_2)Cl]^+$
2. $[Co(en)_2Cl_2]^+$
3. $[Pt(NH_3)_2Cl_4]$
4. $[Cr(en)_3]^{3+}$
5. $[Pt(NH_3)_2Cl_2]$

Wanted:

Names of the above compounds.

1. $[Co(en)_2(NO_2)Cl]^+$

Step 1: Attain the names of the ligands and metal cation. Names can be found here.

Co: Cobalt

en: Ethylenediamine

NO_2: Nitro

Cl: Chloro

Step 2: Add the appropriate pre-fixes to each ligand depending on the number. Pre-fixes can be found here.

$(en)_2$: bis(Ethylenediamine)

Step 3: Find the charges of the ligands. Charges can be found here.

en: 0

NO_2: -1

Cl: -1

Step 4: Algebraically attain the charge of the metal cation using the overall charge of the complex ion and the individual ligand charges.

$Co + 2(en) + (NO_2) + Cl = 1$

$Co + 2(0) + (-1) + (-1) = 1$

$Co = 3$

Step 5: For the name alphabetically place the ligands, pre-fixes should not be accounted, and use roman numerals for the metal cation which should be placed last.

Chlorobis(ethylenediamine)nitrocobalt(III)

2. $[Co(en)_2Cl_2]^+$

Step 1: Attain the names of the ligands and metal cation. Names can be found here.

Co: Cobalt

en: Ethylenediamine

Cl: Chloro

Step 2: Add the appropriate pre-fixes to each ligand depending on the number. Pre-fixes can be found here.

$(en)_2$: bis(Ethylenediamine)

Cl_2: dichloro

Step 3: Find the charges of the ligands. Charges can be found here.

en: 0

Cl: -1

Step 4: Algebraically attain the charge of the metal cation using the overall charge of the complex ion and the individual ligand charges.

$Co + 2(en) + 2(Cl) = 1$

$Co + 2(0) + 2(-1) = 1$

Co = 3

Step 5: For the name alphabetically place the ligands, pre-fixes should not be accounted, and use roman numerals for the metal cation which should be placed last.

Dichlorobis(Ethylenediamine)cobalt(III)

3. $[Pt(NH_3)_2Cl_4]$

Step 1: Attain the names of the ligands and metal cation. Names can be found here.

Pt: Platinum

NH_3: Ammine

Cl: Chloro

Step 2: Add the appropriate pre-fixes to each ligand depending on the number. Pre-fixes can be found here.

$(NH_3)_2$: diammine

Cl_4: tetrachloro

Step 3: Find the charges of the ligands. Charges can be found here.

NH_3: 0

Cl: -1

Step 4: Algebraically attain the charge of the metal cation using the overall charge of the complex ion and the individual ligand charges.

$Pt + 2(NH_3) + 4(Cl) = 0$

$Pt + 2(0) + 4(-1) = 0$

Pt = 4

Step 5: For the name alphabetically place the ligands, pre-fixes should not be accounted, and use roman numerals for the metal cation which should be placed last.

Diamminetetrachloroplatinum(IV)

4. $[Cr(en)_3]^{3+}$

Step 1: Attain the names of the ligands and metal cation. Names can be found here.

Cr: Cromium

en: ethylenediamine

Step 2: Add the appropriate pre-fixes to each ligand depending on the number. Pre-fixes can be found here.

$(en)_3$: tris(ethylenediamine)

Step 3: Find the charges of the ligands. Charges can be found here.

en: 0

Step 4: Algebraically attain the charge of the metal cation using the overall charge of the complex ion and the individual ligand

charges.

Cr + 3(en) = 3

Cr + 3(0) = 3

Cr = 3

Step 5: For the name alphabetically place the ligands, pre-fixes should not be accounted, and use roman numerals for the metal cation which should be placed last.

Tris(ethylenediamine)cromium(III)

5. $[Pt(NH_3)_2Cl_2]$

Step 1: Attain the names of the ligands and metal cation. Names can be found here.

NH_3: Ammine

Cl: Chloro

Pt: Platinum

Step 2: Add the appropriate pre-fixes to each ligand depending on the number.

$(NH_3)_2$: diammine

Cl_2: dichloro

Step 3: Find the charges of the ligands. Charges can be found here.

NH_3: 0

Cl: -1

Step 4: Algebraically attain the charge of the metal cation using the overall charge of the complex ion and the individual ligand charges.

$Pt + 2(NH_3) + 2(Cl) = 0$

Pt + 2(0) + 2(-1) = 0

Pt = 2

Step 5: For the name alphabetically place the ligands, pre-fixes should not be accounted, and use roman numerals for the metal cation which should be placed last.

Diamminedichloroplatinum(II)

A19.2.7

1. Chlorobis(ethylenediamine)nitrocobalt(III)
2. Dichlorobis(Ethylenediamine)cobalt(III)
3. Diamminetetrachloroplatinum(IV)
4. Tris(ethylenediamine)cromium(III)
5. Diamminedichloroplatinum(II)

Q19.2.8

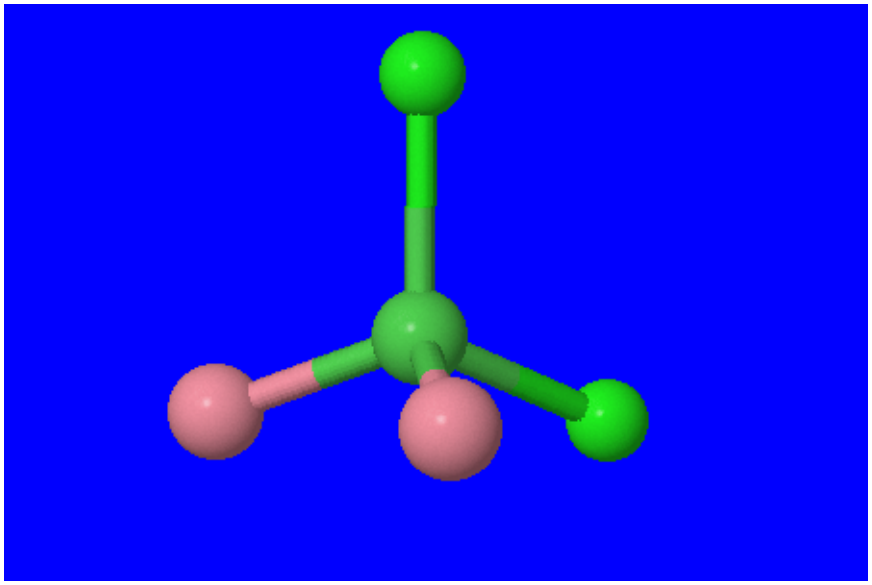
Specify whether the following complexes have isomers.

a. tetrahedral $[Ni(CO)_2(Cl)_2]$
b. trigonal bipyramidal $[Mn(CO)_4NO]$
c. $[Pt(en)_2Cl_2]Cl_2$

S19.2.8

Isomers are compounds that have the same number of atoms, but have different structures. Structural isomers (linkage, ionization, coordination) and stereoisomers (geometric and optical) can occur with several compounds.

1. tetrahedral $[\mathrm{Ni(CO)_2(Cl)_2}]$

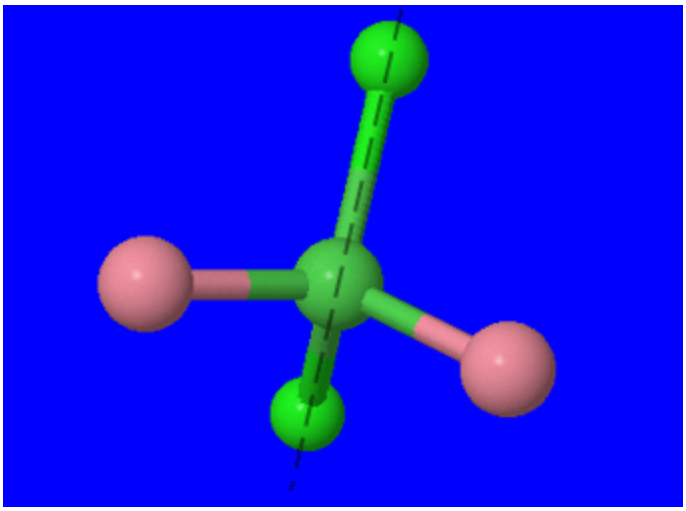


(Fig 1.) *In this model, nickel is the dark green central atom, carbonyl ligands are the pink atom, and chloro ligands are the light green atoms.*

Immediately, we can cancel out the possibility of linkage, ionization, and coordination isomers. There are no other coordination complexes for coordination isomerism, there is no ligand that can bond to the atom in more than one way for it to exhibit linkage isomerism, and there are no ions outside the coordination sphere for ionization isomerism.

This is a tetrahedral structure which immediately rules out any geometric isomers since they require 90° and/or 180° bond angles. Tetrahedral structures have 109.5° angles.

To confirm that the structure has no optical isomer, we must determine if there is a plane of symmetry. Structures that have no plane of symmetry are considered chiral and would have optical isomers.



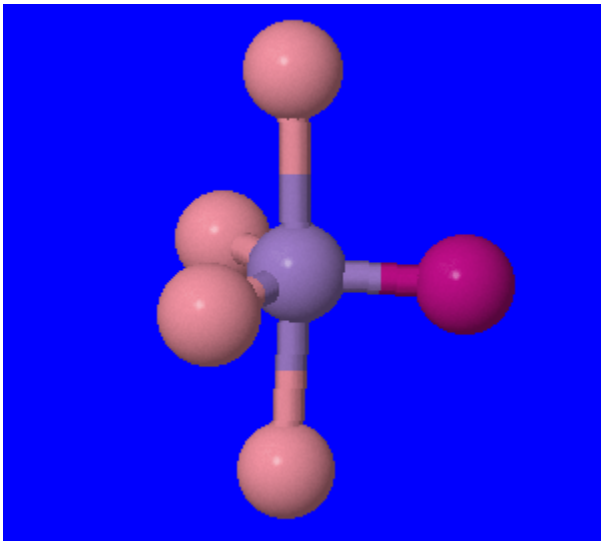
(Fig 2.) *We can rotate the structure and find that there is indeed a plane of symmetry through the two chloro ligands and central atom and between the carbonyl ligands.*

Since there is a plane of symmetry, we can conclude that there are no optical isomers.

Overall, there are no isomers that exist for this compound.

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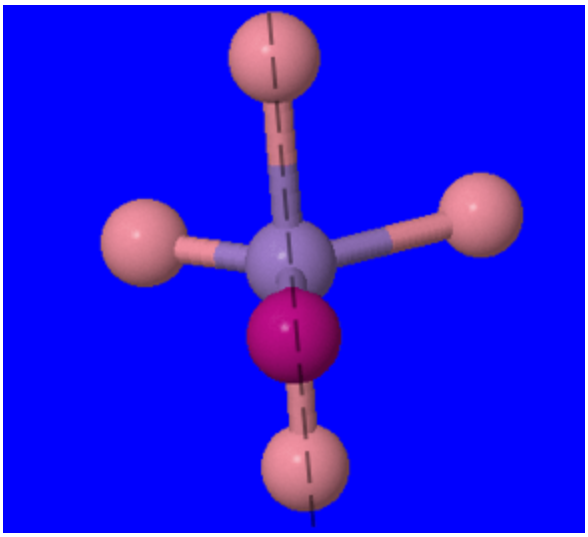
2. trigonal byprimidal $[\mathrm{Mn(CO)_4(NO)}]$



(Fig 3.) *The central purple atom is manganese, the carbonyl ligands are the pink atoms, and the nitrosyl ligand is the fuschia atom.*

There are no ions, other coordination complex, and ambidentate ligands. Therefore, no structural isomers exist for this structure.

Geometric isomers do not exist for this compound because there is only one nitrosyl ligand.



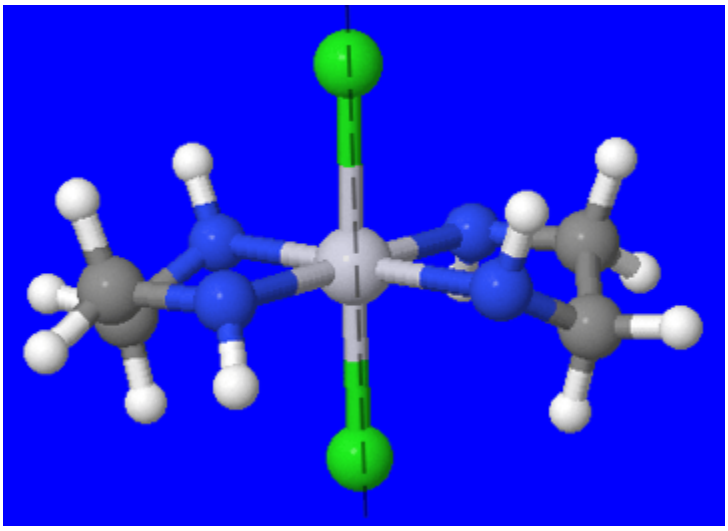
(Fig 4.) *Dashed line bisects molecule and shows plane of symmetry. The molecule is rotated in this image.*

In the image above, after the structure has been rotated, we can see that there is a plane of symmetry. Thus, there are no optical isomers.

No isomers (the ones mentioned above) exist for this compound.

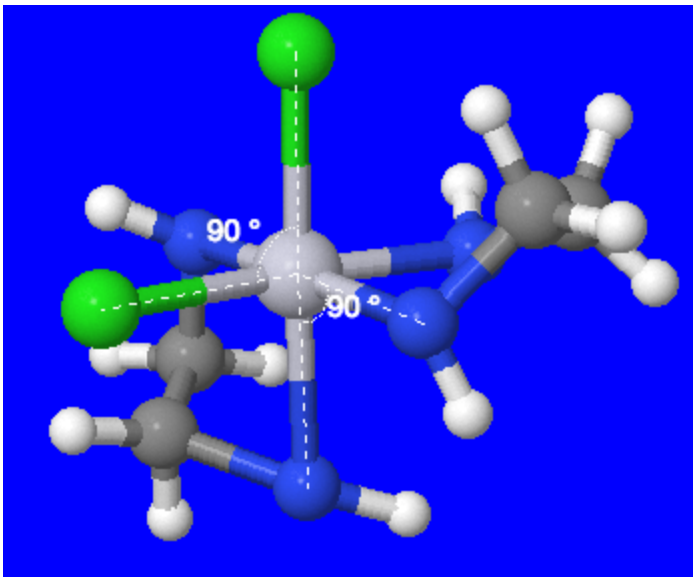
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3. $[\mathrm{Pt(en)_2Cl_2}]\mathrm{Cl_2}$



(Fig 5.) *The green atoms are the chloro ligands, the the central atom is platinum, and the grey/blue atoms are ethyldiamine ligands.*

Coordination isomerism cannot exist for this complex because there are no other complexes. There are no linkage isomers because there are no ambidentate ligands. Ionization isomers cannot exist in this complex either, even though there is a neutral molecule outside the coordination sphere. If we exchange $\mathrm{Cl_2}$ with one ethyldiamine molecule, There would be 5 ligands in the coordination sphere instead of 4. This difference in the ratio of metal atom to ligands means that an ionization isomer cannot exist.



(Fig 6.) *Here, one chloro ligand exchanged places with the ethyldiamine so that it can be at a 90° angle with the other chloro ligand.*

The image above, shows the chloro and ethyldiamine ligands at a 90° angle with its other identical ligand. This is the *cis* isomer, while Fig. 5 shows the *trans* isomer.

Fig 5. shows that there is a plane of symmetry in the *trans* isomer. Therefore, that structure does not have an optical isomer. On the other hand, the *cis* isomer does not have a plane of symmetry and therefore has an optical isomer.

A19.2.8

none; none; The two Cl ligands can be *cis* or *trans*. When they are *cis*, there will also be an optical isomer.

Q19.2.9

Predict whether the carbonate ligand $\mathrm{CO_3^{2-}}$ will coordinate to a metal center as a monodentate, bidentate, or tridentate ligand.

S19.2.9

$\mathrm{CO_3^{2-}}$ can be either monodentate or bidentate, since two of its oxygen atoms have lone pairs as shown above and can form covalent bonds with a transition metal ion. In most cases carbonate is monodentate because of its trigonal planar geometry (there is 120 degrees between the oxygens so it's hard for both to bind to the same metal). However, in some cases it will bind to two different metals, making it bidentate.

A19.2.9

CO_3^{-2} will coordinate to a metal center as a monodentate ligand.

Q19.2.10

Draw the geometric, linkage, and ionization isomers for [$CoCl_5CN$][CN].

S19.2.10

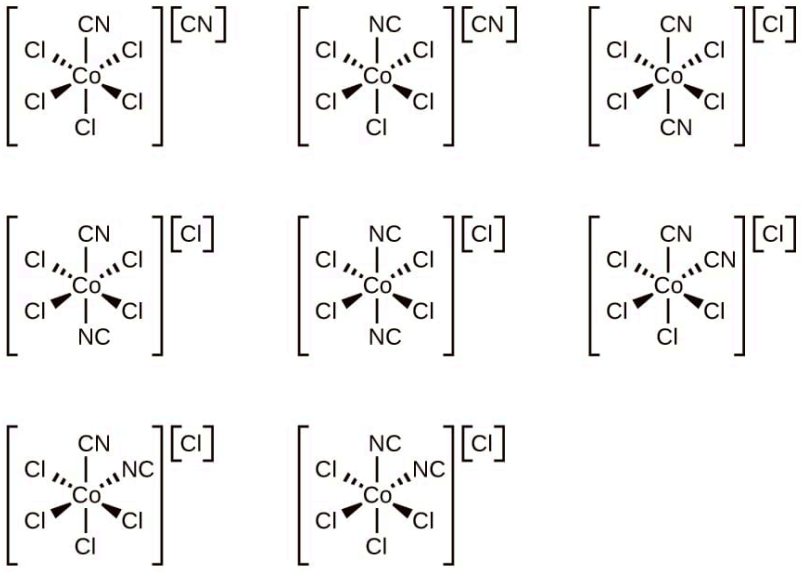
Isomers are compounds with same formula but different atom arrangement. There are two subcategories: **structural isomers**, which are isomers that contain the same number of atoms of each kind but differ in which atoms are bonded to one another, and **stereoisomers**, isomers that have the same molecular formula and ligands, but differ in the arrangement of those ligands in 3D space.

There are three subcategories under structural isomers: **ionization isomers**, which are isomers that are identical except for a ligand has exchanging places with an anion or neutral molecule that was originally outside the coordination complex; **coordination isomers**, isomers that have an interchange of some ligands from the cationic part to the anionic part; and **linkage isomers**, in two or more coordination compounds in which the donor atom of at least one of the ligands is different.

There are also two main kinds of stereoisomers: **geometric isomers**, metal complexes that differ only in which ligands are adjacent to one another (cis) or directly across from one another (trans) in the coordination sphere of the metal, and **optical isomers**, which occurs when the mirror image of an object is non-superimposable on the original object.

Some of the isomers look almost identical, but that is because the CN ligand can be attached by both (but not at the same time) the C or N.

A19.2.10



19.3: Spectroscopic and Magnetic Properties of Coordination Compounds

Q19.3.1

Determine the number of unpaired electrons expected for $[Fe(NO_2)_6]^{3-}$and for $[FeF_6]^{3-}$ in terms of crystal field theory.

S19.3.1

- The crystal field theory is is a model that describes the breaking of degeneracies of electron orbital states, usually d or f orbitals, due to a static electric field produced by a surrounding charge distribution.
    - The degenerate d-orbitals split into two levels, e_g and t_{2g}, in the presence of ligands.
    - The energy difference between the two levels is called the crystal-field splitting energy, Δ_o.
- After 1 electron each has been filled in the three t_{2g} orbitals, the filling of the fourth electron takes place either in the e_g orbital or in the t_{2g}, where the electrons pair up. depending on whether the complex is high spin or low spin.

- If the $\Delta_{\circ}$ value of a ligand is less than the pairing energy (P), then the electrons enter the e_g orbital, but if the $\Delta_{\circ}$ value of a ligand is more than the pairing energy (P), then the electrons enter the t_{2g} orbital.
- when the Δ_o is less than the pairing energy, the electrons prefer then e_g orbitals because there is not enough energy to pair the electrons together. It will be **high** spin
- when the Δ_o is more then the pairing energy, the electrons prefer the t_{2g} because there is enough energy to pair the electrons. It will be **low** spin.

Step 1: Determine the oxidation state of the Fe

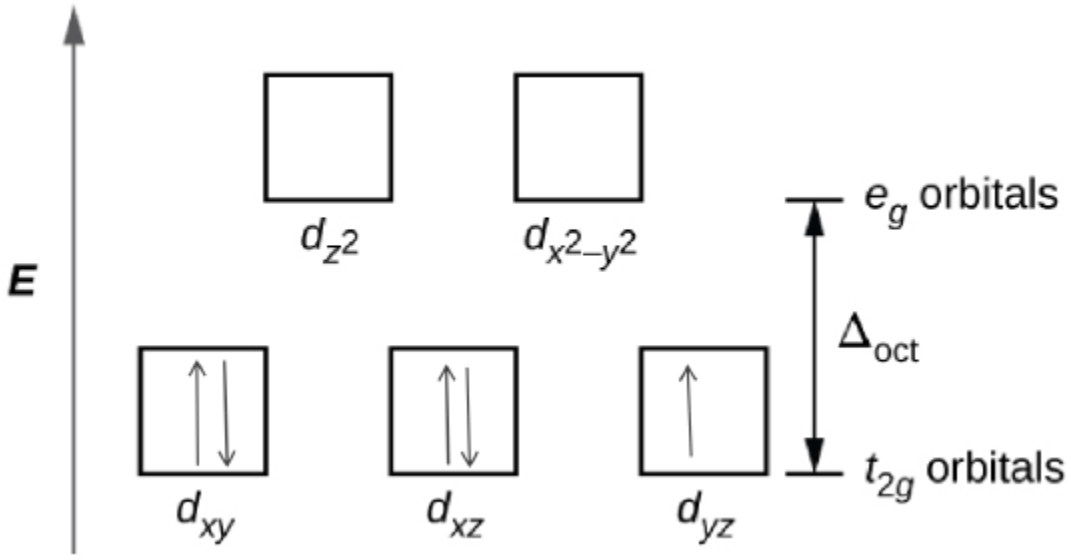
For $[Fe(NO_2)_6]^{3-}$ and $[FeF_6]^{3-}$, both NO_2 and F_6 have a charge of -1. Since there is 6 of them then that means the charge is -6 and in order for there to be an overall charge of -3, Fe has to have a +3 charge.

Step 2: Determine type of ligand

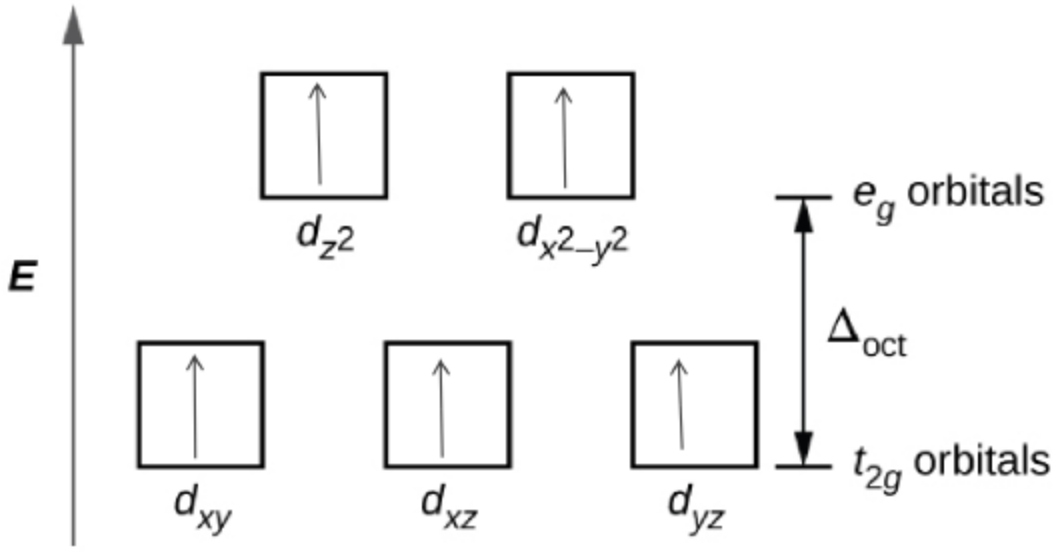
Based on the spectrochemical series we can see that NO_2^- is a stronger field ligand than F^-, and therefore is a low spin complex because it has a high $\Delta_{\circ}$ unlike F^- which is a high spin.

Step 3: Draw the crystal field

$[Fe(NO_2)_6]^{3-}$



$[FeF_6]^{3-}$



There is 1 unpaired electron for $[Fe(NO_2)_6]^{3-}$, and 5 for $[FeF_6]^{3-}$ based on the crystal field theory.

A19.3.1

$[Fe(NO_2)_6]^{3-}$:1 electron

$[FeF_6]^{3-}$:5 electrons

Q19.3.2

Draw the crystal field diagrams for $[Fe(NO_2)_6]^{4-}$ and $[FeF_6]^{2-}$. State whether each complex is high spin or low spin, paramagnetic or diamagnetic, and compare Δ_{oct} to P for each complex.

S19.3.2

a)

$$[Fe(NO_2)_6]^{-4} \tag{9.P.76}$$

- NO_2^- has a -1 charge. The overall ion has a -4 charge, therefore Fe must be +2 charge. (The math: $x + (6)(-1) = -4, x + -6 = -4, x = +2$ **or** 2+(6*-1)=-4)
  - Fe^{2+} has 6 valence electrons.
- Next we look at the ligand bonded to Fe, which is NO_2^- . Based on the spectrochemical Series, NO_2^- is a strong field ligand meaning that it has a large **DELTA$_o$** large splitting energy in comparison to the pairing energy, P. So the electrons would rather pair up, as it takes the least amount of energy.
  - So $[Fe(NO_2)_6]^{4-}$ is low spin.
  - All 6 electrons are paired up, so it is diamagnetic.

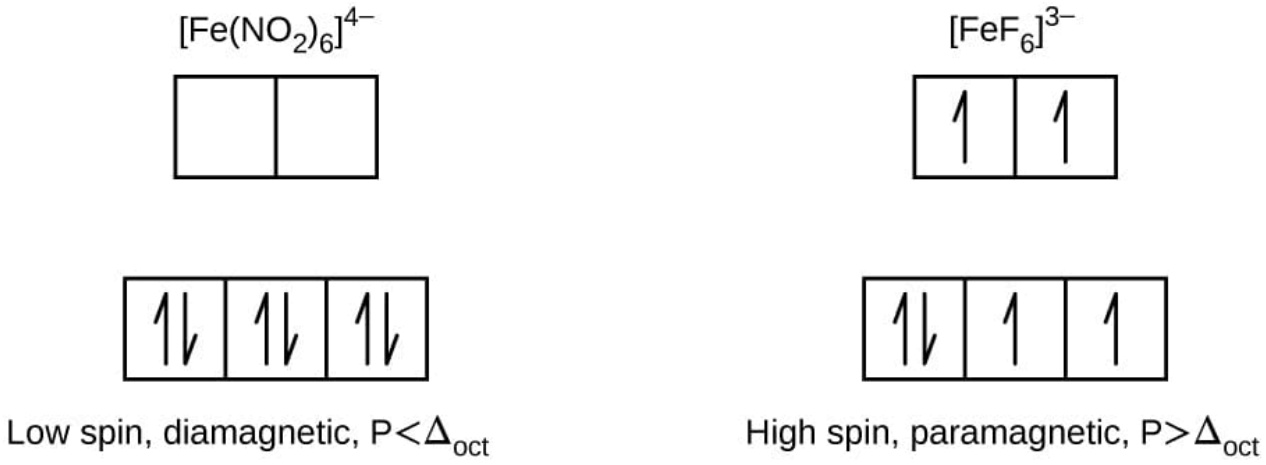
b)

$$[FeF_6]^{-3} \tag{9.P.77}$$

- F^- has a -1 charge. The overall ion has a -3 charge, therefore Fe must be +3 charge. (The math: $x + (-1)(6) = -3, x + -6 = -3, x = +3$ **or** 3+(6*-1)=-3)
  - F^{3+} has 5 valence electrons.

- Next we look at the ligand bonded to Fe, which is F^- . Based on the Spectrochemical Series, F^- is a weak field ligand, meaning that it has a small $DELTA_o$ or small splitting energy in comparison to the pairing energy, P. So the electrons would rather split up and move up to the higher energy level, rather than pairing up, as it takes the least amount of energy.
- So $[Fe(NO_2)_6]^{4-}$ is high spin.
- $[FeF_6]^{3-}$ is paramagnetic because it has unpaired electrons.

A19.3.2



Q19.3.3

Give the oxidation state of the metal, number of *d* electrons, and the number of unpaired electrons predicted for $[Co(NH_3)_6]Cl_3$.

S19.3.3

The oxidation state of the metal can be found by identifying the charge of one of each molecule in the coordinate compound, multiplying each molecule's charge by the respective number of molecules present, and adding the products. This final sum represents the charge of the overall coordination compound. You can then solve for the oxidation state of the metal algebraically. In this case, one chloride anion Cl^- has a charge of -1. So three chloride anions have a total charge of -3. One ammine ligand NH_3 has no charge so six ammine ligands have a total charge of zero. Finally, we are trying to solve for the oxidation state of a cobalt ion. Now we can write the equation that adds the total charges of each molecule or ion and is equal to the total charge of the overall coordinate compound.

$$(\text{oxidation state of Co}) + (-3) + 0 = 0 \tag{9.P.78}$$

$$\text{oxidation state of Co} = +3 \tag{9.P.79}$$

So the oxidation state of Co is +3. Now we need to identify the number of d-electrons in the Co^{3+} ion. The electron configuration for cobalt that has no charge is

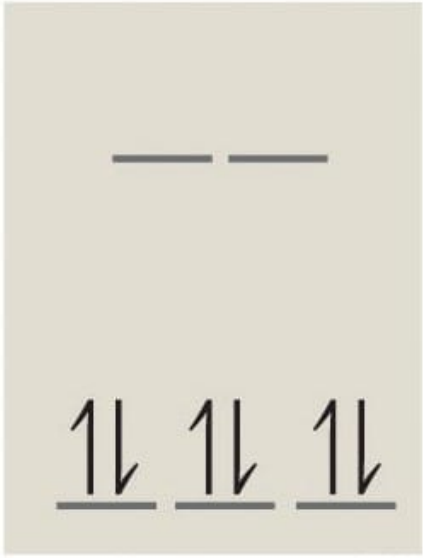
$$[\text{Ar}]4\text{s}^2 3\text{d}^7 \tag{9.P.80}$$

However, a Co^{3+} ion has 3 less electrons than its neutral counterpart and has an electron configuration of

$$[\text{Ar}]3\text{d}^6 \tag{9.P.81}$$

For transition metals, the s electrons are lost first. So cobalt loses its two 4s electrons first and then loses a single 3d electron meaning **Co^{3+} ion has 6 d electrons.** To predict the number of unpaired electrons, we must first determine if the complex is high spin or low spin. Whether the complex is high spin or low spin is determined by the ligand in the coordinate complex.

Specifically, the ligand must be identified as either a weak-field ligand or a strong-field ligand based on the spectrochemical series. Weak-field ligands induce high spin while strong-field ligands induce low spin. We can then construct the energy diagram or crystal field diagram of the designated spin that has the proper electron placings. The geometric shape of the compound must also be identified to construct the correct diagram. Finally, from this crystal field diagram we can determine the number of unpaired electrons. The number of electrons in the diagram is equal to the number of d electrons of the metal. The ligand in this case is NH_3, which is a strong field ligand according to the spectrochemical series. This means that the complex is low spin. Additionally, six monodentate ligands means the ligand field is octahedral. The number of electrons that will be in the diagram is 6 since the metal ion Co^{3+} has 6 d electrons. Now the proper crystal field diagram can be constructed.



From the crystal field diagram, we can tell that **the complex has no unpaired electrons**.

A19.3.3

a) 3+

b) 6 d electrons

c) No unpaired electrons

Q19.3.4

The solid anhydrous solid $CoCl_2$ is blue in color. Because it readily absorbs water from the air, it is used as a humidity indicator to monitor if equipment (such as a cell phone) has been exposed to excessive levels of moisture. Predict what product is formed by this reaction, and how many unpaired electrons this complex will have.

S19.3.4

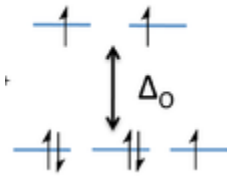
From our knowledge of ligands and coordination compounds (or if you need a refresher Coordination Compounds), we can assume the product of $CoCl_2$ in water. H_2O is a common weak field ligand that forms six ligand bonds around the central Cobalt atom while the Chloride stays on the outer sphere. We can use this to determine the complex:

$$[Co(H_2O)_6]Cl_2$$

From this formation, we can use the Crystal Field Theory (CFT)(Crystal Field Theory) to determine the number of unpaired electrons. This coordination compound has six ligand bonds attached to the central atom which means the CFT model will follow the octahedral splitting. Keep in mind that we know H_2O is a weak field ligand and will produce a high spin. High spin is when

the electrons pairing energy (P) is greater than the octahedral splitting energy. Thus, the electrons spread out and maximize spin.

In order to fill out our crystal field diagram, we need to determine the charge of cobalt. Because the H_2O ligand is neutral, and there are two chlorine ions, we can deduce the charge of cobalt is plus two in order to make the coordination complex neutral. From here, we can use the electron configuration of Co^{2+} is $[Ar]4s^23d^7$. The electrons that are taken away from the cobalt atom in order to form the plus two charge will from the 4s orbital and leave the 3d orbital untouched. Thus, there will be 7 electrons in the crystal field diagram and appear as:



We can see here that there are 3 unpaired electrons.

A19.3.4

$[Co(H_2O)_6]Cl_2$ with three unpaired electrons.

Q19.3.5

Is it possible for a complex of a metal in the transition series to have six unpaired electrons? Explain.

A19.3.5

Is it possible for a complex of a metal in the transition series to have six unpaired electrons? Explain.

It is not possible for a metal in the transition series to have six unpaired electrons. This is because transition metals have a general electron configuration of $(n\text{-}1)d^{1\text{-}10}\ ns^{1\text{-}2}$ where n is the quantum number. The last electron will go into the d orbital which has 5 orbitals that can each contain 2 electrons, yielding 10 electrons total. According to Hund's Rule, electrons prefer to fill each orbital singly before they pair up. This is more energetically favorable. Since there are only 5 orbitals and due to Hund's Rule, the maximum number of unpaired electrons a transition metal can have is 5. Therefore, there cannot be a complex of a transition metal that has 6 unpaired electrons.

For example, lets look at iron's electron configuration. Iron has an electron configuration of $1s^22s^22p^63s^23p^64s^23d^6$. Now the most important orbital to look at is the d orbital which has 6 electrons in it, but there are only 4 unpaired electrons as you can see by this diagram:

3d: [⇅] [↑] [↑][↑][↑]

Each [ ] represents an orbital within the d orbital. This diagram follows Hund's rule and shows why no transition metal can have 6 unpaired electrons.

Q19.3.6

How many unpaired electrons are present in each of the following?

a. $[CoF_6]^{3-}$ (high spin)
b. $[Mn(CN)_6]^{3-}$ (low spin)
c. $[Mn(CN)_6]^{4-}$ (low spin)

d. $[MnCl_6]^{4-}$ (high spin)

e. $[RhCl_6]^{3-}$ (low spin)

S19.3.6

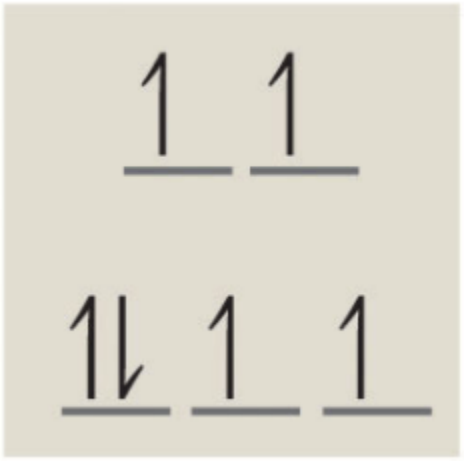
1. For $[CoF_6]^{3-}$, we first found the oxidation state of Co, which is 3+ since F has a 1- charge and since there is 6 F, Co's charge has to be 3+ for the overall charge to be 3-.

$$\text{charge of Co} + \text{-6} = \text{-6} \tag{9.P.82}$$

$$\text{charge of Co} = +3 \tag{9.P.83}$$

After finding the oxidation state, I then go to the periodic table to find its electron configuration: $[Ar]3d^6$

We distribute the 6 d-orbital electrons along the complex and since it is high spin, the electrons is distributed once in each energy level before it is paired. There is only one pair and the other 4 electrons are unpaired, making the answer 4.



2. The same process is repeated. We find the charge of Mn, which is 3+, making the electron configuration: $[Ar]3d^4$

$$\text{charge of Mn} + \text{-6} = \text{-3} \tag{9.P.84}$$

$$\text{charge of Mn} = +3 \tag{9.P.85}$$

There is a difference between this and number 1. This is low spin so instead of distributing one electron in each level before pairing it, I must distribute one electron on the bottom and then pair them all up before I'm able to move to the top portion. So since there is 4, there is only a pair at d_{yz} and the other two electrons are unpaired. Making the number of unpaired electrons 2.



3.The same process as number 2 is applied. The only difference is that the charge of Mn is now 2+ so the electron configuration: [Ar]$3d^5$.

$$\text{charge of Mn} + \text{-6} = \text{-4} \tag{9.P.86}$$

$$\text{charge of Mn} = +2 \tag{9.P.87}$$

Since is it low spin like number 2, I only need to add an extra electron to the next level, making that 2 pairs of electron and only 1 electron unpaired.

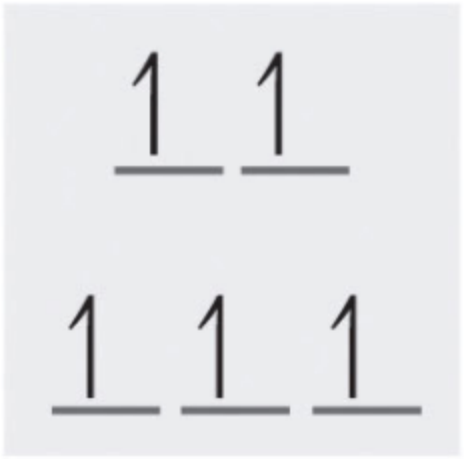


4. Since Cl has a -1 charge like CN, Mn's charge is also 2+ with the same electron configuration as number 3, which is 5.

$$\text{charge of Mn} + \text{-6} = \text{-4} \tag{9.P.88}$$

$$\text{charge of Mn} = +2 \tag{9.P.89}$$

With 5 electrons, this is high spin instead of low. So as stated in number 1, we pair distribute the electrons on all levels first. Since there are 5 electrons and 5 levels and they are al distributed, there are zero pairs, making that 5 unpaired electrons.



5. Using the same process as the problems above, Rh's charge is 3+, with the electron configuration: [Kr]4d^6.

$$\text{charge of Rh} + \text{-6} = \text{-3} \tag{9.P.90}$$

$$\text{charge of Mn} = +3 \tag{9.P.91}$$

With a low spin and 6 electrons, all electrons are paired up, making it 0 electrons that are unpaired.



A19.3.6

4; 2; 1; 5; 0

Q19.3.7

Explain how the diphosphate ion, $[O_3P–O–PO_3]^{4–}$, can function as a water softener that prevents the precipitation of Fe^{2+} as an insoluble iron salt.

S19.3.7

The diphosphate ion, $[O_3P–O–PO_3]^{4–}$ can function as a water softener keeping the iron in a water soluble form because of its more negative electrochemical potential than water's. This is similar to the way plating prevents metals from reacting with oxygen to corrode.

Mineral deposits are formed by ionic reactions. The Fe^{2+} will form an insoluble iron salt of iron(III) oxide-hydroxide when a salt of ferric iron hydrolyzes water. However, with the addition of $[O_3P–O–PO_3]^{4–}$, the Fe^{2+} cations are more attracted to the PO_3 group, forming a $Fe(PO_3)$ complex.

The excess minerals in this type of water is considered hard thus its name hard water.

Q19.3.8

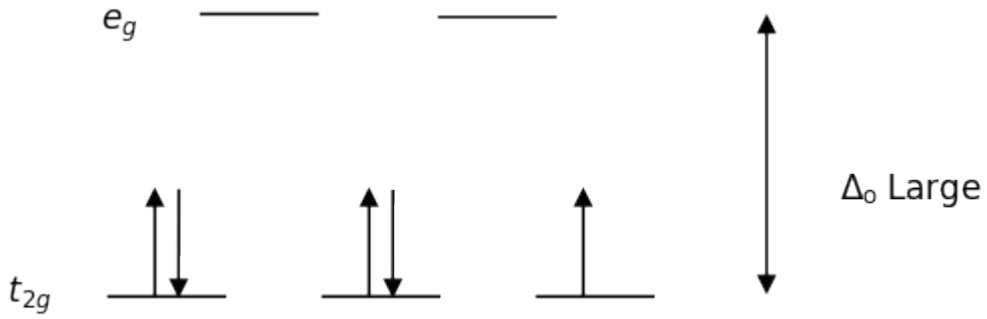
For complexes of the same metal ion with no change in oxidation number, the stability increases as the number of electrons in the t_{2g} orbitals increases. Which complex in each of the following pairs of complexes is more stable?

a. $[Fe(H_2O)_6]^{2+}$ or $[Fe(CN)_6]^{4–}$
b. $[Co(NH_3)_6]^{3+}$ or $[CoF_6]^{3–}$
c. $[Mn(CN)_6]^{4–}$ or $[MnCl_6]^{4–}$

S19.3.8

The Spectrochemical Series is as follows \[I^{-}

The strong field ligands (on the right) are low spin which fills in more electrons in the *t2g* orbitals. The weak field ligands (on the left) are high spin so it can fill electrons in the *t2g* orbitals and *eg* orbitals. In conclusion, more electrons are filled up from the strong field ligands because the electrons don't move up to the *eg* orbitals.



a. $[Fe(CN)_6]^{4–}$

CN is a stronger ligand than H_2O so it is low spin, which fills up the *t2g* orbitals.

b. $[Co(NH_3)_6]^{3+}$

NH_3 is a stronger ligand than F.

c. $[Mn(CN)_6]^{4–}$

CN is a stronger ligand than $Cl^–$.

For more information regarding the shape of the complex and d-electron configuration, libretext provides more information on how to classify high and low spin complexes.

A19.3.8

$[Fe(CN)_6]^{4-}$; $[Co(NH_3)_6]^{3+}$; $[Mn(CN)_6]^{4-}$

Q19.3.9

Trimethylphosphine, $P(CH_3)_3$, can act as a ligand by donating the lone pair of electrons on the phosphorus atom. If trimethylphosphine is added to a solution of nickel(II) chloride in acetone, a blue compound that has a molecular mass of approximately 270 g and contains 21.5% Ni, 26.0% Cl, and 52.5% $P(CH_3)_3$ can be isolated. This blue compound does not have any isomeric forms. What are the geometry and molecular formula of the blue compound?

S19.3.9

1)Find the empirical formula. There is a total of 270 grams. To find out how many grams of each element/compound there are, multiply the percentage by the mass (270).

$$(270g)(0.215) = 58.05gNi \tag{9.P.92}$$

$$(270g)(0.26) = 70.2gCl \tag{9.P.93}$$

$$(270g)(0.525) = 141.75gP(CH_3)_3 \tag{9.P.94}$$

Now that we have the grams of each element/compound, we can convert them to moles by using their molar mass.

$$(58.055gNi)(\frac{1mol.}{58.69gNi}) = 0.989mol.Ni \tag{9.P.95}$$

$$(70.2gCl)(\frac{1mol.}{35.45gCl}) = 1.98mol.Cl \tag{9.P.96}$$

$$(141.75gP(CH_3)_3)(\frac{1mol.}{76.07gP(CH_3)_3}) = 1.86mol.P(CH_3)_3 \tag{9.P.97}$$

Now that we have the moles of all elements/compounds, we can find the ratio of all them to each other. To do this, we take the element/compound with the least amount of moles and divide all element/compound moles by this amount. In this case, Ni has the least number of moles.

$$\frac{0.989mol.Ni}{0.989mol.Ni} = 1 \tag{9.P.98}$$

$$\frac{1.98mol.Cl}{0.989mol.Ni} = approx.2 \tag{9.P.99}$$

$$\frac{1.86mol.P(CH_3)_3}{0.989mol.Ni} = approx.2 \tag{9.P.100}$$

We now know the ratio of all element/compounds in the blue compound.

The empirical formula is: $NiCl(P(CH_3)_3)_2$

This formula shows us there are 4 ligands. There are 2 chlorine ligands and 2 trimethylphosphine ligands. This means that the blue compound has either a tetrahedral or square planar shape, where tetrahedral shapes are capable of different isomeric forms when all ligands are different (because if not, there is only 1 way for them to be arranged), and square planar shapes are capable of cis/trans forms. In the problem, it states this compound does not have any isomeric forms, therefore this has a tetrahedral shape.

A19.3.9

a) $NiCl(P(CH_3)_3)_2$

b) Tetrahedral

Q19.3.10

Would you expect the complex $[Co(en)_3]Cl_3$ to have any unpaired electrons? Any isomers?

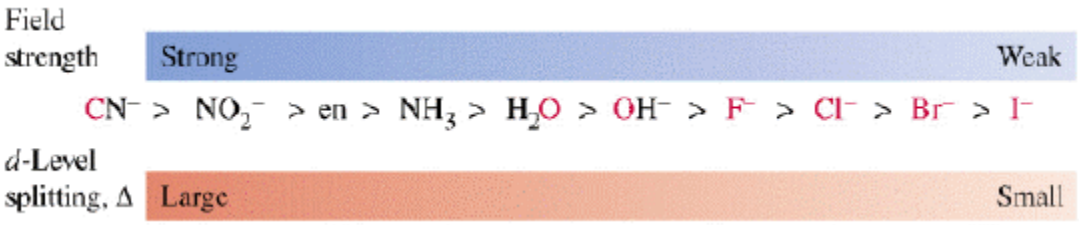
S19.3.10

Assign oxidation states to each element. Cl- has a -1 oxidation state. En is neutral, so 0. The entire complex is also neutral, so in order to balance the charges out, Co must be +3 because there are 3 chlorides, which gives a -3 charge.

STEP 2:

Write the electron configuration for Co^{3+}. $[Ar]3d^6$. There are 6 electrons.

STEP 3:



Check where en lies on the spectrochemical series. Does it have a strong field strength? It does, so these electrons will exist at the d-level with high splitting energy because the magnitude of the pairing energy is less than the crystal field splitting energy in the octahedral field.

You will the notice that there aren't any unpaired electrons when you draw the Crystal Field Theory (CFT) diagram.



This complex does not have any geometric isomers because cis-trans structures cannot be formed. The mirror image is nonsuperimpoasable, which means the enantiomers are chiral molecules; if the mirror image is placed on top on the original molecule, then they will never be perfectly aligned to give the same molecule.

A19.3.10

The complex does not have any unpaired electrons. The complex does not have any geometric isomers, but the mirror image is nonsuperimposable, so it has an optical isomer.

Q19.3.11

Would you expect the $Mg_3[Cr(CN)_6]_2$ to be diamagnetic or paramagnetic? Explain your reasoning.

S19.3.11

The first step to determine the magnetism of the complex is to calculate the oxidation state of the transition metal. In this case, the transition metal is Cr.

Before doing so, we need to find charge of the of the complex ion $[Cr(CN)_6]_2$ given that the oxidation state of Mg_3 is 2+. Using the subscripts of the Mg^{2+} ion and the $[Cr(CN)_6]_2$ complex, we find that the oxidation state of $[Cr(CN)_6]_2$, x, to be:

$$3(+2) + 2(x) = 0$$

$$x = 3$$

Now that we found the charge of the coordination complex, we are able to find the charge of the transition metal Cr given that the charge of CN is -1. Again, using the subscripts we find the oxidation state of Cr, y, to be:

$$y + 6(-1) = -3$$

$$y = 3$$

Therefore, the oxidation state of the transition metal Cr is Cr^{3+}

Next, using the transition metal Cr^{3+} and the periodic table as reference, we can determine the electron configuration of Cr^{3+} to be $[Ar]d^3$. This means that Cr^{3+} has 3 unpaired electrons in the 3d sublevel. Therefore, we find that since at least one electron is unpaired(in this case all 3 electrons are unpaired), $Mg_3[Cr(CN)_6]_2$ is paramagnetic.

A19.3.11

a) Paramagnetic

Q19.3.12

Would you expect salts of the gold ion, Au^+, to be colored? Explain.

S19.3.12

No. **Colored ions have unpaired electrons in their outmost orbital**. A partially filled d orbital, for example, can yield various colors. After completing the noble gas configuration, we see that Au^+ has a configuration of [Xe] $4f^{14}$**$5d^{10}$**. Since Au^+ has a **completely filled d sublevel**, we are certain that any salts of the gold ion, Au^+ will be **colorless.**

*An example of a colored ion would be copper(II). Cu^{2+} has an electron configuration of [Ar]$3d^9$. It has one unpaired electron. Copper(II) appears blue.

A19.3.12

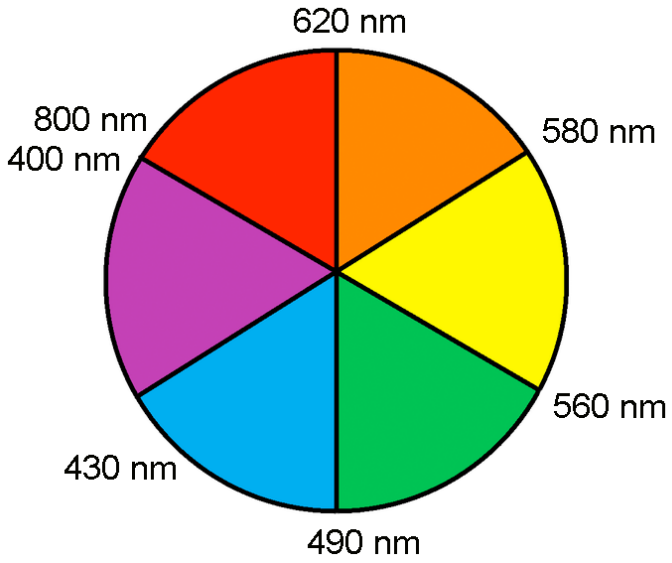
No. Au^+ has a complete 5*d* sublevel.

Q19.3.13

$[CuCl_4]^{2-}$ is green. $[Cu(H_2O)_6]^{2+}$is blue. Which absorbs higher-energy photons? Which is predicted to have a larger crystal field splitting?

S19.3.13

Although a color might appear a certain way, it actual absorbs a different color, opposite of it on the color wheel.



In this case;

$[CuCl_4]^{2-}$ appears green but is opposite of red on the color wheel which is absorbed and is characterized by wavelengths 620-800 nanometers.

$[Cu(H_2O)_6]^{2+}$ appears blue but is opposite of orange on the color wheel which is absorbed and is characterized by wavelengths 580-620 nanometers.

When determining which absorbs the higher energy photons, one must look at the complex itself. A higher energy indicates a high energy photon absorbed and a lower energy indicates a lower energy photon absorbed. How can we determine this? By looking at the complex and more specifically the ligand attached and its location in the spectrochemical series.

Merging to get spectrochemical series

$CO, CN^- > phen > en > NH_3 > NCS^- > H_2O > F^- > RCO_2^- > OH^- > Cl^- > Br^- > I^-$

Strong field, π acceptors, large Δ, low spin — σ only — Weak field, π donors, small Δ, high spin

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

The ligands attached are Water and Chlorine and since Water is a stronger ligand than Chlorine according to the series, it

also has larger energy, indicating a higher energy. This means that the complex $[Cu(H_2O)_6]^{2+}$ absorbs a higher energy photon because of its a stronger ligand than chlorine.

Part 2 of this question also asks which complex is predicted to have a larger crystal field splitting. To determine this you also use the spectrochemical series and see which ligand is stronger. Since H_2O is stronger than Cl^- on the spectrochemical series, we can say $[Cu(H_2O)_6]^{2+}$ has a higher crystal field splitting.

A19.3.13

a) $[Cu(H_2O)_6]^{2+}$

b) $[Cu(H_2O)_6]^{2+}$ has a higher crystal field splitting

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10: COORDINATION CHEMISTRY II - BONDING

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10.9.2.1: Introduction to Substitution Reactions

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10.P: Problems

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10.1: EVIDENCE FOR ELECTRONIC STRUCTURES

This section describes the types of experimental data that give us hints about the electronic structure of coordination complexes (ie the molecular orbitals, their energy levels, and electron configurations). The types of experimental observations discussed here have been used to generate the theories of bonding that are described later in this chapter.

Introduction

The frontier (valence) electrons and orbitals define the chemical and physical properties of any compound. In the transition metals and their coordination compounds, the d orbitals and d electrons are the ones of interest. Thus, the d orbitals and electrons will be the focus of this chapter.

One of the first things you might notice about valence d orbitals is the order of orbital energy levels of atoms and ions in the transition metals. For example, in the first row of transition metals, the 4s orbital fills before the $3d$ *in the atoms*. This indicates that $4s$ is lower in energy than $3d$ *in these atoms*. However, *in the ions* of the same elements, the $3d$ orbital is occupied while the $4s$ orbital is empty. This indicates the opposite, that the $3d$ orbital is lower in energy than $4s$ *in these ions*. The change in the relative energy levels of the $3d$ and $4s$ orbitals in atoms compared to ions is a result of the combined effects of shielding and penetration, as discussed in a previous chapter. The result is that the 3d and 4s orbital energy levels are close enough in energy that subtle changes in the environment can reverse the order.

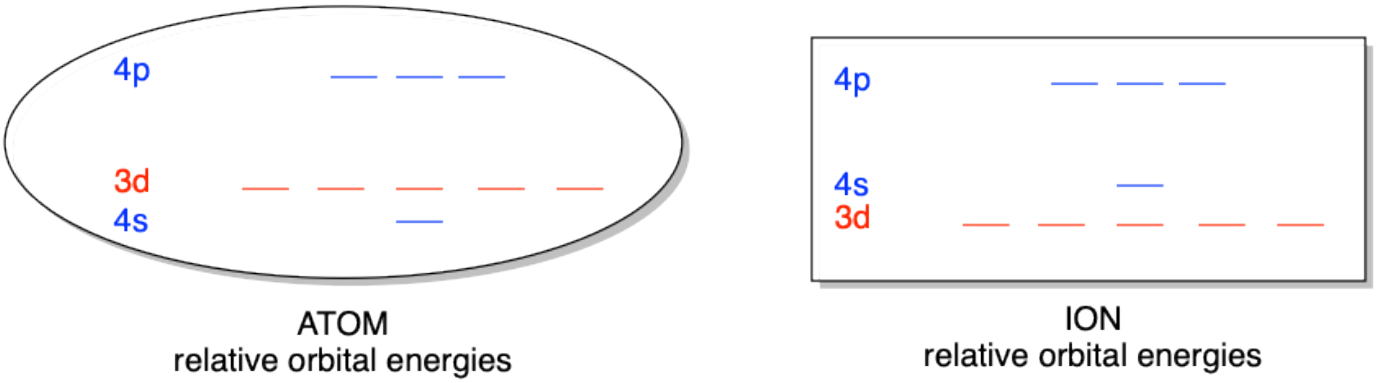


Figure 10.1.1: In early period 4 of the periodic table, the $4s$ orbital energy level is lower than $3d$ for atoms. However, in the ions of the same elements, the $3d$ is lower in energy than $4s$. (CC-BY-NC; Chris Schaller)

Furthermore, you are going to see that once the atom is surrounded by ligands, the five d orbitals are no longer degenerate. In a coordination compound, with ligands bound in a specific geometry, the d orbitals become split into slightly different energy levels. The splitting pattern depends on where the ligands are in space; in other words it depends on the coordination geometry. The patterns of splitting for tetrahedral and octahedral geometries are shown below. Notice that the splitting is reversed between metals in a tetrahedral coordination environment compared to an octahedral environment.

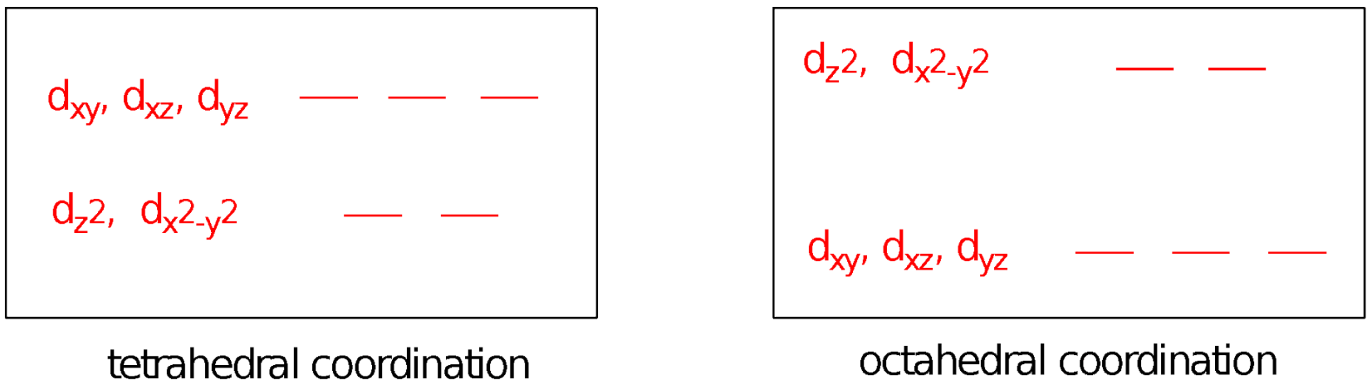


Figure 10.1.2: Splitting of d orbitals for (left) tetrahedral and (right) octahedral ligand geometries. (CC-BY-NC; Chris Schaller)

When the orbitals of a coordination compound are filled with electrons, the electron configuration depends on the energy difference between the lower and higher energy levels. For example, given five d electrons in an octahedral environment, there are two possible electron configurations. All five electrons may occupy the lower level of d orbitals (Fig. $10.1.3$, left), so that some electrons are paired. Another possibility is that all the electrons will be unpaired if they populate both levels of the d orbitals (Fig. $10.1.3$, right).

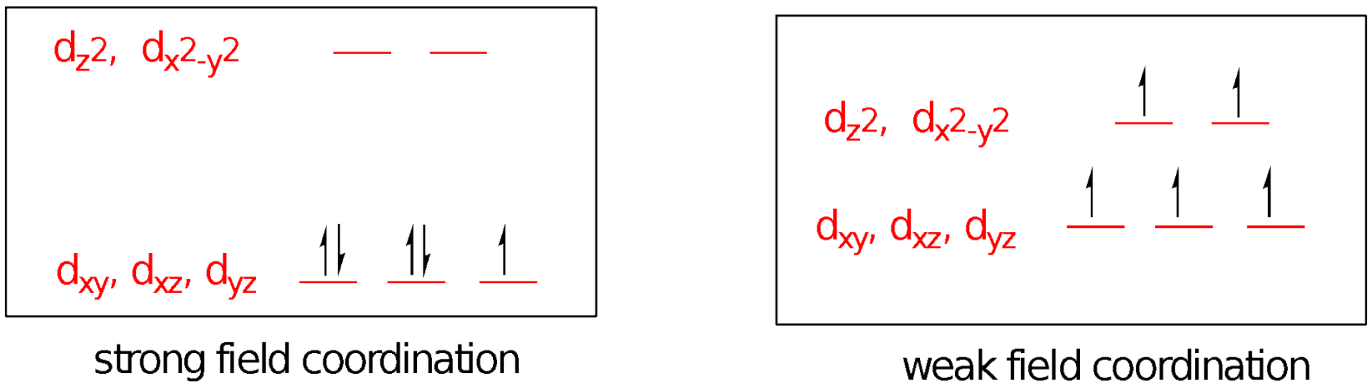


Figure $10.1.3$: Two possible electron configurations for five electrons in an octahedral ligand field. (CC-BY-NC; Chris Schaller)

A number of factors determine which case results, including the identity of the metal ion and the nature of the ligands involved. These different filling orders have consequences, too. The magnetic properties of the complex, its propensity to undergo reactions, and its optical properties all depend on the configuration of these frontier electrons.

This chapter is an exploration of the nature of the metal-ligand bond and how both geometry and the mode of bonding influence the properties of coordination complexes.

10.1.1: Thermodynamic Data

10.1.2: Magnetic Susceptibility

10.1.3: Electronic Spectra

10.1.4: Coordination Number and Molecular Shapes

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10.1.1: Thermodynamic Data

We can get some insight into the stability of coordination complexes by looking at their formation constants. The formation constant is the equilibrium constant for the reaction leading to the formation of a coordination complex. The greater the formation constant, the more thermodynamically stable the product complex compared to the reactant complex.

Many complexation reactions take place in aqueous solution by dissolving a metal ion in water to produce the "aqueous metal ion". An aqueous metal ion is one that is coordinated by a number of water molecules, and since it is charged, there must be counter ions to balance that charge. When an aqueous metal ion reacts to form a new complex, its formation constant indicates the stability of the product compared to the aqueous complex. Depending on the number of ligands that are replaced in the product compared to the reactant, the formation complex is defined as either a **stepwise formation constant** (K) or an **overall formation constant** (β).

For example, the formation of $[Cu(NH_3)(OH_2)_5]^{2+}$ complex ion from $Cu^{2+}_{(aq)}$ can be represented by the following *stepwise* reaction:[1]

$$[Cu(OH_2)_6]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)(OH_2)_5]^{2+} + H_2O \qquad K_1 = 1.9 \times 10^4$$

The formation constant, K_1, is a stepwise formation constant because it represents the substitution of a single aquo ligand (a coordinated water) by an ammine ligand. Another example is the reaction below that represents the substitution of four aquo ligands for four ammine ligands. The *overall* formation of the $[Cu(NH_3)_4(OH_2)_2]^{2+}$ complex ion from $Cu^{2+}_{(aq)}$ would be represented by this equation:

$$[Cu(OH_2)_6]^{2+} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4(OH_2)_2]^{2+} + 4\,H_2O \qquad \beta_4 = 1.1 \times 10^{13}$$

This time, the formation constant represents the substitution of four ammine ligands for four aquo ligands. This transformation does not happen in one step, so the formation constant, β_4 is a composite of the equilibrium constants for four individual steps:

$$[Cu(OH_2)_6]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)(OH_2)_5]^{2+} + H_2O \qquad K_1 = \frac{[Cu(NH_3)(OH_2)_5{}^{2+}]}{[Cu(OH_2)_6{}^{2+}][NH_3]} = 1.9 \times 10^4$$

$$[Cu(NH_3)(OH_2)_5]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_2(OH_2)_4]^{2+} + H_2O \qquad K_2 = \frac{[Cu(NH_3)_2(OH_2)_4{}^{2+}]}{[Cu(NH_3)(OH_2)_5{}^{2+}][NH_3]} = 3.9 \times 10^3$$

$$[Cu(NH_3)_2(OH_2)_4]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_3(OH_2)_3]^{2+} + H_2O \qquad K_3 = \frac{[Cu(NH_3)_3(OH_2)_3{}^{2+}]}{[Cu(NH_3)_2(OH_2)_4{}^{2+}][NH_3]} = 1.0 \times 10^3$$

$$[Cu(NH_3)_3(OH_2)_3]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_4(OH_2)_2]^{2+} + H_2O \qquad K_4 = \frac{[Cu(NH_3)_4(OH_2)_2{}^{2+}]}{[Cu(NH_3)_3(OH_2)_3{}^{2+}][NH_3]} = 1.5 \times 10^2$$

$$\beta_4 = K_1 \times K_2 \times K_3 \times K_4 = (1.9 \times 10^4)(3.9 \times 10^3)(1.0 \times 10^3)(1.5 \times 10^2) = 1.1 \times 10^{13}$$

(\beta\) notation

The β notation is used to distinguish an overall formation constant from a stepwise formation constant. However, sometimes alternative notation will be used. You may see other texts, the literature, or your instructor using alternative ways to distinguish an overall formation constant like β_4 from the stepwise formation constant, like K_4. The important thing is to understand the conventions used for whatever source you are reading.

In both the examples above, the equilibrium lies to the right (in other words, the formation constant is >> 1). Another way to interpret this is that Cu(II) has a higher affinity for ammonia than for water, and thus the ammine complex is more stable than the aqueous metal ion. In the case of the copper tetraammine complex, replacement of each individual water by ammonia is favorable, so the aggregate formation constant β_4 becomes very large. The preference of Cu(II) for ammonia can be explained by the increased basicity of ammonia compared to water.

Formation constants can provide valuable insight into factors that contribute to the stability of coordination complexes, but we may need a more extensive set of data to build a more complete picture. If we look at formation constants in a series of complexes that have something in common, we may get an idea about additional factors that play a role in complex stability. Take

a look at these examples:[2]

$$\begin{aligned} \mathrm{Cu^+(aq) + 2\,Cl^- \rightleftharpoons [CuCl_2]^-} \quad & K = 3.0 \times 10^5 \\ \mathrm{Cu^+(aq) + 2\,Br^- \overset{CuBr_2}{\rightleftharpoons} -} \quad & K = 8.0 \times 10^5 \\ \mathrm{Cu^+(aq) + 2\,I^- \overset{CuI_2}{\rightleftharpoons} -} \quad & K = 8.0 \times 10^8 \end{aligned}$$

The reactions above are simplified by abbreviating the aqueous metal ion, $\mathrm{[Cu(OH_2)n]^+}$ as $\mathrm{Cu^+(aq)}$. This time, we are dealing with Cu(I) rather than Cu(II). Note that basicity does not seem to play a role in this series. The pK_a's of the conjugate acids HCl, HBr, and HI are -6.7, -8.7, and -9.3, respectively. If basicity were important, chloride should bind most tightly, followed by bromide, and then iodide; that trend is reversed here. Instead, this case can be explained by an application of Pearson's hard-soft acid-base theory (HSAB). HSAB theory predicts that small, charge-dense bases will bind more tightly with small, charge-dense acids. Archetypically, hard bases have N, O, or F donor atoms. Conversely, larger, more polarizable bases bind more tightly with larger, more polarizable acids. Soft bases archetypically have P or S donor atoms. In this series of copper complexes, the iodide is the softest, most polarizable of the three halide ions shown, whereas the chloride is the hardest (although not as hard as fluoride). Cu(I) has a relatively low charge density, so it can be considered a soft acid. Soft acids and soft bases form strong bonds because of the pronounced covalency between the donor and acceptor. Of the three halides, iodide is the most capable of providing that soft-soft interaction with the Cu(I) ion.

Let's look at another major contributor to complex stability. In this case, aqueous nickel ion reacts with ammonia to produce the hexaammine complex, $\mathrm{[Ni(NH_3)_6]^{2+}}$. That's similar to the reaction of aqueous copper ion with ammonia; ammonia is a better donor in this case than water. However, ammine is easily displaced by ethylenediamine ($\mathrm{H_2NCH_2CH_2NH_2}$, abbreviated en) to provide an ethylenediamine complex, $\mathrm{[Ni(en)_3]_2{}^+}$.[2,3]

$$\begin{aligned} \mathrm{[Ni(OH_2)_6]^{2+} + 6\,NH_3 \overset{Ni(NH_3)_6}{\rightleftharpoons} {}^2+} \quad & K = 2.0 \times 10^8 \\ \mathrm{[Ni(NH_3)_6]^{2+} + 3\,en \overset{Ni(en)_3}{\rightleftharpoons} {}^2+ + 6\,NH_3} \quad & K = 4.7 \times 10^9 \end{aligned}$$

Once again, we see that an ammine ligand is a much more effective donor than an aquo ligand. The ethylenediamine ligand, however, binds exceptionally tightly, and can even displace ammine ligands. To gain insight into why a metal ion would have higher affinity toward $\mathrm{H_2NCH_2CH_2NH_2}$ (en) than $\mathrm{NH_3}$, despite the fact that the two ligands have similar donor atoms, we can look at the thermodynamic parameters (the entropy and enthalpy) of the reaction for the formation of $\mathrm{[Ni(en)_3]^{2+}}$ from $\mathrm{[Ni(NH_3)_6]^{2+}}$:

$$\begin{aligned} \Delta H^\circ &= -12.1\ \mathrm{kJ\ mol^{-1}} \\ \Delta S^\circ &= 184.9\ \mathrm{J\ mol^{-1} K^{-1}} \\ \text{and at 298 K}, -T\Delta S^\circ &= -55.1\ \mathrm{kJ\ mol^{-1}} \end{aligned}$$

That last term, $-T\Delta S^\circ$, is included for easier comparison to the enthalpy contribution, since these two factors are evaluated via the Gibbs free energy equation, $\Delta G = \Delta H - T\Delta S$. We see that the formation of $\mathrm{[Ni(en)_3]^{2+}}$ from $\mathrm{[Ni(NH_3)_6]^{2+}}$ is slightly favored enthalpically (by $\Delta H^\circ = -12.1\mathrm{kJ\ mol^{-1}}$), even though there are nitrogen atom donor ligands in both reactant and product complexes. However, this small preference is not likely the most important driving force for the large formation constant. The entropy factor is much larger in comparison ($T\Delta S^\circ = -55.1\ \mathrm{kJ\ mol^{-1}}$), indicating entropy is driving the huge formation constant for the ethylenediamine complex.

How do we interpret that large $T\Delta S^\circ$? The simplest approach to interpreting a change in entropy of a reaction is to evaluate the number of molecules in the reactants compared to the products. If there is an increase in the number of molecules, there is an increase in disorder (entropy).

In the replacement of aquo ligands with ammine ligands, there are seven species on either side of the equation:

$$\begin{array}{cc} \mathrm{[Ni(OH_2)_6]^{2+} + 6\,NH_3} & \rightleftharpoons \quad \mathrm{[Ni(NH_3)_6]^{2+}} \\ \text{7 molecules} & \qquad\quad \text{7 molecules} \end{array}$$

We might not expect this reaction to have a large entropic driving force because the number of molecules is the same in the reactants and products.

On the other hand, in the replacement of ammine ligands with ethylenediamine ligands, there are four molecules on the reactant side, and seven on the products side.

$$\underset{4 \text{ molecules}}{[Ni(NH_3)_6]^{2+} + 3\,en} \rightleftharpoons \underset{7 \text{ molecules}}{[Ni(en)_3]^{2+} + 6\,NH_3}$$

That means there is a net increase in the number of molecules in solution when the ethylenediamine replaces the ammines. An increase in the number of molecules represents an increase in the partitioning of energy, which is entropically favorable. The underlying reason for this difference is that each ethylenediamine ligand has two nitrogen donors, allowing one ethylenediamine to replace two ammines. The high formation constant for ligands that contain multiple donor atoms is called the **chelate effect**, from the Greek word for "crab" (which has two claws with which it can grab things). We call donors capable of binding through multiple atoms “polydentate” ligands (for “many-toothed”, indicating they can bite more strongly into the metal and hold on).

Formation constants of coordination complexes affect important processes ranging from industrial catalysis to biology. For example, most people are aware of carbon monoxide poisoning. Carbon monoxide leads to suffocation by displacing molecular oxygen from hemoglobin (Hb), the oxygen-carrying protein in blood cells. Hemoglobin has an Fe(II) ion bound in its active site which in turn coordinates molecular oxygen, increasing the oxygen-carrying capacity of a blood cell. The two relevant equilibria are:[4]

$$Hb + O_2 \rightleftharpoons HbO_2 \quad K = 3.2\ \mu M^{-1}$$
$$Hb + CO \rightleftharpoons HbCO \quad K = 750\ \mu M^{-1}$$

Here, Hb is just a shorthand for hemoglobin. The formation constants shown above indicate that carbon monoxide binds to hemoglobin hundreds of times more tightly than does oxygen. This difference can’t be caused by a chelate effect; both CO and O_2 are monodentate donors in this case. The origin for this difference comes from more subtle differences in metal-ligand binding that we will develop later in this chapter.

Problems

Exercise 10.1.1.1

Show how we can combine the formation constants given above for $[Ni(NH_3)_6]^{2+}$ and $[Ni(en)_3]^{2+}$ from $[Ni(HO_2)_6]^{2+}$ to determine the formation constant for the ethylenediamine complex from aqueous nickel ion.

$$[Ni(OH_2)_6]^{2+} + 3\,en \rightleftarrows [Ni(en)_3]^{2+} + 6\,H_2O \qquad K = ?$$

Answer available at the end of this section.

Exercise 10.1.1.2

The formation constants shown below correspond to the substitution of one ligand on aqueous Cu(II) ion.[5] Propose a trend that explains the different stabilities of the complexes.

NH_3	$K = 2.0 \times 10^3$
F^-	$K = 8.0$
Cl^-	$K = 1.2$
Br^-	$K = 0.9$

Answer available at the end of this section.

Exercise 10.1.1.3

Ethylenediamine can be displaced from nickel by tren, (NH2CH2CH2)3N, another polydentate ligand.[3]

$$[Ni(en)_2(OH_2)_2]^{2+} + tren \rightleftarrows [Ni(tren)(H_2O)_2]^{2+} + 2\,en \qquad K = 76$$

a. What is the denticity of tren?
b. It is reported that $\Delta H° = +13.0$ kJ mol^{-1} and $\Delta S° = 79.5$ J mol^{-1} K^{-1}. Propose a reason for the moderately large formation constant.

Answer available at the end of this section.

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Answers

Exercise 10.1.1.1

We know the formation constants of $[Ni(NH_3)_6]^{2+}$ and $[Ni(en)_3]^{2+}$. Let's call them "reactions i and j":

$$\text{Reaction } i: \quad [Ni(OH_2)_6]^{2+} + 6\,NH_3 \overset{Ni(NH_3)_6}{\rightleftharpoons}{}^{2}+ \qquad K_i = \frac{[Ni(NH_3)_6]}{[Ni(OH_2)_6][NH_3]} = 2.0 \times 10^8$$

$$\text{Reaction } j: \quad [Ni(NH_3)_6]^{2+} + 3\,en \overset{Ni(en)_3}{\rightleftharpoons}{}^{2}+ + 6\,NH_3 \qquad K_j = \frac{[Ni(en)_3][NH_3]^6}{[Ni(NH_3)_6][en]^3} = 4.7 \times 10^9$$

and we want to find the equilibrium constant for the formation of $[Ni(en)_3]^{2+}$ from $[Ni(HO_2)_6]^{2+}$. We'll call this "reaction k".

$$\text{Reaction } k: \quad [Ni(OH_2)_6]^{2+} + 3\,en \rightleftarrows [Ni(en)_3]^{2+} + 6\,H_2O \qquad K_k = ?$$

Reaction "k" is the sum of reaction "i" followed by reaction "j".

$$\begin{aligned} K_k &= K_i \times K_j \\ &= \frac{[Ni(NH_3)_6]}{[Ni(OH_2)_6][NH_3]} \times \frac{[Ni(en)_3][NH_3]^6}{[Ni(NH_3)_6][en]^3} = \frac{[Ni(en)_3]}{[Ni(OH_2)_6][en]^3} \\ &= (2.0 \times 10^8)(4.7 \times 10^9) = 9.4 \times 10^{17} \end{aligned}$$

Exercise 10.1.1.2

This trend could be explained by basicity, since ammonium ion is a weak base and the acidity of the hydrogen halides increase in the order HF < HCl < HBr. The ammine ligand is a better donor than any of the halides to the nickel ion, but fluoride is better than chloride and chloride is better than bromide. The reason for the acidity trend varies in the midst of this series. Among the halides, fluoride is the best donor because it is the least polarizable and least stable ion. However, in the second row of the periodic table, the nitrogen in ammonia is a better donor than fluoride because nitrogen is less electronegative than fluorine. This difference is enough to compensate for the fact that ammine is a neutral ligand, presumably with less Coulombic attraction to the copper ion than fluoride.

Note that this trend is very different for Cu(II) than for a similar series of ligands with Cu(I). Cu(II), with greater charge density, is harder in character than Cu(I). Thus, it doesn't necessarily bind more tightly to softer donors the way Cu(I) does.

Exercise 10.1.1.3

a) Tren has a denticity of 4; it is sometimes described as a tetradentate ligand.

b) The enthalpy of reaction $\Delta H° = +13.0$ kJ mol-1 and at 298 K, $-T\Delta S° = -23.7$ kJ mol-1. That means there are no arguments based on the donor-acceptor strength, such as HSAB or basicity, because the enthalpy of reaction is positive. The tightness of binding must result from the positive entropy, which comes from the net increase in the number of molecules as the reaction proceeds (the chelate effect).

The moderately positive enthalpy change is probably related to ring strain in the multidentate complex.

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10.1.2: Magnetic Susceptibility

Electronic Structure

The electronic structure of coordination complexes can lead to several different properties that involve different responses to magnetic fields. These properties can vary between related compounds because of differences in electron counts, geometry, or donor strength. As a result, magnetic measurement of these materials can be used as a tool to provide insight into the structure of a coordination complex.

Diamagnetic and paramagnetic compounds are two common categories defined by interaction with a magnetic field. Diamagnetic compounds display a very slight repulsion from magnetic fields. The interaction is quite subtle and requires the proper instrumentation if it is to be observed; it's not something you would normally notice by waving a magnet in front of a vial of coordination complex. In contrast, paramagnetic compounds display a very slight attraction to magnetic fields. In terms of electronic structure, diamagnetic compounds have all of their electrons in pairs whereas paramagnetic compounds have one or more unpaired electrons. These definitions are not limited to coordination complexes. Atmospheric oxygen, O_2, is a common example of a paramagnetic compound. Atmospheric nitrogen, N_2, is a common example of a diamagnetic compound.

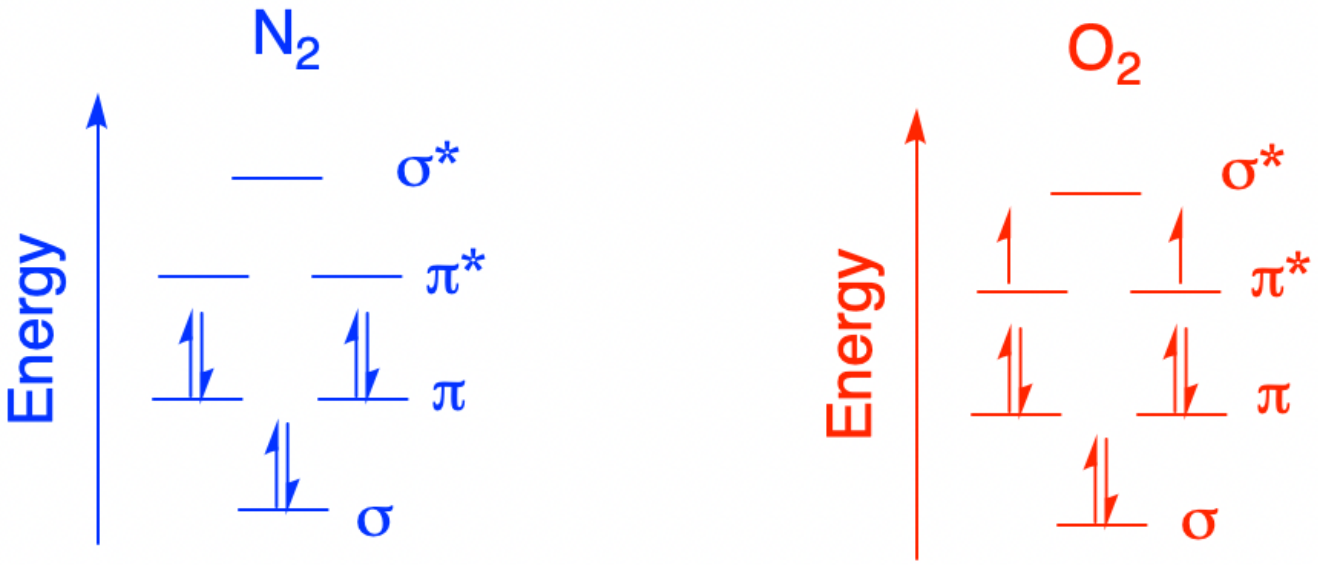


Figure 10.1.2.1: Valence molecular orbital diagrams of N_2 and O_2 show that N_2 is diamagnetic while O_2 is paramagnetic. (CC-BY-NC; Chris Schaller)

These differences arise because of a quantum mechanical property of electrons and other subatomic particles: spin. Spin does not have a direct macroscopic analogy; physical chemists often urge caution about equating it to a phenomenon on the level at which we observe the universe. However, we do know that spin is related to magnetic phenomena. We can think of an electron as having a magnetic moment. There are two allowed values of this magnetic moment ($+\frac{1}{2}$ and $-\frac{1}{2}$) that differ in orientation; spin is a vector quantity. Normally, there is no preference for one orientation over the other. If a coordination complex has one unpaired electron, and we have a million of those coordination complexes in a very tiny sample, about 500,000 of the unpaired electrons would have spin = $+\frac{1}{2}$ and about 500,000 of them would have spin = $-\frac{1}{2}$. The spin of each electron is randomly oriented. As a result, the material would have no net magnetic moment. In the presence of a magnetic field, however, there is a small energy difference between those two spin states. As a result, a majority of the spins adopt the energetically more favorable orientation. Although the material by itself has no net magnetic field, one has temporarily been induced by the influence of an external magnetic field. This is what we mean by magnetic susceptibility.

Measuring Magnetic Susceptibility

All diamagnetic compounds have a roughly similar response to a magnetic field; either their electrons are all paired or they

are not. Paramagnetic compounds, however, can respond quite differently to a magnetic field, depending on the number of unpaired electrons. The more unpaired electrons there are, the stronger the magnetic susceptibility will be, and so the stronger the attraction between the compound and the magnetic field. For this reason, measuring the strength of attraction of a compound for a magnetic field can reveal the number of unpaired electrons in the compound. This relationship is most straightforward for complexes of first row transition metals ($3d$ metals), becoming a little more complicated for the $4d$ and $5d$ series.

A Guoy balance is probably the simplest example of a method for determining the presence of unpaired electrons in a coordination complex.[1] It uses a balance, a sample holder and a magnet. Essentially, the magnet is weighed in the presence and absence of the sample. The discrepancy between the two measurements arises because of the interaction of the sample with the magnetic field. Any diamagnetic sample causes slight downward repulsion, registering as a heavier weight. A paramagnetic sample suspended between the poles of the magnet causes a slight upward pull on the magnet, which registers as a lighter weight. The more unpaired electrons there are, the greater the induced magnetic moment, and so the lighter the weight becomes.

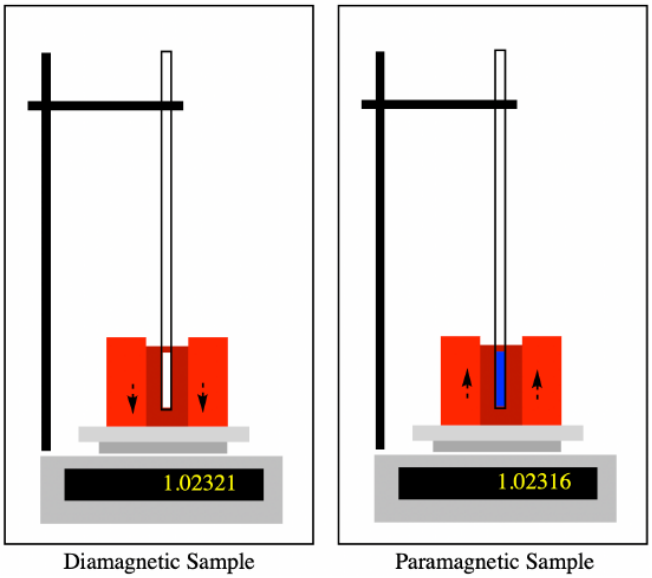


Figure 10.1.2.2: Diagram of a Guoy balance. A magnet (red) sits on a balance and a sample tube is placed in the center cavity of the magnet. (CC-BY-NC; Chris Schaller)

From that measurement, we can extract a parameter that we normally refer to as the effective magnetic moment of the material, μ_{eff}. The magnetic moment is expressed in units called Bohr magnetons. A Bohr magneton (BM or μ_B) is defined as:

$$1\text{BM} = \frac{eh}{4\pi mc}$$

in which *e* is the charge on an electron; h is Planck's constant; m is the mass of the electron; c is the speed of light.

This experimental quantity is fitted to a simple relationship that depends on the number of unpaired electrons. This mathematical model gives a prediction of the "spin-only" magnetic moment. If the magnetic moment arises purely from the number of unpaired electrons without additional complicating factors, the fit to the experimental data is pretty good.

$$\mu_{eff} \approx \mu_{so} = g\sqrt{S(S+1)}$$

Here, *g* is the gyromagnetic ratio, which is a proportionality constant between the angular momentum of the electron and the magnetic moment. It has a value of 2.00023, or approximately 2.0. The term $\sqrt{S(S+1)}$ is the value of the angular momentum, which depends on the number of unpaired electrons; S is the absolute value of the sum of the individual spins of the valence electrons. Of course, the spins would cancel out in electrons that were paired, because one would have $m_s = \frac{1}{2}$ and the other would have $m_s = -\frac{1}{2}$. For unpaired electrons, Hund's rule states that they would have parallel spins; for example, two unpaired electrons gives $S = 1$.



The table above shows how the magnetic moment changes with the number of unpaired electrons. The maximum number of unpaired electrons given is five, because for a transition metal a sixth electron would have to pair up in a previously occupied orbital. In f-block elements, there could be seven unpaired electrons before pairing occurs because there are seven f orbitals rather than just five d orbitals.

Note that the expression for spin-only magnetic moment is sometimes written in an alternative way, based directly on the number of unpaired electrons, n, rather than S.

$$\mu_{eff} \approx \mu_{so} = \sqrt{n(n+2)}$$

There is an additional approximation in these cases, based on how the values of the spin-only magnetic moment correlate with the number of unpaired electrons. If we always round the value of μ_{so}, then it is one greater than the number of unpaired electrons. Thus, $\mu_{so} \approx n + 1$, provided of course that there are any unpaired electrons at all; the relationship doesn't hold if n = 0 because then $\mu_{so} = 0$, not 1.

In reality, observed magnetic moments are slightly different than spin-only magnetic moments. In some cases, the observed magnetic moment is smaller than expected, but those cases are more complicated and we won't consider them here. Very often, the observed magnetic moments are larger than predicted because orbital angular momentum also plays a role in determining the magnitude of the overall magnetic moment. We may use a modified expression that takes this part into account.

$$\mu_{eff} \approx \mu_{s+L} = g\sqrt{S(S+1) + \frac{1}{4}L(L+1)}$$

Just as S is the absolute value of the sum of the spin quantum numbers in the ion, m_s, *L* is the absolute value of the sum of the orbital quantum numbers, m_l. There are five d orbitals, with $m_l = 2, 1, 0, -1, -2$, and the value of *L* has to be maximized according to Hund's rule. That means the value of *L* can be 3, 2, or 0.

As an example, suppose we have a Co^{2+} ion. Co^{2+} ion has a d^7 configuration. It has five d orbitals, so four of these electrons are paired, leaving only three unpaired electrons with parallel spins, so $S = 3/2$. In order to maximize the orbital quantum number, L , two electrons will be in an orbital with $m_l = 2$, two electrons will be in an orbital with $m_l = 1$, and one electron will be in each orbital with m_l = 0, -1, and -2. When we take the sum, we find $L = 2 + 2 + 1 + 1 + 0 - 1 - 2 = 3$. That gives us:

$$\mu_{s+L} = g\sqrt{3/2(3/2+1) + \frac{1}{4}3(3+1)} = 5.20$$

In comparison, $m_{so} = 3.87$ in this case. Observed values of μ_{eff} vary between different Co^{2+} complexes but are generally in the range 4.1 – 5.2 BM.[2] The orbital contribution is often smaller than expected, so magnetic susceptibilities frequently fall somewhere between μ_{so} and μ_{S+L}.

The use of a simple Guoy balance is an historically important method of determining magnetic susceptibility, and it is sometimes used in undergraduate laboratory experiments. Other methods are frequently used to measure magnetic susceptibility in the research laboratory. A magnetic susceptibility balance operates on a similar principle to the one behind the Guoy balance. A sample is placed within the poles of an electromagnet, causing the electromagnet to move very slightly. The current in the electromagnet is adjusted, changing its magnetic field, until the magnet comes back to its initial position. The magnitude of the current adjustment is proportional to the magnetic susceptibility of the sample.

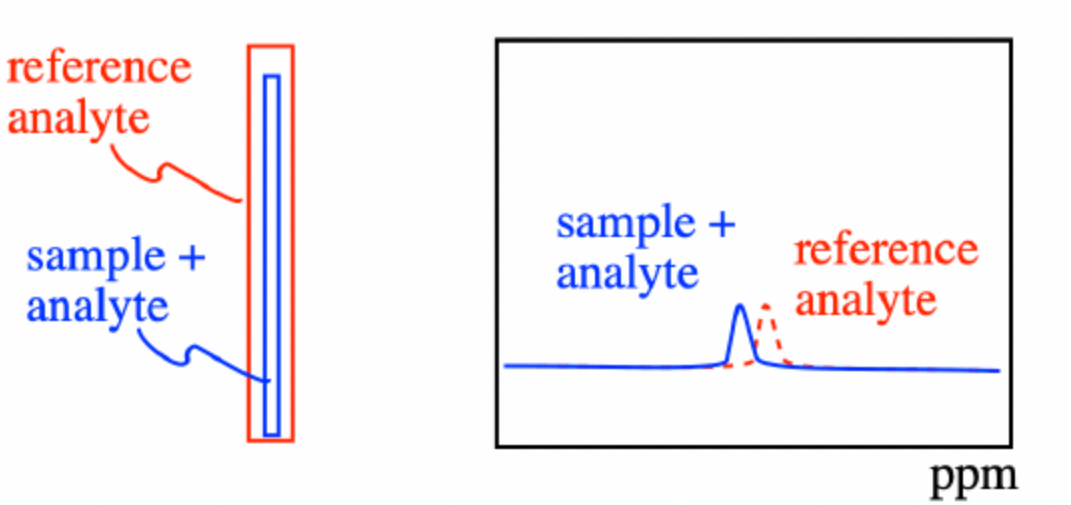


Figure 10.1.2.3: The Evans Method uses chemical shifts (from NMR) to measure magnetic susceptibility. Left: A capillary tube containing sample and a reference analyte is bathed in a larger tube containing reference analyte solution. Right: The NMR signal of a reference analyte (red) is shifted when that analyte is mixed with a paramagnetic sample (blue). (CC-BY-NC; Chris Schaller)

A superconducting quantum interference device (SQUID) uses a superconducting loop in an external magnetic field to measure magnetic susceptibility of a sample.[3] The sample is mechanically moved though the superconducting loop, inducing a change in current and magnetic field that are proportional to the magnetic susceptibility of the sample. Commercially produced SQUID magnetometers often have variable temperature controls, allowing magnetic susceptibility to be measured across a range of temperatures.

The Evans NMR method is quite common because of the widespread availability of high-field NMR spectrometers in research labs. A capillary containing the paramagnetic sample and a reference analyte is placed in an NMR tube containing the same reference analyte but without the paramagnetic sample. The analyte in the presence of the paramagnetic material will experience a local, induced magnetic field owing to the effect of the superconducting magnet of the NMR instrument on the paramagnetic sample. Its NMR signals will shift as a result. The NMR signal of the analyte outside the capillary will undergo no such shift, and the difference in the two signals is an indicator of the magnetic susceptibility of the sample.

There are other types of magnetic behavior in addition to diamagnetism and paramagnetism. Ferromagnetic materials have long-range order with spins oriented parallel to each other, even in the absence of an external magnetic field. Common, permanent magnets are made from ferromagnetic materials. Antiferromagnetic materials also have long-range order, but the magnetic moments are arranged in opposing pairs. These three different magnetic behaviors are diagnosed by the temperature dependence of the magnetic susceptibility. Paramagnetic materials display magnetic susceptibility (χ_M, related to μ_{eff}) that increases with the inverse of temperature. Ferromagnetic materials have a critical temperature below which magnetic susceptibility rapidly rises. Antiferromagnetic materials have a critical temperature below which magnetic susceptibility rapidly falls. However, these behaviors are largely beyond the scope of the current discussion.

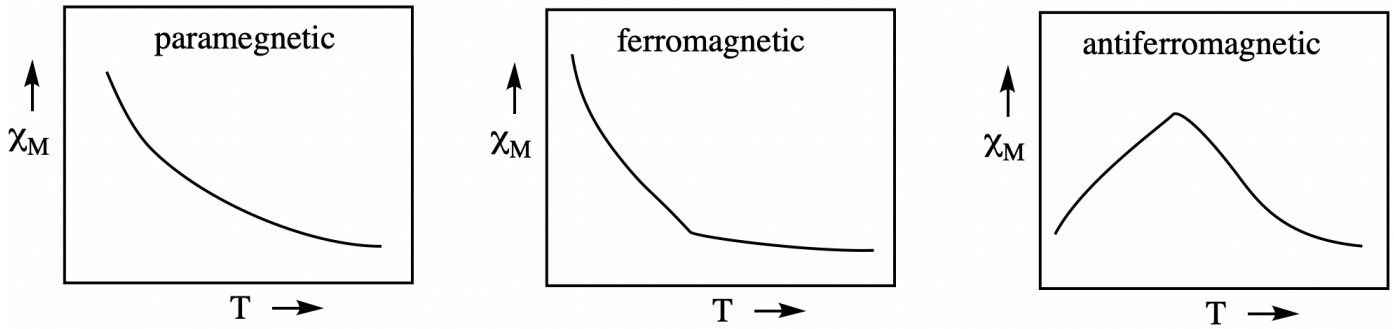


Figure 10.1.2.4: Magnetic behavior depends on temperature. Shown are plots of magnetic behaviour in terms of magnetic susceptibility χ_M versus temperature (T). (CC-BY-NC; Chris Schaller)

Problems

Exercise 10.1.2.1

Show that, given g = 2.00, then $g\sqrt{S(S+1)} = \sqrt{n(n+2)}$.

Answer available at the end of this section.

Exercise 10.1.2.2

Calculate the value of μ_{so} in the following cases:

a) V^{4+} b) Cr^{2+} c) Ni^{2+} d) Co^{3+} e) Mn^{2+} f) Fe^{2+}

Answer available at the end of this section.

Exercise 10.1.2.3

Calculate the value of μ_{eff} in the following cases:

a) V^{4+} b) Cr^{2+} c) Ni^{2+} d) Co^{3+} e) Mn^{2+} f) Fe^{2+}

g) Cr^{3+} h) V^{3+}

Answer available at the end of this section.

References

1. Lancashire, R. J. Magnetic Susceptibility https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Map%3A_Inorganic_Chemistry_(Housecroft)/04%3A_Experimental_techniques/4.14%3A_Magnetism/Magnetic_Susceptibility_Measurements (accessed Jun 27, 2021).
2. Cotton, F.A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th Ed. John Wiley & Sons: New York, 1980, p 628.
3. Raja, P. M. V.; Barron, A. R. Magnetism https://chem.libretexts.org/@go/page/55872 (accessed Jun 27, 2021).

Answers

Exercise 10.1.2.1

$$\begin{aligned}\mu_{so} &= g\sqrt{S(S+1)} \\ &= 2\sqrt{S(S+1)} \\ &= \sqrt{4S(S+1)} \\ &= \sqrt{2S(2S+2)}\end{aligned}$$

but $S = n(1/2)$ or $n = 2S$ then

$$\mu_{so} = \sqrt{n(n+2)}$$

Exercise 10.1.2.2

a) V^{4+} is $d^1; n = 1; \sqrt{n(n+2)} = 1.73$
b) Cr^{2+} is $d^4; n = 4; \sqrt{n(n+2)} = 4.90$
c) Ni^{2+} is $d^8; n = 2; \sqrt{n(n+2)} = 2.83$
d) Co^{3+} is $d^6; n = 0; \sqrt{n(n+2)} = 0$
e) Mn^{2+} is $d^5; n = 5; \sqrt{n(n+2)} = 5.92$
f) Fe^{2+} is $d^6; n = 4; \sqrt{n(n+2)} = 4.90$
g) Cr^{3+} is $d^3; n = 3; \sqrt{n(n+2)} = 3.87$

h) V^{3+} is $d^2; n = 2; \sqrt{n(n+2)} = 2.83$

Exercise 10.1.2.3

a) V^{4+} is $d^1; S = 1/2; L = 2; \mu_{s+L} = g\sqrt{1/2(1/2+1) + \frac{1}{4}2(2+1)} = 3.00$

b) Cr^{2+} is $d^4; S = 2; L = 2+1+0-1 = 2; \mu_{s+L} = g\sqrt{2(2+1) + \frac{1}{4}2(2+1)} = 5.48$

c) Ni^{2+} is $d^8; S = 1; L = 2+2+1+1+0+0-1-2 = 3; \mu_{s+L} = g\sqrt{1(1+1) + \frac{1}{4}3(3+1)} = 2.24$

d) Co^{3+} is $d^6; S = 2; L = 2+2+1+0-1-2 = 2; \mu_{s+L} = g\sqrt{(2+1) + \frac{1}{4}2(2+1)} = 5.48$

e) Mn^{2+} is $d^5; S = 5/2; L = 2+1+0-1-2 = 0; \mu_{s+L} = g\sqrt{5/2(5/2+1) + \frac{1}{4}0(0+1)} = 5.92$

f) Fe^{2+} is $d^6; S = 2; L = 2+2+1+0-1-2 = 2; \mu_{s+L} = g\sqrt{2(2+1) + \frac{1}{4}2(2+1)} = 5.48$

g) Cr^{3+} is $d^3; S = 3/2; L = 2+1+0 = 3; \mu_{s+L} = g\sqrt{3/2(3/2+1) + \frac{1}{4}3(3+1)} = 5.20$

h) V^{3+} is $d^2; S = 1; L = 2+1 = 3; \mu_{s+L} = g\sqrt{1(1+1) + \frac{1}{4}3(3+1)} = 2.24$

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10.1.3: Electronic Spectra

The interaction of different wavelengths of electromagnetic radiation with matter provides a vast amount of information about material structure. The absorption of UV-visible light is connected to the excitation of electrons to higher orbitals. Inherently, this spectroscopy reveals information about the electronic structure of compounds, including coordination complexes. This topic is important enough that it is the subject of a later chapter.

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10.1.4: Coordination Number and Molecular Shapes

Examination of physical properties, such as electronic spectra or magnetic susceptibility, can often be used to distinguish between possible molecular geometries of coordination complexes. It can be difficult to predict the coordination number of a complex formed from a specific metal ion and a given set of ligands, to say nothing of its geometry. Steric crowding and valence electron count around the metal in the complex are just two of the factors that influence coordination number. Even for a given coordination number, there are sometimes different possible coordination geometries. For example, five-coordinate can adopt square pyramidal or trigonal bipyramidal geometry. In most cases, it is especially difficult to predict which geometry prevails. In fact, many complexes adopt a geometry somewhere between the two. Four-coordinate geometry offers a similar choice between square planar and tetrahedral geometry, although in this case it can be easier to predict which one is likely to occur. The energetic difference between these two possible geometries can often be explained based on the electronic structure of the complex.

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10.2: Bonding Theories

Coordination complexes caused great fascination among chemists during the nineteenth century, although it wasn't until the century's end that Alfred Werner determined the fundamental principles of their structure. A fuller understanding of their structures was developed over the first half of the twentieth century. This understanding developed in stages, with newer theories and models building on previous ones rather than replacing them completely.

Crystal Field Theory

In the early 1930's, American physicists John Hasbrouck van Vleck and Hans Bethe developed a theoretical treatment of crystalline transition metal compounds that explained their magnetic and optical properties. This treatment did not consider bonding in any way, but it did concern itself with the geometry of ligands, or counterions, around a central metal ion. Electrostatic considerations formed the basis of the theory, with attention to repulsive forces between ligand electrons and d electrons on the metal ion. The model gave good predictions about the effect of ligand geometry on the electronic structure of the metal ion.

Ligand Field Theory

During the 1950's, British chemists John Stanley Griffith and Leslie Orgel combined some aspects of crystal field theory with molecular orbital theory to produce a bonding model for coordination complexes. Rather than just considering electrostatic interactions between metal and ligand, this approach used orbital interactions to model the role of covalency in determining the electronic structure of the complex.

Angular Overlap Model

This model is a specific approach to considering how ligand and metal orbitals combine to produce molecular orbitals in a coordination complex. It uses the symmetry and orientation of atomic orbitals to determine what combinations of these orbitals should be considered.

Computational Chemistry

The three "pencil-and-paper models" described above for bonding in coordination complexes have been greatly augmented by the power of modern computational chemistry. Although based on the same principles, computational methods offer a much higher level of quantitative information about electronic energy and allow relatively easy assessment of possible structural features such as coordination geometry. Pioneering methods included extended Hückel theory, originally developed by Roald Hoffman and Robert Burns Woodward to study pericyclic reactions. The method was later adapted by Hoffman and others to investigate inorganic and organometallic complexes. More recently, developments such as density functional theory have greatly facilitated computational work on transition metal systems because of their simplified treatment of many-electron systems. These approaches and others like them allow for the prediction of coordination complex properties through a computer interface.

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10.2.1: Crystal Field Theory

As the name implies, crystal field theory was developed as a way of explaining phenomena in ionic crystalline solids. Bethe and van Vleck wished to provide a rationale for the magnetic properties of these materials, as well as their colors. The latter resulted from the wavelength of light absorbed, revealing something about differences in electronic energy levels in the ions of the crystalline solid. The magnetic properties also depended on electronic energy levels, because magnetism depended upon whether electrons were paired, and whether or not electrons are paired depends on the presence or absence of orbitals at the same energy level.

They first considered a transition metal ion in an octahedral hole formed between layers of counterions packed in a crystalline lattice. The metal ion would have six near neighbors: three above and three below. Of course, the ions would be held together by electrostatics: the negative charges on the counterions would be attracted to the positive charge on the metal ion.

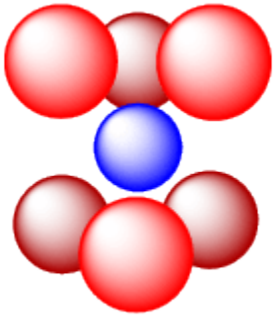


Figure 10.2.1.1: Illustration of a positively charged metal ion (blue) surrounded by six near neighbors with negative charges (red). (CC-BY-NC; Chris Schaller)

But in addition to that positive charge, the metal ion also has electrons of its own. How did the electrons of those neighboring counterions affect the energy of those metal electrons? "...If we're going to work this out carefully, we need to consider three different situations", thought the physicists. "We need to start by considering the energy of the metal valence orbitals in the absence of counterions. Since these are transition metal ions, we will pay close attention to the five d orbitals. What happens when those d orbitals are placed in a field of surrounding electrons, if the field is evenly distributed around them? In other words, what happens to them in a spherical field of negative charge? And then, what happens if those electrons are not evenly distributed? What happens if the surrounding electrons approach only along the Cartesian axes?"

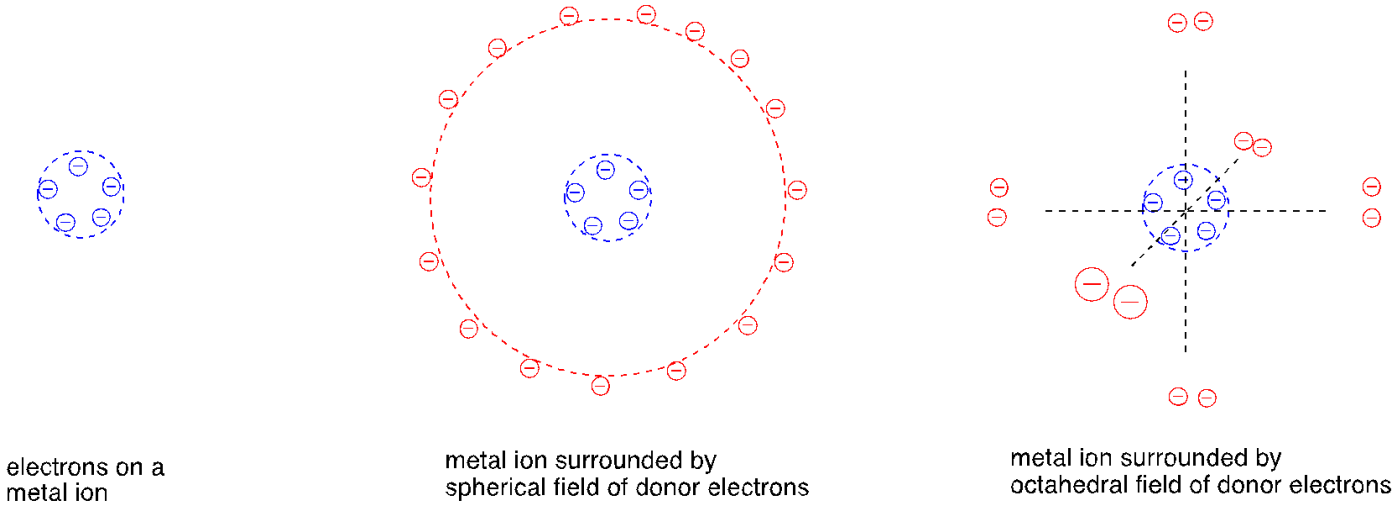


Figure 10.2.1.2: Illustration of the electrostatic charges to consider in idealized situations. (Left) imaginary situation of a "lone" metal ion with five d electrons in its valence shell. (Middle) Imaginary situation where a d^5 metal ion is surrounded by a spherical distribution of donor (Lewis base) electrons from a set of ligands. (Right) Imaginary situation where a d^5 metal ion is surrounded by a set of ligand donor electrons that are located along Cartesian coordinates (in an octahedral geometry). (CC-BY-NC; Chris Schaller)

The Cartesian axes are important here because, in an octahedron, the six ligands are ninety degrees ($90°$) apart from each other in space. We can think of two of those ligand electrons as lying in either direction from the metal ion along the z axis; two of them along the x axis; and the last two along the y axis.

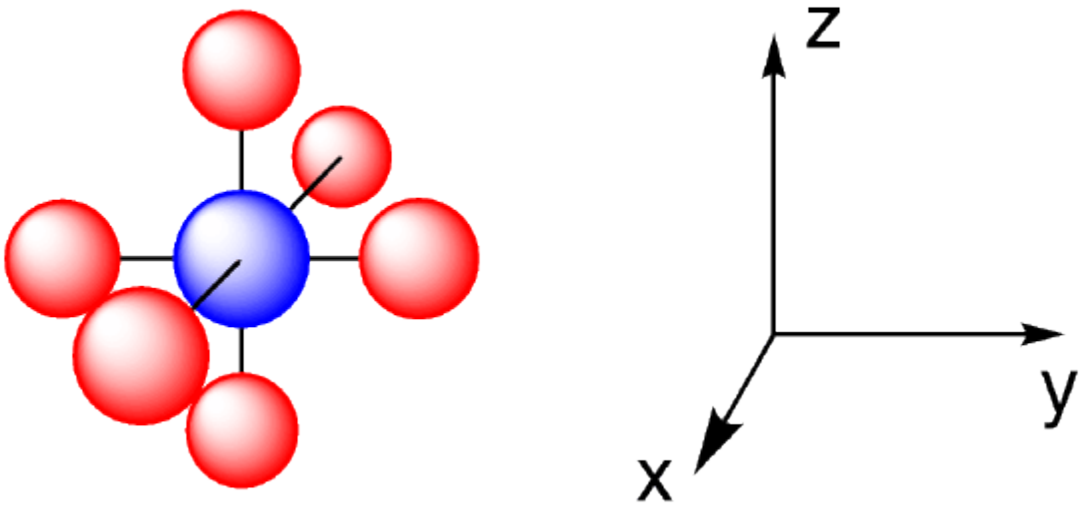


Figure 10.2.1.3: Illustration of a positively charged metal ion (blue) surrounded by six ligands (red) in an octahedral geometry where each ligand lies along the Cartesian axes. (CC-BY-NC; Chris Schaller)

Of course, when these metal electrons are placed in a field of negative charge, repulsion results, and the electrons on the metal go up in energy. They all increase in energy by the same amount.

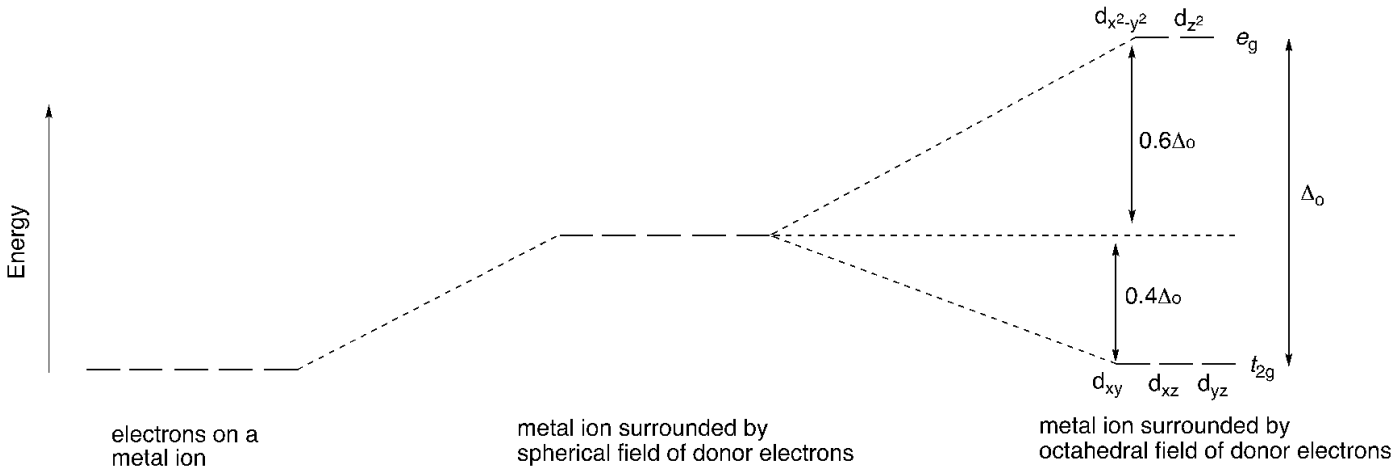


Figure 10.2.1.4: The relative energy levels of the valence d orbitals corresponding to the imaginary situations pictured in Figure 10.2.1.2 above. (Left) The five valence d orbitals of a "lone" metal ion are degenerate. (Middle) The electrons in the five valence d orbitals of a metal ion would be uniformly repelled by a spherical distribution of negative charge, and thus would be higher in energy than a "lone" metal ion. (Right) The electrons in each of the five valence d orbitals of a metal ion would interact to different extents with ligands located along each of the Cartesian coordinates, and thus their energies would be raised or lowered compared to the situation where charge was distributed in a uniform sphere. (CC-BY-NC; Chris Schaller)

The octahedral field is a different question, however, because the five d orbitals have different spatial distributions. Two of them (the d_{z^2} and $d_{x^2-y^2}$) lie along the axes. These orbitals are referred to as having e_g symmetry. The other three (the d_{xy}, d_{xz}, and d_{yz}) lie in between the axes. These three are referred to as having t_{2g} symmetry.

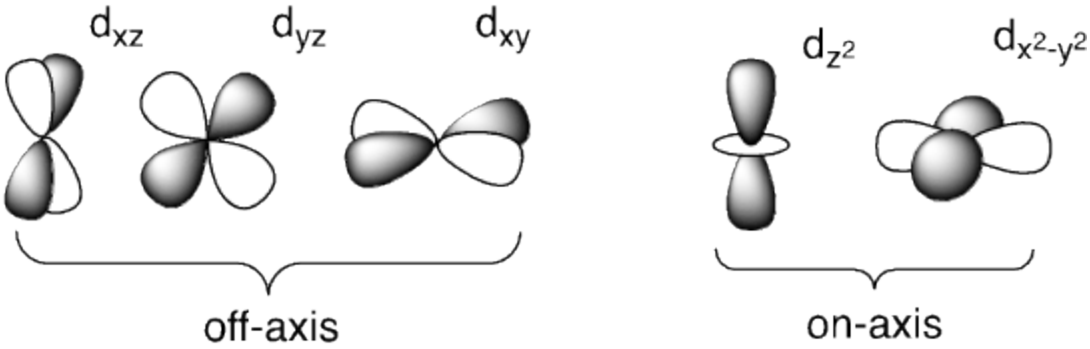


Figure 10.2.1.5: Illustration of the boundary surfaces of the five d orbitals. (CC-BY-NC; Chris Schaller)

Those two orbitals along the axes experience repulsion from the neighboring anions. Because all of the negative charge is focused in six positions rather than being uniformly distributed, the repulsion experienced by these orbitals is greater than it would be in a spherical field. On the other hand, the three orbitals between the axes experience very little repulsion; their energy is actually much lower than it would be in a spherical field of negative charge.

These two sets of orbitals are therefore found at two different energy levels. The energy difference between them is called the octahedral field splitting, Δ_o. Because the total amount of repulsion is the same in the octahedral field and the spherical field – it is just distributed differently – the average energy level of the orbitals should be the same in the two fields. This average energy of the orbitals is called the **barycenter**, a term borrowed from astronomy. Because two of the orbitals are raised above the barycenter in the octahedral field and three are lowered below the barycenter, then the e_g set must be $\frac{3}{5}\Delta_o$ ($= 0.6\Delta_o$) above the barycenter and the t_{2g} set must be $\frac{2}{5}\Delta_o$ ($= 0.4\Delta_o$) below the barycenter. That means the average energy lies at the barycenter.

A parameter called the crystal field stabilization energy (CFSE) was developed to assess the energy difference between the metal ion in an octahedral coordination geometry and a spherical field. To determine CFSE, we simply add up the energy of all the electrons relative to the energy level of electrons in the spherical field, in units of Δ_o. For an octahedral case:

Misplaced '#'

Problems

Exercise 10.2.1.1

Determine the crystal field stabilization energy (CFSE) in the following octahedral ions:

a) V^{3+} b) Ni^{2+} c) Cr^{3+} d) Zn^{2+}

Answer a available at the end of this section.

Answer b available at the end of this section.

Answer c available at the end of this section.

Answer d available at the end of this section.

Answers

Exercise 10.2.1.1

V^{3+} is d^2, with two electrons in the t_{2g} and zero electrons in e_g.

CFSE = $[2(-0.4) + 0(0.6)] \times \Delta_o = -0.8\Delta_o$

Exercise 10.2.1.1

Ni^{2+} is d^8, with six electrons in t_{2g} and two electrons in e_g.

CFSE = $[6(-0.4) + 2(0.6)] \times \Delta_o = -1.2\Delta_o$

Exercise 10.2.1.1

Cr^{3+} is d^3, with three electrons in t_{2g} and zero electrons in e_g.
CFSE = $[3(-0.4) + 0(0.6)] \times \Delta_o = -1.2\Delta_o$

Exercise 10.2.1.1

Zn^{2+} is d^{10}, with six electrons in t_{2g} and four electrons in e_g.
CFSE = $[6(-0.4) + 4(0.6)] \times \Delta_o = 0\Delta_o$.

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10.3: LIGAND FIELD THEORY

10.3.1: Ligand Field Theory - Molecular Orbitals for an Octahedral Complex
10.3.2: Orbital Splitting and Electron Spin
10.3.3: Ligand Field Stabilization Energy
10.3.4: Tetrahedral Complexes
10.3.5: Square-Planar Complexes

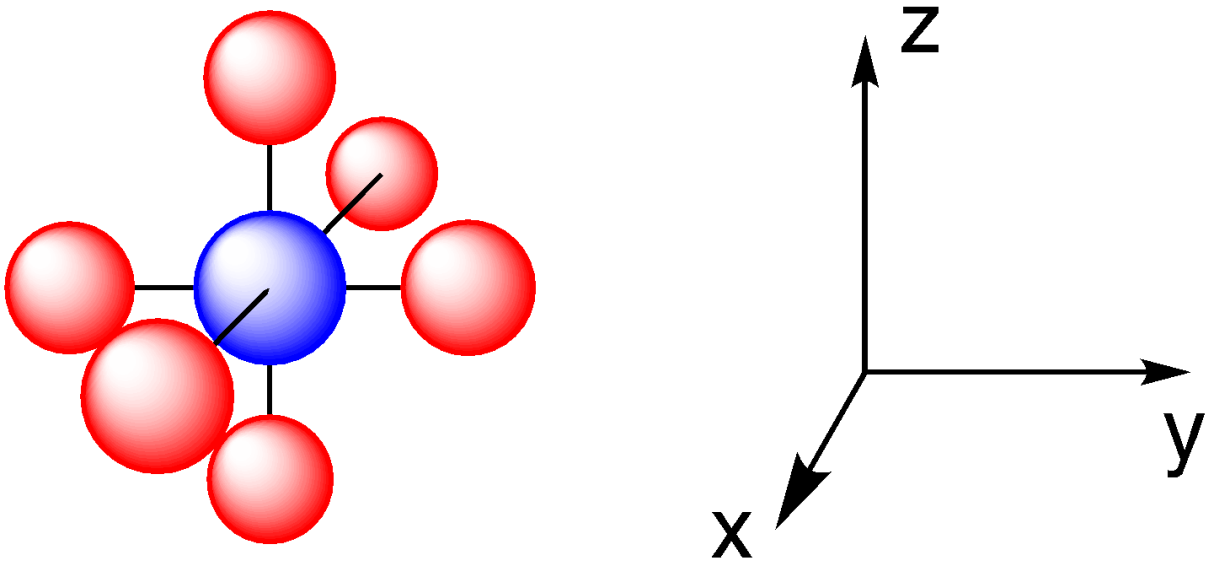
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10.3.1: Ligand Field Theory - Molecular Orbitals for an Octahedral Complex

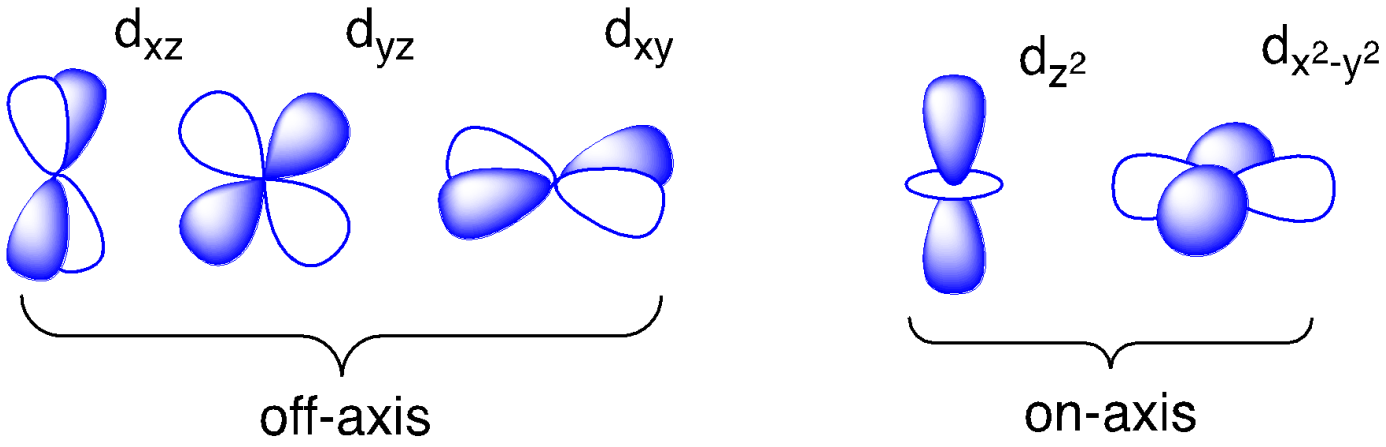
Crystal field theory is successful at providing some general insights into the differing energy levels of d orbitals in coordination complexes. That knowledge can help us to understand some of the magnetic properties of these compounds, which are determined by the number of unpaired electrons. It can also help us to understand some of the absorbed wavelengths of light in the UV-visible spectrum, which in some cases depends on the energy difference between different sets of d orbitals.

Ligand field theory picks up where crystal field theory left off by taking into consideration the importance of orbital overlap for covalent bonding. That factor adds another level of detail to our model of metal complex behavior, and it provides additional nuance to our understanding of why two related complexes may have very different properties.

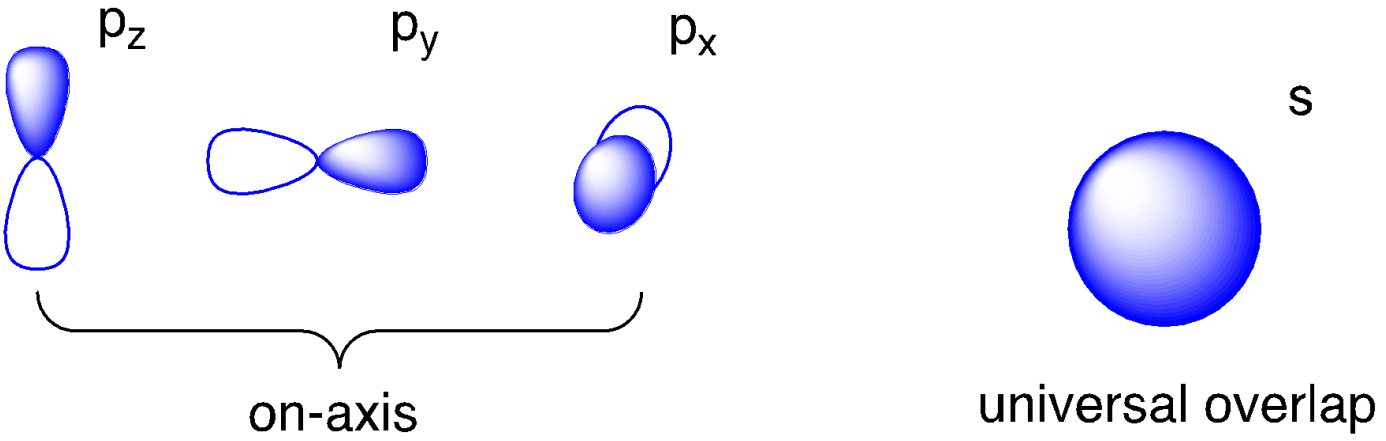
We can start by taking another look at octahedral coordination geometry. That's probably the most common coordination geometry. It's also the one we looked at when we considered crystal field theory. In this geometry, all six ligands are located along the x, y, or z axes.



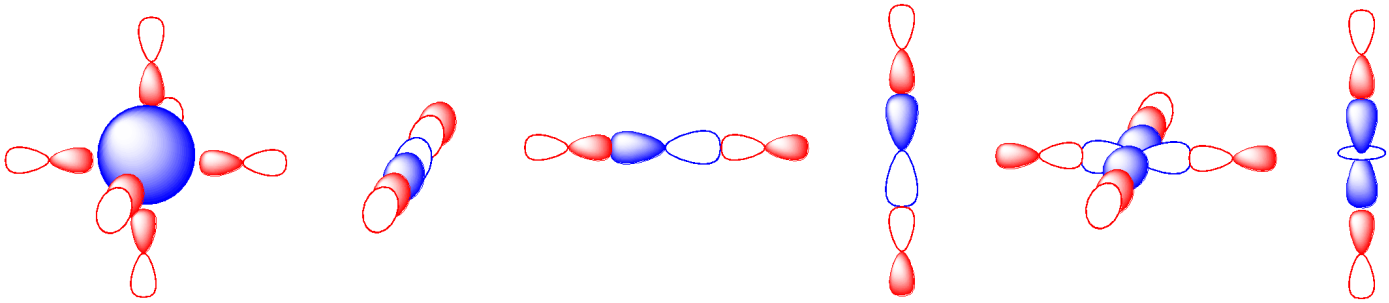
Once again, only two of the valence d orbitals are located along those axes. In crystal field theory, we considered that orientation as an opportunity for electron-electron repulsion between ligand lone pairs (or charges on neighboring anions) and the d electrons. This time, we'll think about the opportunity for covalent bonding that exists between ligand orbitals and the d orbitals along these axes.



In addition to the d orbitals, we should also think about the potential for bonding with the metal's valence s and p orbitals. All three p orbitals are located along the axes where we find the ligands. They are ideally located for bonding with ligand orbitals along those axes. The s orbital is different: it is non-directional. No matter where a ligand is located, if it has sigma bonding, it will have the same overlap with that spherical s orbital. That means the s orbital is a good candidate for forming a covalent sigma bond with any ligand, no matter what the geometry.

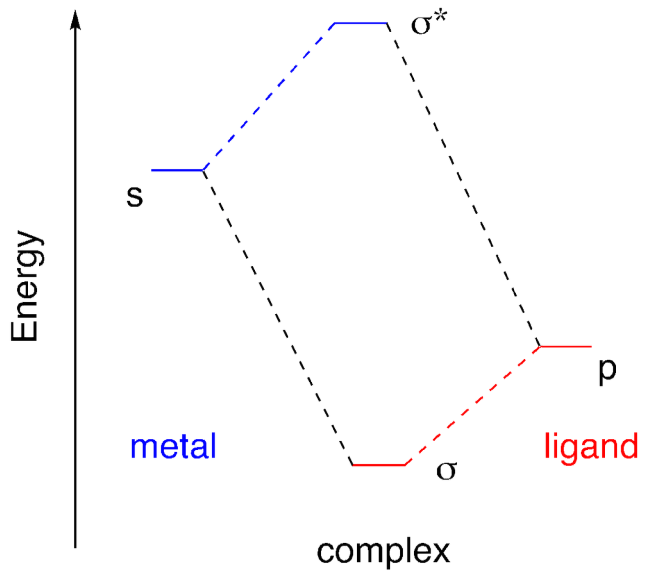


That leaves us with six possible metal orbitals that could potentially overlap with the six ligands. Each metal orbital could potentially interact with any one of a number of these ligands. In the illustration below, we've made the assumption that the ligand orbitals are p orbitals. That's not a bad bet given that we are generally considering p-block elements as donor atoms in most ligands. The s orbital could presumably interact with up to six ligands. The metal p orbitals could interact with ligand orbitals in either direction along the axis. By inspection, it appears that the d orbitals could interact with two or four orbitals.



That ratio of six ligand orbitals to six ligand orbitals is coincidental. A one-to-one correspondence between metal orbitals and ligand orbitals isn't strictly required, but it's easier to think about that way. Let's begin by assuming that the s orbital interacts with just one donor orbital. Just like in MO construction for main group diatomics, if we start with two atomic orbitals and combine them, we get two molecular orbitals. One of them is the in-phase combination and the other one is the out-of-phase combination.

The number of molecular orbitals we obtain is the same as the number of atomic orbitals we start with.

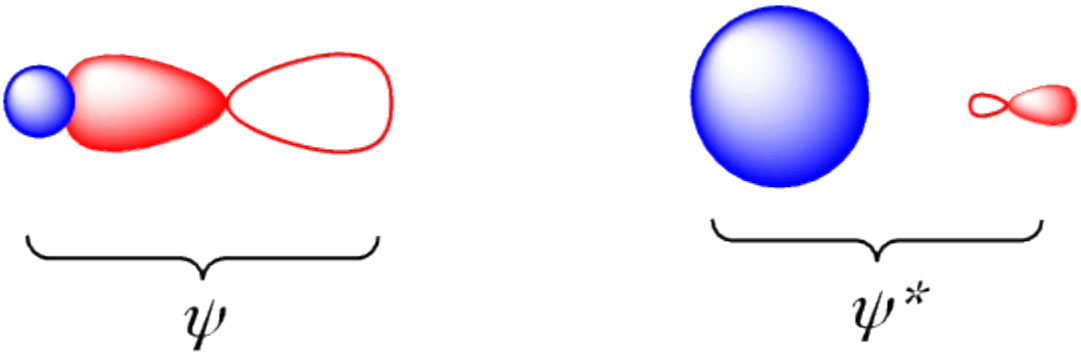


We can think of these two combinations as the addition of two orbitals together, with a positive coefficient if they are in phase and a negative coefficient if they are out of phase.

$$\psi M\text{-}L = a\psi M(s) + b\psi L(p)$$

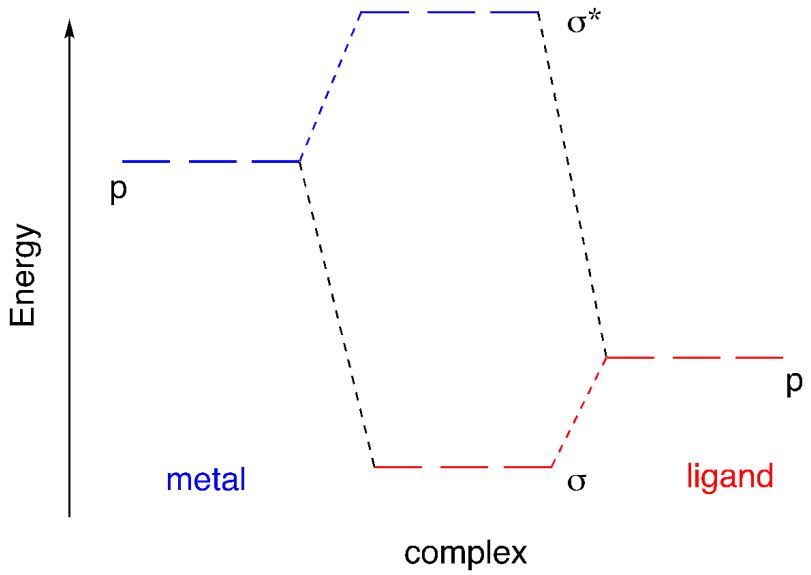
$$\psi^* M\text{-}L = c\psi M(s) - d\psi L(p)$$

Notice that the molecular orbital interaction diagram is asymmetric. The ligand orbital is at lower energy than the metal orbital. The donor atom is a p block element; it's to the right of the transition metals in the periodic table. The donor atom is more electronegative than the transition metal, so its electrons are at lower energy. In a case like that, the coefficients in the orbital combination follow a pattern. In the in-phase combination, the more electronegative element gets a larger coefficient than the less electronegative element ($b > a$). The opposite is true in the out-of-phase combination ($c > d$).

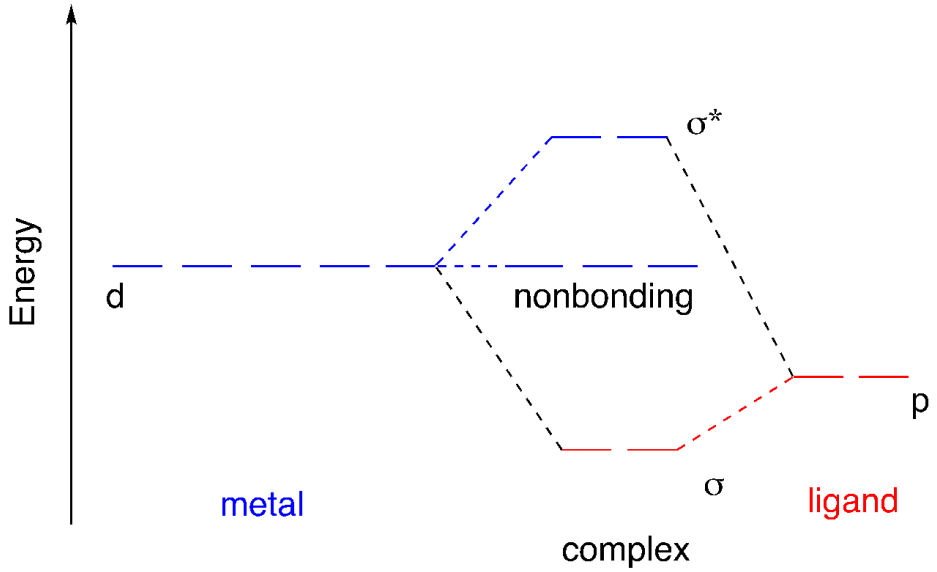


The molecular orbital more closely resembles the atomic orbital to which it is closest in energy, both spatially and energetically. Consequently, we often talk about the bonding orbital, σ, as though it is still a ligand p orbital, and the antibonding orbital, σ, as though it is still a metal s orbital. The bonding orbital is ligand-centered and the antibonding orbital is metal-centered.

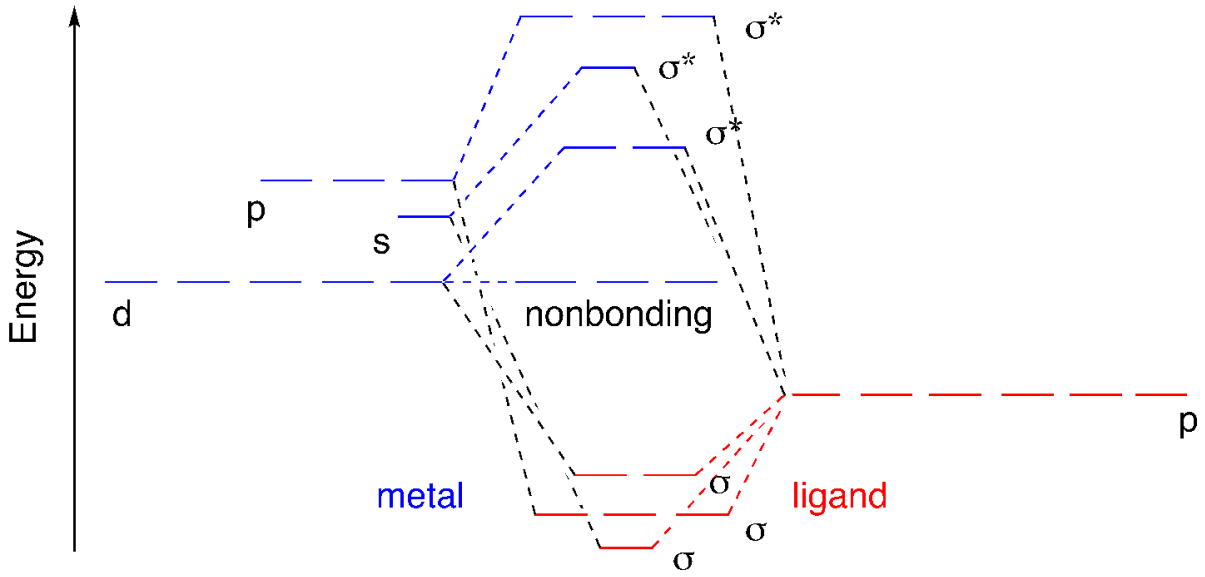
If we consider the three metal p orbitals and their overlap with three of the ligand donor orbitals, we find a very similar outcome. The three σ* orbitals are metal-centered, whereas the three σ orbitals are ligand-centered.



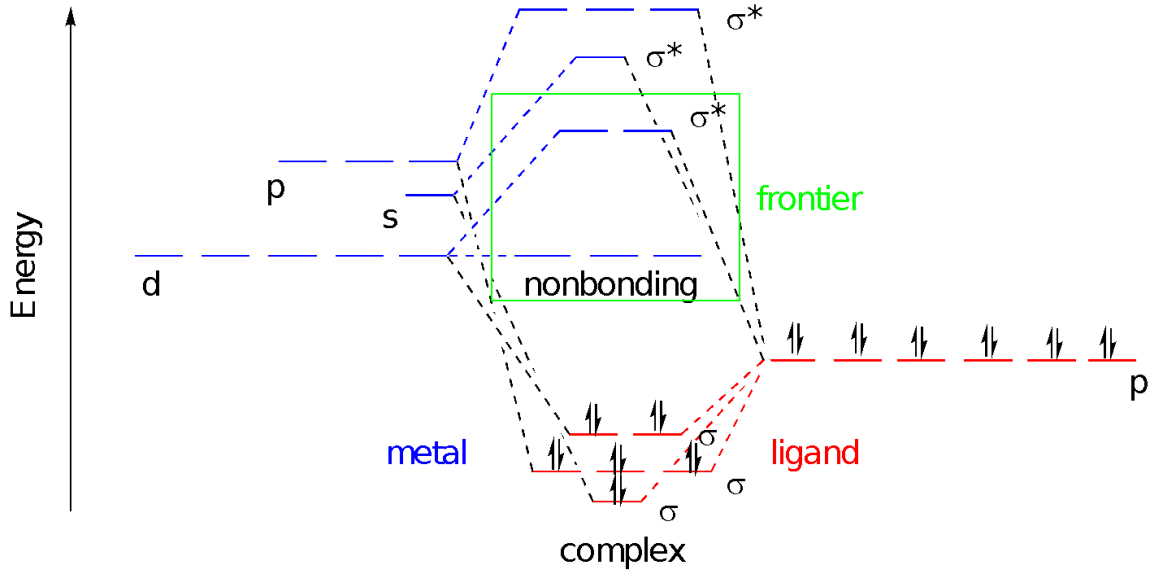
The d orbitals, on the other hand, present a significant variation. Only two of them appear to be capable of overlap with ligand p orbitals. If we pair those two d orbitals off with the remaining two ligand donor orbitals, we have three leftover metal d orbitals. Those three metal orbitals do not overlap with the ligand and so they are non-bonding.



We can superimpose those three pictures to get a look at the full molecular orbital interaction diagram. It is still somewhat simplified. We are ignoring any core orbitals on the metal and we are also ignoring any ligand orbitals that aren't involved in sigma bonding to the metal. Maybe we have ammine ligands but we are ignoring all of those N-H bonds and focusing solely on the M-N bonds.

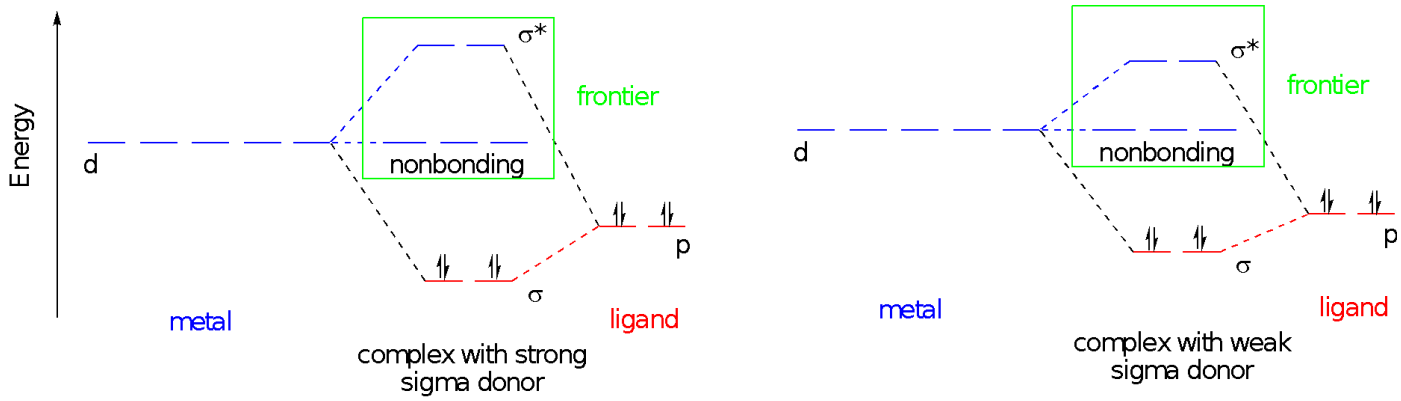


The six donor atoms are each donating a pair of electrons to the metal. Upon covalent bond formation, each of those lone pairs slides down into an energy well; they are stabilized by formation of the metal-ligand bond.

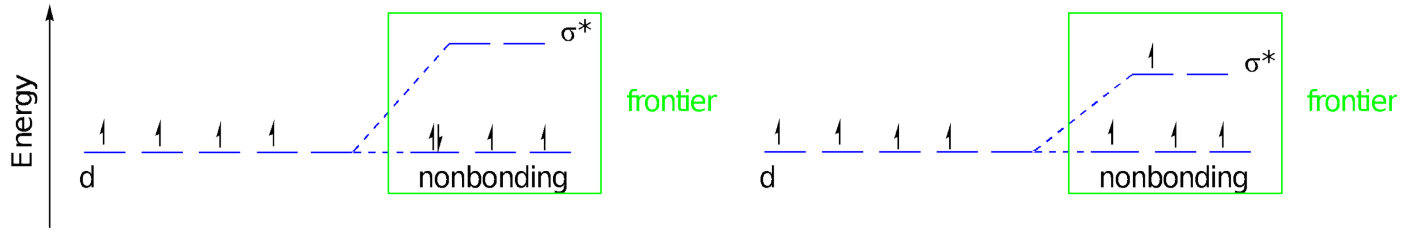


So far, we have ignored the electrons on the metal because we are looking at a general case. There could be anywhere from zero to ten electrons in the atomic d orbitals, depending on the metal and its oxidation state. These electrons will be crucial to many aspects of the behavior of the complex because they are found at the frontier. Frontier orbitals are often the key to understanding reactivity as well as physical properties such as magnetism and interaction with light.

We often consider only these frontier orbitals when we consider the properties of transition metal complexes. We ignore what seems like the most important part of the picture: the bonding orbitals. We do that because those bonding orbitals are not frontier orbitals. Furthermore, the stability of those bonding orbitals is reflected in the antibonding level. The lower the bonding electrons sink, the higher the antibonding levels rise. One immediate consequence of that connection is that the bond strength may control the gap between nonbonding and antibonding d orbitals. Strong sigma donors provide a large d-d gap, whereas weak sigma donors give a smaller d-d gap. Understanding donor strength can be a difficult task, but remember for example that more basic ligands are often stronger donors.



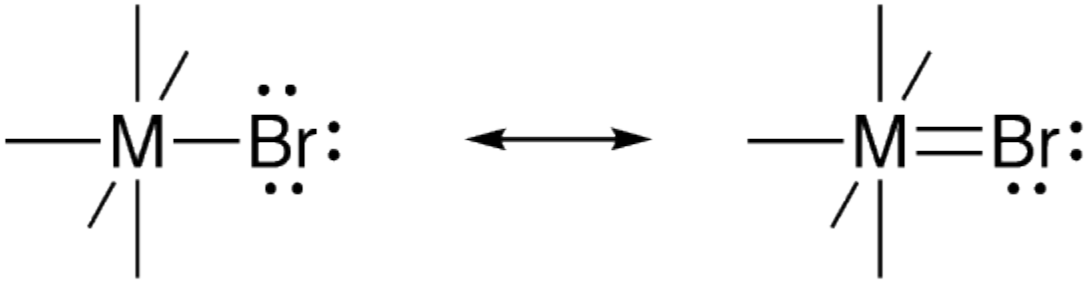
If we think about a specific case of metal ion, we can add some d electrons to the picture. Suppose we have a d^4 metal ion. Maybe it's a Cr^{2+} ion. This ion can take on two different electron configurations in an octahedral environment. With stronger donors, the d-d gap is potentially too large to promote a fourth electron into the next energy level, so the complex is left with two unpaired electrons. With weaker donors, the relatively small d-d gap may be smaller than the energy it takes to put two electrons into the same orbital, so there are four unpaired electrons. We'll return to the consequences of these situations on an upcoming page.



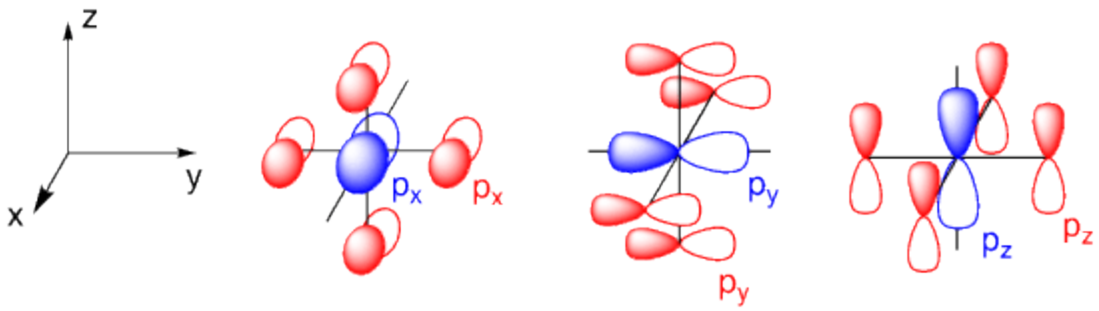
Pi Donor Ligands

The sigma donor strength of the ligand can have an appreciable effect on the d orbital splitting in the complex, and that might influence the properties of the complex. That's not something that we considered in crystal field theory, but thinking about bonding interactions has provided another layer of information. What other variations in ligand donation might play a role in the d orbital splitting?

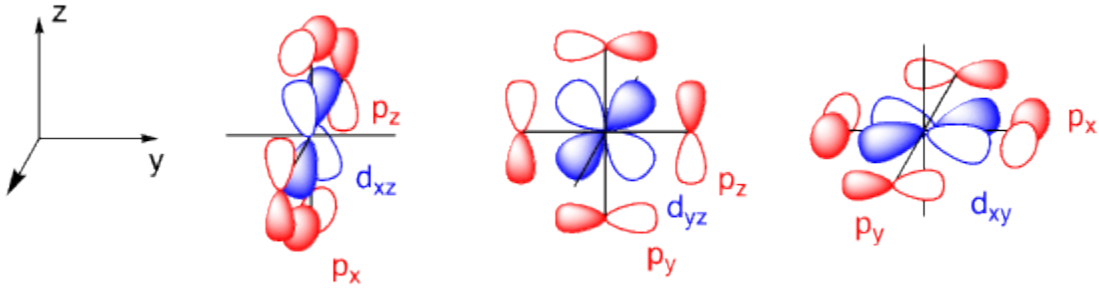
Suppose a donor atom had more than one lone pair. Could it donate a second? On paper, that makes another bond between the ligand and the metal. Bond formation is energy-releasing and stabilizing, although sometimes we get in trouble when we draw too many bonds, because we've run out of orbitals to interact with each other.



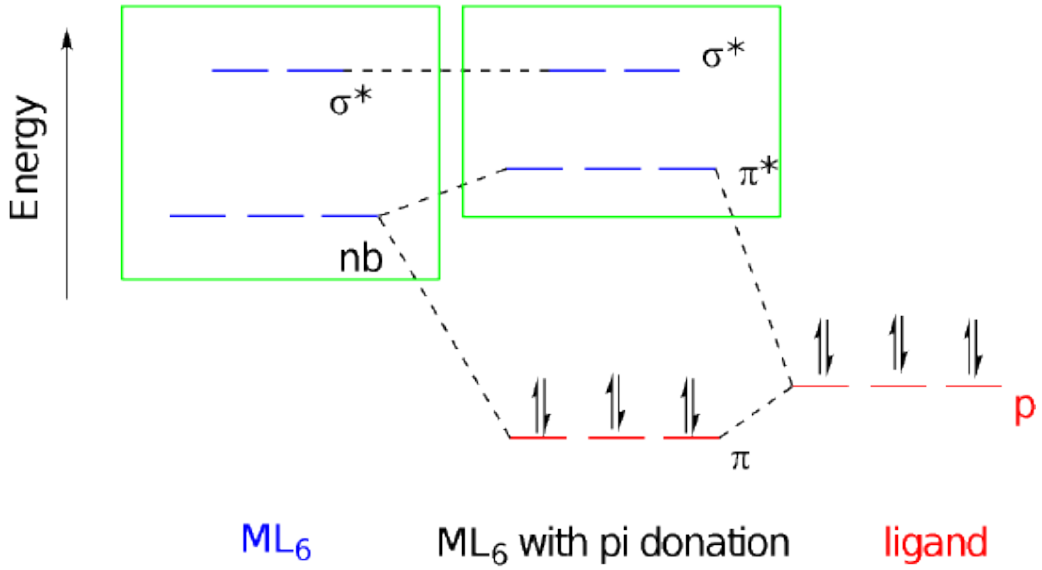
When we draw a pair of bonds between two atoms, we usually think of the first bond as a sigma bond and the second one as a pi bond. The question here is, can bromine form a pi bond with a transition metal? When we learn about pi bonds, we start by looking at two nitrogen atoms or two carbon atoms using parallel p orbitals to bond with each other. The resulting pi bond avoids the sigma bond because it is above and below the bond axis. We have already established that the metal can use its p orbitals for bonding. On paper, a metal p orbital in an octahedral complex could pi bond with four different ligands.



The trouble with that scheme is that we are already using these metal p orbitals for sigma bonding. We have other metal orbitals that could overlap with these ligand p orbitals, however, and we aren't using them for sigma bonding. These are the d_{xy}, d_{xz}, and d_{yz} orbitals. This set looks even more promising for pi bonding; the d orbitals reach out towards the ligand p orbitals, maximizing overlap. Once again, each d orbital could potentially form pi bonds with up to four ligands.

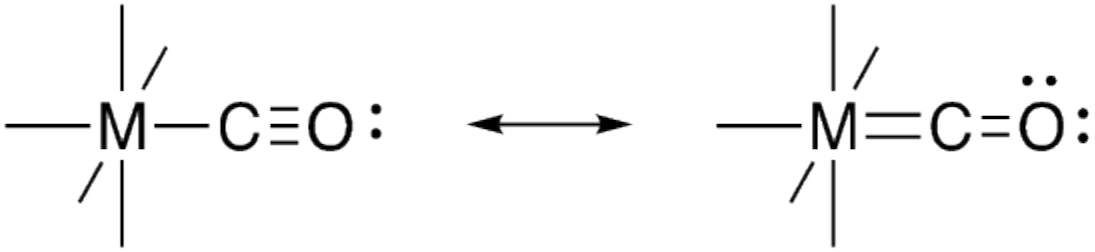


Let's consider the consequences of pi bond formation using the molecular orbital interaction diagram. This time we're just considering lone pairs on three ligands that could donate to the three different d orbitals of appropriate symmetry: the d_{xy}, d_{yz}, and d_{xz}. We get a bonding and an antibonding combination, but the three ligand pairs all go down in energy. As long as there are fewer than six d orbitals there is a net decrease in energy. Just like before, when these orbitals combine, the bonding combination has more ligand character whereas the antibonding combination has more metal character. The key change in terms of the frontier orbitals is that the d orbital splitting becomes smaller than in the case of the simple sigma bond donor.



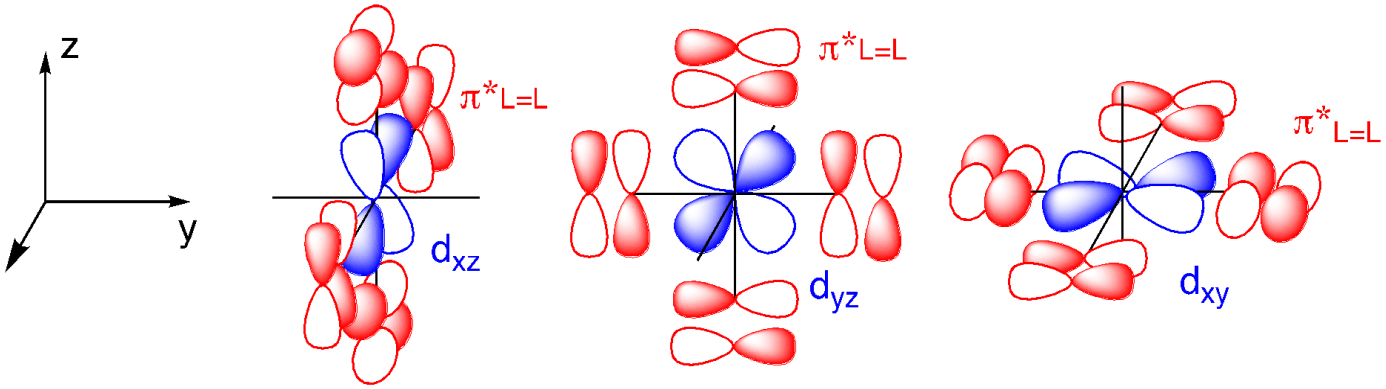
Ligand-to-metal donation is just one way to make a metal-ligand double bond. In those cases in which the metal has d electrons, the double bond could also be formed by donation from the metal to the ligand. The d electrons are most likely to occupy the d_{xy}, d_{xz}, and d_{yz}, as those orbitals are the lowest available ones. Those are the same orbitals that were involved in π bonding in ligand-to-metal donation. In addition to d electrons, there must also be an acceptor orbital on the ligand. That is to say, there

must be an empty orbital on the ligand with π symmetry. Instead of a lone pair, this acceptor takes the form of a π* orbital on the ligand. That means there has to be a π bond between the donor atom and a second atom within the ligand. Carbon monoxide is the classic example of such a ligand.

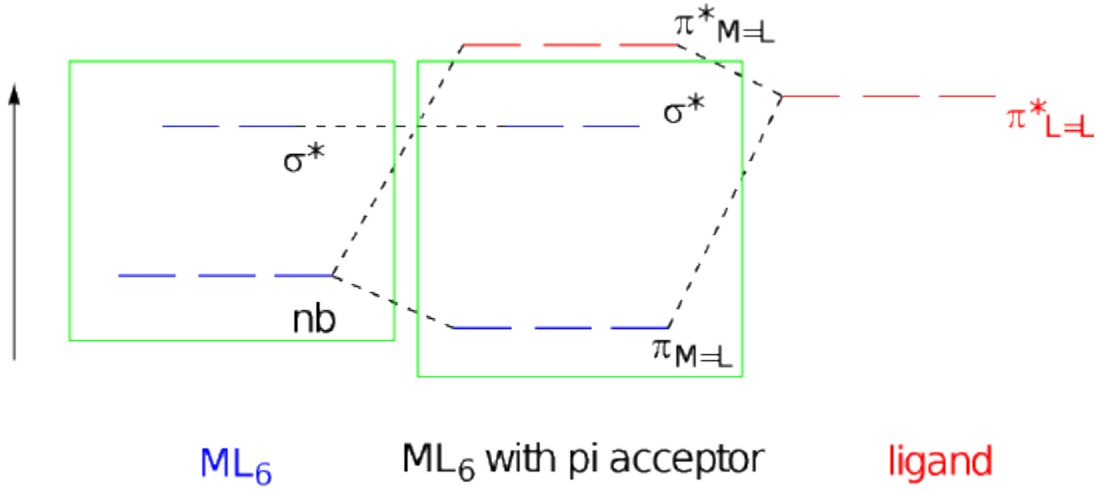


Metal-to-ligand π donation has the effect of breaking a π bond in the ligand because of the fact that electrons are donated into a ligand π* orbital. In terms of Lewis structures, this looks like an interaction that would strengthen the metal-ligand bond but weaken bonds within the ligand itself. When a metal π donates into a carbon monoxide, populating the CO π* orbital, the CO bond gets weaker.

Because we are still looking at π bond formation, the orbital pictures look somewhat similar to the ones for ligand-to-metal π donation, but with π* molecular orbitals instead of p atomic orbitals.



This time, the relevant ligand orbitals are higher in energy than the metal orbitals because they are antibonding. Antibonding orbitals are typically higher in energy than atomic orbitals. That means that when we construct orbital combinations from these pairs, the metal-ligand pi bonding orbital has more metal character. Conversely, the metal-ligand pi antibonding orbital has more ligand character. If there are any d electrons, they will drop into a lower energy well through formation of the pi bond. The ligand π* molecular orbitals are raised in energy, but that change has no energetic consequences since there aren't any electrons there.



In contrast to ligand-to-metal pi bond donation, metal-to-ligand pi bond formation has the effect of increasing the d orbital splitting. That gives us three different magnitudes of d orbital splitting for three different categories of ligand. The splitting follows the order pi donors < sigma donors < pi acceptors, at least as a rough trend; individual ligands may deviate from this trend for other reasons, such as the strength of sigma donation.

Group Theory as a Tool in Ligand Field Theory

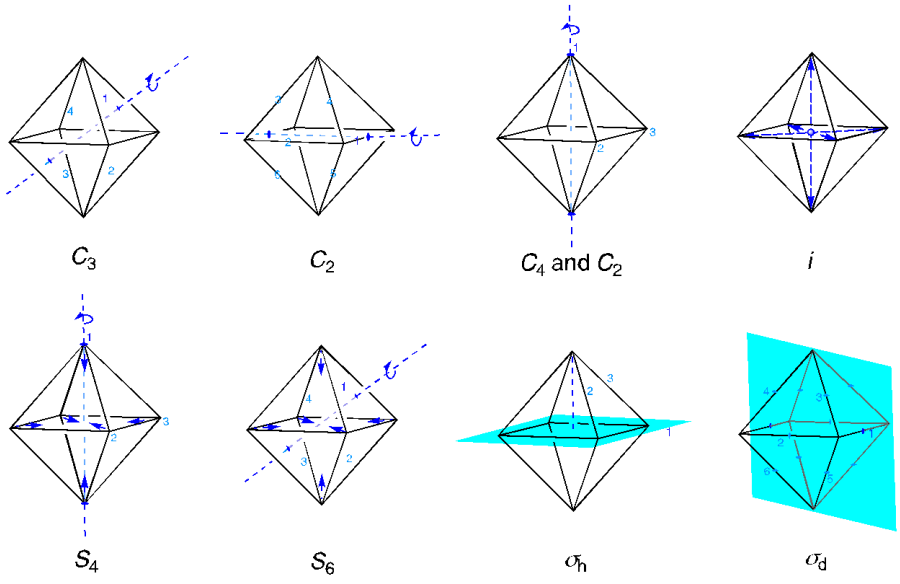
What if the orbital combinations are not obvious? What if you can't decide by inspection which ligand orbital would overlap with which metal orbital? There is a more general method of evaluating these things using group theory. We should use that approach for the octahedral geometry, because we already have a concrete example of what that should look like. We can use our knowledge of that outcome to build confidence in our results from group theory. Group theory may be a newer approach to us, and so it will be helpful to validate the results.

To get started, we are going to need a character table for an octahedral geometry, and we will need to consider how the bonding orbitals behave under the symmetry operations of this group. You can brush up on point groups and symmetry here.1

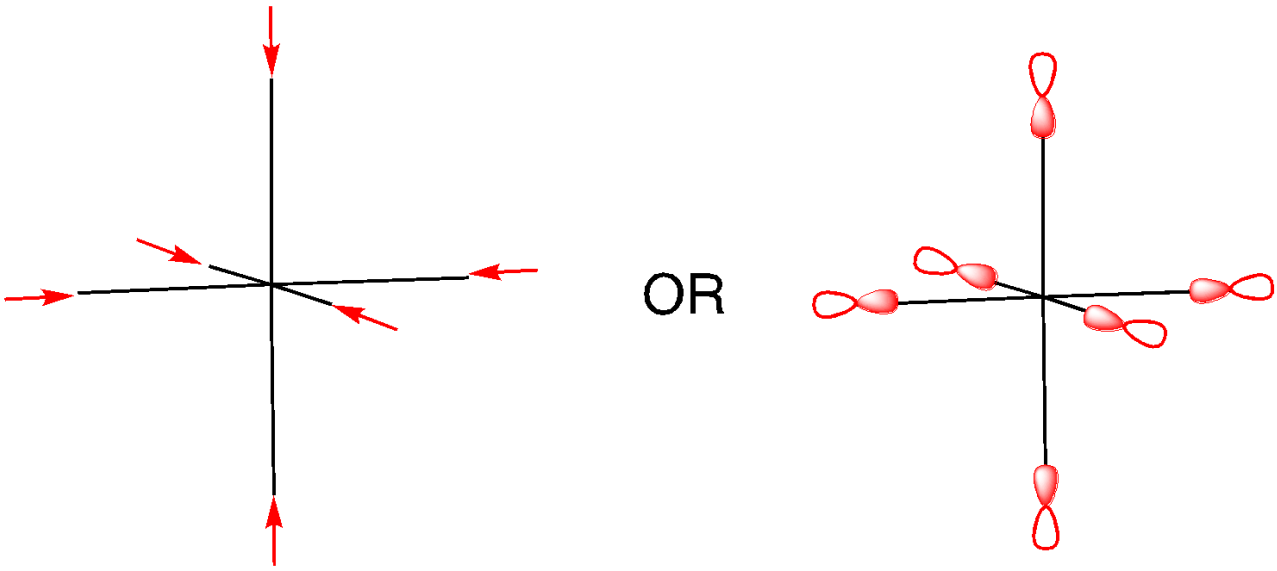
The top row of the character table for the octahedral point group organizes the symmetry operations and tells us how many of each operation we can find.

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 (= C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$3\sigma_d$

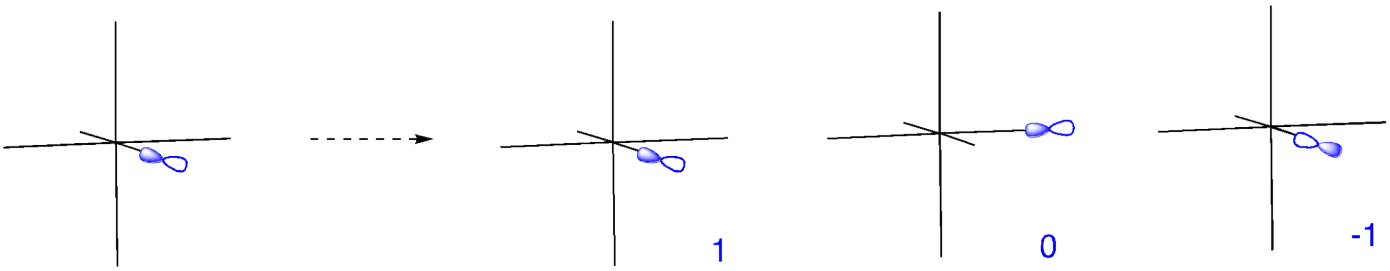
Apart from the identity element, there are ten additional symmetry elements in this point group. The C_3 axis passes through the four pairs of opposite faces of the octahedron. We can rotate by either 120 degrees or 240 degrees, making a total of eight operations. Six different C_2 axes pass through opposite edges of the octahedron. Additional C_2 axes are coincident with the C_4 axis passing through opposite corners of the octahedron (because $C_2 = C_4^2$, but not C_4^1 or C_4^3). There is an inversion center at the position of the metal ion. That inversion element makes possible an S_4 axis coincident with the C_4 axis and an S_6 axis coincident with the C_3 axis. Finally, there are two sets of mirror planes, one set in the equatorial planes and one set bisecting the faces of the octahedron.



We can use the character table to determine appropriate orbitals for bonding with the ligands. A set of vectors is often used for this purpose but p orbitals can be used just as well. We consider how each of the p orbitals will change under a particular symmetry element.



Has a p orbital remained in place, unchanged? That counts as 1. Has it moved into an entirely different position? That counts as 0. Has it remained in place, but with the opposite orientation? That counts as -1.



Looking at each of the symmetry elements gives us a reducible representation.

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 (= C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$3\sigma_d$
Γ	6	0	0	2	2	0	0	0	4	2

If we look at the complete character table, we can find the irreducible representations that this reducible representation is composed of.

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 (= C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$3\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1		
E_g	2	-1	0	0	2	2	0	-1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1		(xz, yz, xy)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1		
E_u	2	-1	0	0	2	-1	0	1	-2	0		

T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(*x*, *y*, *z*)	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1		

We find that $\Gamma = A_{1g} + T_{1u} + E_g$. If we add together the characters for each of the symmetry elements in those three representations, we get the characters in our reducible representation for the ligand p orbitals.

The A_{1g} representation corresponds to the metal s orbital. The T_{1u} representation corresponds to the three metal p orbitals. The E_g representation corresponds to two of the d orbitals: $2z^2 - x^2 - y^2$ (usually abbreviated as z^2) and $x^2 - y^2$. The other three d orbitals (d_{xy}, d_{xz}, and d_{yz}) have T_{1u} symmetry and are not a match for the set of ligand orbitals that we examined. This is exactly the outcome that we established by looking at metal orbitals and ligand orbitals and deciding which ones would overlap. The match between the two approaches should provide some confidence about the use of character tables to make decisions about symmetry-appropriate bonding.

References

(1) Point Groups https://chem.libretexts.org/@go/page/269925 (accessed Jul 2, 2021).

Example 10.3.1.1

The formula for decomposing a reducible representation is based on taking the dot product and normalizing:

$$ai = 1hQN \bullet \chi(R) \bullet \chi(R)Q$$

in which ai is the number of times the irreducible representation appears in the reducible representation; *h* is the order of the point group (the total number of symmetry operations); *N* is the number of operations for a given symmetry element, *Q*; *χ(R)*is the character of the reducible representation and *χ(R)*is the character of the irreducible representation.

Use the formula to confirm the finding that, for sigma bonding in an octahedral geometry:

$$\Gamma = A_{1g} + T_{1u} + E_g.$$

Solution

ai = 1h QN· χ(R)·χ(R)Q

A_{1g}: ai = 148 [1·6·1+8·0·1+6·0·1+6·2·1+3·2·1+ 1·0·1+6·0·1 + 8·0·1+3·4·1+6·2·1] = 148 (6+12+ 6+12+12)= 148·48=1

A_{2g}: ai = 148 [1·6·1+8·0·1+6·0·(-1)+6·2·(-1)+3·2·1+ 1·0·1+6·0·(-1) + 8·0·1+3·4·1+6·2·(-1)] = 148 (6-12+ 6+12-12)= 148·0=0

E_g: ai = 148 [1·6·2+8·0·(-1)+6·0·0+6·2·0+3·2·2+ 1·0·2+6·0·0 + 8·0·(-1)+3·4·2+6·2·0] = 148 (12+12+ 24)= 148·48=1

T_{1g}: ai = 148 [1·6·3+8·0·0+6·0·(-1)+6·2·1+3·2·(-1)+ 1·0·3+6·0·1 + 8·0·0+3·4·(-1)+6·2·(-1)] = 148 (18+12- 6-12-12)= 148·0=0

T_{2g}: ai = 148 [1·6·3+8·0·0+6·0·1+6·2·(-1)+3·2·(-1)+ 1·0·3+6·0·(-1) + 8·0·0+3·4·(-1)+6·2·1] = 148 (18-12- 6-12+12)= 148·0=0

A_{1u}: ai = 148 [1·6·1+8·0·1+6·0·1+6·2·1+3·2·1+ 1·0·(-1)+6·0·(-1) + 8·0·(-1)+3·4·(-1)+6·2·(-1)] = 148 (6+12+ 6-12-12)= 148·0=0

A_{2u}: ai = 148 [1·6·1+8·0·1+6·0·(-1)+6·2·(-1)+3·2·1+ 1·0·(-1)+6·0·1 + 8·0·(-1)+3·4·(-1)+6·2·1] = 148 (6-12+ 6-12+12)= 148·0=0

E_u: ai = 148 [1·6·2+8·0·(-1)+6·0·0+6·2·0+3·2·2+ 1·0·(-2)+6·0·0 + 8·0·1+3·4·(-2)+6·2·0] = 148 (12+12- 24)= 148·0=0

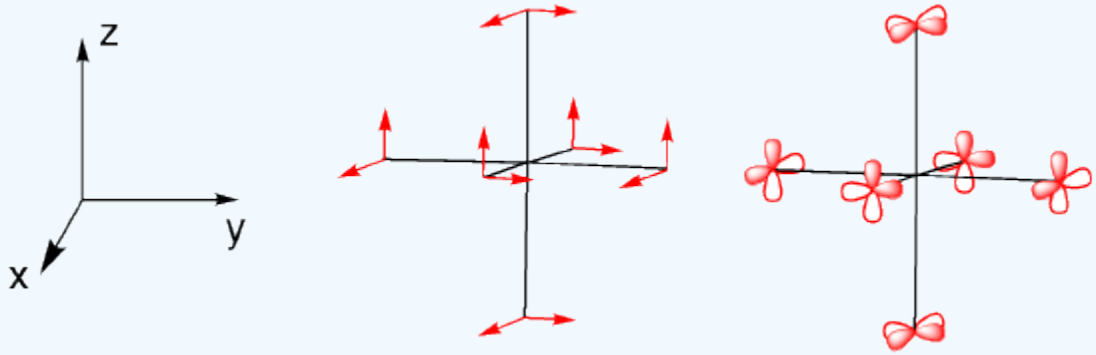
T_{1u}: ai = 148 [1·6·3+8·0·0+6·0·(-1)+6·2·1+3·2·(-1)+ 1·0·(-3)+6·0·(-1) + 8·0·0+3·4·1+6·2·1] = 148 (18+12- 6+12+12)= 148·48=1

T_{2u}: ai = 148 [1·6·3+8·0·0+6·0·1+6·2·(-1)+3·2·(-1)+ 1·0·(-3)+6·0·1 + 8·0·0+3·4·1+6·2·(-1)] = 148 (18-12- 6+12-12)= 148·0=0

$$\Gamma = A_{1g} + T_{1u} + E_g.$$

Example 10.3.1.1

Determine the reducible representation for the symmetry of the pi-bonding orbitals in an octahedral geometry. You can use simple vectors to represent the bias of the p orbitals.



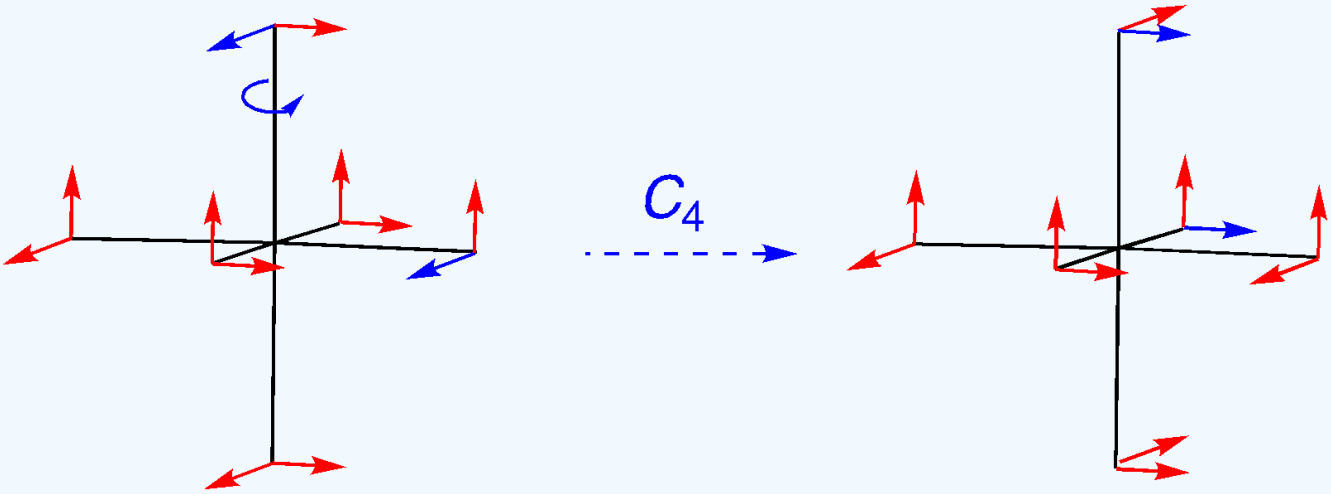
Solution

E: All 12 vectors remain in same place in same orientation. The character is 12.

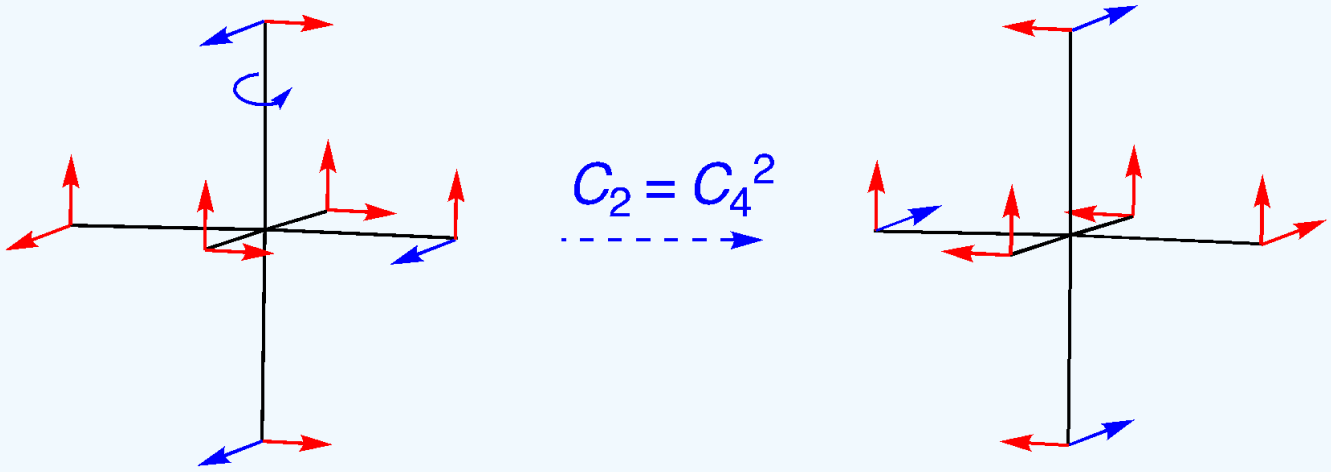
C_3: An off-axis rotation, so all vectors have moved. The character is 0.

C_2: An off-axis rotation, so all vectors have moved. The character is 0.

C_4: An on-axis rotation, but the vectors are off-axis. Note how the labeled vectors make the movement out of position clear. The character is 0.

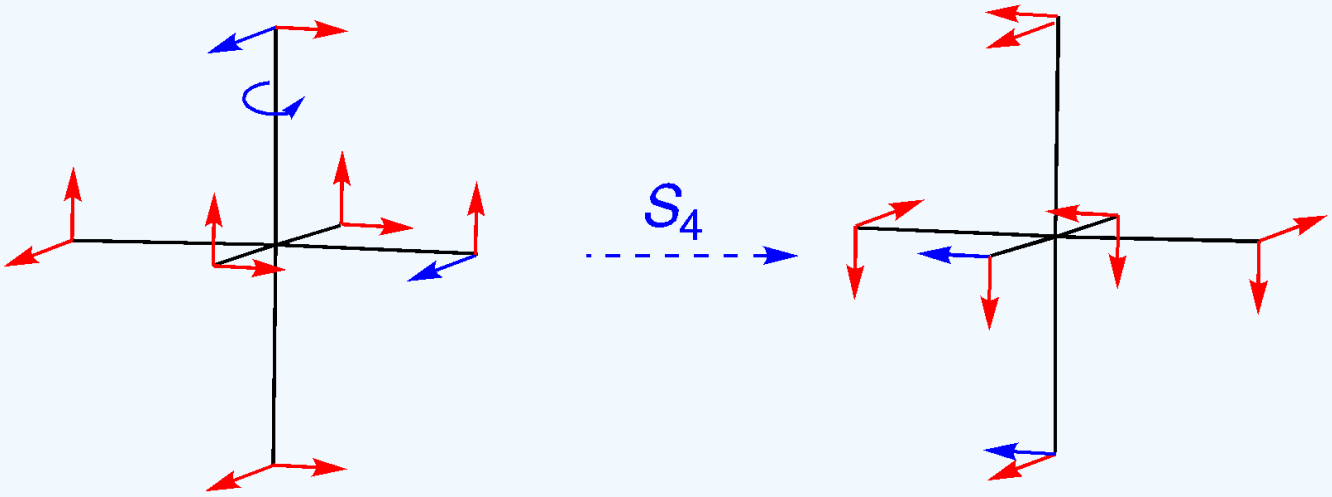


C_2 (= C_4^2): An on-axis rotation, but this time the four vectors located along the rotational axis just switch bias. The others move out of position. The character is -4.



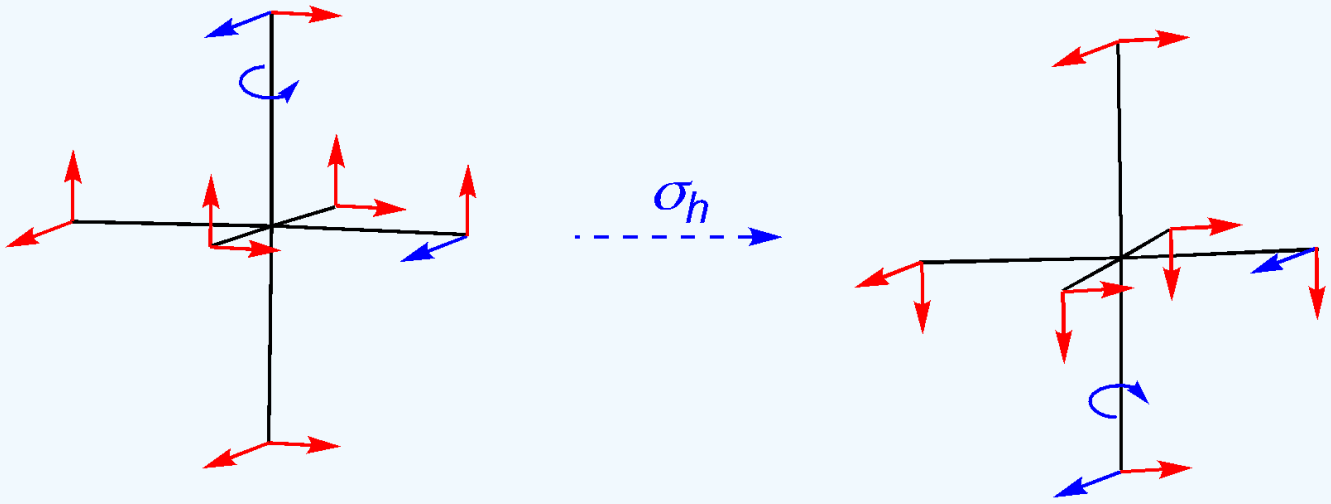
i: All 12 vectors move to the opposite side of the structure. The character is 0.

S_4: An on-axis rotation, followed by inversion. Note how the labeled vectors make the movement out of position clear. The character is 0.



S_6: An off-axis rotation, so all vectors have moved. The character is 0.

σ_h: Four vectors change position (character is 0); four vectors remain in position and keep original bias (character is 4); four vectors remain in position and switch bias (character is -4); net character is 0.



σ_d: An off-axis reflection, so all vectors have moved. The character is 0.

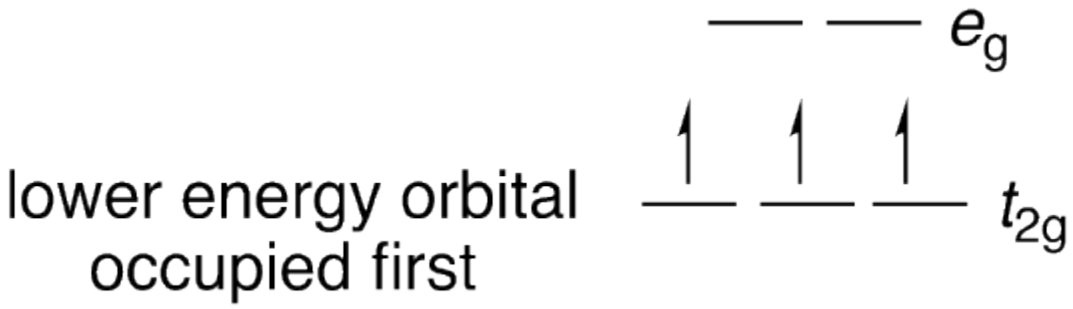
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 (= C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$3\sigma_d$
Γ	12	0	0	0	-4	0	0	0	0	0

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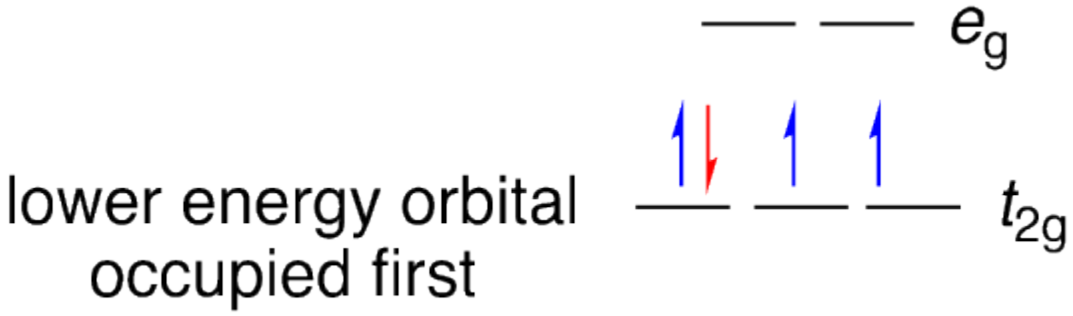
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10.3.2: Orbital Splitting and Electron Spin

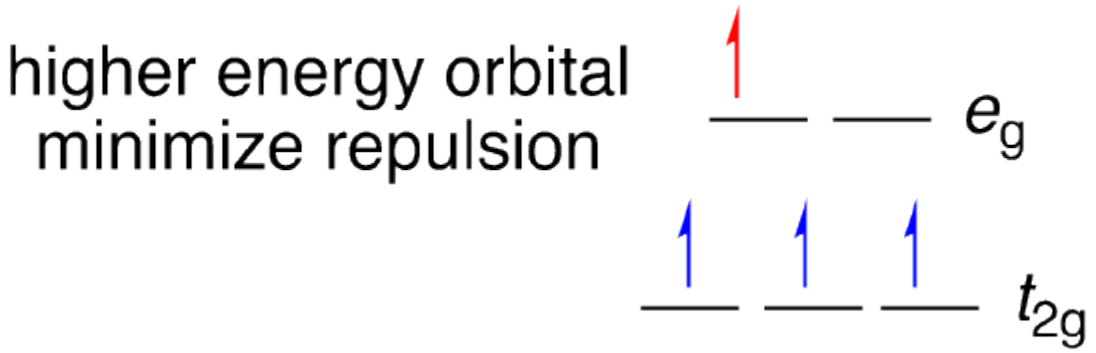
Once we have a d orbital splitting diagram for a particular geometry of a complex, we can populate the diagram with the known number of d electrons for a specific metal ion. If the complex is octahedral and the metal ion has 1, 2, or 3 d electrons, then the electrons will simply go in the lower level, the t_{2g} orbitals. For the d^3 case, one electron will occupy each orbital, with parallel spins.



What about a fourth electron? If the metal ion has a d^4 configuration, we could imagine two situations. The electron may also occupy one of the t_{2g} orbitals, which lie at lower energy. To do so, the fourth electron must be spin-paired with the other occupant of that orbital.



That's the low-spin configuration. The fourth electron has gone into the lower possible orbital rather than the higher possible one. Alternatively, the fourth electron could occupy one of the e_g orbitals. It would be at a higher energy level, but it would avoid that repulsive interaction with the other electron in the t_{2g} orbital. That would be the high-spin case. The fourth electron has gone into the higher possible orbital rather than the lower one.



The terms "high-spin" and "low-spin" really refer to the net spin of the atom. Each electron has a spin of a certain magnitude, but spin is a vector quantity. If two spins are pointing in the same direction, they add together, so the overall spin of the atom increases. If two spins are pointing in opposite directions, they cancel out, so the overall spin of the atom decreases. Having

electrons paired in the same orbital leads to a lower spin for the atom.

The electron configuration of a d^4 metal ion in an octahedral complex depends broadly on two factors: the difference in energy between the t_{2g} and e_g levels (the octahedral field splitting, Δ_o) and the energy associated with pairing two electrons in the same orbital. We have already looked at some of the factors that influence the field splitting, so let's start by looking at that factor.

It is useful to be aware of some general trends in Δ_o. First, comparison between Δ_o measured for +3 cations and for +2 cations of the first-row transition metals manganese, iron, and cobalt shows that charge exerts a significant influence. The higher the charge on an ion, the larger Δ_o becomes. These examples are illustrated in Table 1.

Table 1. Comparison of Octahedral Field Splitting Between M(II) and M(III) Ions[1]

Complex	Δ_o (cm^{-1})	Complex	Δ_o (cm^{-1})
$Cr(OH_2)_6^{2+}$	14,000	$Cr(OH_2)_6^{3+}$	17,600
$Mn(OH_2)_6^{2+}$	7,500	$Mn(OH_2)_6^{3+}$	21,000
$Fe(OH_2)_6^{2+}$	10,000	$Fe(OH_2)_6^{3+}$	14,000

In each case, the M(III) ion has an octahedral field splitting that is significantly larger than the corresponding value in the M(II) case. However, comparisons of the field splitting between metals in different columns is complicated, with no simple trend.

Second, Δ_o is much larger for second-row than for first-row metals of the same group, as shown in Table 2. The value of Δ_o is even larger for third-row transition metals than second-row transition metals. As a result, transition metal ions from the second and third rows are usually low-spin. First-row transition metal ions, with their smaller Δ_o values, are often high spin, but they can also be low spin, and charge is an important factor in determining which case will occur.

Table 2. Comparison of Octahedral Field Splitting Between Ions from Different Periods of the Periodic Table[2]

Complex	Δ_o (cm^{-1})	Complex	Δ_o (cm^{-1})
$CoCl_6^{3-}$	Not available	$Co(NH_3)_6^{3+}$	23,000
$RhCl_6^{3-}$	20,300	$Rh(NH_3)_6^{3+}$	33,900
$IrCl_6^{3-}$	24,900	$Ir(NH_3)_6^{3+}$	Not available

Although the available data is limited here, second-row rhodium has a larger octahedral field splitting than first-row cobalt, and third-row iridium displays a larger field splitting than second-row rhodium. Note that these examples are compared using complexes with identical ligands.

The configuration of first-row transition metals is also strongly influenced by the ligands in the complex, indicated in Table 3. For a given ion, we would expect π-acceptors to give relatively large values of Δ_o, whereas σ-donors would give a smaller Δ_o and π-donors would give a smaller value still. There may be some overlap between these groups, because there are stronger and weaker π-acceptors, for example, or stronger and weaker σ-donors, but that is the general trend that we would expect.

Table 3. Comparison of Octahedral Field Splitting Between Ions from Different Periods of the Periodic Table[2]

Complex	Δ_o (cm^{-1})	Complex	Δ_o (cm^{-1})
$CrBr_6^{3-}$	Not available	$NiBr_6^{2-}$	7,000
$CrCl_6^{3-}$	13,600	$NiCl_6^{2-}$	7,300
$Cr(OH_2)_6^{3+}$	17,400	$Ni(OH_2)_6^{2+}$	8,500
$Cr(NH_3)_6^{3+}$	21,600	$Ni(NH_3)_6^{2+}$	10,800

Complex	Δ_o (cm^{-1})	Complex	Δ_o (cm^{-1})
$Cr(CN)_6^{3-}$	26,300	$Ni(CN)_6^{2-}$	Not available

Among the chromium complexes, the π-accepting cyanide gives a much larger value of Δ_o than the π-donating chloride, as expected from molecular orbital considerations. In both the chromium and nickel cases, the ammine ligand, a simple σ-donor, provides a larger splitting that the aquo ligand, which is a π-donor. We may not be able to make predictions about electron configuration based solely on the type of ligand, but generally we would expect that a complex with π-accepting ligandswould be more likely to be low-spin than a complex with π-donating ligands.

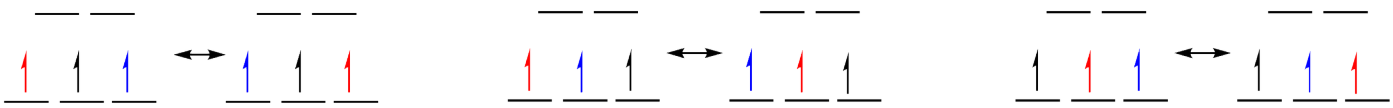
In addition to comparing ligands of different classes, we may also want to look at differences between ligands of the same class. Frequently, among σ-donors and π-donors, basicity of the ligand plays a valuable predictive role. For example, when coordinated to Ni(II), chloride results in a larger field splitting than bromide. Chloride is more basic than bromide, as shown by the pKa of the conjugate acids (pK_a = -6 for HCl vs. -9 for HBr), leading to stronger coordination in the case of chloride; that means a lower energy for the donor electrons but a higher energy for the σ* orbital compared to bromide coordination.

Let's take a look at the other factor that plays a role in determining the electron configuration: the pairing energy. We refer generally to the pairing energy as Π, but it actually has two components. Π_c is the coulombic portion of this energy. It arises from repulsion between two electrons that occupy the same region of space (the same orbital). Repulsion between the electrons causes energy to increase, so Π_c is a positive unit of energy.

The second component involves quantum mechanical exchange between like spins: Π_e is a stabilizing factor. When two electrons of like spin can exchange with each other, energy decreases: Π_e is a negative unit of energy. For example, in a d^2 octahedral metal, the two electrons are both at the t_{2g} level and have the same spin; that situation allows them to freely exchange with each other, which results in a decrease in energy.



In a d^3 system, the addition of just one more electron leads to a significant lowering of energy because the amount of exchange triples. Now, the electron in the first orbital can exchange with either the electron in the second or the third orbital. The electrons in the second and third orbitals can also exchange with each other. That makes a total of three possible exchanges.



These two factors, repulsion and exchange, contribute to an overall or total pairing energy. Some values of total pairing energy are shown in Table 4.

Table 4. Comparison of Total Pairing Energies Between M(II) and M(III) Ions[3]

Complex	Π (cm^{-1})	Complex	Π (cm^{-1})
$Mn(OH_2)_6^{2+}$	25,500	$Mn(OH_2)_6^{3+}$	28,000
$Fe(OH_2)_6^{2+}$	17,600	$Fe(OH_2)_6^{3+}$	30,000
$Co(OH_2)_6^{2+}$	22,500	$Co(OH_2)_6^{3+}$	21,000

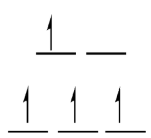
Like the field splitting, pairing energy is somewhat complex and is governed by more than one factor. However, it is worth pointing out that pairing energy is frequently (but not always) larger for more highly charged ions. For example, the pairing energy for both Mn(III) and Fe(III) are greater than the respective values for Mn(II) and Fe(II). That fact reflects the contraction of the more highly-charged ions. Confined to a smaller volume, repulsion between the electrons becomes greater.

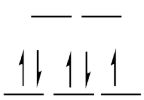
In general, notice that the magnitudes of these pairing energies are pretty large compared to many of the octahedral field splitting values in the previous tables. In particular, they are larger than most of the values of Δ_o for first-row transition metals. That's why many first-row ions are high spin: the energy required to pair electrons in a low-spin configuration is often greater than the energy required to place an electron in the e_g level. The pairing energies are not that large compared to Δ_o for second- and third-row transition metals, so ions of those metals are more likely to be low spin.

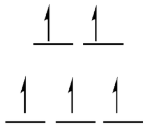
So, if we are comparing the energy difference between two configurations, we need to take into account both the energy difference between the two orbital energy levels and the energy difference resulting from spin pairing. That could include both differences in electron-electron repulsion and differences in energy because of exchange.

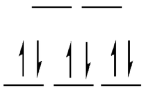
Problems

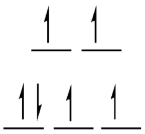
1. Demonstrate the exchanges possible in the following configurations.

a) 

b) 

c) 

d) 

e) 

2. Determine the difference in Π_c between the high spin and low spin configuration in each of the following cases:

a) d^4 b) d^5 c) d^6

3. Determine the difference in Π_e between the high spin and low spin configuration in each of the following cases:

a) d^5 b) d^6 c) d^7

4. Given the value of Δ_o and Π in each case, predict whether the complex will be high spin or low spin.

a) $[Mn(OH_2)_6]^{2+}$

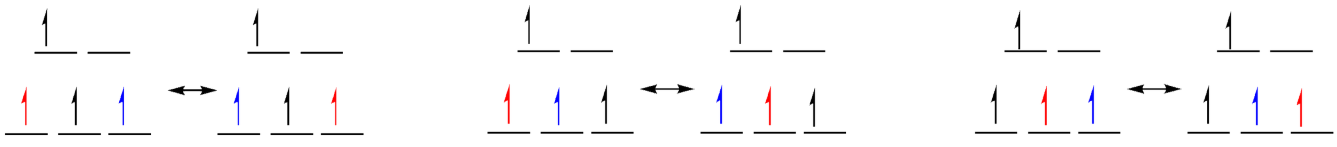
b) $[Mn(OH_2)_6]^{3+}$

c) $[Co(OH_2)_6]^{2+}$ (Δ_o = 14,000 cm^{-1})4

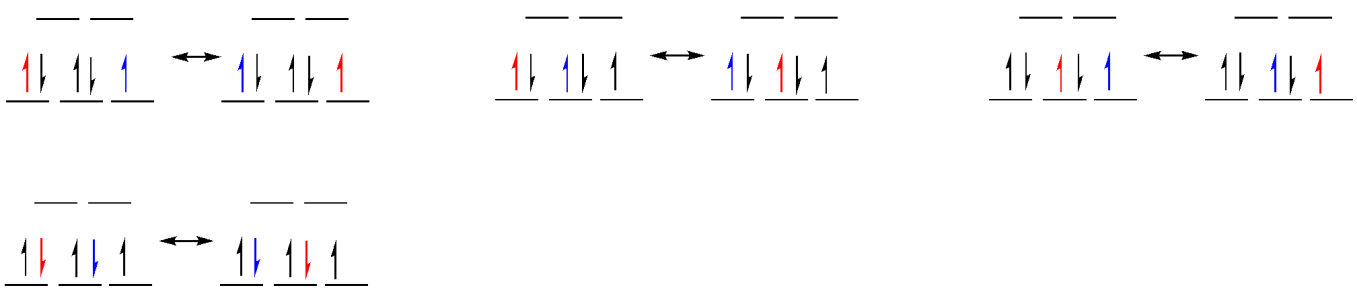
d) $[Co(OH_2)_6]^{3+}$ (Δ_o = 19,000 cm^{-1})4

Solutions

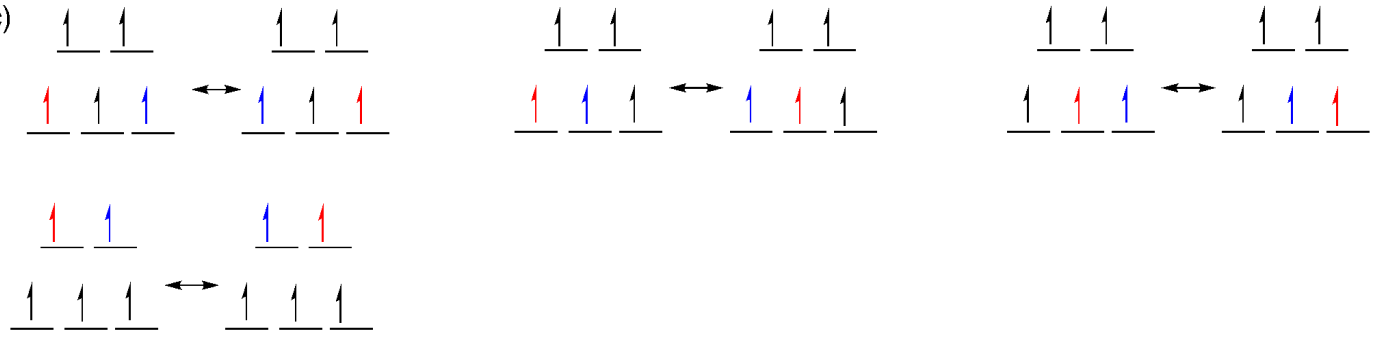
1.

a) 

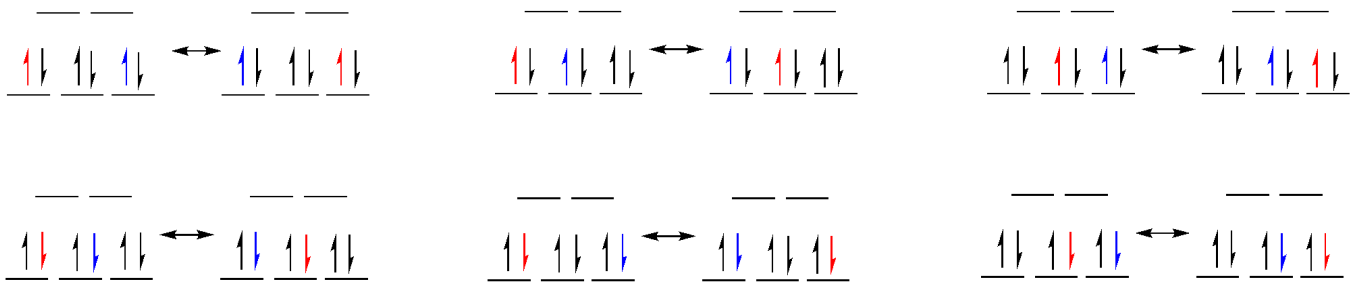
b)



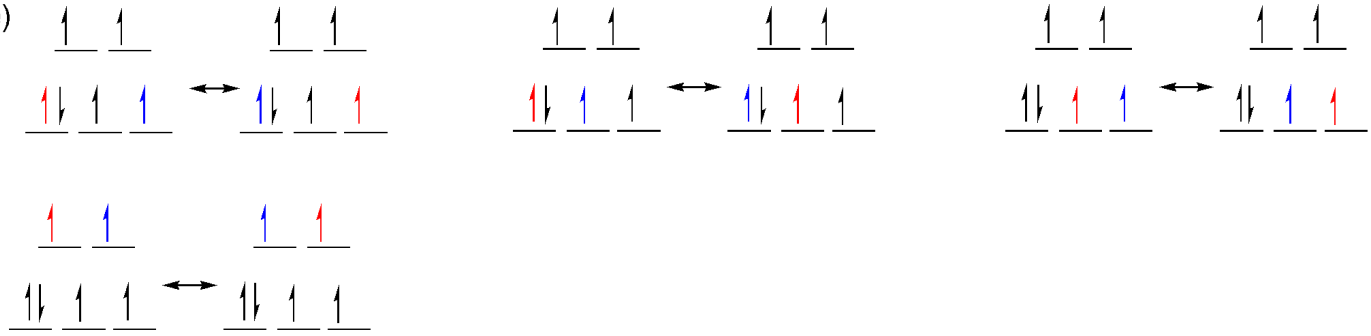
c)



d)

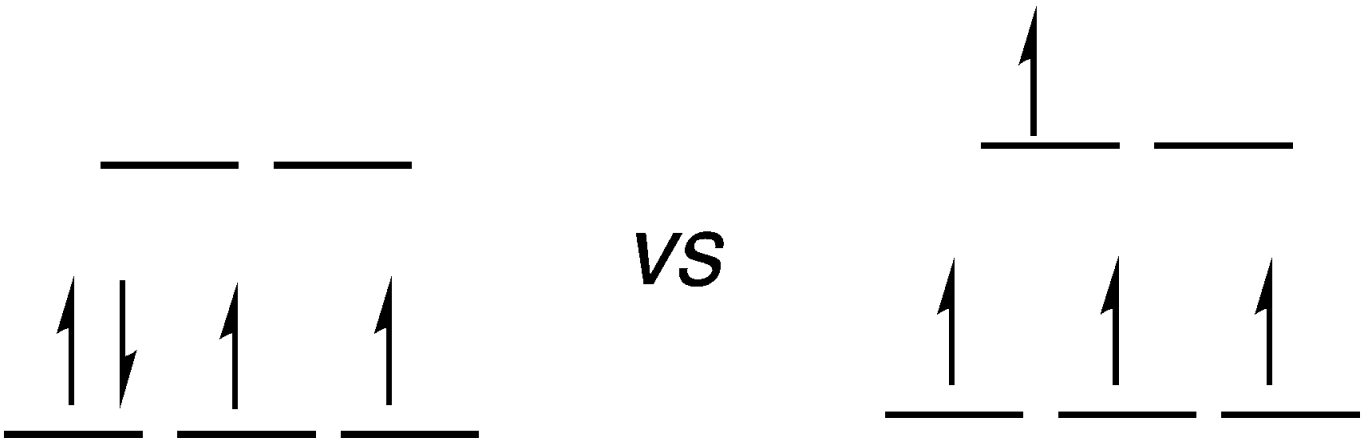


e)



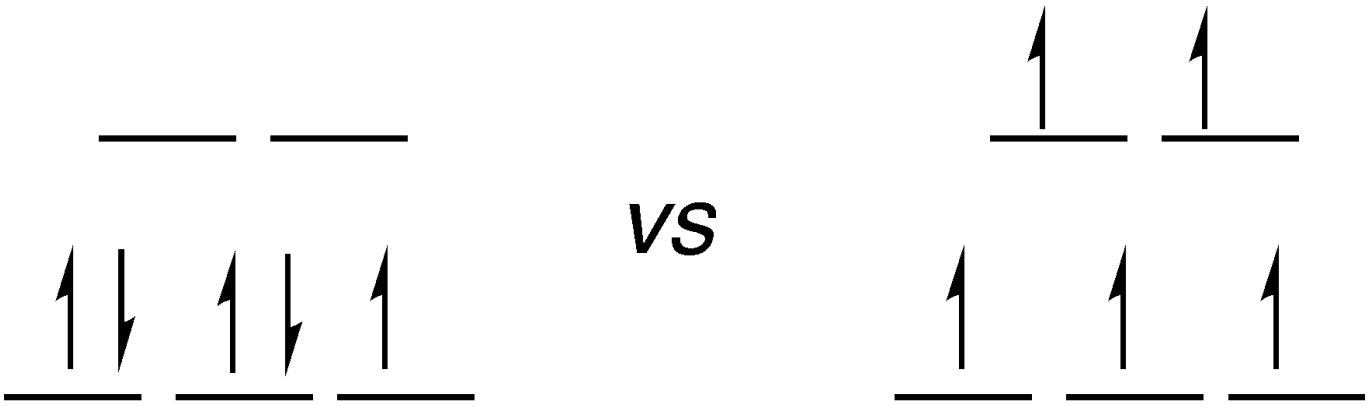
2. Determine the difference in Π_c between the high spin and low spin configuration in each of the following cases:

a) d^4



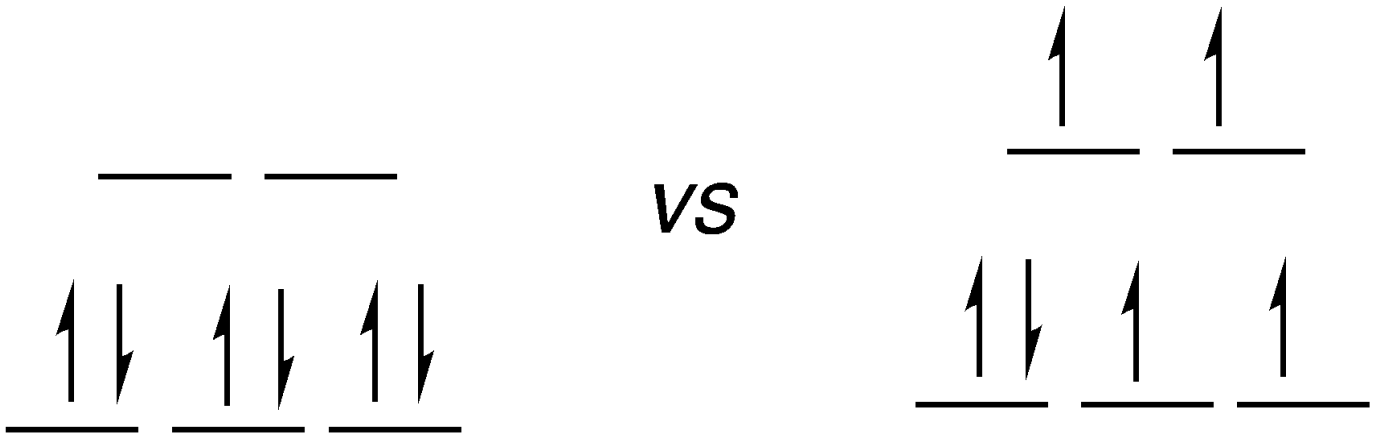
The difference is: $\Delta E = ls - hs = \Pi_c - 0 = \Pi_c$.

b) d^5



The difference is: $\Delta E = ls - hs = 2\Pi_c - 0 = 2\Pi_c$.

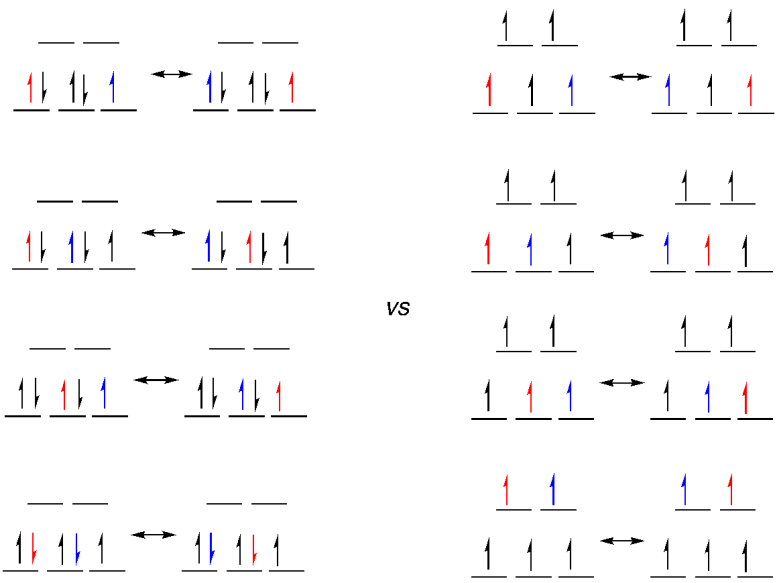
c) d^6



The difference is: $\Delta E = ls - hs = 2\Pi_c - 0 = 2\Pi_c$.

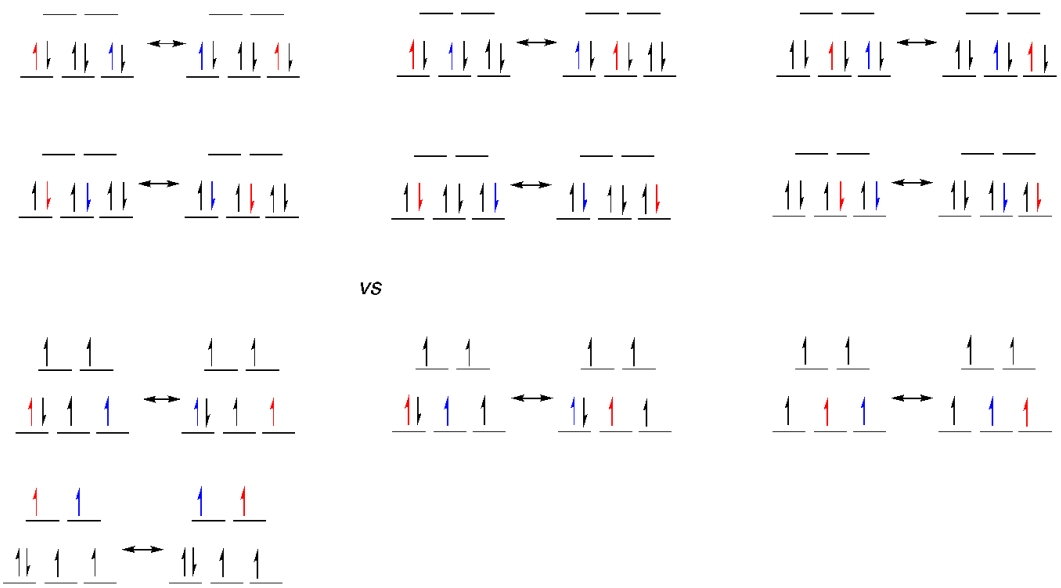
3. Determine the difference in Π_e between the high spin and low spin configuration in each of the following cases:

a) d^5



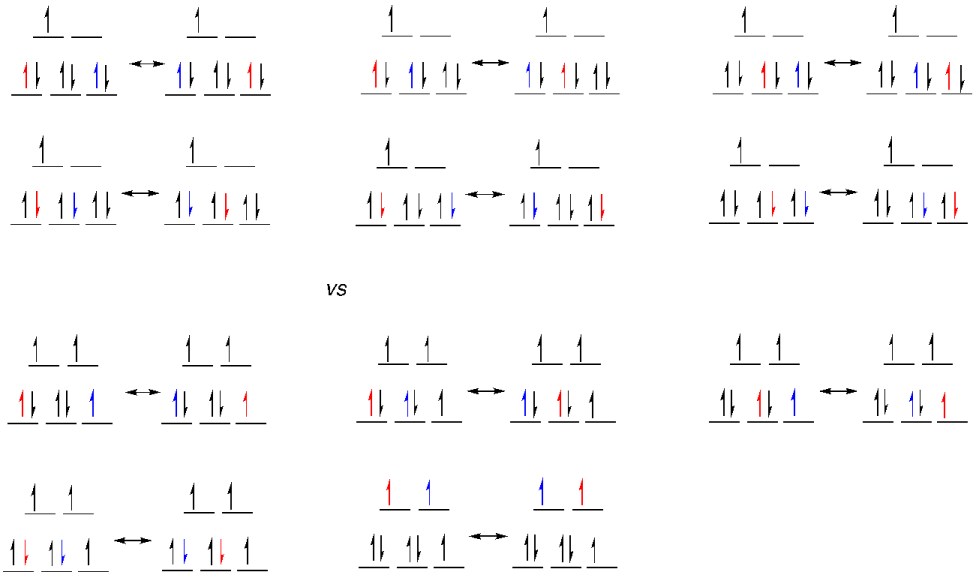
The difference is: ΔE = ls – hs = $4\Pi_e$ - $4\Pi_e$ = 0

b) d_6



The difference is: ΔE = ls – hs = $6\Pi_e$ - $4\Pi_e$ = $2\Pi_e$

c) d^7



The difference is: ΔE = ls – hs = $6\Pi_e$ - $5\Pi_e$ = Π_e

4. Given the value of Δ_o and Π in each case, predict whether the complex will be high spin or low spin.

a) $[Mn(OH_2)_6]^{2+}$

Δ_o = 7,500 cm^{-1} and Π = 25,500 cm^{-1}; because it costs more to pair electrons than to promote one, this complex will be high spin.

b) $[Mn(OH_2)_6]^{3+}$

Δ_o = 21,000 cm^{-1} and Π = 28,000 cm^{-1}; because it costs more to pair electrons than to promote one, this complex will be high spin.

c) $[Co(OH_2)_6]^{2+}$ (Δ_o = 10,000 cm^{-1})4

Δ_o = 10,000 cm^{-1} and Π = 22,500 cm^{-1}; because it costs more to pair electrons than to promote one, this complex will be high spin.

d) $[Co(OH_2)_6]^{3+}$ (Δ_o = 19,000 cm^{-1})4

Δ_o = 19,000 cm^{-1} and Π = 21,000 cm^{-1}; because it costs more to pair electrons than to promote one, this complex will be high spin, but note how similar the values are. Many Co(III) complexes are low spin.

References.

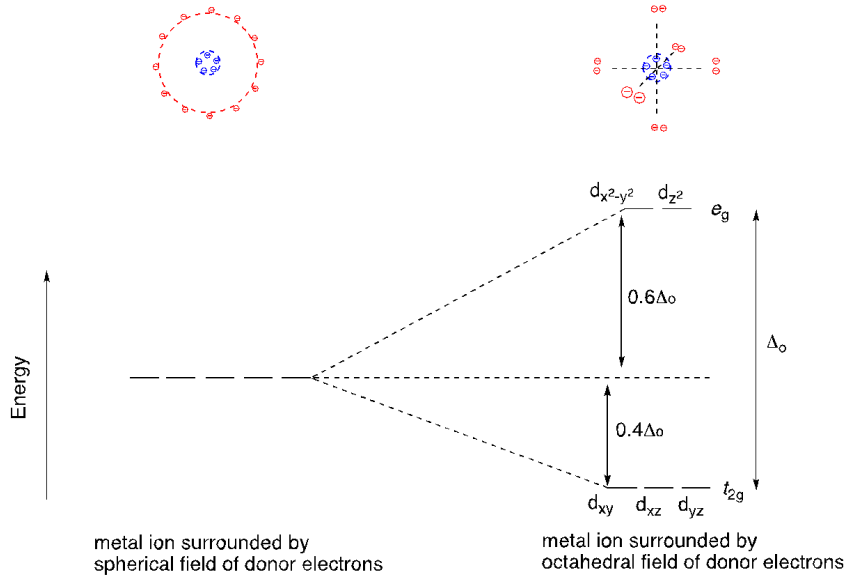
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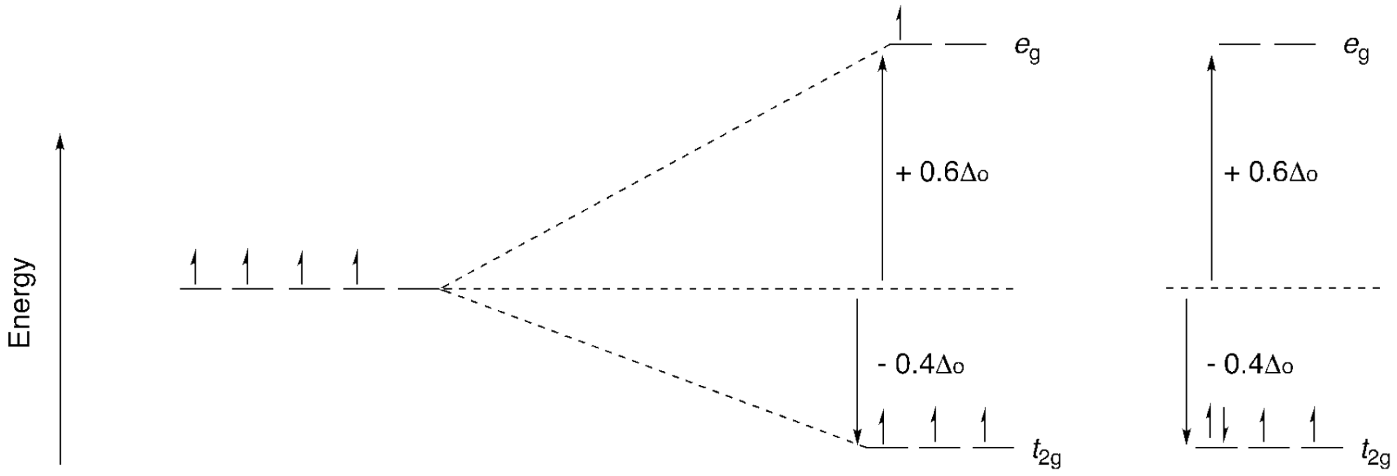
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10.3.3: Ligand Field Stabilization Energy

If we want to compare the stability of a particular electron configuration compared to the imaginary d electron configuration in a spherical electric field, we can calculate the ligand field stabilization energy. Remember, in crystal field theory, we compared the d electrons in a spherical field to the situation in which ligands approached in an octahedral geometry. The e_g level is destabilized by $0.6\Delta_o$ compared to undifferentiated d orbitals in a spherical field, whereas the t_{2g} level is $0.4\Delta_o$ lower in energy than the d orbitals in a spherical field.



Let's look at the case of a d^4 complex. That's an interesting case, because as we fill in the d electrons one by one, it is the first example in which there is the possibility of either a high spin or a low spin configuration. If we first consider the high-spin case, then we see that three of the electrons drop into the t_{2g} level and the last one goes into the e_g level.



The ligand field stabilization energy is the difference between energy in a spherical field and in an octahedral field. In the high spin d^4 case, that means three electrons are lower in energy and one is higher in an octahedral environment.

- High spin d^4:

$$\begin{aligned}\text{LFSE} &= [0.6(1)–0.4(3)]\Delta_o \\ &= [0.6–1.2]\Delta_o \\ &= -0.6\Delta_o\end{aligned}$$

For comparison, in the low spin case, all four of the electrons are lower in energy in the presence of the octahedral field.

- Low spin d^4:

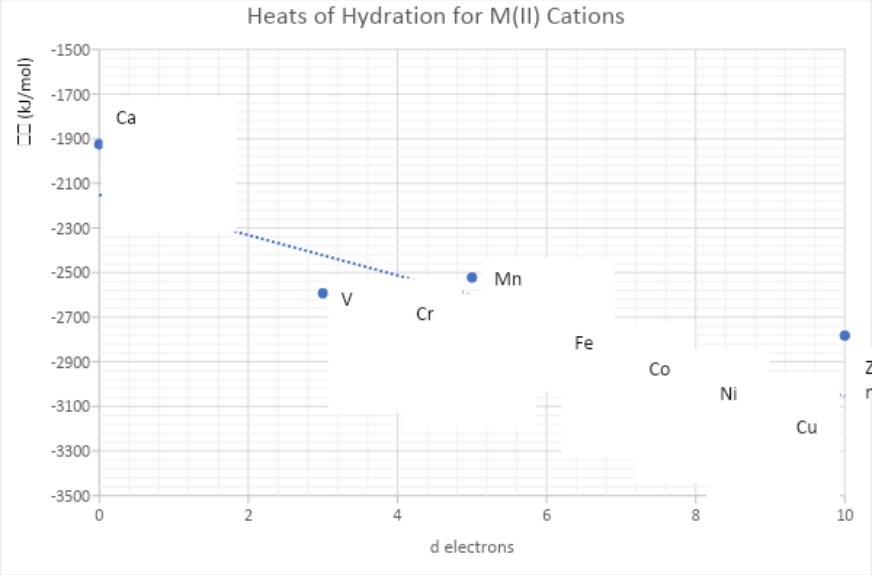
$$\begin{aligned}\text{LFSE} &= [0.6(0)–0.4(4)]\Delta_o \\ &= -1.6\Delta_o\end{aligned}$$

Of course, the ligand field stabilization energy isn't the only contributor to energetic differences between possible electron configurations. Pairing energy will also play a role, including Coulombic or repulsive terms as well as exchange terms. The total energy difference between a high spin and low spin configuration will compare those energies as well. For the d^4 case:

$$\begin{aligned}\Delta E(\text{low spin} - \text{high spin}) &= (-1.6\Delta_o + \Pi_c + 3\Pi_e) - (-0.6\Delta_o + 3\Pi_e) \\ &= -\Delta_o + \Pi_c\end{aligned}$$

One application of ligand field stabilization energy is found in the hydration energies of metal ions. As a first approximation, we might expect that the energy released when a bond is formed between a ligand and a metal ion would be related to Coulomb's Law. If we look at values for the hydration of gas-phase ions, we expect the energies of reaction to become more negative as we move across the transition metals from left to right. That increase in magnitude of the exothermicity of hydration reflects the periodic trend in sizes of the ions. Ions of the same charge get smaller as we go to the right because of the increasing number of protons in the nucleus. As the radius of the atom decreases, the energy released upon binding a ligand increases.

The following graph illustrates this general phenomenon for a series of M^{2+} ions. There are gaps in the graph where data was unavailable. Some of the early transition metals are rarely observed as divalent ions.

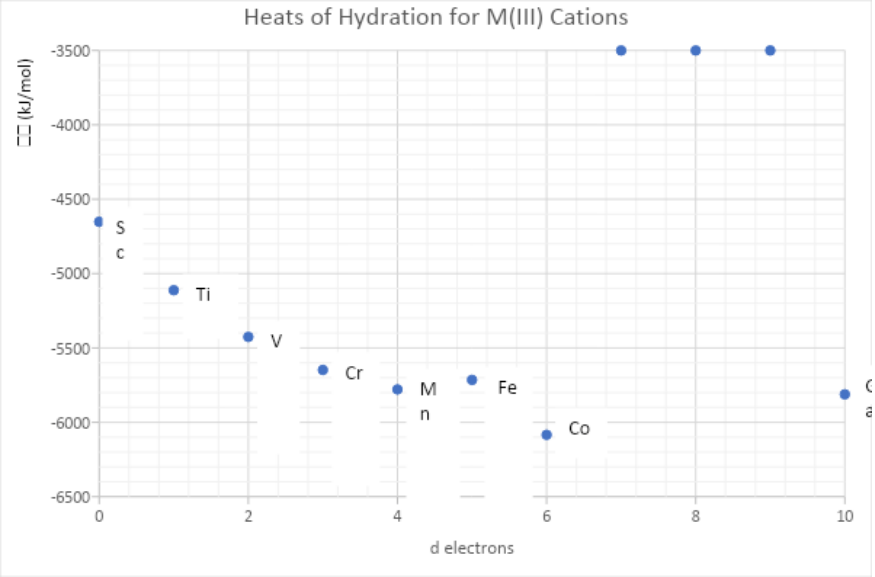


Overall, we can see a general progression towards more negative heats of hydration as we move across the series. That observation is consistent with Coulomb's Law. However, if we look carefully, we can see that some of the data points are a little higher compared to the rest (or a little lower, depending on your perspective). The higher data points occur at d^0, d^5 and d^{10} (Ca^{2+}, Mn^{2+} and Zn^{2+}). Assuming we are dealing with high spin configurations, which is often the case for the first row of transition metals, then these are exactly the cases in which we expect ligand field stabilization energy to be absent. The table below illustrates that point.

Table 3.3.1. Ligand Field Stabilization Energy for High Spin Configuration

Electron count (dn)	LFSE (Δo)
0	0
1	-0.2
2	-0.4
3	-0.6
4	-0.3
5	0
6	-0.2
7	-0.4
8	-0.6
9	-0.3
10	0

We can confirm that what we are seeing is related to the d electron count, rather than some intrinsic property of individual metals, by looking at a similar series of M^{3+} ions. Once again, we observe the overall agreement with Coulomb's Law, and we see that the d^0 cases display a lower heat of hydration than the others because of a lack of ligand field stabilization energy.



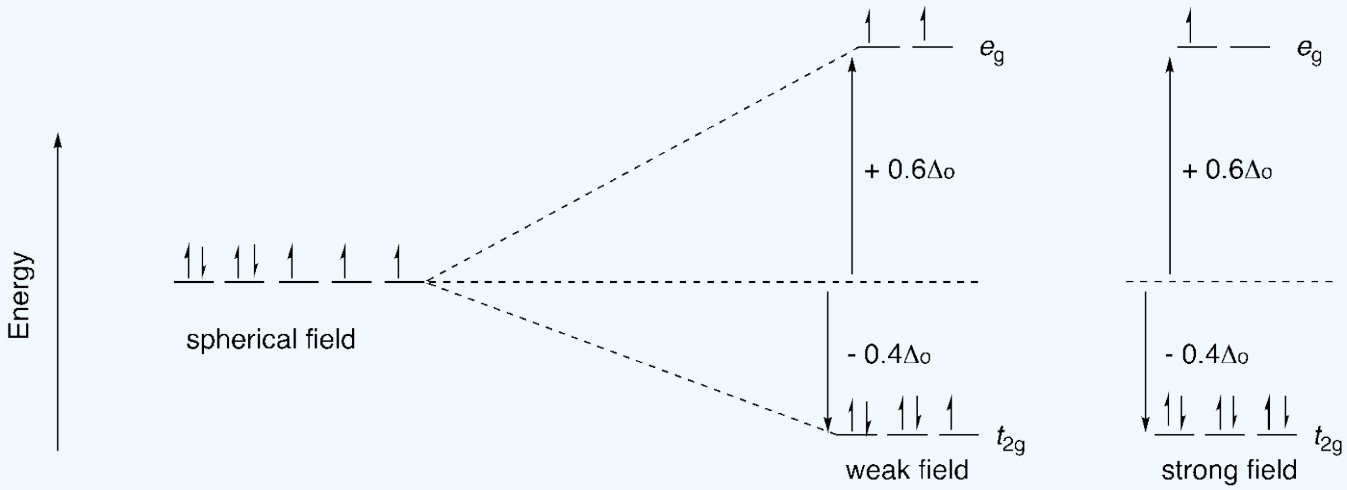
This time, Fe^{3+} is an outlier because it is d^5, rather than the d^4 Mn^{3+}. Again, some of the data is missing here because some of the later transition metals are rarely found as trivalent ions. Conversely, the ions that exhibit ligand field stabilization energies are depressed from the overall trend, displaying additional stabilization in an octahedral coordination environment.

Neither the hydration energies for the M^{2+} ions nor the hydration energies for the M^{3+} ions track perfectly with ligand field stabilization energies. There are a number of other factors that also impact these observed hydration energies, but they are beyond the scope of the current discussion. These factors include the nephelauxetic ("cloud-expanding") effect, in which interelectron repulsion in complexes can be lower than in free ions based on the degree of covalency in the complex.

Example 10.3.3.1

Draw a diagram showing the energetic differences between d^7 metal ions in a spherical field, a weak field octahedral environment, and a strong field octahedral environment.

Solution



Example 10.3.3.2

Show how you would calculate the ligand field stabilization energy in the following cases:

a. Low-spin d^5
b. High-spin d^5
c. Low-spin d^7
d. High-spin d^7

Solution

a. Low-spin d^5: LFSE = $[0.6\ (0) - 0.4\ (5)]\Delta_o = -2.0\Delta_o$
b. High-spin d^5: LFSE = $[0.6\ (2) - 0.4\ (3)]\Delta_o = [1.2 - 1.2]\Delta_o = 0\Delta_o$
c. Low-spin d^7: LFSE = $[0.6\ (1) - 0.4\ (6)]\Delta_o = [0.6 - 2.4]\Delta_o = -1.8\Delta_o$
d. High-spin d^7: LFSE = $[0.6\ (2) - 0.4\ (5)]\Delta_o = [1.2 - 2.0]\Delta_o = -0.8\Delta_o$

Example 10.3.3.3

Calculate the difference between low spin and high spin electronic configurations in the following cases:

a. d^5
b. d^7

Solution

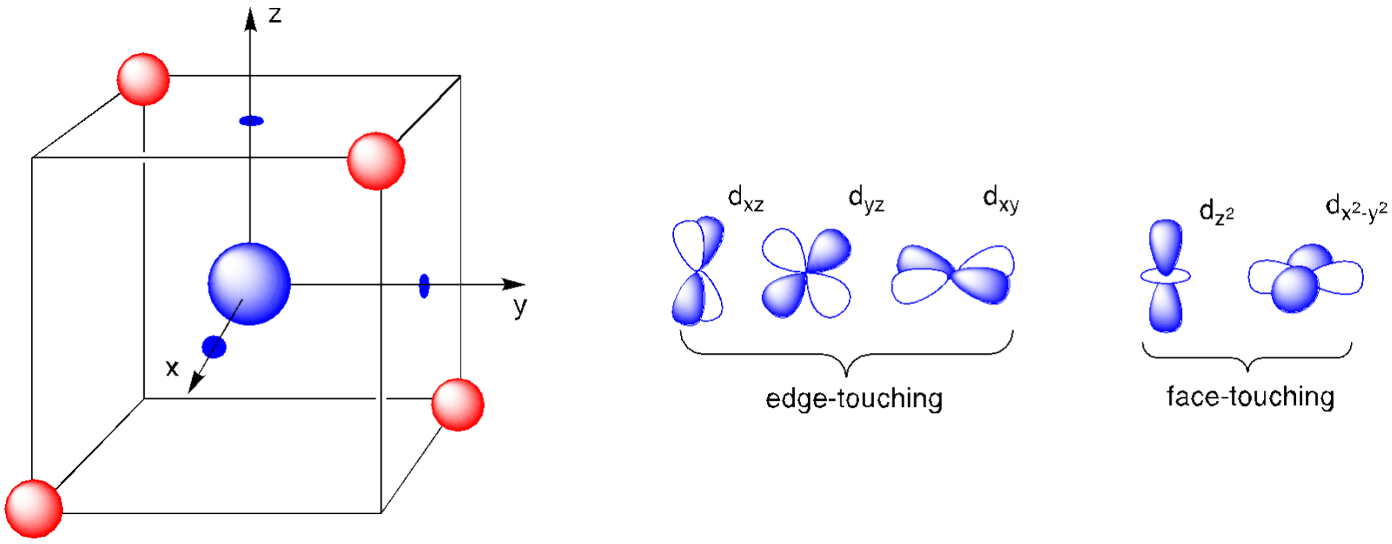
1. d^5: ΔE low spin – high spin = $(-2.0\Delta_o + 2\Pi_c + 4\Pi_e) - (0\Delta_o + 4\Pi_e) = -2\Delta_o$

2. d^7: ΔE low spin – high spin = $(-1.8\Delta_o + 3\Pi_c + 6\Pi_e) - (-0.8\Delta_o + 2\Pi_c + 5\Pi_e) = -\Delta_o + \Pi_c + \Pi_e$

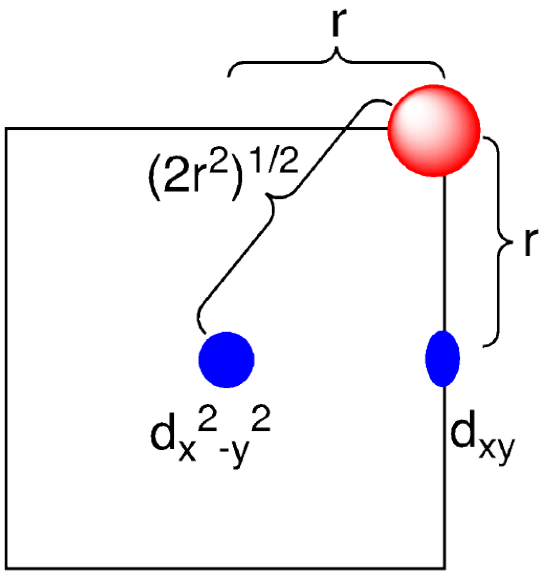
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10.3.4: Tetrahedral Complexes

Tetrahedral geometry is even more common in chemistry than square planar geometry. Assessing the orbital interactions in tetrahedral geometry is somewhat more complicated, however, and it is common to proceed directly to a group theory approach. Nevertheless, let's take a look at this geometry and see what we can determine through simple observation before we see the results from a more rigorous approach. To begin, it helps to know that a tetrahedral geometry is defined as having four atoms arranged at alternating corners of a cube around a central atom.



If we consider the orientation of the d orbitals, we find that they fall into two different groups. Although all five orbitals lie off-axis with respect to the ligands, some of them are pointed directly at the edges of the cube (d_{xy}, d_{xz}, d_{yz}) whereas the others point at the faces of the cube ($d_{x^2-y^2}$, d_{z^2}). The edge-touching orbitals lie a little closer to the ligands; we'll define this distance as *r*, which in this case is half the edge length of the cube. The face-touching orbitals are slightly farther away: based on the Pythagorean theorem, they are $r^2 + r^2 = 2\,r^2 = r^2$ away from the ligands.



Based on that simple observation, we might start to think about the dxy, dxz and dyz group as forming the antibonding orbitals upon interaction with the ligands. The dz2 and dx2-y2 would be left as non-bonding orbitals. This result would be exactly

the opposite of the octahedral case. We would therefore expect an orbital splitting diagram that is exactly the inverse of the octahedral one. Maybe the splitting between orbital levels would be a little smaller, though, because of the lack of direct overlap between the ligands and the metal orbitals. After all, even the closest set of metal orbitals don't point directly at the ligands like in the octahedral case.





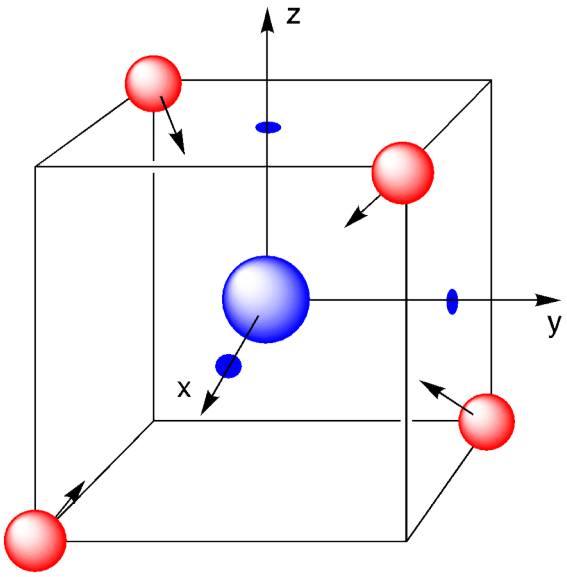
d_{xy}, d_{xz}, d_{yz} — — —

$d_{x^2-y^2}$, d_{z^2} — —

$d_{x^2-y^2}$, d_{z^2} — —

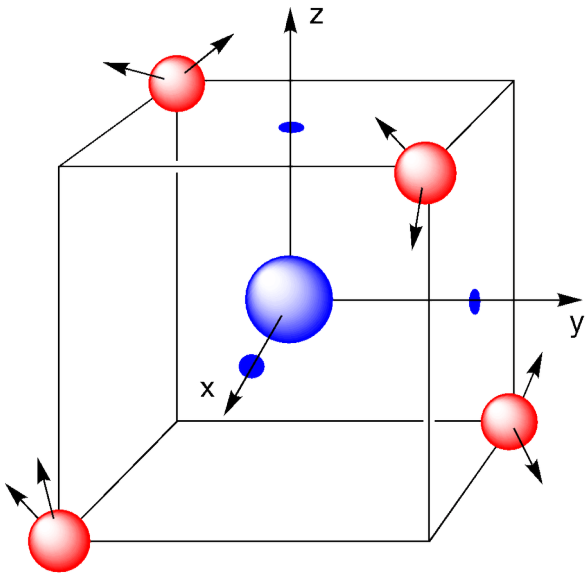
d_{xy}, d_{xz}, d_{yz} — — —

This supposition is confirmed through a group theory approach. We can use vectors pointing along the ligand-metal axes to examine sigma bonding, as shown below. We would subject these vectors to the symmetry transformations in the tetrahedral space group, T_d, shown in the table.



T_d	E	$8C_3$	$6C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)
Γ_σ	4	1	0	0	2		$A_1 + T_2$
Γ_π	8	-1	0	0	0		$E + T_1 + T_2$

That analysis leads to the reducible representation for sigma bonding, Γ_σ , shown in the table. This representation reduces to the irreducible representations, $A_1 + T_2$. The d orbitals represented here, the T_2 set, are indeed the d_{xy}, d_{xz} and d_{yz}. The non-bonding d orbitals are the E group, corresponding to d_{z^2} and $d_{x^2-y^2}$.



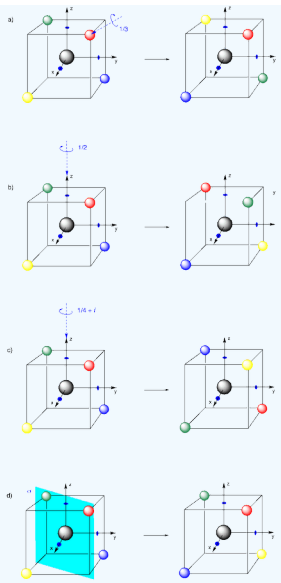
We can go further with the group theory approach and to determine the reducible representation for pi bonding, Γ_π , also shown in the table. Pi bonding is otherwise even more difficult to assess via simple inspection than was sigma bonding. The resulting representation reduces to $E + T_1 + T_2$. The d orbitals represented here include the expected d_{z^2} and $d_{x^2-y^2}$. Note, however, that they also include the d_{xy}, d_{xz}, and d_{yz} orbitals. That means that in the presence of a pi-donor ligand, the latter set are antibonding with respect to both sigma and pi bonding.

Example 10.3.4.1

Demonstrate these symmetry operations on the drawing of the tetrahedron within a cube shown above.

a. C_3
b. C_2
c. S_4
d. σ_d

Solution

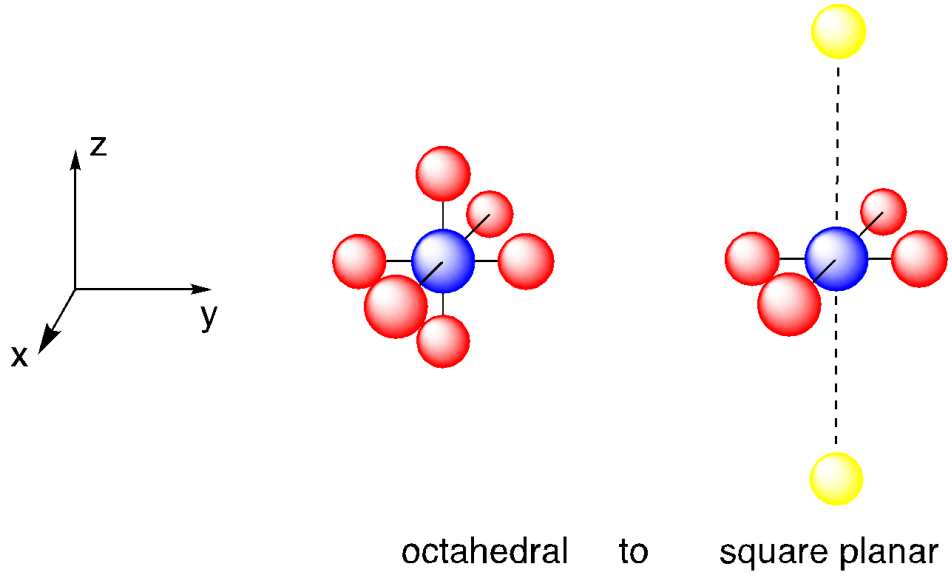


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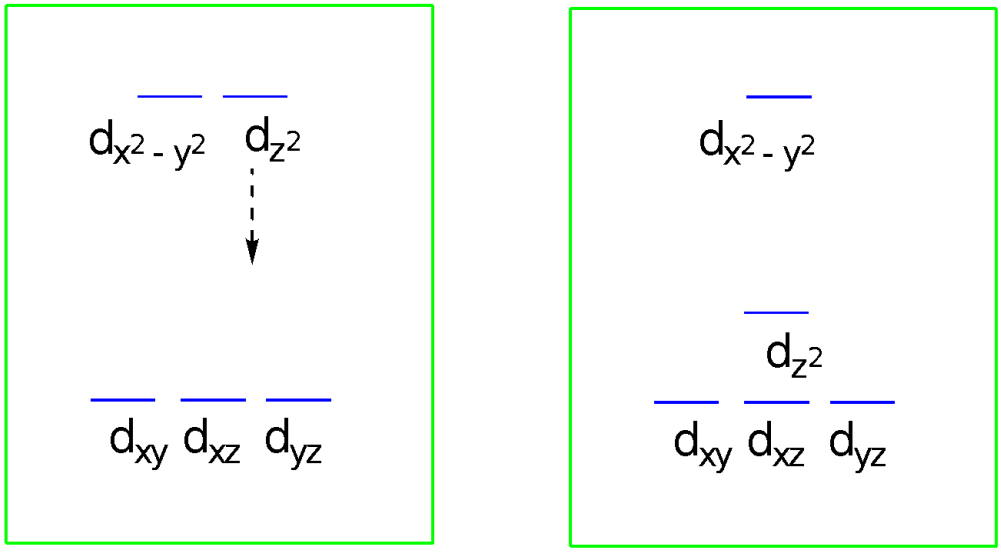
10.3.5: Square-Planar Complexes

Square planar geometry is much less common than octahedral, but square planar complexes assert their importance through their frequent appearance in key catalytic processes and other settings. Furthermore, having learned something about bonding in octahedral complexes, we can make some educated guesses about metal-orbital interactions in square planar complexes. Both geometries are nicely described by Cartesian coordinates and so it is relatively easy to draw comparisons between the two.

We can imagine how we might arrive at a square planar geometry simply by taking an octahedral geometry and removing two axial ligands. The four remaining equatorial ligands form a square planar complex.

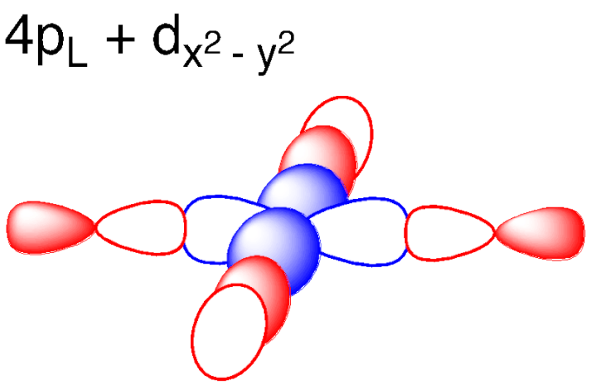


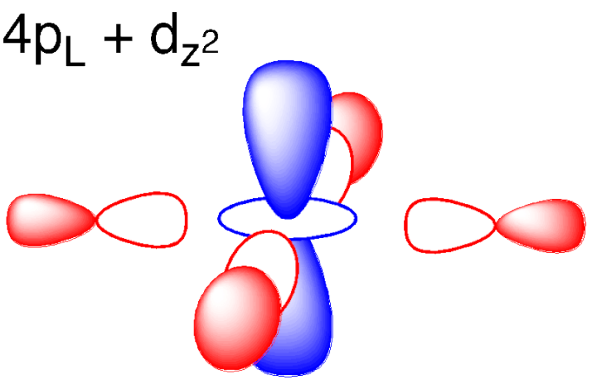
Since we already know something about the d orbital splitting diagram in an octahedral case, we can draw some rational conclusions about the consequence of this change. The axially-oriented d_{z^2} orbital drops in energy because it is no longer forming the antibonding combination with ligand orbitals along the z axis.



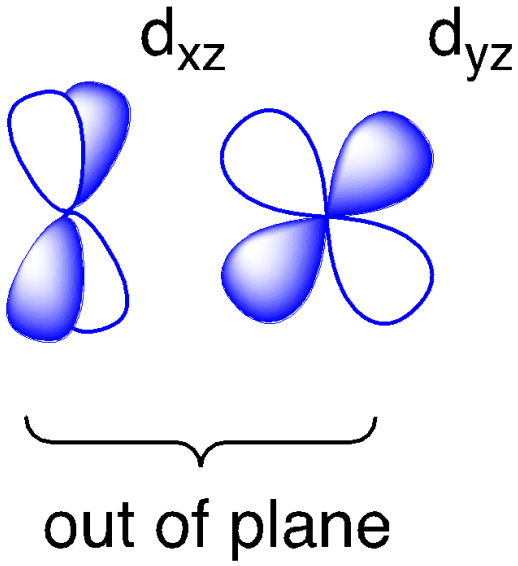
The d_{z^2} orbital does not drop all the way to the non-bonding level, however, because the toroid (the donut around the central node of the orbital) is still in plane with ligand orbitals along the x and y axes. Nevertheless, the d_{z^2} orbital overlaps with these ligand

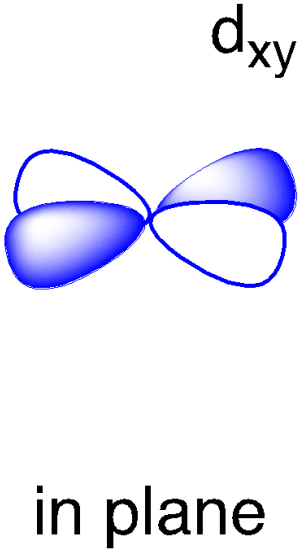
orbitals to a much lesser extent than the $d_{x^2-y^2}$ orbitals, so it drops to a level well below the $d_{x^2-y^2}$ orbital.



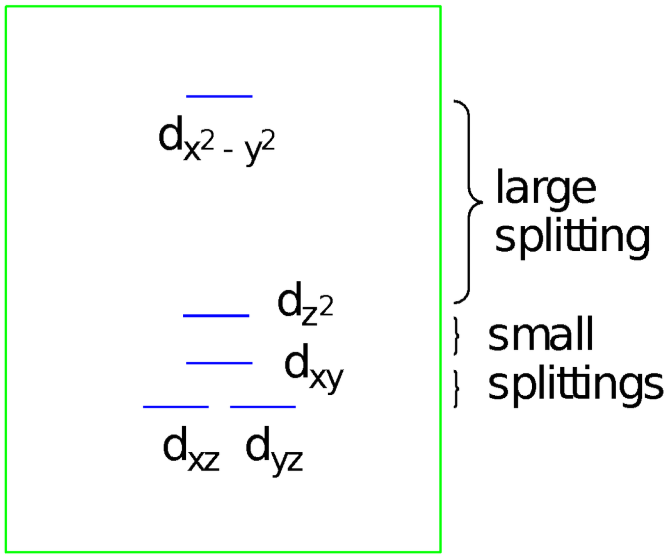


The d orbital splitting diagram shown above is not the one you will normally see for a square planar complex. The three non-bonding orbitals, d_{xy}, d_{xz} and d_{yz}, are degenerate in an octahedral geometry but not in a square planar one. The d_{xy} orbital is in the plane of the metal and ligands whereas the d_{xz} and d_{yz} are above and below that plane.





We therefore might not expect all three of these orbitals to be at the exact same energy level in the square planar coordination environment. We usually think of the d_{xy} orbital as lying at higher energy than the d_{xz}, d_{yz} pair because of the potential for interaction with the ligands that lie in the same plane as the d_{xy} orbital. The typical drawing of a d orbital splitting diagram reflects that subtle difference, showing the five metal d orbitals lying at four different energy levels with just one degenerate set (the d_{xz}, d_{yz} pair).



Note that there is a large splitting and two smaller splittings between the d orbitals, rather than the single splitting observed in an octahedral environment. As a result, when we talk about possible high spin and low spin electron population in the square planar environment, we are generally concerned with whether the electrons can surmount the large splitting and occupy the top orbital, the $d_{x^2-y^2}$.

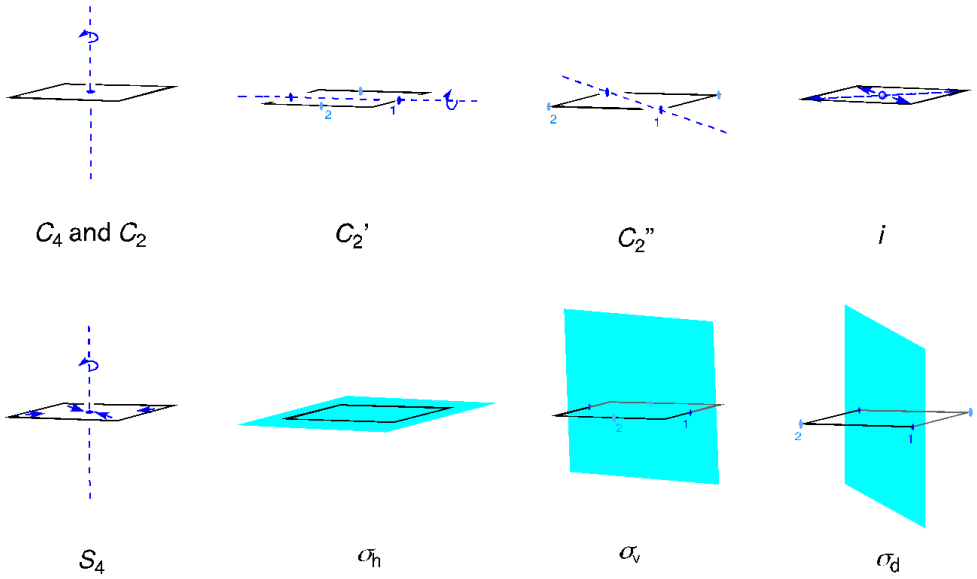
Sometimes, square planar d orbital splitting diagrams show the d_{xy} orbital above the d_{z^2} orbital and sometimes *vice versa*; the exact order varies with the ligands involved. The reasons for these differences are somewhat complicated. For example, this order can reflect the importance of pi bonding in a particular complex, as we will see later.

Group Theory Treatment of Square Planar Complexes

In octahedral coordination, we were able to use group theory to confirm the bonding picture we had arrived at through simple observation. We can do the same thing in the square planar case. This time, we need to use a character table for D_{4h} symmetry.

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2$, z^2
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1		$x^2 - y^2$
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E_g	2	0	-2	0	0	2	0	-2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E_u	2	0	-2	0	0	-1	0	2	0	0	(x, y)	

The ten symmetry elements listed in this table may be easier to grasp than the ones in the higher-symmetry octahedral point group. In this case, we see several two- or four-fold axes and some mirror planes. They are illustrated below.



If we consider only sigma bonding from the ligands, which was the initial consideration we thought about earlier, then we could look at how this picture operates when transformed by these symmetry elements:



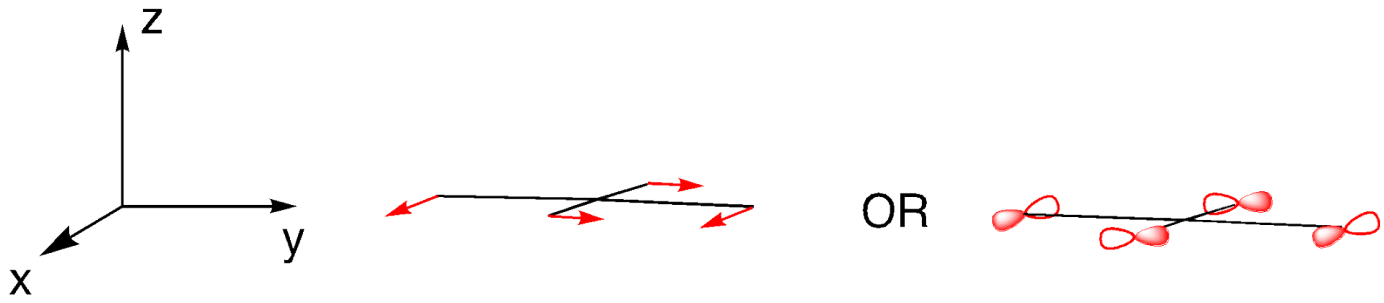
In that case, we obtain a reducible representation that can be reduced to the following:

$$\Gamma_\sigma = A_{1g} + B_{1g} + Eu$$

Returning to the character table, we find that the matching orbitals on the metal include the d_{z^2} and the $d_{x^2-y^2}$, as well as the s (represented by x^2+y^2), the p_x and p_y. If we are just interested in the d orbital splitting diagram, that gives us the picture that we had obtained before. Two d orbitals display some antibonding character whereas the other three are non-bonding. Of course, this treatment does not take into account the subtly different interactions of the ligands with the d_{z^2} and the $d_{x^2-y^2}$ orbitals. Although they are of like symmetry, these orbitals overlap with the ligands to different extents.

Pi Bonding

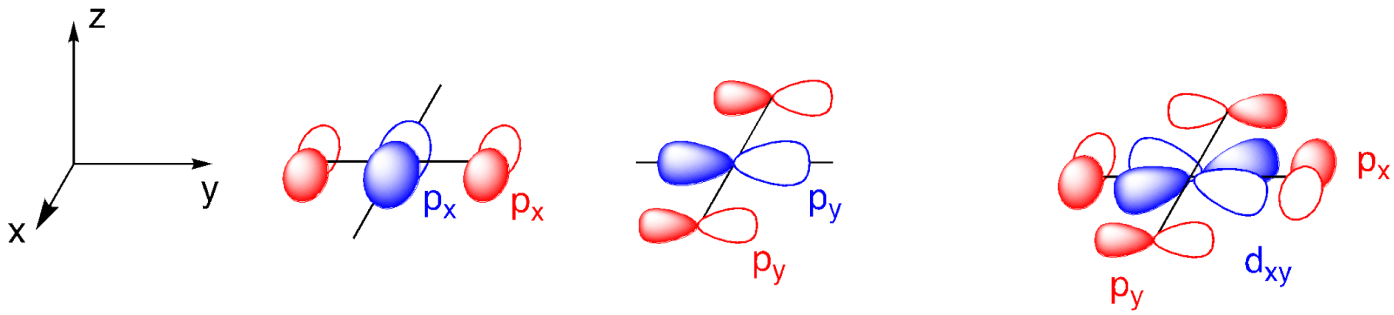
If we also want to include pi bonding in our understanding of these complexes, we have to think about two different orientations of the ligand p orbitals, which are not symmetrically equivalent in this case. The first orientation is parallel to the plane of the metal-ligand complex. It looks like this:



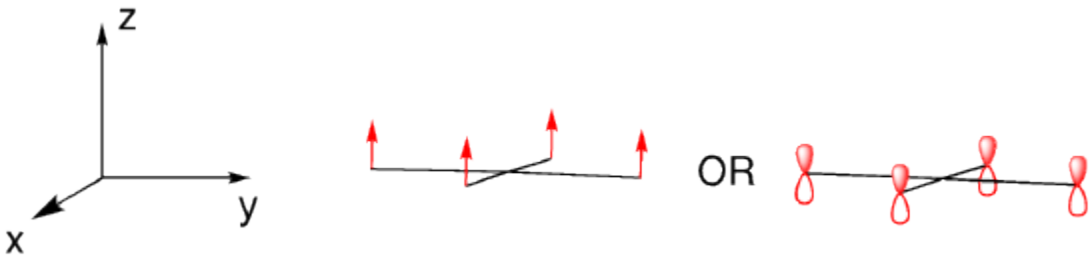
Treatment of those vectors with the symmetry elements leads to a reducible representation that can be represented by this one:

$$\Gamma_{\pi} \parallel = A_{2g} + B_{2g} + E_u$$

Consulting the character table, we find that the corresponding orbitals on the central atom are d_{xy}, p_x and p_y. In reality, the interaction with the d_{xy} is likely to be much more pronounced than with either the p_x or the p_y because of stronger overlap between the d_{xy} and the ligand p orbital.



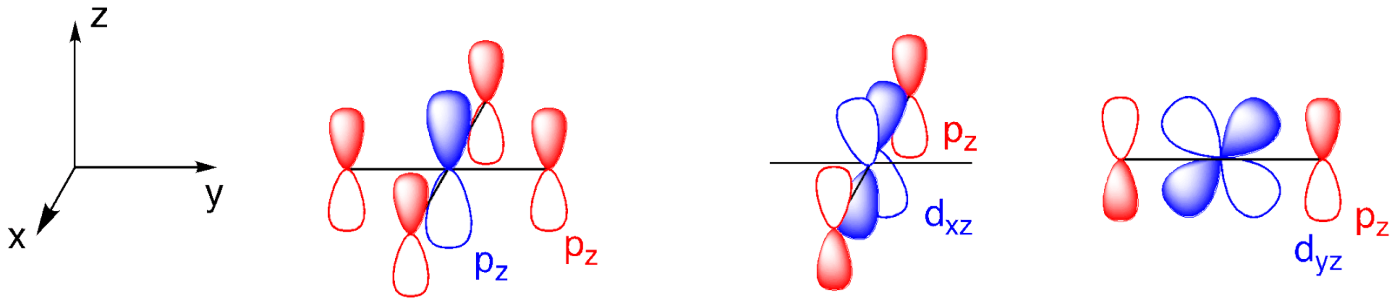
The second orientation is perpendicular to the plane of the complex.



This time, the irreducible representation is as follows:

$$\Gamma_{\pi} \perp = A_{2g} + B_{2g} + E_u$$

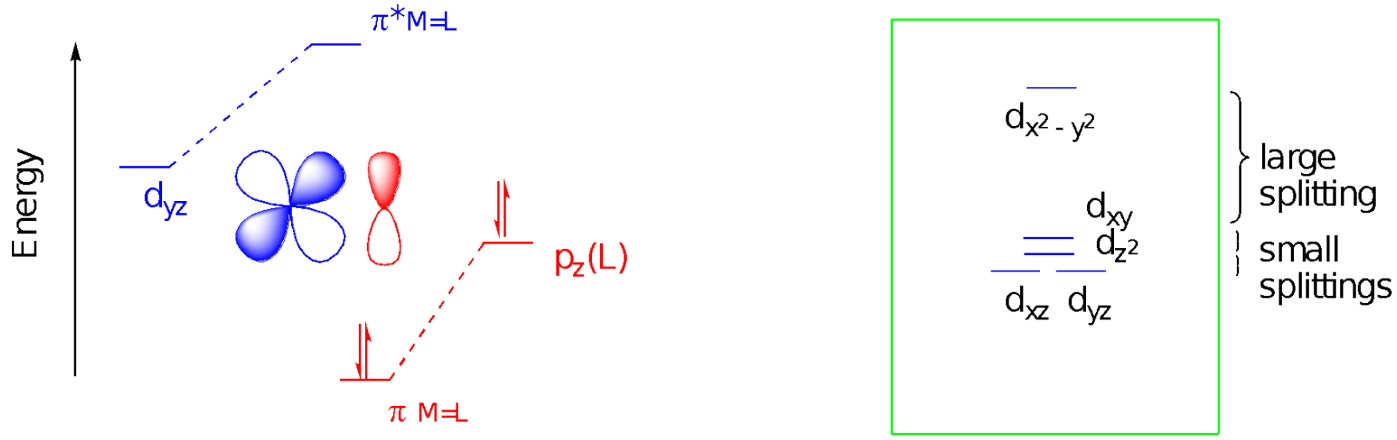
According to the character table, this time the corresponding orbitals on the central atom are d_{xz}, d_{yz}, and p_z. Once again, because of stronger overlap between the d_{xy} or d_{yz} with the ligand p orbital compared to ligand overlap with the metal p_z, the former case is likely to be much more important than the latter.



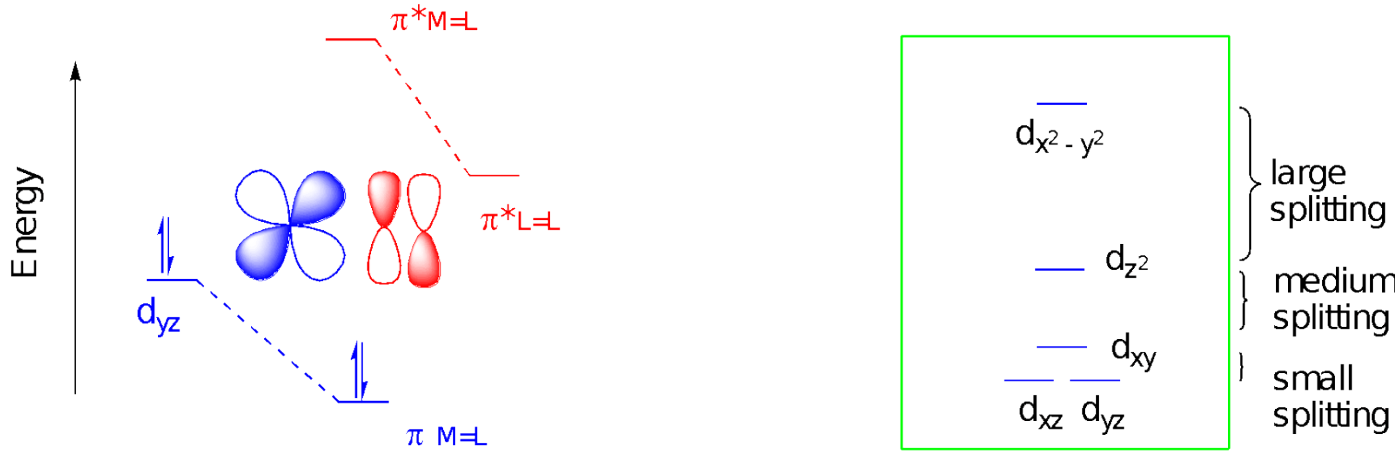
Thus, we see that the d orbitals that were not originally involved in sigma bonding have the potential to be involved in pi bonding. Which ones will actually be involved depends on the orientations of the ligands that are capable of pi bonding with these orbitals. That may be all of them in a more symmetric case (such as a homoleptic complex, in which all four ligands are the same as each other). It may be fewer in a complex with lower symmetry, in which the overall D_{4h} symmetry is broken by different ligands.

The nature of the ligands is probably of greater significance in terms of the magnitude of splittings in the d orbital diagram. If the metal forms a pi bond with the ligand via interaction with a p orbital on the ligand, then the resulting pi bond will be closer in both energy and character to the lower-energy ligand p orbital. We still think of that orbital as largely based on the more electronegative ligand. That means that the corresponding antibonding combination is more like the metal orbital in energy and character. It is still mostly a d orbital, for example. That results in a decrease in the splittings between d orbitals as the otherwise

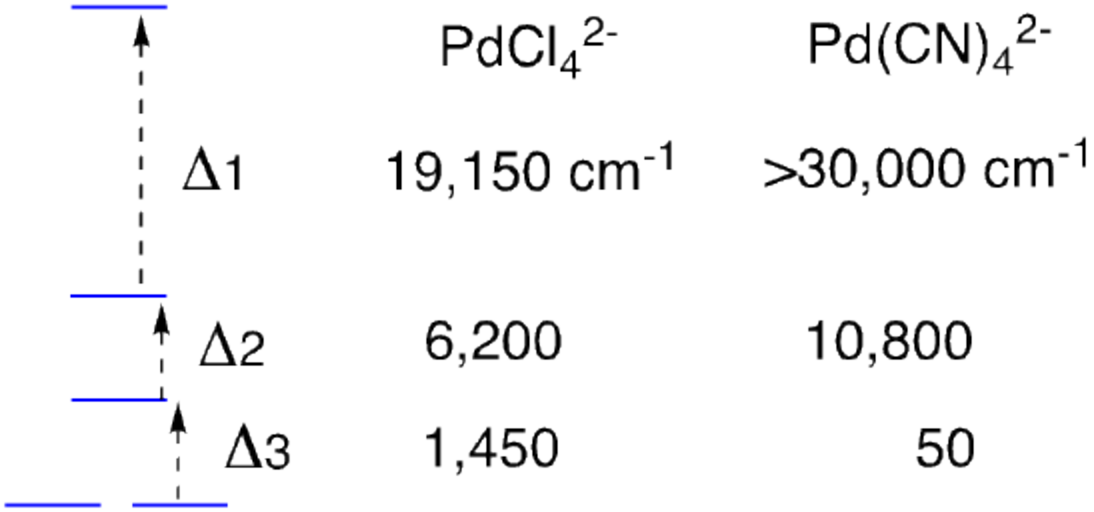
non-bonding set is pushed up in energy. We might even see the d_{xy} orbital at a higher energy level than the nominally sigma-antibonding d_{z^2} orbital, given a strong enough pi-bonding interaction.



On the other hand, if the metal orbital interacts with the empty π* orbital of a ligand such as cyanide or carbon monoxide, this situation will be reversed. Because of its antibonding nature, the ligand π* orbital lies above the metal d orbital in energy. When the two orbitals combine, the ligand π* orbital becomes the metal-ligand π* orbital. The metal d orbital drops in energy to form the metal-ligand bonding combination. Consequently, the metal orbitals involved in pi bonding to a pi acceptor drop in energy and splittings get larger. In particular, the gap between the pi bonding metal orbitals and the purely sigma bonding metal orbitals grows wider in this case.



The difference in overall splitting in these cases can be quite significant. For example, the differences between energy levels, denoted Δ1 and Δ2 below, are about 50% greater with the strongly pi-accepting cyanide ligand than with the pi-donating chloride in the corresponding homoleptic palladium complexes.[1]



In all of these cases, the splitting between the highest-lying $d_{x^2-y^2}$ orbital and the next highest is much larger than the other splittings. That factor leads to square planar complexes generally adopting a low-spin configuration, which in this case means the lower orbitals are all occupied before the $d_{x^2-y^2}$. Square planar complexes are most often observed with d^7 or d^8 metal ions, which avoids populating that highest-energy d orbital.

Problems

1. a) Demonstrate how to arrive at the reducible representation for sigma bonding under the D_{4h} symmetry of a square planar complex.

b) Determine the irreducible representation.

2. a) Demonstrate how to arrive at the reducible representation for pi bonding in the plane of the complex under the D_{4h} symmetry of a square planar complex.

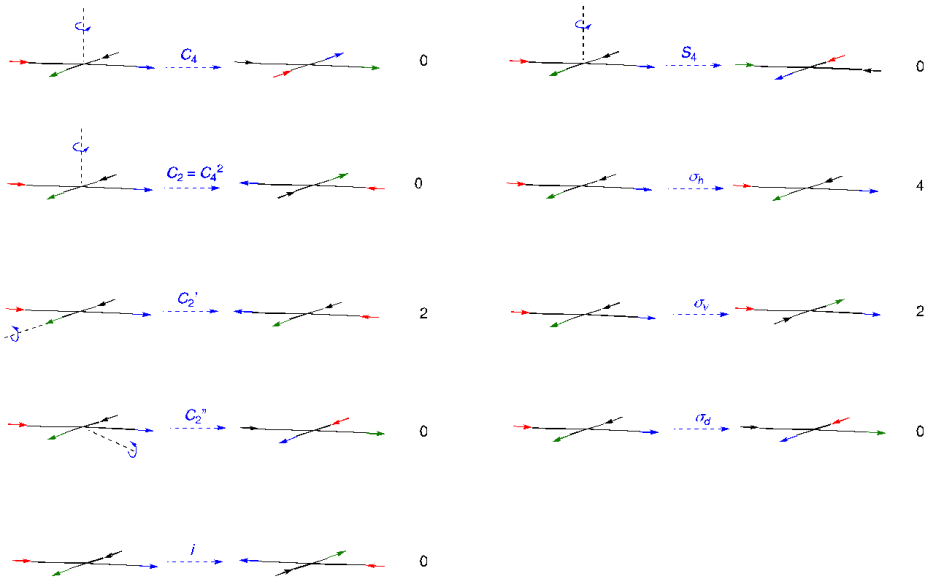
b) Determine the irreducible representation.

3. a) Demonstrate how to arrive at the reducible representation for pi bonding perpendicular to the plane of the complex under the D_{4h} symmetry of a square planar complex.

b) Determine the irreducible representation.

Solutions.

1. a) There are 4 unchanged vectors for *E*. For the others:



b) Γ_σ: Remember, ai = 1hQN·χ(R)·χ(R)Q

A_{1g}: ai = 1/16 [1·4·1 + 2·0·1 + 1·0·1 + 2·2·1 + 2·0·1 + 1·0·1 + 2·0·1 + 1·4·1 + 2·2·1 + 2·0·1] = 1/16 [4 + 4 + 4 + 4] = 1/16(16) = 1

A_{2g}: ai = 1/16 [1·4·1 + 2·0·1 + 1·0·1 + 2·2·(-1) + 2·0·(-1) + 1·0·1 + 2·0·1 + 1·4·1 + 2·2·(-1) + 2·0·(-1)] = 1/16 [4 - 4 + 4 - 4] = 1/16(0) = 0

B_{1g}: ai = 1/16 [1·4·1 + 2·0·(-1) + 1·0·1 + 2·2·1 + 2·0·(-1) + 1·0·1 + 2·0·(-1) + 1·4·1 + 2·2·1 + 2·0·(-1)] = 1/16 [4 + 4 + 4 + 4] = 1/16(16) = 1

B_{2g}: ai = 1/16 [1·4·1 + 2·0·(-1) + 1·0·1 + 2·2·(-1) + 2·0·1 + 1·0·1 + 2·0·(-1) + 1·4·1 + 2·2·(-1) + 2·0·1] = 1/16 [4 - 4 + 4 - 4] = 1/16(0) = 0

E_g: ai = 1/16 [1·4·2 + 2·0·0 + 1·0·(-2) + 2·2·0 + 2·0·0 + 1·0·2 + 2·0·0 + 1·4·(-2) + 2·2·0 + 2·0·0] = 1/16 [8 - 8] = 1/16(0) = 0

A_{1u}: ai = 1/16 [1·4·1 + 2·0·1 + 1·0·1 + 2·2·1 + 2·0·1 + 1·0·(-1) + 2·0·(-1) + 1·4·(-1) + 2·2·(-1) + 2·0·(-1)] = 1/16 [4 + 4 - 4 - 4] = 1/16(0) = 0

A_{2u}: ai = 1/16 [1·4·1 + 2·0·1 + 1·0·1 + 2·2·(-1) + 2·0·(-1) + 1·0·(-1) + 2·0·(-1) + 1·4·(-1) + 2·2·1 + 2·0·1] = 1/16 [4 - 4 - 4 + 4] = 1/16(0) = 0

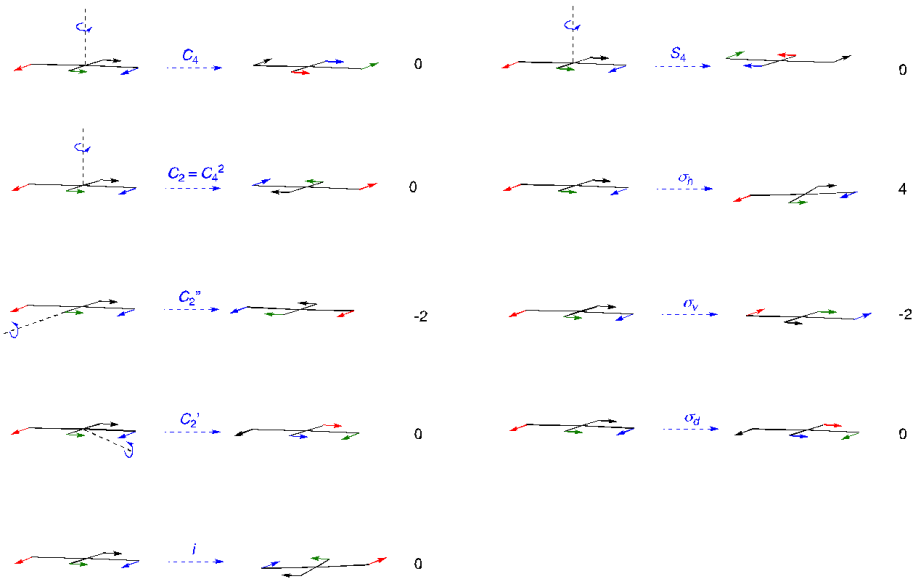
B_{1u}: ai = 1/16 [1·4·1 + 2·0·(-1) + 1·0·1 + 2·2·1 + 2·0·(-1) + 1·0·(-1) + 2·0·1 + 1·4·(-1) + 2·2·(-1) + 2·0·1] = 1/16 [4 + 4 - 4 - 4] = 1/16(0) = 0

B_{2u}: ai = 1/16 [1·4·1 + 2·0·(-1) + 1·0·1 + 2·2·(-1) + 2·0·1 + 1·0·(-1) + 2·0·1 + 1·4·(-1) + 2·2·1 + 2·0·(-1)] = 1/16 [4 - 4 - 4 + 4] = 1/16(0) = 0

E_u: ai = 1/16 [1·4·2 + 2·0·0 + 1·0·(-2) + 2·2·0 + 2·0·0 + 1·0·(-2) + 2·0·0 + 1·4·2 + 2·2·0 + 2·0·0] = 1/16 [8 + 8] = 1/16(16) = 1

$\Gamma_\sigma = A_{1g} + B_{1g} + E_u$

2. a) There are 4 unchanged vectors for *E*. For the others:



b) $\Gamma_{\pi||}$:

A_{1g}: ai = 1/16 [1·4·1 + 2·0·1 + 1·0·1 + 2·(-2)·1 + 2·0·1 + 1·0·1 + 2·0·1 + 1·4·1 + 2·(-2)·1 + 2·0·1] = 1/16 [4 - 4 + 4 - 4] = 1/16(0) = 0

A_{2g}: ai = 1/16 [1·4·1 + 2·0·1 + 1·0·1 + 2·(-2)·(-1) + 2·0·(-1) + 1·0·1 + 2·0·1 + 1·4·1 + 2·(-2)·(-1) + 2·0·(-1)] = 1/16 [4 + 4 + 4 + 4] = 1/16(16) = 1

B_{1g}: ai = 1/16 [1·4·1 + 2·0·(-1) + 1·0·1 + 2·(-2)·1 + 2·0·(-1) + 1·0·1 + 2·0·(-1) + 1·4·1 + 2·(-2)·1 + 2·0·(-1)] = 1/16 [4 - 4 + 4 - 4] = 1/16(0) = 0

B_{2g}: ai = 1/16 [1·4·1 + 2·0·(-1) + 1·0·1 + 2·(-2)·(-1) + 2·0·1 + 1·0·1 + 2·0·(-1) + 1·4·1 + 2·(-2)·(-1) + 2·0·1] = 1/16 [4 - 4 + 4 - 4] = 1/16(16) = 1

E_g: ai = 1/16 [1·4·2 + 2·0·0 + 1·0·(-2) + 2·(-2)·0 + 2·0·0 + 1·0·2 + 2·0·0 + 1·4·(-2) + 2·(-2)·0 + 2·0·0] = 1/16 [8 - 8] = 1/16(0) = 0

A_{1u}: ai = 1/16 [1·4·1 + 2·0·1 + 1·0·1 + 2·(-2)·1 + 2·0·1 + 1·0·(-1) + 2·0·(-1) + 1·4·(-1) + 2·(-2)·(-1) + 2·0·(-1)] = 1/16 [4 - 4 - 4 + 4] = 1/16(0) = 0

A_{2u}: ai = 1/16 [1·4·1 + 2·0·1 + 1·0·1 + 2·(-2)·(-1) + 2·0·(-1) + 1·0·(-1) + 2·0·(-1) + 1·4·(-1) + 2·(-2)·1 + 2·0·1] = 1/16 [4 + 4 - 4 - 4] = 1/16(0) = 0

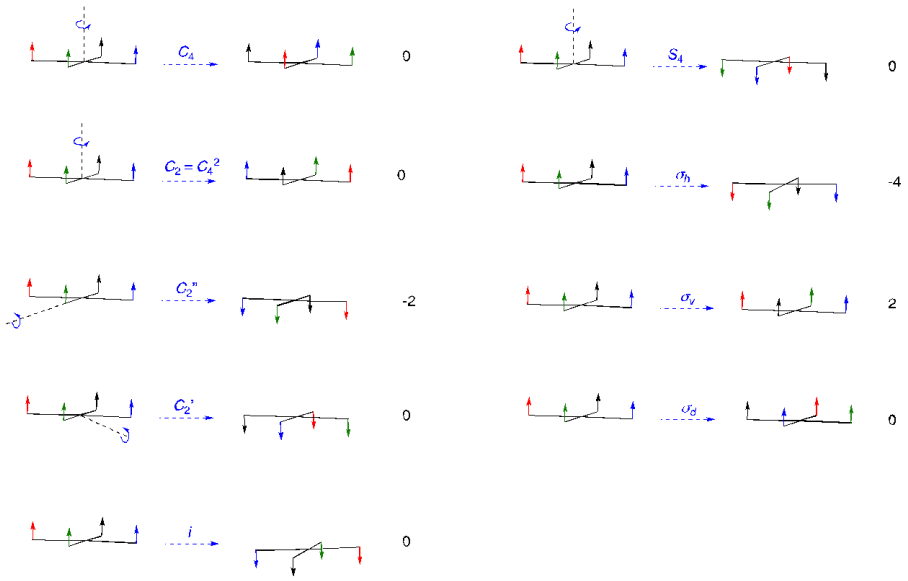
B_{1u}: ai = 1/16 [1·4·1 + 2·0·(-1) + 1·0·1 + 2·(-2)·1 + 2·0·(-1) + 1·0·(-1) + 2·0·1 + 1·4·(-1) + 2·(-2)·(-1) + 2·0·1] = 1/16 [4 - 4 - 4 + 4] = 1/16(0) = 0

B_{2u}: ai = 1/16 [1·4·1 + 2·0·(-1) + 1·0·1 + 2·(-2)·(-1) + 2·0·1 + 1·0·(-1) + 2·0·1 + 1·4·(-1) + 2·(-2)·1 + 2·0·(-1)] = 1/16 [4 + 4 - 4 - 4] = 1/16(0) = 0

E_u: ai = 1/16 [1·4·2 + 2·0·0 + 1·0·(-2) + 2·(-2)·0 + 2·0·0 + 1·0·(-2) + 2·0·0 + 1·4·2 + 2·(-2)·0 + 2·0·0] = 1/16 [8 + 8] = 1/16(16) = 1

$\Gamma_{\pi||} = A_{2g} + B_{2g} + E_u$

3. a) There are 4 unchanged vectors for *E*. For the others:



b) $\Gamma_{\pi\perp}$:

A_{1g}: ai = 1/16 [1·4·1 + 2·0·1 + 1·0·1 + 2·(-2)·1 + 2·0·1 + 1·0·1 + 2·0·1 + 1·(-4)·1 + 2·2·1 + 2·0·1] = 1/16 [4 - 4 - 4 + 4] = 1/16(0) = 0

A_{2g}: ai = 1/16 [1·4·1 + 2·0·1 + 1·0·1 + 2·(-2)·(-1) + 2·0·(-1) + 1·0·1 + 2·0·1 + 1·(-4)·1 + 2·2·(-1) + 2·0·(-1)] = 1/16 [4 + 4 - 4 - 4] = 1/16(0) = 0

B_{1g}: ai = 1/16 [1·4·1 + 2·0·(-1) + 1·0·1 + 2·(-2)·1 + 2·0·(-1) + 1·0·1 + 2·0·(-1) + 1·(-4)·1 + 2·2·1 + 2·0·(-1)] = 1/16 [4 - 4 - 4 + 4] = 1/16(0) = 0

B_{2g}: ai = 1/16 [1·4·1 + 2·0·(-1) + 1·0·1 + 2·(-2)·(-1) + 2·0·1 + 1·0·1 + 2·0·(-1) + 1·(-4)·1 + 2·2·(-1) + 2·0·1] = 1/16 [4 + 4 - 4 - 4] = 1/16(0) = 0

E_g: ai = 1/16 [1·4·2 + 2·0·0 + 1·0·(-2) + 2·(-2)·0 + 2·0·0 + 1·0·2 + 2·0·0 + 1·(-4)·(-2) + 2·2·0 + 2·0·0] = 1/16 [8 + 8] = 1/16(16) = 1

A_{1u}: ai = 1/16 [1·4·1 + 2·0·1 + 1·0·1 + 2·(-2)·1 + 2·0·1 + 1·0·(-1) + 2·0·(-1) + 1·(-4)·(-1) + 2·2·(-1) + 2·0·(-1)] = 1/16 [4 - 4 + 4 - 4] = 1/16(0) = 0

A_{2u}: ai = 1/16 [1·4·1 + 2·0·1 + 1·0·1 + 2·(-2)·(-1) + 2·0·(-1) + 1·0·(-1) + 2·0·(-1) + 1·(-4)·(-1) + 2·2·1 + 2·0·1] = 1/16 [4 + 4 + 4 + 4] = 1/16(16) = 1

B_{1u}: ai = 1/16 [1·4·1 + 2·0·(-1) + 1·0·1 + 2·(-2)·1 + 2·0·(-1) + 1·0·(-1) + 2·0·1 + 1·(-4)·(-1) + 2·2·(-1) + 2·0·1] = 1/16 [4 - 4 + 4 - 4] = 1/16(0) = 0

B_{2u}: ai = 1/16 [1·4·1 + 2·0·(-1) + 1·0·1 + 2·(-2)·(-1) + 2·0·1 + 1·0·(-1) + 2·0·1 + 1·(-4)·(-1) + 2·2·1 + 2·0·(-1)] = 1/16 [4 + 4 + 4 + 4] = 1/16(16) = 1

E_u: ai = 1/16 [1·4·2 + 2·0·0 + 1·0·(-2) + 2·(-2)·0 + 2·0·0 + 1·0·(-2) + 2·0·0 + 1·(-4)·2 + 2·2·0 + 2·0·0] = 1/16 [8 - 8] = 1/16(0) = 0

$\Gamma_{\pi\perp} = A_{2u} + B_{2u} + E_g$

References

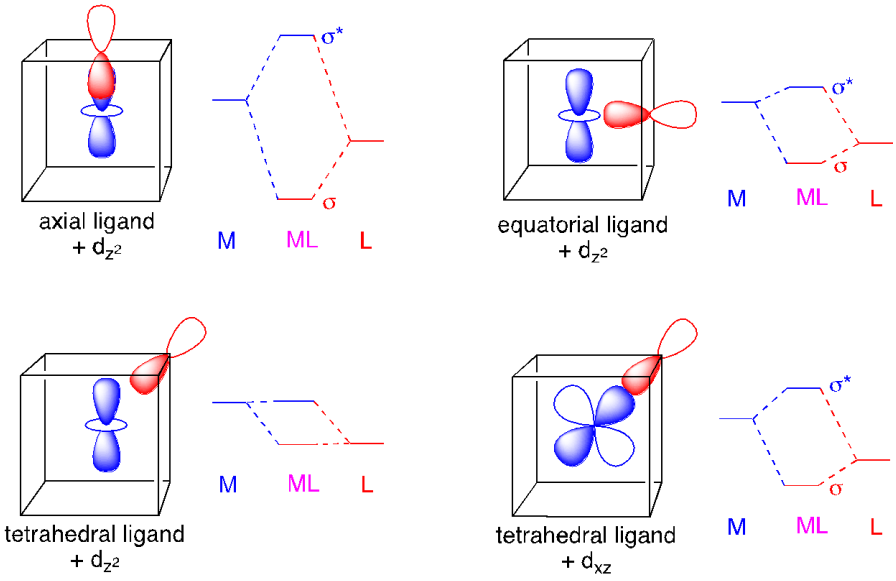
1. Gray, H. B.; Ballhausen, C. J. *J. Am. Chem. Soc.* **1963**, *85*, 260-264.

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10.4: Angular Overlap

The angular overlap model is an approach to quantifying the interaction between metal and ligand orbitals in different geometries, with a focus on the metal d orbitals. Although developed in the 1970's, this approach is still used as a starting point for theoretical calculations using advanced computational chemistry methods available today.1

The core concept of the angular overlap model is that different ligand orbitals will overlap with metal d orbitals to different extents because of the variety of angles at which these orbitals would approach each other. Stronger overlap leads to greater interaction. That means both greater stabilization of the ligand-centered bonding orbital and greater destabilization of the metal-centered antibonding orbital.



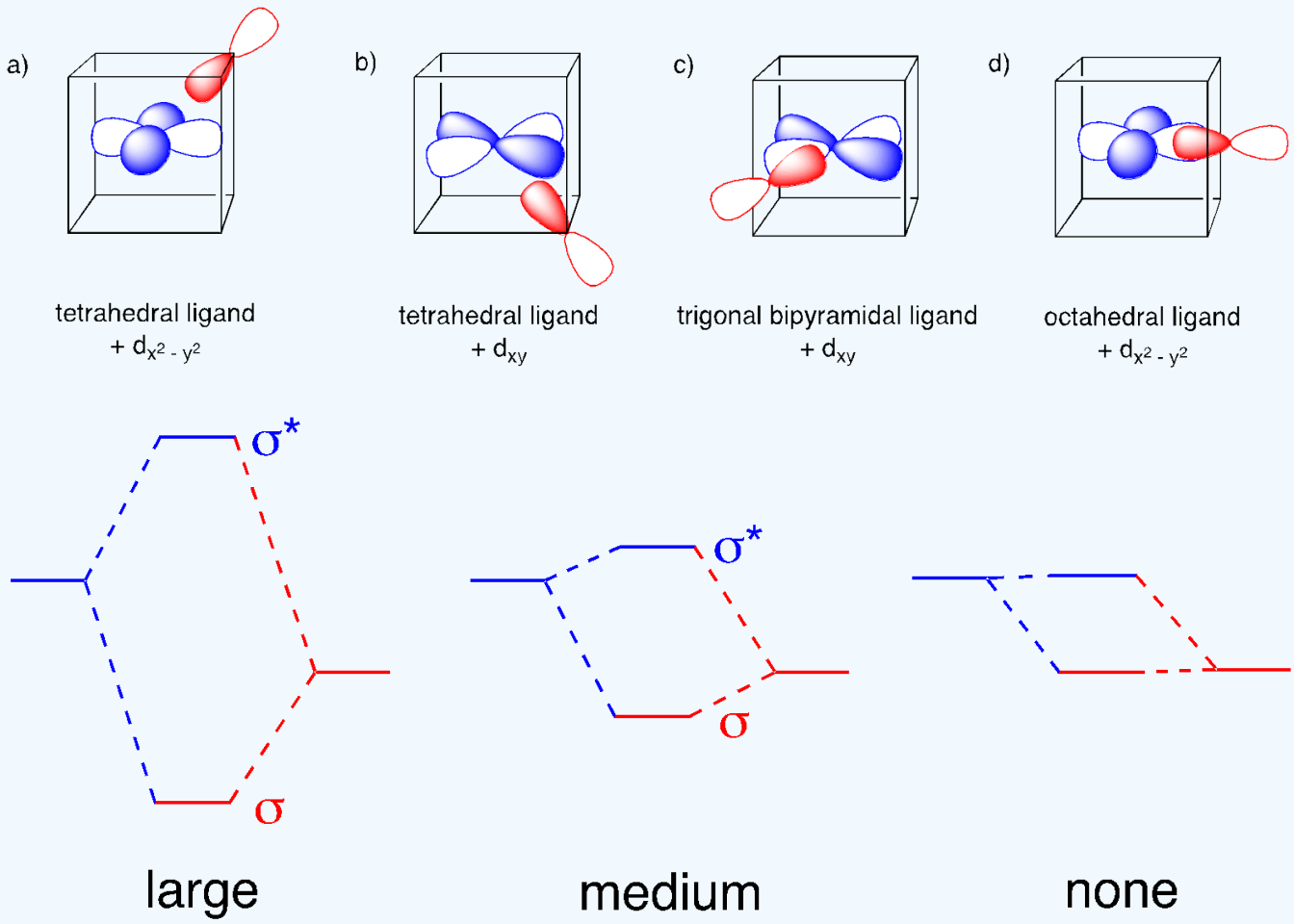
Let's look at some examples. Consider the overlap of the d_{z^2} orbital with an axial ligand in octahedral geometry, with the assumption that the d_{z^2} orbital lies in the axial direction. There should be considerable overlap between the metal and ligand orbitals, leading to both significant stabilization of the ligand donor electrons and similar destabilization of an electrons in the metal d_{z^2} orbital. By comparison, an equatorial ligand would have significantly less overlap with the d_{z^2} orbital. Instead of overlapping with the substantial lobe along the z axis, the ligand would be interacting with the minimal d_{z^2} toroid in the xy plane. The bonding orbital would be stabilized to a significantly lesser extent compared to the axial ligand. The antibonding orbital would be destabilized by a correspondingly smaller amount.

In the case of a tetrahedral ligand, there is essentially no overlap with the d_{z^2} orbital because its on-axis lobe is too far away from the cubic corner positions occupied by ligands in a tetrahedral array. There is really no bonding or antibonding in this case. On the other hand, the dxz orbital reaches a little closer to that corner position, allowing for some overlap with the ligand orbital. Consequently, there is some stabilization of the bonding electrons and destabilization of the antibonding d orbital. At first glance, the amount of overlap in this case, and the amount of stabilization or destabilization, appears much more similar to the case of the equatorial ligand with the d_{z^2} orbital than the axial ligand with the d_{z^2} orbital.

We will not go into the mathematics that explore the exact extent of overlap expected in each case. Instead, we will go straight to a summary of the results in the next section.

Exercise 10.4.1

Estimate the degree of interaction between the ligand and metal orbital: large, medium, or none.



Answer available at the end of this section.

References

1. For example: Chilkuri, V. G.; DeBeer, S.; Neese, F. Ligand Field Theory and Angular Overlap Model Based Analysis of the Electronic Structure of Homovalent Iron–Sulfur Dimers. *Inorg. Chem.* **2020**, *59*(2), 984-995.

Answers

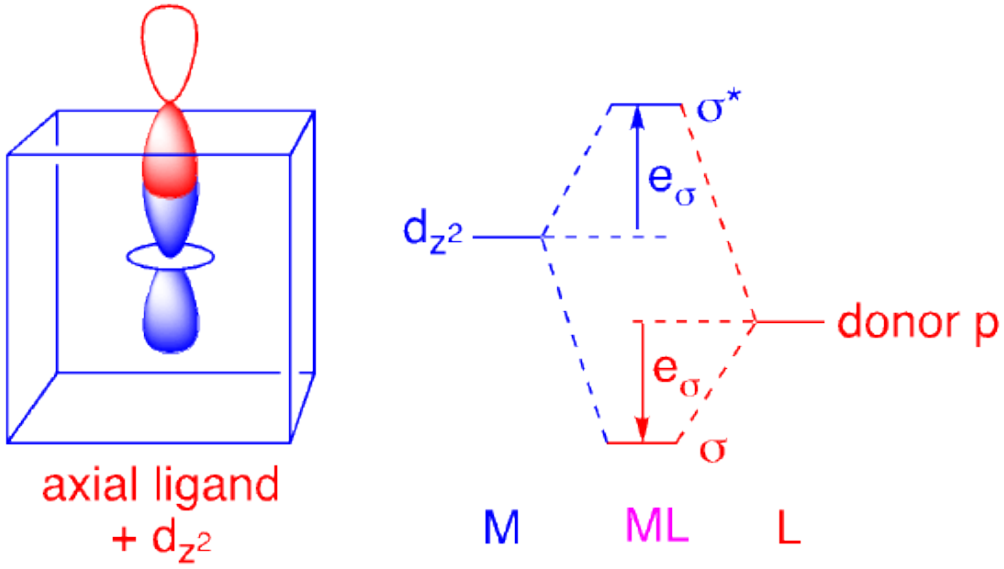
Exercise 10.4.1

a) none b) medium c) medium (although it may appear greater than in (b), and it is) d) large

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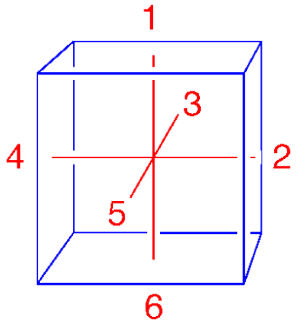
10.4.1: Sigma Bonding in the Angular Overlap Model

The pictures we considered previously explicitly addressed sigma overlap between the ligand donor orbital and the metal d acceptor orbital. The donor electrons drop in energy into the new sigma bonding combination and any electrons in the d orbital are raised into the new sigma antibonding combination. For example, when an axial ligand interacts with a metal dz2 orbital, the in-phase, bonding combination drops in energy by a quantity that we will call eσ. At the same time, the out-of-phase, antibonding combination is raised in energy by the same quantity, eσ. A real computational treatment would reveal that this is not exactly true; the amount of energy by which the bonding orbital is stabilized is slightly different from the amount by which the antibonding orbital is destabilized. However, the distinction is pretty minor for our purposes.

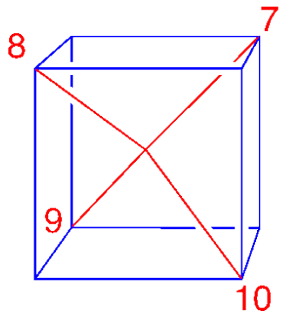


From the interactions we have already looked at, we know that this specific interaction is a strong one. Other metal-ligand interactions may involve less overlap than this one and will lead to smaller changes in energy. For this reason, other metal-ligand interactions are expressed as fractions of the quantity, eσ, found in the case of the dz2 orbital interacting with an axial ligand.

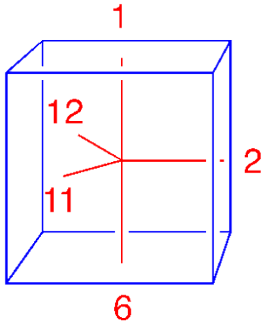
Our first task is to label the positions that will be occupied by ligands in a number of different geometries. To avoid a cluttered diagram of these positions, we can use three separate illustrations to illustrate the ligand positions in some common geometries. The first drawing below includes all the geometries in which ligands are found along Cartesian coordinates. The second drawing describes tetrahedral geometry, whereas the third one describes trigonal structures.



octahedral (1 - 6)
square pyramidal (1 - 5)
square planar (2 - 4)
linear (1, 6)



tetrahedral (7 - 10)



trigonal bipyramidal (1, 2, 6, 11, 12)
trigonal planar (2, 11, 12)

Given those ligand positions, we can assess the interactions that would occur if ligands were purely sigma donors. For reference, the dz2 orbital is assumed to lie along the axis between positions 1 and 6 and the magnitudes of the interactions are all scaled relative to the interaction of a ligand at position 1 or 6 with the dz2 orbital. We will not address the approach that was taken to arrive at these relative numbers; we will simply use the results tabulated here.

Sigma Interactions of Ligands with Metal d Orbitals (units of eσ)

Ligand Positions	dz2	dx2-y2	dxy	dxz	dyz
1	1	0	0	0	0
2	1/4	3/4	0	0	0
3	1/4	3/4	0	0	0
4	1/4	3/4	0	0	0
5	1/4	3/4	0	0	0
6	1	0	0	0	0
7	0	0	1/3	1/3	1/3
8	0	0	1/3	1/3	1/3
9	0	0	1/3	1/3	1/3
10	0	0	1/3	1/3	1/3
11	1/4	3/16	9/16	0	0
12	1/4	3/16	9/16	0	0

In order to quantify the interactions between ligands and metal orbitals, we simply tally up the interactions for each orbital. For example, consider a complex like hexaamminecobalt(III) chloride, [Co(NH3)6]Cl3. It has six sigma donor ligands, forming an octahedral structure. The total interactions with each orbital in this geometry would be calculated by totaling the interactions at all the ligand positions for each orbital.

Looking under the dz2 column and totaling only the values for positions 1 through 6, we find:

dz2: (1 + 1/4 + 1/4 + 1/4 + 1/4 + 1) eσ = 3eσ

A similar approach using the dx2-y2 column leads to:

dx2-y2: (0 + 3/4 + 3/4 + 3/4 + 3/4 + 0) eσ = 3eσ

However, the remaining three d orbitals have no interactions with the ligands in these six positions:

dxy: 0; dxz: 0; dyz: 0

So, we find that the dz2 and dx2-y2 orbitals are both raised in energy by 3eσ. At the same time, we know that the ligand donor orbitals are stabilized by their interaction with the metal orbitals. To see how much, we can tally up the interaction for each ligand at its position. That is, for the ligand in position 1, we would add in its interaction with each of the five d orbitals to determine the amount by which it is stabilized by bonding. We simply add up the values across that row.

Ligand in position 1: - (1 + 0 + 0 + 0 + 0) eσ = - eσ

Ligand in position 2: - (1/4 + 3/4 + 0 + 0 + 0) eσ = - eσ

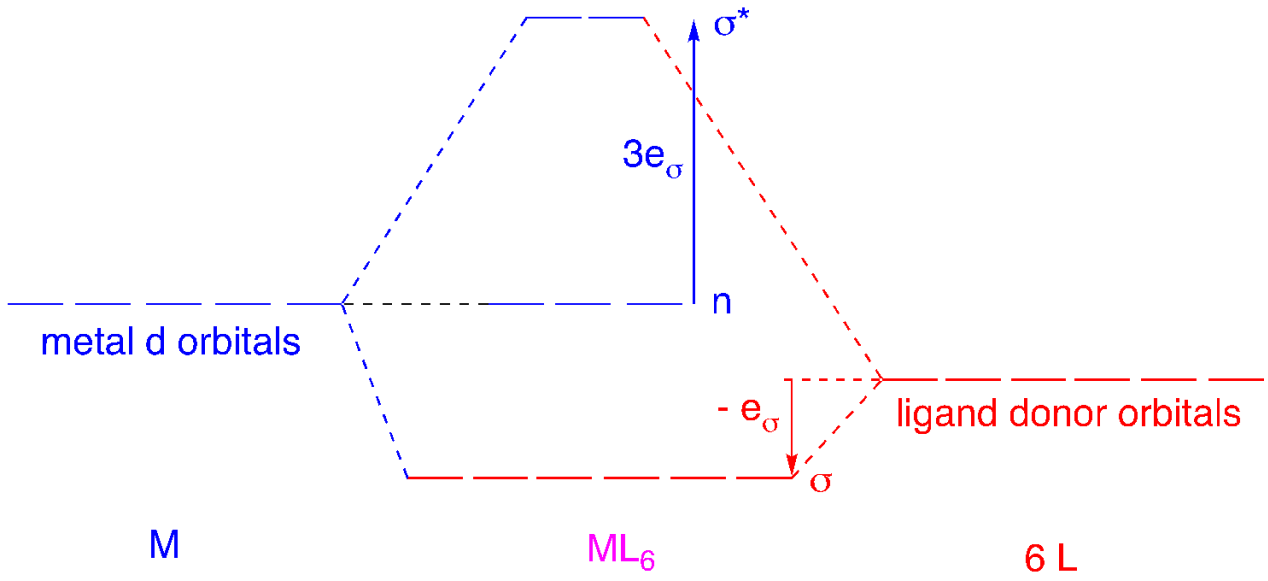
Ligand in position 3: - (1/4 + 3/4 + 0 + 0 + 0) eσ = - eσ

Ligand in position 4: - (1/4 + 3/4 + 0 + 0 + 0) eσ = - eσ

Ligand in position 5: - (1/4 + 3/4 + 0 + 0 + 0) eσ = - eσ

Ligand in position 6: - (1 + 0 + 0 + 0 + 0) eσ = - eσ

We have now generated a diagram that looks very much like what we saw from ligand field theory. We see the familiar d orbital splitting diagram for octahedral geometry as well as stabilization of the ligand donor orbitals in sigma bonds.



The results from the angular overlap model are somewhat simplified compared to the results from ligand field theory. For example, they completely neglect any interaction between ligand orbitals and metal s or p orbitals. However, this model allows a very straightforward calculation of the relative d orbital energy levels.

Problems

1. Use the results of the calculation for the octahedral geometry to calculate the net stabilization due to bonding (in units of eσ) for the following complexes.

a) [Co(NH3)6]Cl3 (assume low spin) b) [Fe(NH3)6](NO3)3 (assume high spin)

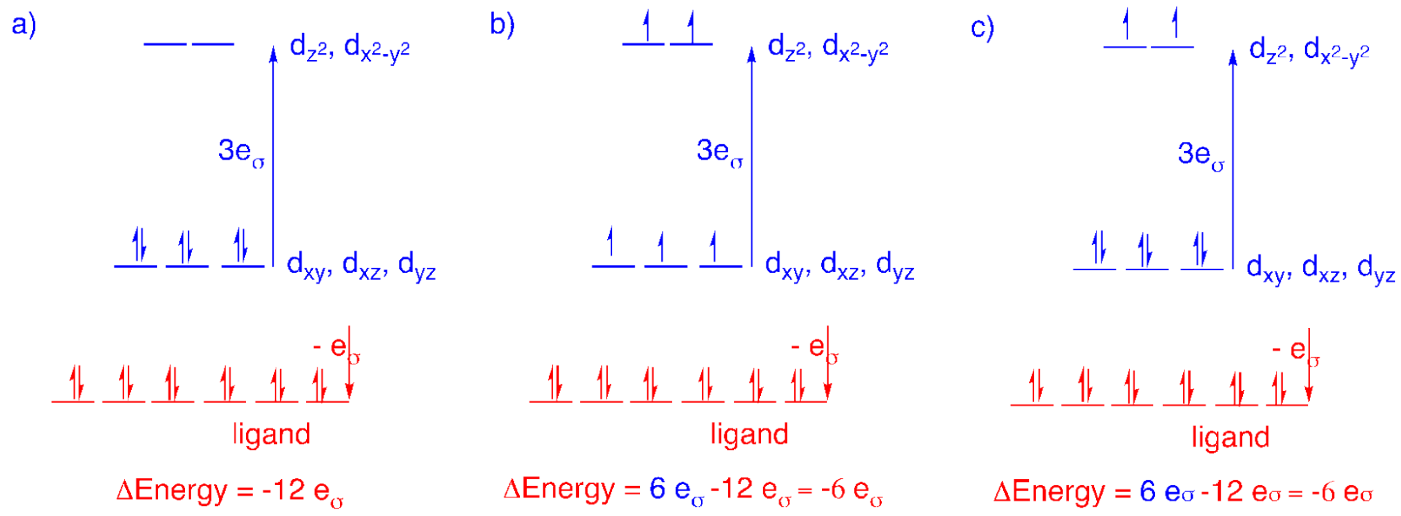
c) [Ni(NH3)6]Cl2

2. Use the table of sigma interactions to calculate orbital energy stabilization or destabilization for the following geometries.

a) trigonal planar ML3 b) square planar ML4 c) trigonal bipyramidal ML5

Solutions

1.



2. a) Positions 2, 11, 12.

dz2: (1/4 + 1/4 + 1/4) eσ = 3/4 eσ

dx2-y2: (3/4 + 3/16 + 3/16) eσ = 18/16 = 9/8 eσ

dxy: (0 + 9/16 + 9/16) eσ = 18/16 = 9/8 eσ

dxz: 0

dyz: 0

Ligand in position 2: - (1/4 + 3/4 + 0 + 0 + 0) eσ = - eσ

Ligand in position 11: - (1/4 + 3/16 + 9/16 + 0 + 0) eσ = - eσ

Ligand in position 12: - (1/4 + 3/4 + 9/16 + 0 + 0) eσ = - eσ

b) Positions 2, 3, 4, 5.

dz2: (1/4 + 1/4 + 1/4 + 1/4) eσ = eσ

dx2-y2: (3/4 + 3/4 + 3/4 + 3/4) eσ = 3 eσ

dxy: 0

dxz: 0

dyz: 0

Ligand in position 2: - (1/4 + 3/4 + 0 + 0 + 0) eσ = - eσ

Ligand in position 3: - (1/4 + 3/4 + 0 + 0 + 0) eσ = - eσ

Ligand in position 4: - (1/4 + 3/4 + 0 + 0 + 0) eσ = - eσ

Ligand in position 5: - (1/4 + 3/4 + 0 + 0 + 0) eσ = - eσ

c) Positions 1, 2, 6, 11, 12.

dz2: (1 + 1/4 + 1+ 1/4 + 1/4) eσ = 11/4 eσ

dx2-y2: (0 + 3/4 + 0 + 3/16 + 3/16) eσ = 18/16 = 9/8 eσ

dxy: (0 + 0 + 0 + 9/16 + 9/16) eσ = 18/16 = 9/8 eσ

dxz: 0

dyz: 0

Ligand in position 1: - (1 + 0 + 0 + 0 + 0) eσ = - eσ

Ligand in position 2: - (1/4 + 3/4 + 0 + 0 + 0) eσ = - eσ

Ligand in position 6: - (1 + 0 + 0 + 0 + 0) eσ = - eσ

Ligand in position 11: - (1/4 + 3/16 + 9/16 + 0 + 0) eσ = - eσ

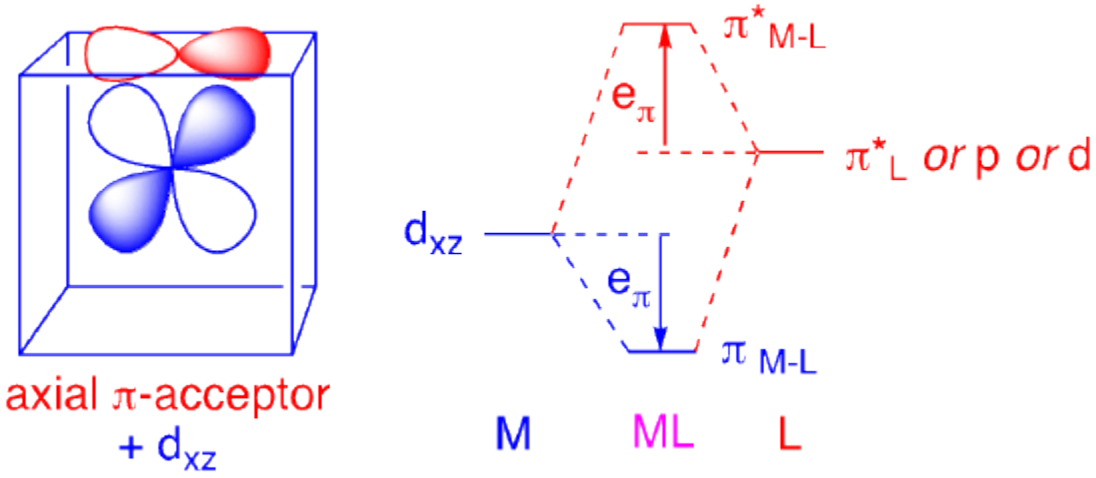
Ligand in position 12: - (1/4 + 3/4 + 9/16 + 0 + 0) eσ = - eσ

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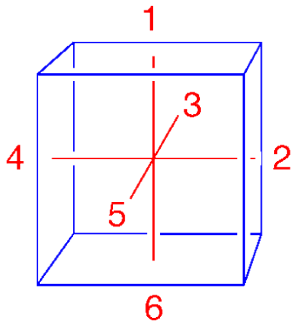
10.4.2: Pi Acceptors in the Angular Overlap Model

So far, we have considered only the effects of sigma donation on the d orbital splitting diagram using the angular overlap model. When we looked at ligand field theory, we saw that pi-donor and pi-acceptor effects produced significant changes in these diagrams. We generally see these effects in any ligands that have orbitals that can accept electron density from the metal (back-bonding). The paradigm of a pi acceptor is carbon monoxide, of course. Similar effects can be found in related ligands in which the donor atoms participate in pi bonding with another atom in the ligand, thus making a pi* orbital available for back-bonding. In addition, back-bonding is a feature of phosphine ligands and some N-heterocyclic carbenes.

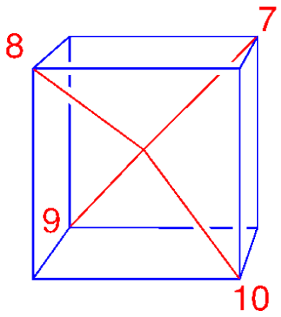
We usually think about this interaction as illustrated below. The empty ligand orbital approaches so that it is perpendicular to the bond axis, allowing overlap with the filled metal d orbital. The interaction lowers the energy of the d electrons, which become bonding in nature, and raises the energy of the empty ligand orbital.



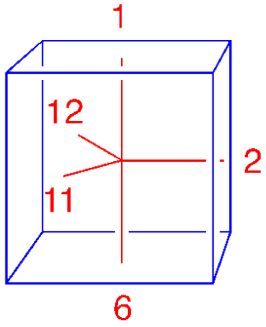
We can use the same ligand positions for pi acceptors that we already used for sigma donors. The orbitals will be oriented differently than the sigma donor orbitals but they will approach from the same directions..



octahedral (1 - 6)
square pyramidal (1 - 5)
square planar (2 - 4)
linear (1, 6)



tetrahedral (7 - 10)



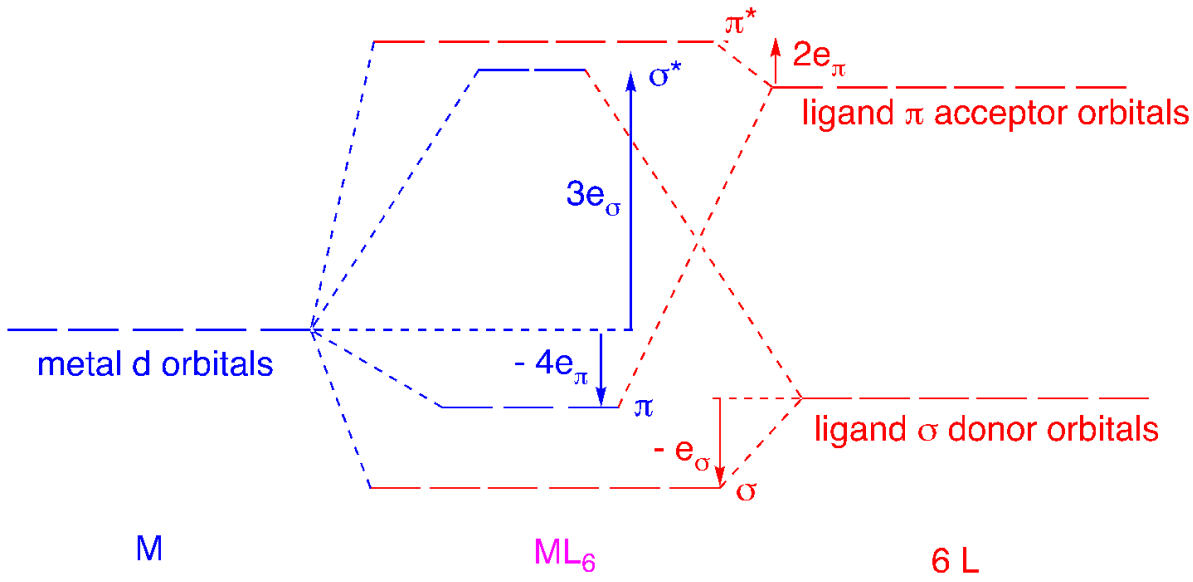
trigonal bipyramidal (1, 2, 6, 11, 12)
trigonal planar (2, 11, 12)

As before, we can use the results of calculations of the strengths of these interactions based on the amount of overlap; we don't need to know exactly how the numbers in the table below came about. This time, the maximum overlap occurs between a dxz orbital and a p orbital approaching in position 1, perpendicular to the bond axis. Several other combinations will be equally strong. This time, the stabilization is expressed in terms of eπ rather that eσ. The amount of energy in this case is somewhat smaller than in sigma donation because of a lesser degree of metal-ligand orbital overlap.

Sigma Interactions of Ligands with Metal d Orbitals (units of eπ)

Ligand Positions	dz2	dx2-y2	dxy	dxz	dyz
1	0	0	0	1	1
2	0	0	1	1	0
3	0	0	1	0	1
4	0	0	1	1	0
5	0	0	1	0	1
6	0	0	0	1	1
7	2/3	2/3	2/9	2/9	2/9
8	2/3	2/3	2/9	2/9	2/9
9	2/3	2/3	2/9	2/9	2/9
10	2/3	2/3	2/9	2/9	2/9
11	0	3/4	1/4	1/4	3/4
12	0	3/4	1/4	1/4	3/4

These interactions modify the picture we built previously for simple sigma donors. In the new interaction diagram, a second set of ligand p orbitals is destabilized by the pi interaction. At the same time, some of the d orbitals are stabilized by the additional interaction. This modification is illustrated below for octahedral geometry.



Problems

1. Use the table of pi interactions to calculate orbital energy stabilization or destabilization for the following geometries.

a) trigonal planar ML3 b) square planar ML4 c) trigonal bipyramidal ML5

Solutions

1. a) Positions 2, 11, 12.

dz2: 0

dx2-y2: - (0 + 3/4 + 3/4) eπ = 6/4 = - 3/2 eπ

dxy: - (1 + 1/4 + 1/4) eσ = 6/4 = - 3/2 eπ

dxz: - (1 + 1/4 + 1/4) eσ = 6/4 = - 3/2 eπ

dyz: - (0 + 3/4 + 3/4) eσ = 6/4 = - 3/2 eπ

Ligand in position 2: (0 + 0 + 0 + 1 + 1) eπ = 2eπ

Ligand in position 11: (0 + 3/4 + 1/4 + 1/4 + 3/4) eπ = 2eπ

Ligand in position 12: (0 + 3/4 + 1/4 + 1/4 + 3/4) eπ = 2eπ

b) Positions 2, 3, 4, 5.

dz2: 0

dx2-y2: 0

dxy: - (1 + 1 + 1 + 1) = -4 eπ

dxz: - (1 + 0 + 1 + 0) = -2 eπ

dyz: - (0 + 1 + 0 + 1) = -2 eπ

Ligand in position 2: (0 + 0 + 1 + 1 + 0) eπ = 2 eπ

Ligand in position 3: (0 + 0 + 1 + 0 + 1) eπ = 2 eπ

Ligand in position 4: (0 + 0 + 1 + 1 + 0) eπ = 2 eπ

Ligand in position 5: (0 + 0 + 1 + 0 + 1) eπ = 2 eπ

c) Positions 1, 2, 6, 11, 12.

dz2: 0

dx2-y2: - (0 + 0 + 0 + 3/4 + 3/4) eπ = -3/2 eπ

dxy: - (0 + 1 + 0 + 1/4 + 1/4) eπ = -3/2 eπ

dxz: - (1 + 1 + 1 + 1/4 + 1/4) eπ = -7/2 eπ

dyz: - (1 + 0 + 1 + 3/4 + 4/4) eπ = -7/2 eπ

Ligand in position 1: (0 + 0 + 0 + 1 + 1) eπ = 2 eπ

Ligand in position 2: (0 + 0 + 1 + 1 + 0) eπ = 2 eπ

Ligand in position 6: (0 + 0 + 0 + 1 + 1) eπ = 2 eπ

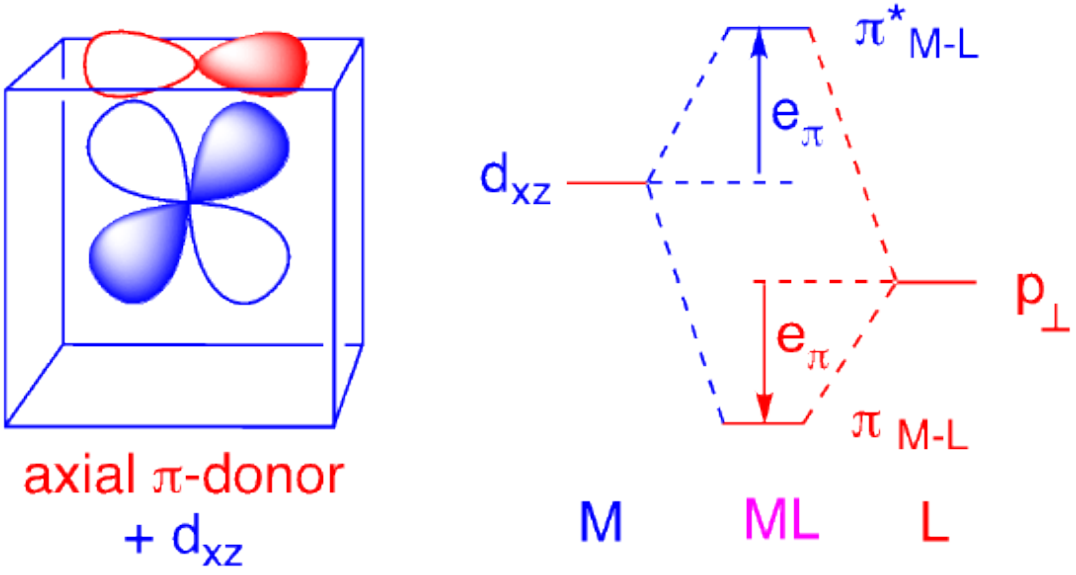
Ligand in position 11: (0 + 3/4 + 1/4 + 1/4 + 3/4) eπ = 2 eπ

Ligand in position 12: (0 + 3/4 + 1/4 + 1/4 + 3/4) eπ = 2 eπ

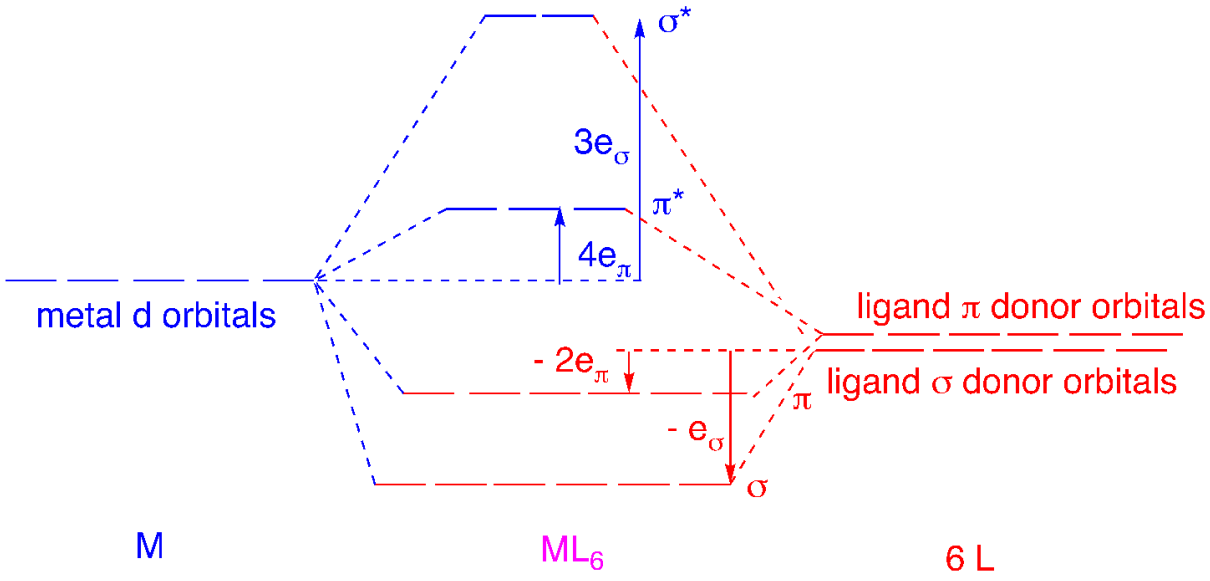
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10.4.3: Pi Donors in the Angular Overlap Model

Ligands in which the donor atom has more than one lone pair are capable of pi donation to the metal. Common examples include halide and alkoxide ligands. The overlap question in this case is exactly the same as in the case of pi acceptors; the same table of interactions applies here. However, since the ligand electrons are forming the pi bond in this case, the ligand electrons are stabilized and the d orbitals with which they overlap are destabilized.



In octahedral geometry, for example, we see the off-axis d orbitals raised modestly in energy in the presence of pi donor ligands. The angular overlap model allows us to quantify the relative changes in energy because of these ligand interactions.



Example 10.4.3.1

Confirm the stabilization and destabilization of orbitals due to pi donation in the octahedral interaction diagram shown above.

Solution

Positions 1, 2, 3, 4, 5, 6.

- dz2: 0
- dx2-y2: 0
- dxy: (0 + 1 + 1 + 1 + 1 + 0) = 4 eπ
- dxz: (1 + 1 + 0 + 1 + 0 + 1) = 4 eπ
- dyz: (1 + 0 + 1 + 0 + 1 + 1) = 4 eπ

- Ligand in position 1: (0 + 0 + 0 + 1 + 1) eπ = 2 eπ
- Ligand in position 2: (0 + 0 + 1 + 1 + 0) eπ = 2 eπ
- Ligand in position 3: (0 + 0 + 1 + 0 + 1) eπ = 2 eπ
- Ligand in position 4: (0 + 0 + 1 + 1 + 0) eπ = 2 eπ
- Ligand in position 5: (0 + 0 + 1 + 0 + 1) eπ = 2 eπ
- Ligand in position 6: (0 + 0 + 0 + 1 + 1) eπ = 2 eπ

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10.4.4: The Spectrochemical Series

The spectrochemical series was determined through an examination of the absorption spectra of a series of octahedral $\mathrm{Co(III)}$ complexes by Tsuchida in the 1930's. The position of the d-d absorption band is influenced by the field strength of the ligand, which leads to greater or lesser values of Δ_o. That interaction depends on both the relative energies of the metal and ligand orbitals and the degree of overlap between these orbitals. The closer in energy the two orbitals are to each other, the greater the interaction. Also, the greater the overlap between the two orbitals, the greater the interaction.

Recall that sigma donors simply donate a lone pair to the metal but do not have additional metal-ligand interactions. The classic example is ammonia. The nitrogen in ammonia has only one lone pair to donate and is a simple sigma donor. Ethylenediamine, $\mathrm{NH_2CH_2CH_2NH_2}$ (en), is also a sigma donor because it has a single lone pair on each nitrogen atom. The en ligand is a slightly stronger sigma donor than ammonia. The difference is explained by the slightly stronger basicity of en compared to ammonia; the nitrogen lone pairs in en are better donors to both protons and metal ions.

en > NH3 (basicity)

The common pi donors include the halides and some oxygen donors. In these cases, the donor atom has an additional lone pair (or more) which may engage in formation of a pi bond by donation to a metal d orbital. Among the halides, fluoride produces the largest field splitting and iodide the smallest. This trend is also explained in terms of the relative basicity of these halides; fluoride is more basic than bromide. In addition, there is also understood to be better overlap between fluorine's p orbital and the d acceptor of a positively charged metal ion, compared to larger halides such as iodine.

F- > Cl- > Br- > I- (basicity)

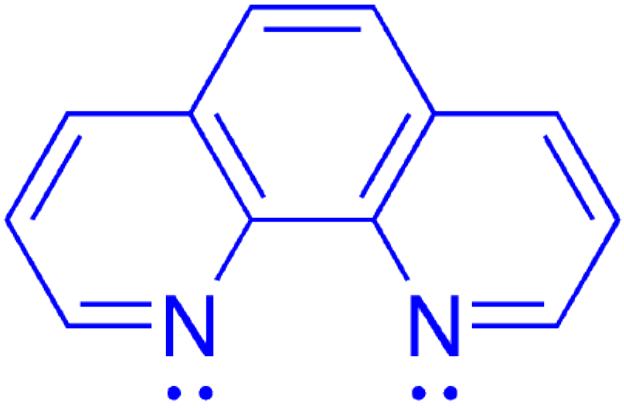
Oxygen donors do not follow this basicity trend. Hydroxide is thought to act as a better pi donor than water, partly because of its negative charge. A carboxylate ligand is not quite as strong a pi donor as hydroxide, probably because its lone pair is delocalized into the carbonyl group.

H20 > RCO2- > HO- (pi donation anion vs neutral)

The pi acceptors include familiar examples such as carbon monoxide (carbonyl ligand) as well as the aromatic phenanthroline.

CO > -CN > phenanthroline > NO2- > SCN-

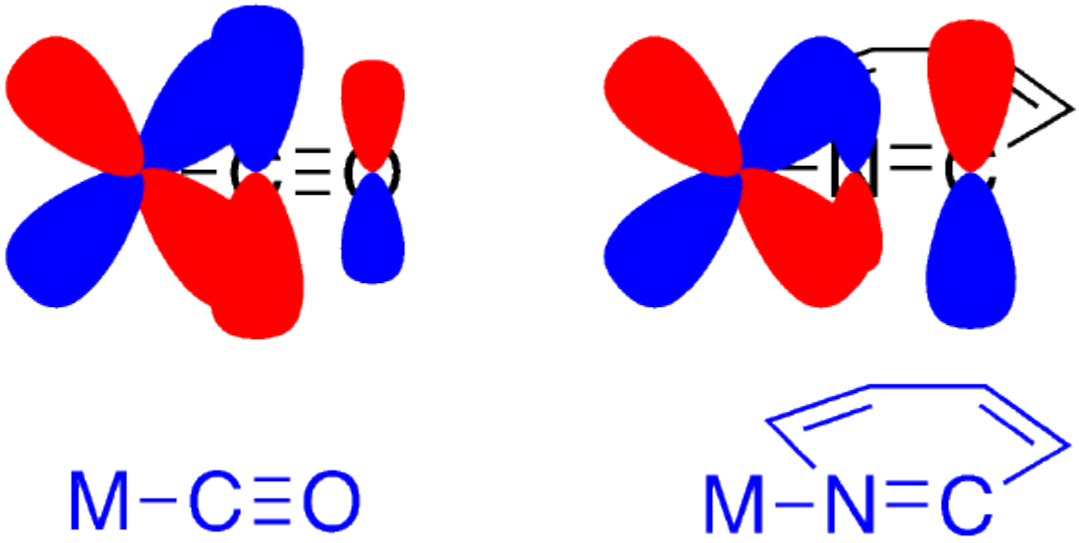
The phenanthroline may be an unfamiliar ligand. It is an aromatic amine, like pyridine. Other aromatic ligands, if they donate through a lone pair such as a phenyl, $\mathrm{C_6H_5^-}$, can also be considered pi acceptors. These compounds feature a pi bond that includes the donor atom, so there is a pi* orbital at that position capable of undergoing back-donation from the metal.



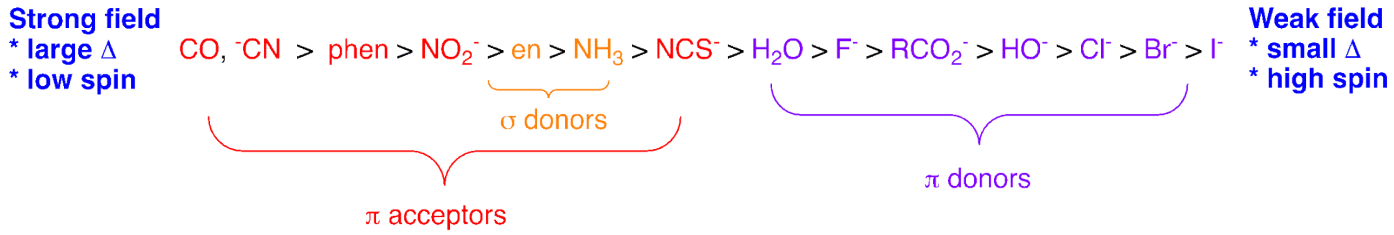
phenanthroline (phen)

Again, there are subtle variations among the field strengths exhibited by these pi acceptors, and there may be several factors contributing to those differences. For example, the cyanide is only slightly weaker field than the isoelectronic carbon monoxide. That small difference may be due to the negative charge on the cyanide rendering it a weaker electron acceptor. On the other hand, phenanthroline is neutral, but it is still a weaker donor than carbon monoxide. That weaker field may be due to the smaller lobe on the nitrogen atom in the pi* orbital in phenanthroline. Because nitrogen is more electronegative than carbon, it makes a greater contribution to the C=N pi bonding orbital than carbon; the opposite is true in the antibonding orbital. Carbon monoxide, in contrast, features a larger lobe on carbon in its pi* orbital. The result is better metal-ligand pi overlap with carbon monoxide than with phenanthroline.

Phosphines are also commonly considered to be pi acceptors, for subtle reasons that have been subject to some debate.1

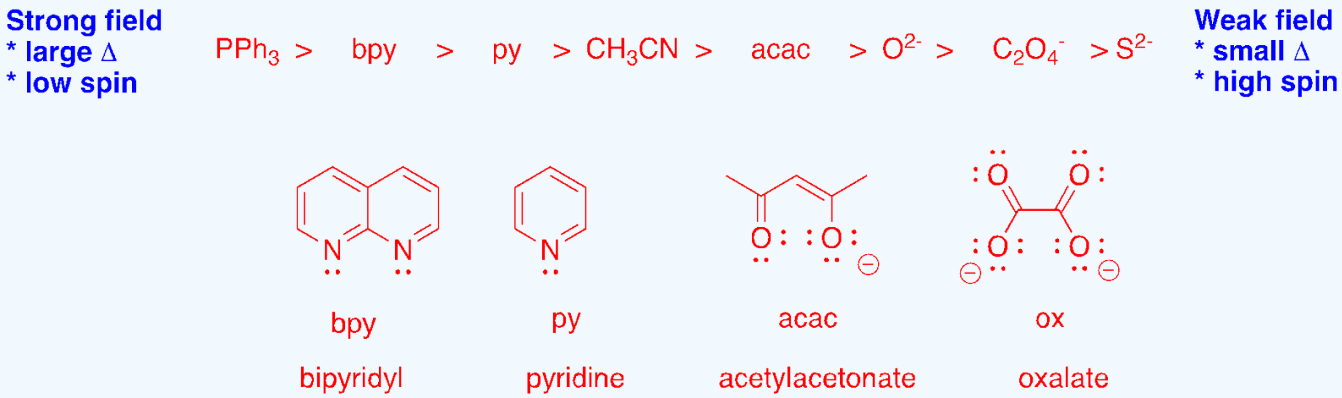


All three of these series can be collated to arrive at a combined list, which is a more complete spectrochemical series. Note that there may be some overlap between the different types of donors. Nevertheless, the overall trend holds: pi acceptors lead to the greatest field splitting on average, whereas di donors lead to the smallest.



Example 10.4.4.1

Some additional common ligands are displayed according to field strength, below. Classify these ligands as pi donors, sigma donors, or pi acceptors.



Solution

Ph3, based on its structure, appears to be a sigma donor only because it has just one lone pair on the donor atom. However, phosphines tend to behave as pi acceptors; that is, they appear to withdraw some electron density from the metal as indicated by the response of reporter ligands such as CO.

Bpy, py and CH3CN (acetonitrile) all appear to be pi acceptors. Like phen, they behave as weak pi acceptors.

Acac, oxide, oxalate and sulfide are all pi donors. The donor atom in each case has a lone pair in addition to the sigma donor pair.

References

1. Wolczanski, P. T. "Flipping the Oxidation State Formalism: Charge Distribution in Organometallic Complexes as Reported by Carbon Monoxide". *Organometallics* **2017**, *36*, 622-631.

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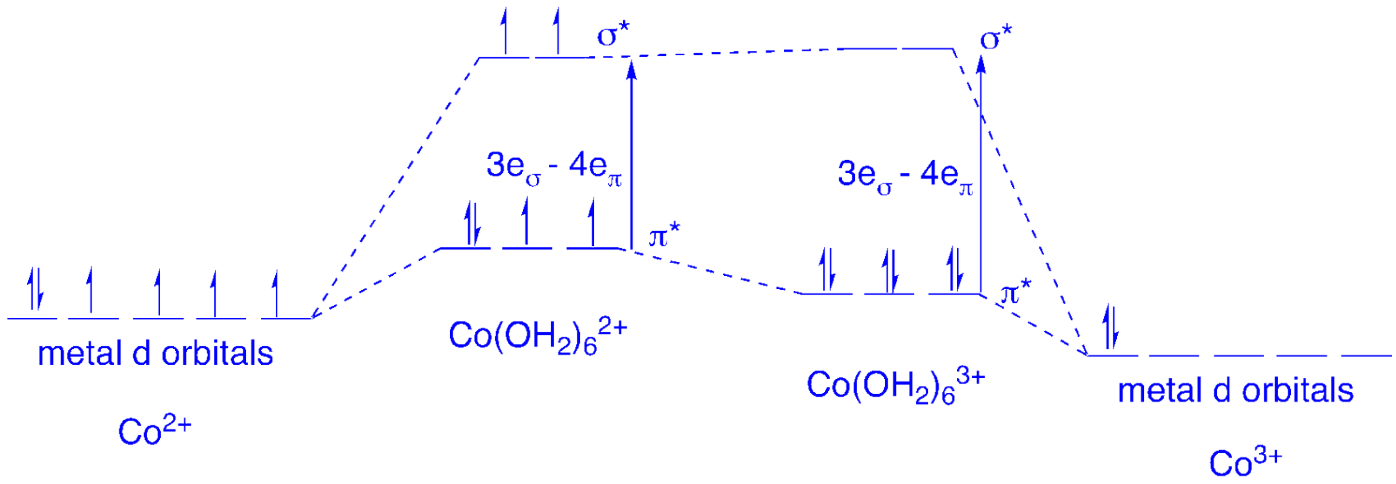
10.4.5: The Magnitude of Parameters eσ, eπ and Δ

In the angular overlap model (AOM), the field splitting, Δ, can be shown to result from a combination of the interaction parameters eσ and eπ. For example, in octahedral geometry,

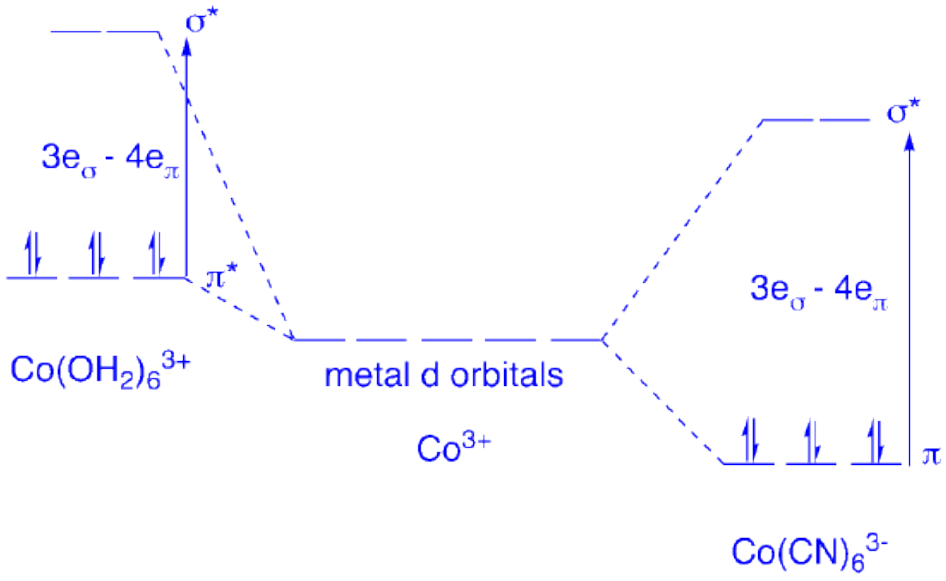
$$\Delta = 3e\sigma - 4e\pi \tag{10.4.5.1}$$

in which the value of eπ is positive for a pi donor but negative for a pi acceptor.

The magnitude of these parameters varies from one complex to another. As we have seen previously in examination of ligand field theory, both the metal ion and the identity of the ligand play a role in determining the magnitude of the field splitting. As outlined in the previous section on ligand field theory, the identity of the metal influences the d orbital splitting. Even for the same element, an increase in charge translates into a significant increase in the splitting parameter. For this reason, aqueous $\mathrm{Co(II)}$ ion is high spin, whereas the aqueous $\mathrm{Co(III)}$ ion is low spin.



The spectrochemical series tells us that the ligands also play a major role in determining the magnitude of the field splitting, with pi donors producing a smaller splitting than pi acceptors. The splitting produced by an aquo ligand is much smaller than the produced by a cyano ligand, for example.



Spectroscopic data can be used to determine the parameters eσ and eπ. A series of examples for different ligands coordinated to the Cr^{3+} ion are outlines in Table 10.4.5.1.

Table 10.4.5.1: Angular Overlap Parameters in Octahedral Cr(III) Complexes[1]

Ligand	eσ	eπ	Δ (cm-1)
π acceptors			
-CN	7,530	-930	26,310
pyridine	6,150	-330	19,770
σ donors			
en	7,260	assumed 0	21,780
NH3	7,180	assumed 0	21,540
π donors			
HO-	8,600	2,150	17,200
H2O	7,550	1,850	15,250
F-	8,200	2,000	16,600
Cl-	5,700	980	13,180
Br-	5,380	950	12,430
I-	4,100	670	9,620

It is worth noting that the parameters observed for Cr(III), although mostly consistent with the spectrochemical series, are not identical to those seen in Co(III). In particular, the places of water and hydroxide are switched in the series. Once again, the identity of the metal plays a role in the strength of interaction with the ligand, and certain ligands may be observed to interact more strongly with some metals than with others.

Example 10.4.5.1

Calculate Δ for tetrahedral Ni^{2+} when coordinated with the following ligands, given the parameters eσ and eπ.[1]

a. PPh_3 with $e\sigma = 5,000\ \text{cm}^{-1}$ and $e\pi = -1,750\ \text{cm}^{-1}$
b. Cl^- with $e\sigma = 3,900\ \text{cm}^{-1}$ and $e\pi = 1,500\ \text{cm}^{-1}$
c. Br^- with $e\sigma = 3,600\ \text{cm}^{-1}$ and $e\pi = -1,000\ \text{cm}^{-1}$

Solution

This question is a direct application of Equation 10.4.5.1:

a. PPh_3:

$$\begin{aligned}\Delta &= 3e\sigma - 4e\pi \\ &= 3(5,000) - 4(-1,750)cm^{-1} \\ &= 22,000\,\text{cm}^{-1}.\end{aligned}$$

b. Cl^-:

$$\begin{aligned}\Delta &= 3(3,900) - 4(1,500) \\ &= 5,700\,\text{cm}^{-1}.\end{aligned}$$

c. Br^-:

$$\begin{aligned}\Delta &= 3(3,600) - 4(1,000) \\ &= 6,800\,\text{cm}^{-1}.\end{aligned}$$

Example 10.4.5.2

AOM parameters eσ were calculated from spectroscopic data for a series of bidentate nickel complexes with octahedral geometry, $\mathrm{Ni(en')_2(NCS)_2}$.[2]

- en' = $\mathrm{H_2NCH_2CH_2NH_2}$ with eσ = 4,010 cm-1
- en' = $\mathrm{(CH_3)_2NCH_2CH_2N(CH_3)_2}$ with eσ = 3,165 cm-1
- en' = $\mathrm{(CH_3CH_2)_2NCH_2CH_2NH_2}$ with eσ = 2,485 cm-1 ($\mathrm{-NEt_2}$); eσ = 4,650 cm-1 ($\mathrm{-NH_2}$)

Explain the reasons for the differences in the eσ values.

Solution

Greater steric hindrance appears to decrease the interaction between the sigma donor and the metal. Thus, the magnitude of eσ decreases from the least hindered $\mathrm{-NH_2}$ group to the most hindered $\mathrm{NEt_2}$ group.

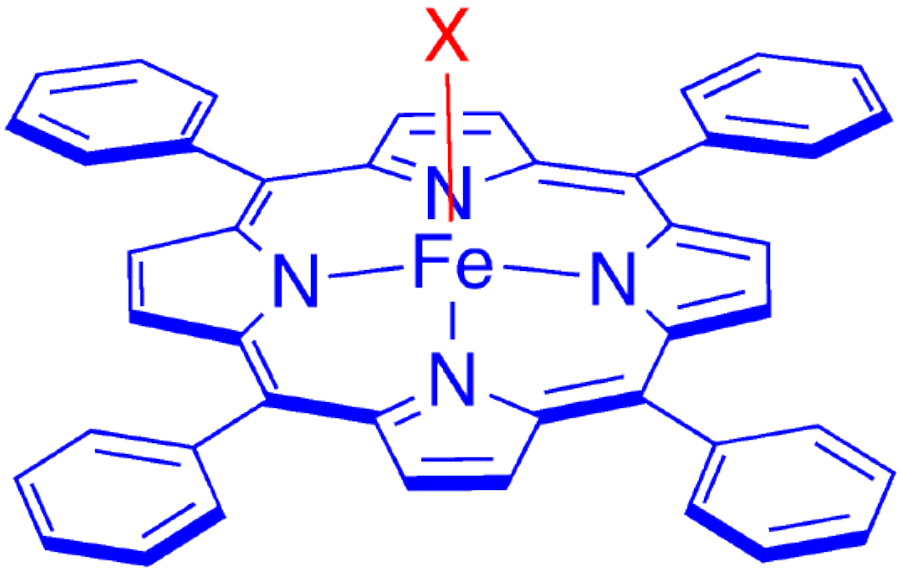
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2. Lever, A. B. P.; Walker, I. M.; McCarthy, P. J.; Mertes, K. B.; Jircitano, A.; Sheldon, R. "Crystallographic and Spectroscopic Studies of Low-Symmetry Nickel(II) Complexes Possessing Ling Nickel-Nitrogen Bonds", *Inorg. Chem.* **1983**, *22*, 2252-8.

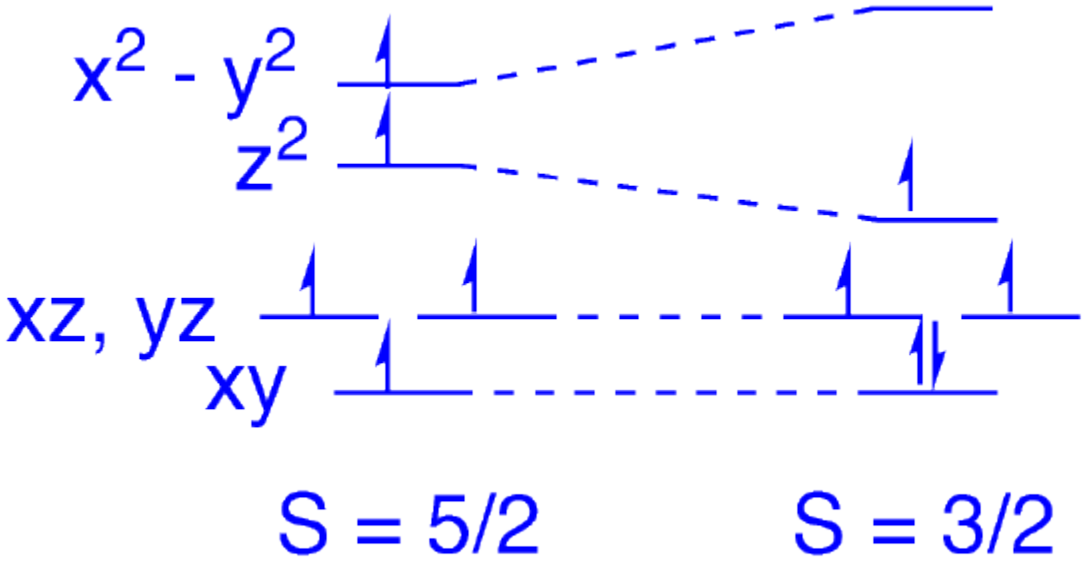
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10.4.6: The Magnetochemical Series

The relative strengths of metal-ligand binding interactions distilled into the spectrochemical series depend on an inference drawn from the difference between the ground and excited states. In contrast, the **magnetochemical series** offers similar information based solely on observation of the ground state. These observations are possible in iron(III) porphyrin complexes because of a subtle change in spin state that occurs upon substitution of the axial position with different ligands. The result is a series analogous to the spectrochemical series that is called the magnetochemical series. This series was developed chiefly by the lab of Christopher Reed at University of Southern California and University of California, Riverside.1



There are two unusual things that happen with these porphyrin complexes that allow measurement of metal-ligand interactions in this way. A distortion that occurs in the weak field case of these square pyramidal complexes results in spin pairing in the weak field configuration rather than the high field case. Also, in these porphyrin complexes, a quantum mechanical admixture occurs in which the 5/2 and 3/2 states exist in superposition with each other. As a result, the spin state in these complexes is often intermediate between these two cases.



One additional feature makes these porphyrin complexes quite useful in measuring a magnetochemical series. Paramagnetic

complexes produce dramatic shifts in nuclear magnetic resonance spectroscopy. In this case, the hydrogen atoms of the 5-membered pyrrole rings in the porphyrin system shift from about -60 ppm in the S = 3/2 case to about +80 ppm in the S = 5/2 case. In the case of a quantum admixture, the shift ranges in between these two limiting values. This NMR shift can be used to compare the field strength of the axial ligand.

An array of experiments eventually lead to a magnetochemical series. Example ligands from this series are shown in order here, from strong field to weak field:

$$NO^+ = CO > R_3Sn^- > -CH_3 > RS^- > F^- > -OPh > N_3^- = -OAc > NCS^- > Cl^- = -OH > Br^- > I^-$$

In addition, this method has allowed the inclusion of several very weakly bound ligands. These can be appended to the series as follows:

$$I^- > ReO_4^- > BF_4^- > CF_3SO_3^- > ClO_4^- > H_2O > SbF_6^- > CB_{11}H_{12}^-$$

Note the unusual position of water, which shows up as a much lower field ligand than in the Co(III) based spectrochemcial series for octahedral complexes. The difference is thought to come from the low spin Co(III) vs. the usually high spin Fe(III). Pi bonding is less favourable in the latter case and so the order in the iron porphyrin complexes is more strongly reflective of sigma donating effects. The anionic hydroxide is a better sigma donor than water because of greater electrostatic attraction to the metal.

Example 10.4.6.1

Organometallic ligands such as $-CH_3$ are not typically included in the spectrochemical series.

a. Characterize $-CH_3$ in terms of ligand type (pi donor, sigma donor, pi acceptor).
b. Explain why it appears so high in the magnetochemical series compared to other anions such as F-.

Solution

a. -CH3 is a sigma donor.
b. The -CH3 anion would be extraordinarily basic. The pKa of CH4 is estimated to be approximately 50, compared to a pKa of approximately 4 for HF. The -CH3 anion is a very strong sigma donor.

References

1. Reed, C.; Guiset, F. "Reversal of H2O and OH- Ligand Field Strength on the Magnetochemical Series Relative to the Spectrochemical Series. Novel 1-equiv Water Chemistry of Iron(III) Tetraphenylporphyrin Complexes." *J. Am. Chem. Soc.*, **2000**, *122*, 3281-2.

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10.5: The Jahn-Teller Effect

Certain metal ions frequently display distortions from ideal geometry, such that the symmetry of the compound is lowered. In tetragonal distortions of octahedral complexes, for example, the metal-ligand bond distances of two axial ligands may be significantly longer than the distances of the equatorial ligands. Alternatively, two of the metal-ligand distances may be compressed compared to others.

Sometimes, these distortions can be experimentally observed. For example, EXAFS (X-ray absorption fine structure) data for [Cu(OH2)6](BrO3)2, an octahedral complex in which all six Cu-O bonds ought to be the same length, show two different Cu-O distances of 1.96(1) and 2.32(2) Å (the digit in parentheses is used to convey the degree of uncertainty in X-ray measurements).1 That's an approximately 20% difference between the same kind of metal-ligand bond distances within the same complex.

These distortions, often called **Jahn-Teller distortions**, are observed in complexes of transition metals with specific electron configurations: high spin d4, low spin d7, and d9 (for which there is neither a low nor high spin case). These configurations give rise to unequally occupied degenerate orbitals. Degenerate orbitals are multiple orbitals at the same energy. The three p orbitals in an atomic shell are degenerate, for example. In contrast, non-degenerate orbitals occur at different energy levels. These two cases are illustrated below with the simplest conceivable case, a pair of orbitals.

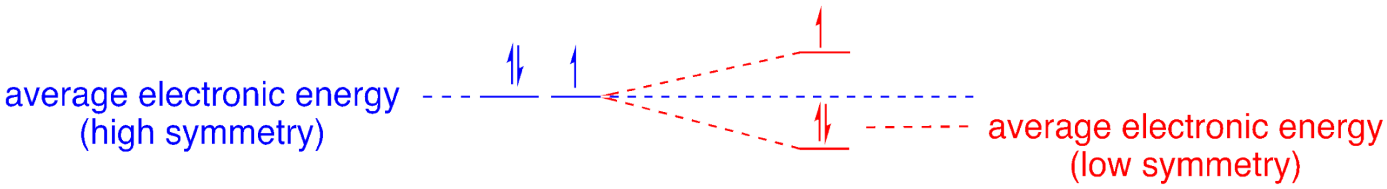


A set of degenerate orbitals might be equally or unequally occupied depending on the number of available electrons. For example, in the simple case of two degenerate orbitals, equal occupancy would occur if there were two electrons or four electrons because those even numbers of electrons could be divided evenly between the two orbitals. Either one or three electrons would lead to unequally occupied orbitals; there is no way to put the same number of electrons in each orbital in this case.

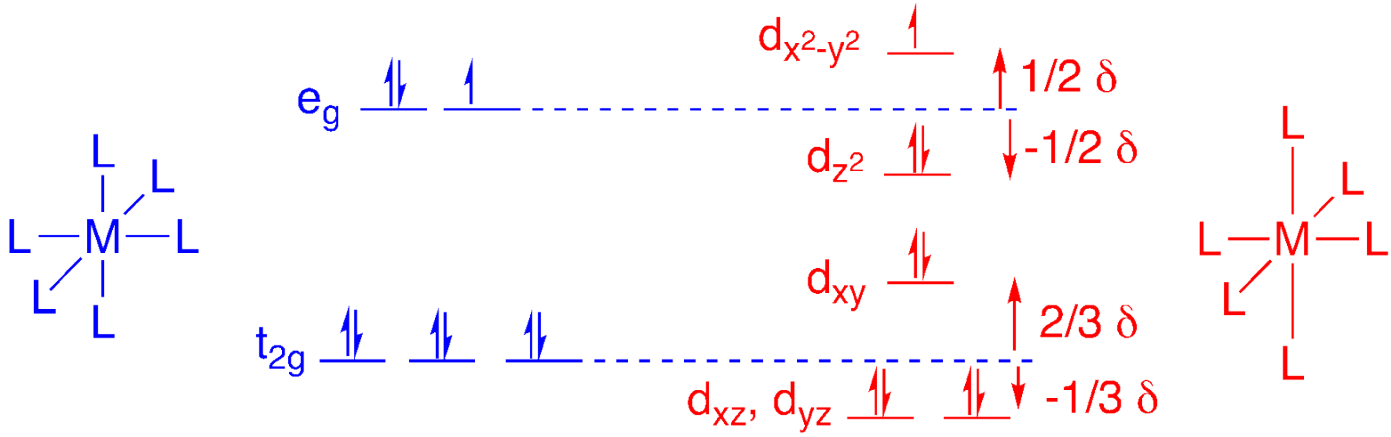




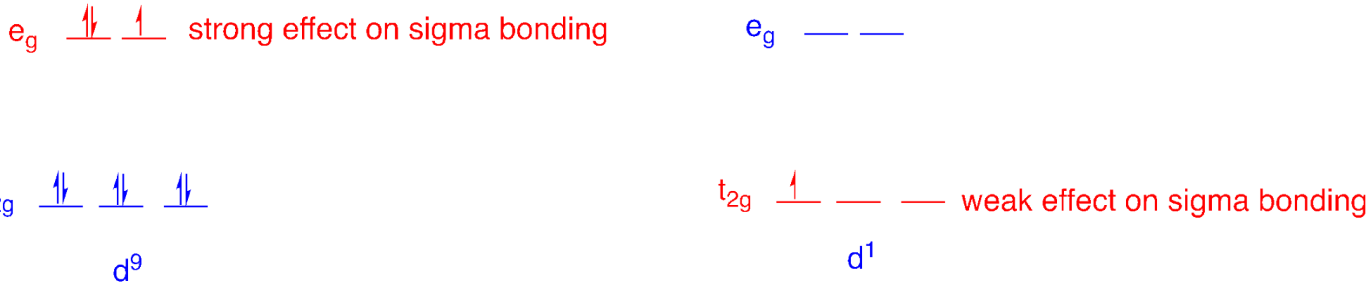
These cases of unequally occupied degenerate orbitals can lead to opportunities for distortion. When the symmetry of a complex drops, two otherwise degenerate orbitals might no longer exist at the same energy as each other. That means, for example, that instead of having three electrons at the same energy, we would have two electrons at lower energy and one at higher. There would be a net decrease in energy in the non-symmetric, distorted case.



In the context of an octahedral d9 complex, elongation of the bonds to the axial ligands leads to a very slight lowering of the d orbitals that interact with ligands along the z axis: the dz2 and the dxz and dyz. The other orbitals are shown increasing slightly according to the principle that the average energy of the orbitals is preserved at the orbital barycenter (as opposed to the energy of the electrons, which decreases in this case).



Not all cases of unequally occupied degenerate orbitals produce measurable Jahn Teller distortions. In octahedral geometry, examples of strong Jahn Teller effects are seen when the unequally occupied orbitals are in the eg set rather than the t2g set. The eg set is the one that is linked to sigma bonding, after all, so the orbitals in that level are strongly influenced by the strength of that sigma bonding interaction, and hence the bond length.



Changes in bond length are not the only observable result of the Jahn Teller effect. The absorption spectra of some octahedral complexes show two distinct d-d bands rather than the one band absorbed for pure octahedral symmetry. This observation is a consequence of having additional orbital levels giving rise to distinct electronic transitions. This phenomenon is also seen if the excited state, rather than the ground state, experiences Jahn Teller distortion.

The Jahn Teller effect also plays a role in reactivity. For example, it is thought to promote the lability of octahedral Cu(II) complexes by weakening the bonds to axial ligands via the tetragonal distortion.

References

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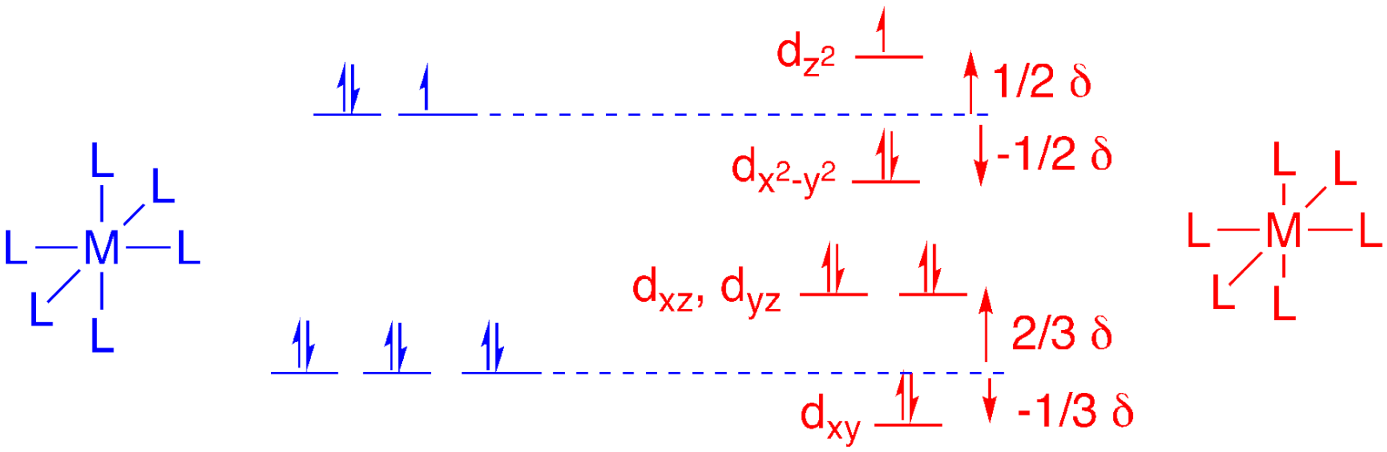
Problems

1. Given the effect of axial bond elongation on the d orbital energy levels in an octahedral complex, show the corresponding effects that would result from shortening of the axial metal ligand bonds.

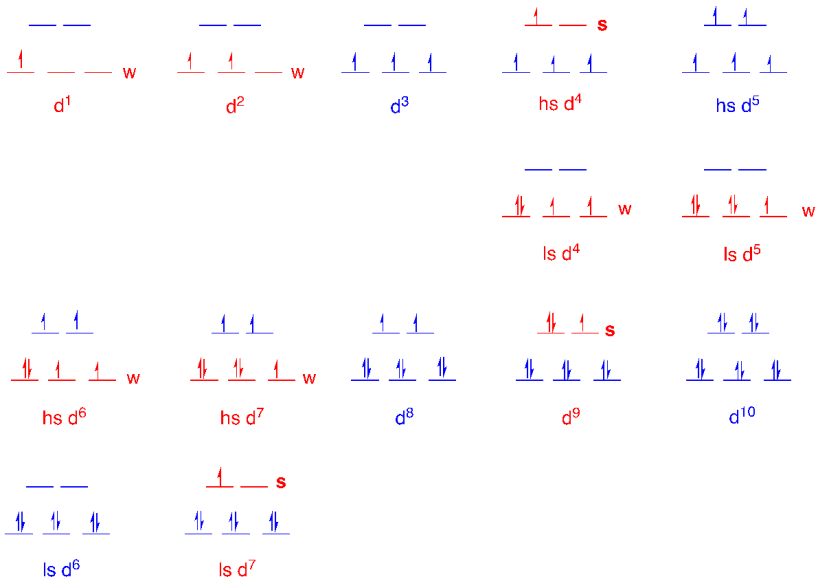
2. Fill in octahedral d orbital splitting diagrams for d1 to d10 configurations to show why only high spin d4, low spin d7 and d9 configurations exhibit strong Jahn Teller distortions.

Solutions

1. This time, dz2 is elevated, along with the dxz and dyx.



2. The w indicates a weak Jahn Teller effect. The s indicates a strong Jahn Teller effect.



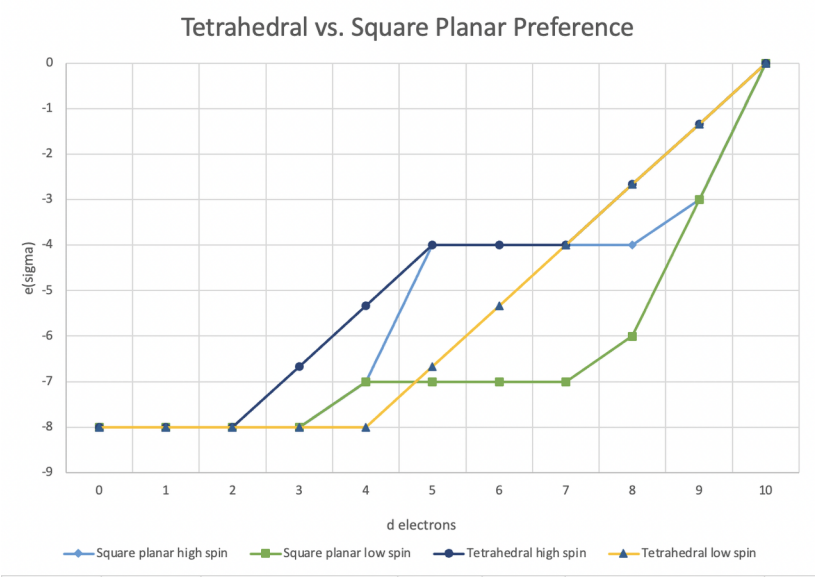
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10.6: Four- and Six-Coordinate Preferences

Students sometimes want to be able to predict the coordination geometry that will be adopted by a particular combination of metal ion and ligands. In reality, there are enough variables involved in both the ligand and the metal that such predictions are not possible with any certainty.

Nevertheless, there are some broad trends that can be highlighted by looking at what the angular overlap model says about geometric preferences. One of the most common questions is whether a four coordinate complex will adopt a tetrahedral or square planar geometry. Probably the most important factor in this case is the steric bulk of the ligands. The ligand-metal-ligand bond angles in tetrahedral geometry are ideally 109 degrees, compared to 90 degrees in square planar geometry. As a result, ligands are spaced further apart in tetrahedral geometry than in square planar geometry, so bulkier ligands favor tetrahedral complexes.

On the other hand, the angular overlap model (as well as other approaches) suggests some advantages of square planar geometry. A comparison of eσ at a range of d electron configurations for both high spin and low spin cases is plotted below.



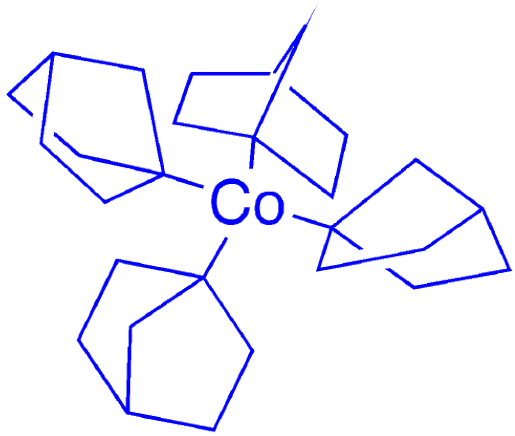
From the outset, we should note that low spin tetrahedral complexes are almost unheard of, so we should really compare square planar to the high spin tetrahedral case. In the comparison between high spin tetrahedral and high spin square planar geometry, square planar is favored only for d3, d4, d8 and d9 configuration. However, as we will see shortly, square planar complexes of d3 and d4 metals are not very common because metals with those electron configurations are more likely to adopt higher coordination geometries, such as five or six coordination. All of the other cases are more likely to adopt a tetrahedral geometry because if electronic stabilization factors are equal then steric factors (relief of ligand crowding) will prevail.

If we are comparing low spin square planar to high spin tetrahedral cases, there is an increased preference for the square planar geometry for all but the d1, d2 and d10 configurations. That suggests square planar geometry is usually favored unless there are steric factors that push the geometry to tetrahedral. Of course, the comparison we have used ignores eπ. Because the magnitude of eσ and eπ vary with different ligands and metals, we can't easily include both factors in one graph. However, we do know that π donors will make it more likely that we are dealing with a high spin square planar case, whereas π acceptors will lead to a low spin square planar case. These two cases have a dramatic effect on the d orbital splitting diagram. The angular overlap model suggests a dramatic reordering of the square planar d orbital splitting diagram in these cases.

Consequently, square planar geometry is expected to be much more common in cases with π acceptor ligands, whereas tetrahedral geometry should be more common in cases with π donor ligands.

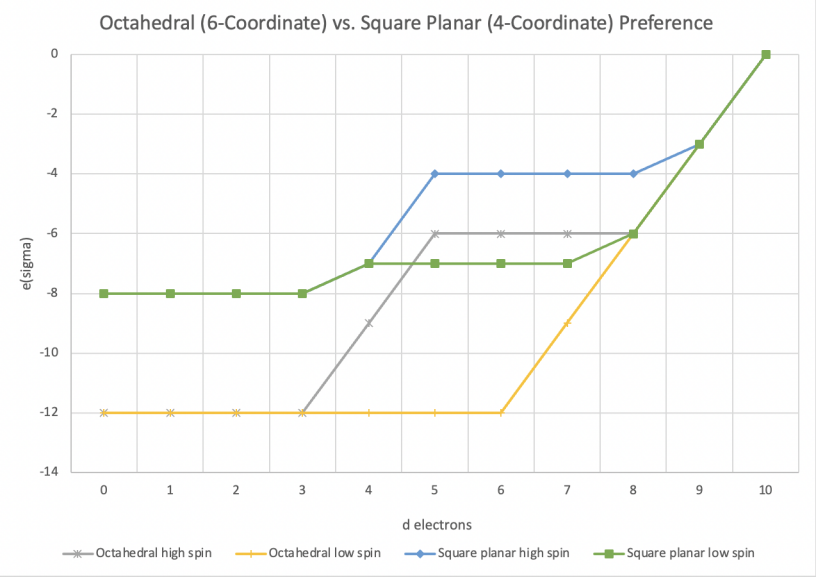
It is worth noting that the first reported group of low spin tetrahedral complexes, the crystallographically characterized tetrakis(norbornyl)cobalt(IV), (nor)4Co, as well as the cationic and anionic (nor)4Co+ and (nor)4Co-, are d5, d4 and d6 complexes,

respectively.1 AOM predicts very similar stabilization in low spin square planar and low spin tetrahedral geometries in these cases. However, the tetrahedral geometry is largely enforced by the bulky norbornyl ligands.



$(nor)_4Co$

As mentioned above, there is a general preference for six coordination over four coordination, especially at lower d electron counts. A simple AOM comparison indicates octahedral geometry is favored for the low spin case between d0 and d7. Even high spin octahedral geometry is favored electronically over low spin square planar up to d4, with only a modest preference for square planar between d5 and d7. It isn't surprising that octahedral geometry is so common. In very simple terms, this preference comes from the energetically favored formation of six metal-ligand bonds rather than only four metal-ligand bonds.



Example 10.6.1

Confirm the stabilization values from the angular overlap model for (a) high spin and (b) low spin tetrahedral geometry.

Solution

Stabilization (σ only) ΔE = 0(# *e* electrons) - 43(# *t2* electrons) - 4(2 electrons per ligand) eσ

a) For high spin:

- d0: ΔE = 0(0) + 43(0) - 8 eσ = -8 eσ
- d1: ΔE = 0(1) + 43 (0) - 8 eσ = -8 eσ
- d2: ΔE = 0(2) + 43 (0) - 8 eσ = -8 eσ
- d3: ΔE = 0(2) + 43 (1) - 8 eσ = -623 eσ
- d4: ΔE = 0(2) - 43(2) - 8 eσ = -513 eσ
- d5: ΔE = 0(2) - 43 (3) - 8 eσ = -4 eσ
- d6: ΔE = 0(3) - 43 (3) - 8 eσ = -4 eσ
- d7: ΔE = 0(4) - 43 (3) - 8 eσ = -4 eσ
- d8: ΔE = 0(4) - 43 (4) - 8 eσ = -223 eσ
- d9: ΔE = 0(4) - 43 (5) - 8 eσ = -113 eσ
- d10: ΔE = 0(4) - 43 (6) - 8 eσ = 0 eσ

b) For low spin:

- d0: ΔE = 0(0) + 43 (0) - 8 eσ = -8 eσ
- d1: ΔE = 0(1) + 43 (0) - 8 eσ = -8 eσ
- d2: ΔE = 0(2) + 43 (0) - 8 eσ = -8 eσ
- d3: ΔE = 0(3) + 43 (0) - 8 eσ = -8 eσ
- d4: ΔE = 0(4) -43 (0) - 8 eσ = -8 eσ
- d5: ΔE = 0(4) - 43 (1) - 8 eσ = -623 eσ
- d6: ΔE = 0(4) - 43 (2) - 8 eσ = -513 eσ
- d7: ΔE = 0(4) - 43 (3) - 8 eσ = -4 eσ
- d8: ΔE = 0(4) - 43 (4) - 8 eσ = -223 eσ
- d9: ΔE = 0(4) - 43 (5) - 8 eσ = -113 eσ
- d10: ΔE = 0(4) - 43 (6) - 8 eσ = 0 eσ

Example 10.6.2

Calculate the preference for square planar geometry for each d electron count in (a) the case of high spin square planar vs. high spin tetrahedral, and (b) the case of low spin square planar vs. high spin tetrahedral.

Solution

Preference = ΔΔE = ΔE(square planar) - ΔE(tetrahedral)

a) For high spin:

- d0: ΔΔE = - 8 -(- 8) eσ = 0 eσ
- d1: ΔΔE = - 8 -(- 8) eσ = 0 eσ
- d2: ΔΔE = - 8 -(- 8) eσ = 0 eσ
- d3: ΔΔE = - 8 - (-623)eσ = -113eσ
- d4: ΔΔE = -7 - (-513) eσ = -123eσ
- d5: ΔΔE = -4 - (4) eσ = 0 eσ
- d6: ΔΔE = -4 - (4) eσ = 0 eσ
- d7: ΔΔE = -4 - (4) eσ = 0 eσ
- d8: ΔΔE = -4 - (223) eσ = -113 eσ
- d9: ΔE = -3 - (113) eσ = -123 eσ
- d10: ΔE = 0 - (0) eσ = 0 eσ

b) For low spin:

- d0: ΔΔE = - 8 -(- 8) eσ = 0 eσ
- d1: ΔΔE = - 8 -(- 8) eσ = 0 eσ
- d2: ΔΔE = - 8 -(- 8) eσ = 0 eσ
- d3: ΔΔE = - 8 - (-623)eσ = -113eσ

- d4: ΔΔE = -7 - (-513) eσ = -123eσ
- d5: ΔΔE = -7 - (4) eσ = -3 eσ
- d6: ΔΔE = -7 - (4) eσ = -3 eσ
- d7: ΔΔE = -7 - (4) eσ = -3 eσ
- d8: ΔΔE = -6 - (223) eσ = -313 eσ
- d9: ΔE = -3 - (113) eσ = -123 eσ
- d10: ΔE = 0 - (0) eσ = 0 eσ

References

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10.7: Other Shapes

Although four- and six-coordinate geometries are probably the most commonly observed in inorganic chemistry, a range of other shapes have also been reported.1 The other most common coordination number is five. Geometries for five-coordination include both trigonal bipyramidal and square pyramidal. Both are common, and distorted geometries in between these two limiting cases are even more commonly observed. The fractional parameter, τ (tau), is usually reported with structural analyses of five-coordinate compounds to convey where the structure falls on this continuum. A value of τ = 1 corresponds to perfect trigonal bipyramidal and a value of τ = 0 corresponds to perfect square pyramidal. Most reported complexes have values solidly in between these extremes. However, there are some ligands, such as porphyrins, in which a rigid ring of four basal donors enforces square pyramidal geometry more closely.

Lower coordination numbers are less common but are reported in certain cases. Two-coordinate compounds are sometimes observed in complexes of the coinage metals. They include a range of ligands, including σ donors in [Ag(NH3)2]+ ion, π donors in [CuCl2]- ion and π acceptors in [Au(CN)2]- ion, for example. Three coordinate complexes have been reported from across the periodic table, especially with sterically demanding ligands such as Bradley and Chisholm's [(Me3Si)2N]3M (Sc, Ti, V, Cr, Fe) or Wolczanski's (t-Bu3SiO)3Ta.2,3

Coordination numbers higher than six are sometimes observed. These cases often involve early transition metals in high oxidation states that are less electronically saturated. Examples are also seen in the lanthanides and actinides owing to their large size. There is even a reported sixteen-coordinate complex, although it is of an alkali metal ion and not a transition metal ion.

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Problems

1. Use the angular overlap model to

i) calculate d orbital energy destabilization and

ii) construct d orbital splitting diagrams for linear (two-coordinate) geometry with the following ligand types.

a) sigma donor b) pi acceptor c) pi donor

2. Use the angular overlap model with sigma-only interactions to calculate d orbital energy destabilization in square pyramidal geometry.

3. Use the angular overlap model with sigma-only interactions to construct d orbital splitting diagrams for the following geometries.

a) trigonal planar b) trigonal pyramidal c) square bipyramidal

Solutions

1. i) a) Positions 1, 6.

dz2: (1 + 1) eσ = 2 eσ

dx2-y2: (0 + 0) eσ = 0

dxy: (0 + 0) eσ = 0

dxz: 0

dyz: 0

b) Positions 1, 6.

dz2: 0

dx2-y2: - (0 + 0) eπ = 0

dxy: - (0 + 0) eπ = 0

dxz: - (1 + 1) eπ = -2 eπ

dyz: - (1 + 1) eπ = -2 eπ

c) Positions 1, 6.

dz2: 0

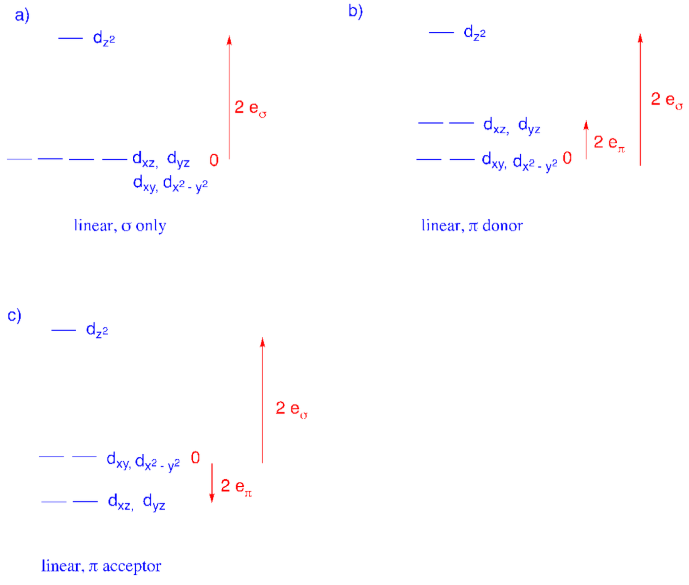
dx2-y2: (0 + 0) eπ = 0

dxy: (0 + 0) eπ = 0

dxz: (1 + 1) eπ = 2 eπ

dyz: (1 + 1) eπ = 2 eπ

ii)



2. Positions 1, 2, 3, 4, 5:

dz2: (1 + 1/4 + 1/4 + 1/4 + 1/4) eσ = 2eσ

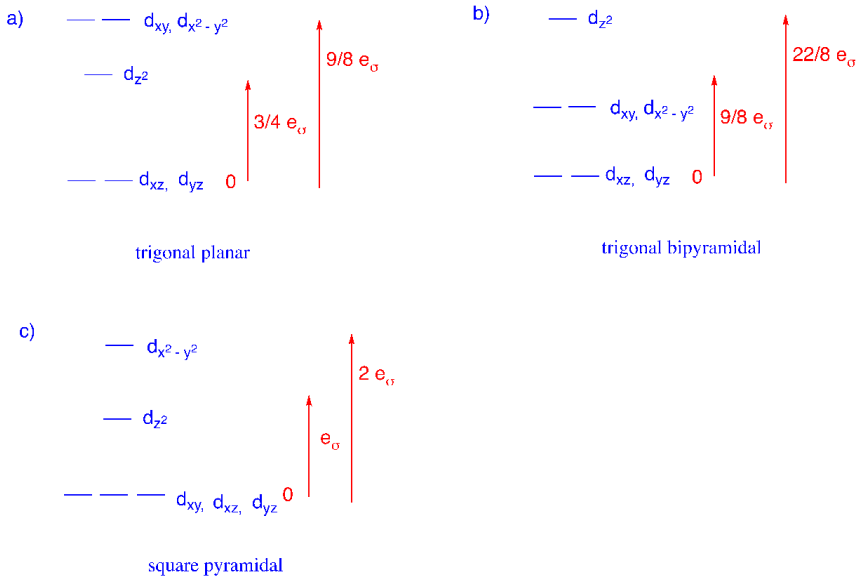
dx2-y2: (0 + 3/4 + 3/4 + 3/4 + 3/4) eσ = 3eσ

dxy: 0

dxz: 0

dyz: 0

3.



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10.8: Coordination Chemistry III - Electronic Spectra

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10.9: COORDINATION CHEMISTRY IV - REACTIONS AND MECHANISMS

10.9.1: Introduction to Reactions of Metal Complexes

10.9.2: Substitutions Reactions

10.9.2.1: Introduction to Substitution Reactions

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10.9.1: Introduction to Reactions of Metal Complexes

Although there are a vast array of reactions that occur at transition metal centers, we will touch on only a subset of the possibilities. This chapter will focus on the reactions of octahedral and square planar metal complexes, and the reactions will be divided into three types:

1. **Substitution reactions at the metal center**: these are reactions in which one ligand is replaced with another ligand within the metal's inner coordination sphere.
2. **Redox**: these are reactions in which the metal oxidation state formally changes by gaining or loosing electrons.
3. **Ligand reactions**: these are reactions that occur primarily on the ligands that are bound to metal ions.

Review of reaction coordinate diagrams and terms

Before we begin our discussion of reactions, let's review some of the vocabulary and models that chemists use to understand reactions.

A chemical reaction can be represented with a reaction coordinate diagram in which the total potential energy of a state is plotted in the vertical y axis, and the "**reaction coordinate**" (sometimes also referred to as "reaction progress", or "extent of reaction") is plotted on the horizontal x axis. The reaction coordinate is often drawn as the progress of a reaction from reactants (R) on the left to products (P) on the right.* Examples of reaction coordinate diagrams for a one-step and a two-step reaction are shown in Figure $10.9.1.1$. Notice the difference in the reaction profile that depends on the number of reaction steps. A one-step reaction has one "hill" shape, while a two step reaction takes on a "saddle" shape.

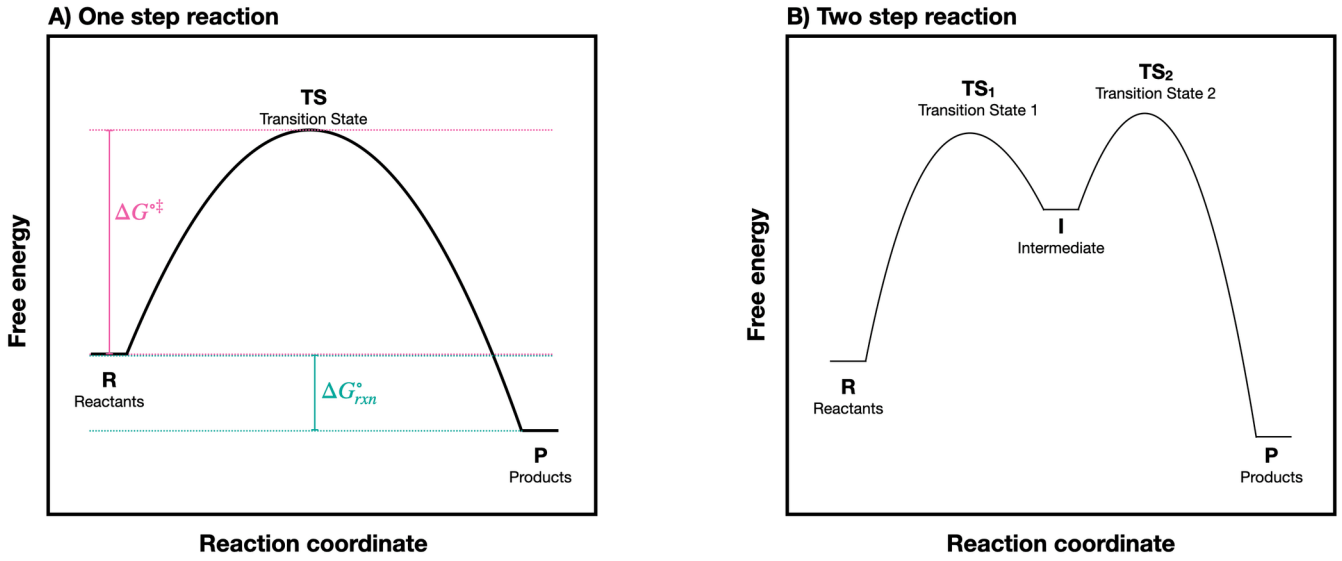


Figure $10.9.1.1$: Examples of a reaction coordinate diagram for a one-step reaction (left), and a two-step reaction (right). (CC-BY-SA; Kathryn Haas)

*Many students find it helpful to envision the horizontal axis in an reaction coordinate diagram as being analogous to the progress bar at the bottom of a youtube video.

Thermodynamics

The difference in energy between reactants (R) and products (P) indicates whether reactants or products will dominate at thermodynamic equilibrium. At standard conditions, this difference is the standard Gibbs Free Energy of the reaction (ΔG°_{rxn} or ΔG°). The Gibbs free-energy change is a combination of enthalpy change (ΔH°) and entropy change (ΔS°):

$$\Delta G^{\circ} = \Delta H^{o} - T\Delta S^{o}$$

where

- T is the temperature in Kelvin (recall that the Kelvin temperature is simply the Celsius temperature plus 273.15).
- Enthalpy change (ΔH°) is the heat released or absorbed by the reaction.
- Entropy change (ΔS°) is the change in disorder from reactants to products. In a reaction in which one molecule cleaves into two smaller molecules, for example, disorder increases, so ΔS° is positive.

The standard Gibbs free energy change for a reaction can be related to the reaction's equilibrium constant K_{eq} by the equation:

$$\Delta G^\circ = -RT \ln K_{eq}$$

where R is the gas constant (8.314 J/mol×K) and T is the temperature in Kelvin (K).

A negative value for $\Delta \mathrm{G_{rnx}}^\circ$ (an exergonic reaction) corresponds to $\mathrm{K_{eq}}$ being greater than 1, an equilibrium constant which favors product formation. Conversely, an endergonic reaction has a positive value of $\Delta \mathrm{G}^\circ$, and a $\mathrm{K_{eq}}$ between 0 and 1.

Kinetics

The highest point between two energy minima is a transition state (TS). The difference in energies of the reactant and the highest-energy TS is the standard free energy of activation ($\Delta \mathrm{G}^{\circ\ddagger}$). The activation energy, in combination with the temperature at which the reaction is being run, determines the rate of a reaction: the higher the activation energy, the slower the reaction. The rate constant (k) is the proportionality constant relating the rate of the reaction to the concentrations of reactants. The relationship between activation energy and the rate constant, k, is given by the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}} \qquad \text{or} \qquad \ln k = \ln A - \frac{E_A}{RT}$$

A rate law is an expression showing the relationship of the reaction rate to the concentrations of each reactant. The rate is defined as the change in reactants or products over time. For example, in a reaction of two reactants (R_1 and R_2) to form product (P), a rate law could be written as follows:

$$\frac{d[\mathrm{P}]}{dT} = \mathrm{k[R_1][R_2]}$$

The rate law above is second order overall, and first order with respect to both R_1 and R_2. The order indcates the power of reactant concentrations for individual reactants or overall for the reaction.

In a one-step reaction, the product is formed in one step. There is an energy barrier to overcome so that this process can happen. At the height of that energy barrier is the TS. In a one-step reaction, there is one transition state. In contrast, in a two-step reaction, there are two transition states and an intermediate (denoted by the letter I). The first step from R to I, passes over transition state TS_1, is endergonic. The second step passing through transition state TS_2 is exergonic. The intermediate (I) is thus depicted as an energy 'valley' (a local energy minimum) situated between the two energy maxima; TS_1 and TS_2.

In Figure $10.9.1.1$B, notice that the energy barrier for the first step is larger than the energy barrier for the second step. This means that the first step is slower than the second. In a multi-step reaction, the slowest step - the step with the largest energy barrier - is referred to as the rate-limiting or rate-determining step. The rate-determining step can be thought of as the 'bottleneck' of the reaction: a factor which affects the rate-determining step will affect the overall rate of the reaction. Conversely, a factor which affects only a much faster step will not significantly affect the rate of the overall reaction.

Summary and Key Terms

Reaction coordinate diagrams convey some very important ideas about how the reaction can proceed, and about the thermodynamics and kinetics of the reaction. In the sections that follow, the following key terms will be used:

Description of Key Terms

Reactants (R): The molecular species that are the starting materials for a chemical reaction. These are often written at the left side of a reaction coordinate diagram.

Products (P): The molecular species that result from a chemical reaction. These are often written at the right side of a reaction coordinate diagram.

Transition State (TS): a transition state is the transient species that exists at an energy maximum. In other words, TS's are highest-energy structures along a reaction pathway. Hammond's postulate suggests that the structure of a transition state should resemble the lower-energy species (R, P, or I) adjacent to it along the reaction coordinate, and most closely resembles the structure of the species closest in energy.

Intermediate (I): an intermediate is a high-energy structure at a local minimum. Intermediates are sometimes thought of as long-lived transition states. Unlike transition states, intermediates sometimes exist long enough and in high enough concentration to be detectable experimentally.

Microscopic reversibility: if a reaction can proceed in the forward direction from R to P, then in principle, it can also proceed in the reverse direction from P to R. There may be many possibilities for how a reaction *could* happen, but the lowest-energy pathway in the forward direction is also the lowest energy pathway in the reverse direction. In other words, the reactions passes through the same lowest-energy I and TS in the forward and reverse directions.

Steady-State Approximation: the concentration of an intermediate is assumed to react as quickly as it forms. This approximation allows us to assume that concentration of an intermediate remains "steady" throughout the reaction progress. This approximation is useful for analysis of reaction kinetics.

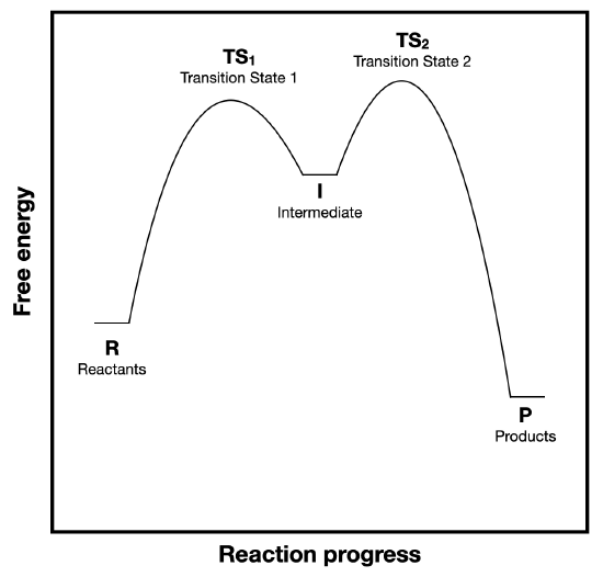
Order: The order of a reaction indicates the power of total reactant concentration in a kinetic rate law. The order of a reactant indicates that reactant's power in the rate law. For example, is a rate law that is $\mathrm{Rate} = \mathrm{k}\ [\mathrm{A}]^2[\mathrm{B}]$, the reaction is second order in A, first order in B and third order overall. If there were also a reactant, C, that was not part of the rate law, the reaction would be zero order with respect to C.

Exercise 10.9.1.1

Figure $10.9.1.1$ is replicated below for convenience. This figure shows a reaction coordinate diagram for a two-step reaction.

a. (ΔG°) and $\Delta G^{\circ\ddagger}$) are labeled on Figure $10.9.1.1A$, but not on Figure $10.9.1.1B$. Add the appropriate labels to diagram B. (copied below for convenience).

b. Consider the energy barriers for the first and second steps and explain why the steady-state approximation is a valid assumption.

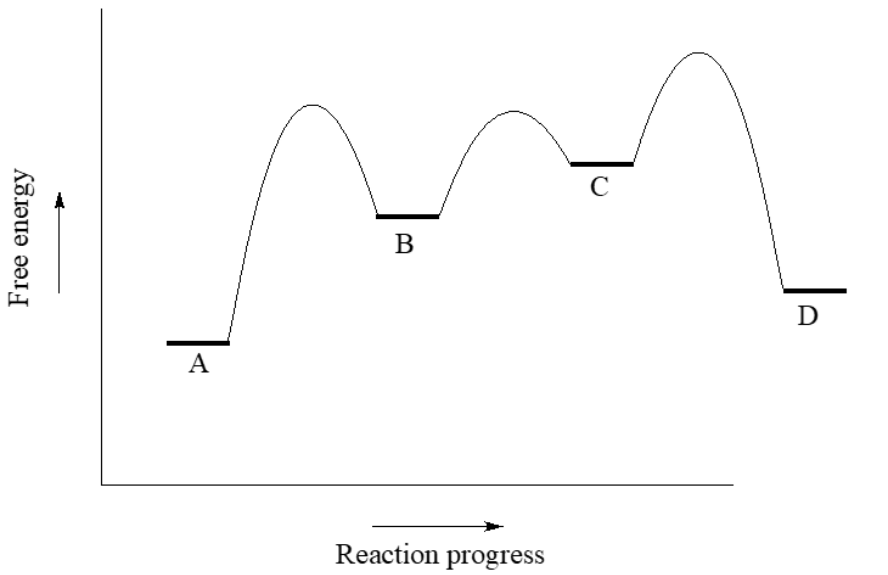


Answer available at the end of this section.

Exercise 10.9.1.1

Use the reaction coordinate diagram below to answer the questions.

a. Is the overall reaction endergonic or exergonic in the forward (A to D) direction?
b. How many steps does the reaction mechanism have?
c. How many intermediates does the reaction mechanism have?
d. Redraw the diagram if necessary. Add a label showing the energy barrier for the rate-determining step of the forward reaction.
e. Add a label showing ΔG°_{rxn} for the reverse reaction (D to A).
f. What is the fastest reaction step, considering both the forward and reverse directions?



Answer available at the end of this section.

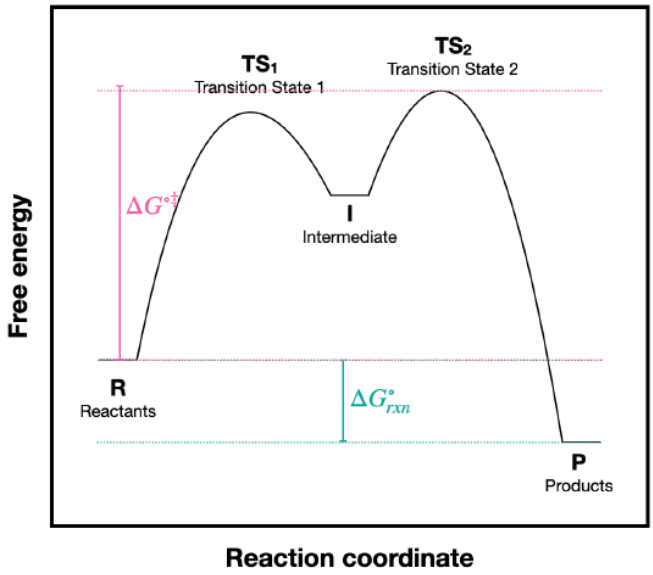
Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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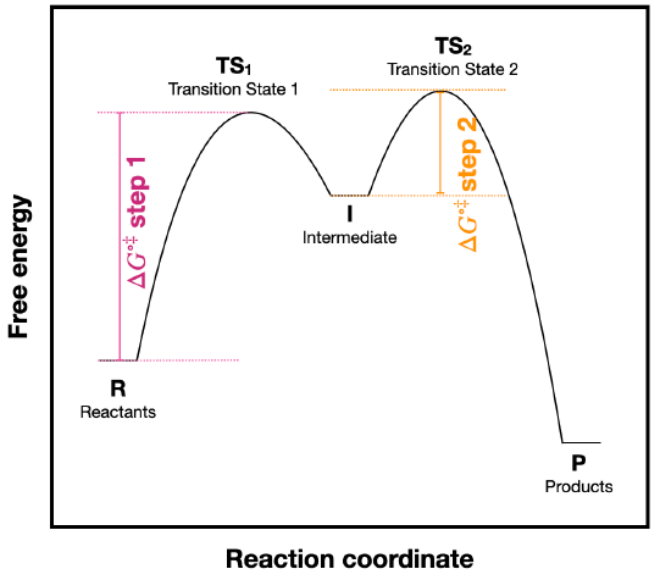
Answers

Exercise 10.9.1.1

a) The activation energy for this reaction is the difference between R and TS_2 because TS_2 is the highest energy along the reaction pathway.

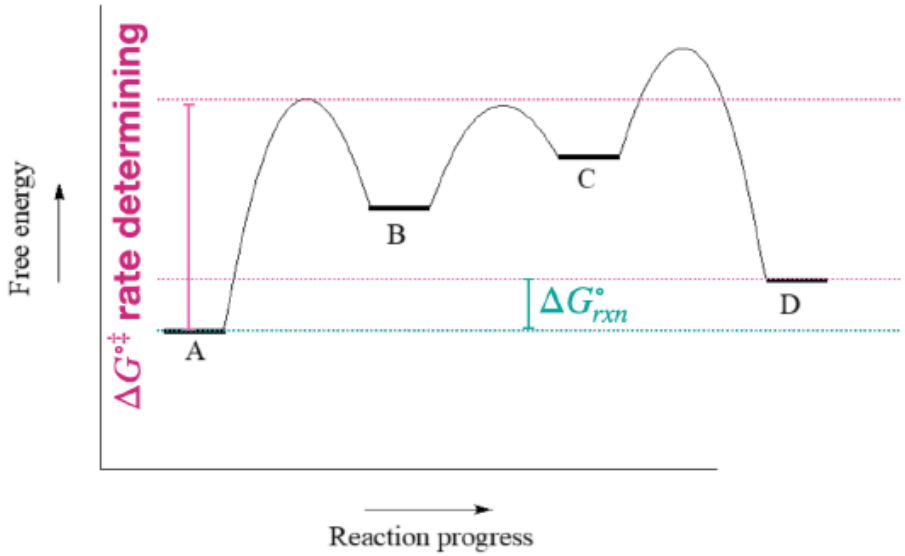


b) The activation energy for step 2 is much smaller than for step 1. This tells us that step 2 occurs faster than step 1. So, the concentration of intermediate should not increase over the course of the reaction, and it should react at least as fast as it is formed. The fact that the activation barrier for step 2 is less than for step one allows us to assume that [I] does not change over the course of the reaction. This should generally be true for all intermediates.



Exercise 10.9.1.1

a. D is higher energy than A, so the reaction is endergonic
b. Three steps
c. Two: B and C are intermediates.
d. The first step is rate determining since it has the largest activation barrier.
e. ΔG°_{rxn} for the reverse reaction (D to A) is the same as for the froward direction, with a reverse of its sign.



f. The fastest step has the lowest barriers: this would be the step to/from B and C.

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10.9.2: SUBSTITUTIONS REACTIONS

10.9.2.1: Introduction to Substitution Reactions
10.9.2.2: Inert and Labile Complexes
10.9.2.3: Mechanistic Possibilities

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10.9.2.1: Introduction to Substitution Reactions

Ligand substitution refers to the replacement of one ligand in a coordination complex with another ligand.

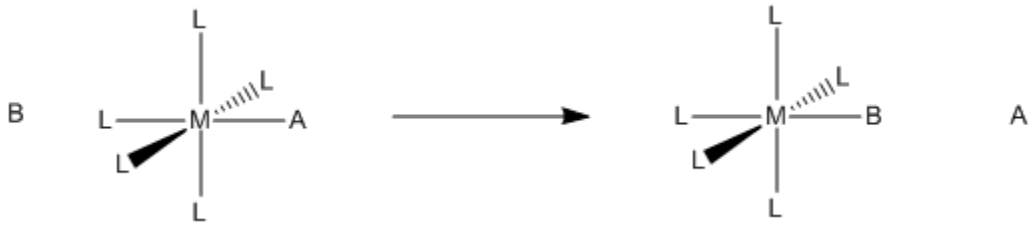


Figure 10.9.2.1.1: Substitution of one ligand for another in a coordination complex.

Remember, a ligand in coordination chemistry is just a Lewis base that binds to a metal atom or ion. It does so by donating a lone pair (or other pair of electrons). Generallly, this donation is reversible. The donor can always take its electrons back. Typically, there may be some balance between the metal's need for more electrons and the donor's attraction for its own electrons; donor atoms are frequently more electronegative than the metal.

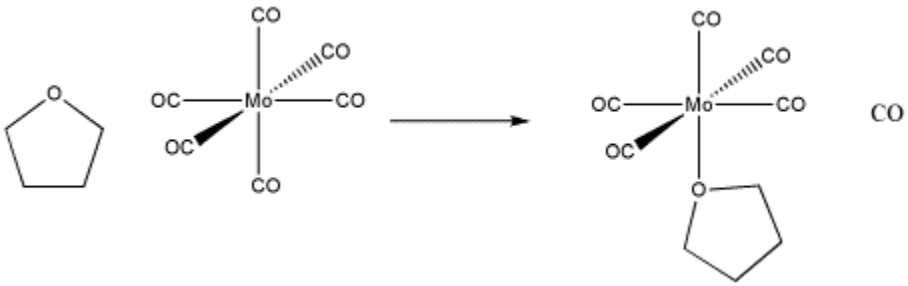


Figure 10.9.2.1.2: An example of ligand substitution. THF replaces a carbon monoxide in this molybdenum complex.

Even though the reaction is pretty simple, it can occur in different ways.

That is, the elementary steps involved in the reaction can occur in different orders. The elementary reactions are the individual bond-making or bond-breaking events that lead to an overall change. Sometimes the order of steps is referred to as the mechanism or the mechanistic pathway.

- The mechanism is the order of elementary reaction steps.
- Elementary reaction steps are individual bond-making and breaking steps.

You may have seen reaction mechanisms before. For example, carbonyl addition chemistry can involve lengthy mechanisms, in which a number of proton transfers and other bond-making and bond-breaking steps must occur to get from one state to another. Because ligand substitution is simpler than that, it is a good place to study mechanism in a little more depth, without getting overwhelmed by the details.

The sequence of steps in the mechanism influences how different factors will impact the reaction. For example, changing concentrations of different components in a reaction mixture can affect the time it takes for a reaction to finish.

- The mechanism can have a dramatic impact on the outcome of the reaction under different circumstances.

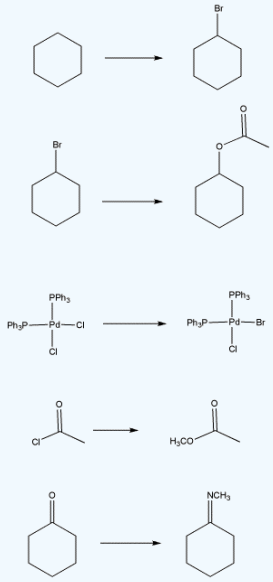
These kinds of considerations have a dramatic impact on industrial processes such as pharmaceutical production. In that setting, chemical engineers need to make decisions about how much of each reactant must be admitted to a reaction mixture and how long they should be allowed to react together. If they allow the reaction to proceed for too, long, there may be “side-reactions” that start to occur, interfering with the quality of the product, and they will waste valuable time in the production pipeline. If they don’t allow it to react long enough, the reaction may not finish, and the product will be contaminated with leftover starting materials.

In this chapter, we will look at how this simple reaction can occur in different ways. We will see some different methods that are

used to tell which way the reaction occurs (i.e. evidence of what is really happening). We will also look at some different factors that may influence whether the reaction is likely to occur one way or the other (i.e. reasons it is happening that way, or reasons we expect it will happen that way).

Exercise 10.9.2.1.1

Some kind of substitution occurs in each of the following reactions: an atom or group replaces another. In each case, identify what is being replaced, and what replaces it.



Answer a available at the end of this section.

Answers

Exercise 10.9.2.1.1

a bromine atom replaces a hydrogen atom
an acetate group (ethanoyl ester) replaces a bromine atom
a bromine atom replaces a chlorine atom (or ions)
a methoxy group replaces a chlorine atom
a methylamino group replaces an oxygen atom

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10.9.2.2: Inert and Labile Complexes

Kinetics of Substitution Reactions

Kinetics is a branch of chemistry that is concerned with the rates of chemical reactions. In this section, we will discuss the rates of metal-ligand (M-L) substitution reactions.

Let's start with some examples. In the table below are three examples of ligand substitution reactions of hexaaquo metal complexes to form hexaammine complexes. These reactions are nearly identical with the exception of the metal ion. The products are thermodynamically favored in all cases.

Reaction	Rate constant (k)	Labile or Inert
$[\mathrm{Ni(OH_2)}]^{2+} + 6\,\mathrm{NH_3} \rightleftharpoons [\mathrm{Ni(NH_3)_6}]^{2+}$	$k = 10^{4} s^{-1}$ (1 ns)	Labile (happens in < 1 min)
$[\mathrm{Cr(OH_2)}]^{3+} + 6\,\mathrm{NH_3} \rightleftharpoons [\mathrm{Cr(NH_3)_6}]^{3+}$	$k = 10^{-3} s^{-1}$ (6 days)	Inert (slow, takes hours)
$[\mathrm{Cu(OH_2)}]^{2+} + 6\,\mathrm{NH_3} \rightleftharpoons [\mathrm{Cu(NH_3)_6}]^{2+}$	$k = 10^{8} s^{-1}$	Very Labile (happens in seconds)

Definitions

- **Kinetically Labile** - Metal complexes that undergo "kinetically fast" substitution reactions are **kinetically labile**. Taube suggested that these are reactions in which half of the reactant is consumed in one minute or less ($t_{1/2}$ <1 min).
- **Kinetically Inert** - Metal complexes that undergo "kinetically slow" substitution reactions are **kinetically inert** or **non-labile**. Taube suggested that these are reactions in which $t_{1/2}$ >1 min.

A common pitfall is to confuse the meaning of kinetic terms, like *labile* and *inert,* with thermodynamic terms, like *stable* and *unstable*. It is important to distinguish between kinetics and thermodynamics. For example, the complex $[Fe(H_2O)Cl]^{2+}$ has a large formation constant and is thermodynamically stable; yet it is also labile. On the other hand, the complex $[Co(NH_3)_6]^{3+}$ is unstable in acidic aqueous solution and decomposes spontaneously to $[Co(H_2O)_6]^{3+}$; yet it decomposes slowly because it is inert. It is good practice to use clear terms such as "*kinetically* labile" or "*kinetically* inert" and "*thermodynamically* stable" and "*thermodynamically* unstable".

Exercise 10.9.2.2.1

Draw the reaction coordinate diagrams for a reaction of the form $[ML_6]^{n+} + X \rightleftharpoons [ML_5X]^{n+} + L$ in the following scenarios:

a. $[ML_6]^{n+}$ is theromdynamically stable and kinetically inert.
b. $[ML_6]^{n+}$ is theromdynamically unstable and kinetically inert.
c. $[ML_6]^{n+}$ is theromdynamically stable and kinetically labile.
d. $[ML_6]^{n+}$ is theromdynamically unstable and kinetically labile.

Answer a) available at the end of this section.

Answer b) available at the end of this section.

Answer c) available at the end of this section.

Answer d) available at the end of this section.

Factors that affect rates of substitution reactions:

Some of the factors that affect the kinetic rates of ligand substitution are the same factors that affect thermodynamic stability (see Chapter 10). The same factors that make a complex stable can also make it more inert. Why are kinetic factors related to thermodynamic stability? It is because the structure and stability of the reactant complex is related to the structure and stability of the transition state. The reactant complex must change its geometry to form an intermediate or transition state. When the reactant is particularly stable, it can result in a higher activation energy associated with moving away from the stable configuration. However, it is incorrect to assume that stability is *always* correlated with reaction rates. Kinetic and thermodynamic factors are related, yet separate.

There are three important factors that influence kinetic rate of substitution:

1. Ligand Field Stabilization Energy (LFSE): Electron configurations that place electrons in higher-energy orbitals (particularly antibonding orbitals) result in more labile complexes. As long as there are not electrons in higher-energy orbitals, the lability correlates roughly with LFSE. The more negative the LFSE, the more inert.
2. Coulombic attraction between the metal and ligand: In general, higher charge density on the metal ion or on the ligand(s) leads to stronger electrostatic attraction between metal and ligand. Stronger Coulombic attraction generally leads to slower dissociation steps and faster association steps. The effect that these have on the reaction rate depends on elementary steps that take part in the rate-determine step(s).
3. Denticity: Multi-dentate ligands create particularly inert complexes as a result of the kinetic chelate effect.

All three considerations are described in more detail below.

Exercise 10.9.2.2.2

In which compound from each pair would you expect the strongest ionic bonds? Why?

a) LiF vs KBr
b) $CaCl_2$ vs. KCl

Answer a available at the end of this section.

Taube's observations of metal complex substitution rates

Henry Taube (Nobel Prize, 1983) tried to understand kinetic lability by comparing the factors that govern bond strengths to observations about the rates of reaction of coordination complexes. He saw some things that were unsurprising. He also drew some new conclusions based on ligand field theory.

Taube observed that **many M^{+1} ions (M = metal) are more labile than many M^{+3} ions**, in general. That isn't too surprising, since metal ions function as electrophiles (Lewis acids) and ligands function as nucleophiles (Lewis bases) in forming coordination complexes. In other words, *metals with higher charges ought to be stronger Lewis acids, and so they should bind ligands more tightly*. However, there were exceptions to that general rule. For example, Taube also observed that Mo_5^+ compounds are more labile than Mo_3^+ compounds. So, there must be more going on here than *just* the effects of electrostatic attraction.

Another factor that governs ionic bond strengths is the *size of the ion*. Typically, **ions with smaller atomic radii form stronger bonds** than ions with larger radii. Taube observed that Al^{3+}, V^{3+}, Fe^{3+} and Ga^{3+} ions are all about the same size. All these ions exchange ligands at about the same rate. That isn't surprising, because they have the same charge and the same radius. However, Cr^{3+} is also about the same size as those ions and it also has the same charge, but it is much less labile. Once again, there are exceptions to our regular expectations based on simple electrostatic considerations. Furthermore, 4d and 5d transition metals (Y→Cd, and Ac→Hg) are much more inert than 3d transition metals (Sc→Zn). This is unexpected when we consider size; the 4d and 5d metals are much larger than the 3d metals. This unexpected behavior tells us that electrostatics alone cannot predict lability.

Taube came up with a hypothesis that could explain the seeming contradictory oservations described above: *kinetic lability must be affected by d-electron configuration*. This idea forms the basis of Taube's rules about lability.

For example, metals like Ni^{2+} and Cu^{2+} are very labile. The d orbital splitting diagrams for those compounds would have d electrons in the e_g set. Remember, the e_g set arises from interaction with the ligand donor orbitals; this set corresponds to a σ antibonding level.

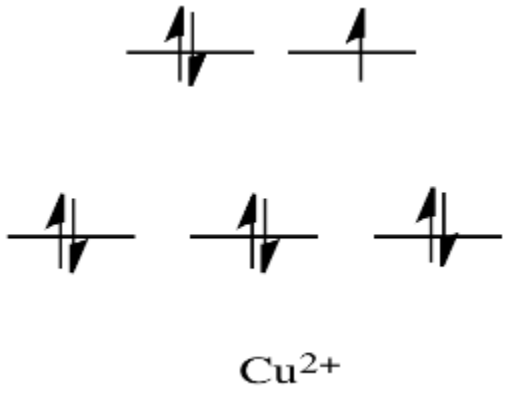


Figure 10.9.2.2.1: d^9-electron configuration assuming octahedral geometry.

By comparison, V^{2+} is rather inert. The d orbital splitting diagram in this case has electrons in the t_{2g} set, but none in the e_g set.

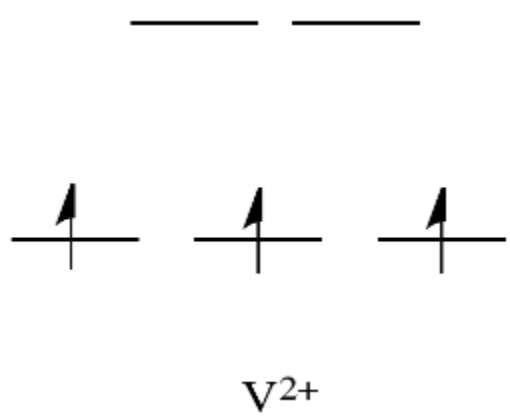


Figure 10.9.2.2.2: d^3-electron configuration assuming octahedral geometry.

So, having electrons in the higher energy, antibonding e_g level weakens the bond to the ligand, so the ligand can be replaced more easily. In the absence of those higher energy electrons, the bond to the ligand is stronger, and the ligand isn't replaced as easily.

On the other hand, metals like Ca^{2+}, Sc^{3+} and Ti^{4+} are pretty labile. The d orbital splitting diagrams in those cases are pretty simple: there are no d-electrons at all in these ions.

That means having no electrons in these mostly non-bonding levels leaves the complex susceptible to ligand replacement. But it's hard to see why population of an orbital that is mostly non-bonding would have an effect on ligand bond strength.

Instead, this factor probably has something to do with the part of ligand substitution that we have ignored so far. Not only does one ligand need to leave, but a second one needs to bond in its place. So, having an empty orbital for the ligand to donate electrons into (or, put another way, not having electrons in the way that may complicate donation from the ligand) makes that part of the reaction easier.

Exercise 10.9.2.2.3

Consider all possible electron configurations for octahedral complexes (d^0 to d^{10}, high spin and low spin cases): predict whether each case would be inert, intermediate, or labile.

Answer available at the end of this section.

Exercise 10.9.2.2.4

Put the metal ions in order of decreasing reaction rate (from labile to inert):

a) Al^{3+}, Na^{+}, Mg^{2+}

b) $Ca^{2+}, Mg^{2+}, Sr^{2+}$

Answer (a) available at the end of this section.

Answer (b) available at the end of this section.

Exercise 10.9.2.2.5

Some metals, like Mn^{2+}, can be either labile or inert, depending on whether they are high spin or low spin. Explain why using d orbital splitting diagrams.

Answer available at the end of this section.

Exercise 10.9.2.2.6

Predict whether the following metals, in octahedral complexes, are labile or not.

a) Co^{3+} (high spin)

b) Co^{3+} (low spin)

c) Fe^{2+} (low spin)

d) Fe^{2+} (high spin)

e) Zn^{2+}

Answer available at the end of this section.

Generalizations for how metal ion affects kinetics:

These are some generalizations about how the kinetics of substitution is affected by the metal ion identity and the d^n electron configuration.

1. s-block metals are very labile, except for those with very high charge density (eg. $Mg^{2+}\ is\ inert$)
2. d^{10} metals are labile (eg: Zn^{2+}, Cu^{+}, Hg^{2+})
3. Other ions with a full shell are labile (eg: Ln^{3+} of f-block)
4. 3d M^{2+}, *when high spin,* are generally labile (eg. $Cu^{2+}is\ very\ labile$)

5. 4d and 5d are usually inert due to higher LFSE (low spin, high LFSE)
6. M^{2+} is more labile than the same metal as M^{3+}
7. d^3 and low spin d^6 are inert (eg. Cr^{3+}, Co^{3+}, low spin Fe^{2+})

Chelate Complexes

In addition to considering factors related to the metal ion and charge or covalent character of metal-ligand bonds, an important consideration is the effect a chelate ligand on reaction kinetics. This effect is also discussed in more detail later in this chapter (Section 12.4.5).

Recall the Thermodynamic Chelate Effect

Chelating complexes tend to be more stable than complexes with monodentate ligands. This is called the "thermodynamic chelate effect". The effect deserves an explanation. The explanation is the increase of entropy that occurs when two or more monodentate ligands are replaced by a chelating ligand. The entropy increases because the overall number of particles increases as the substitution takes place.

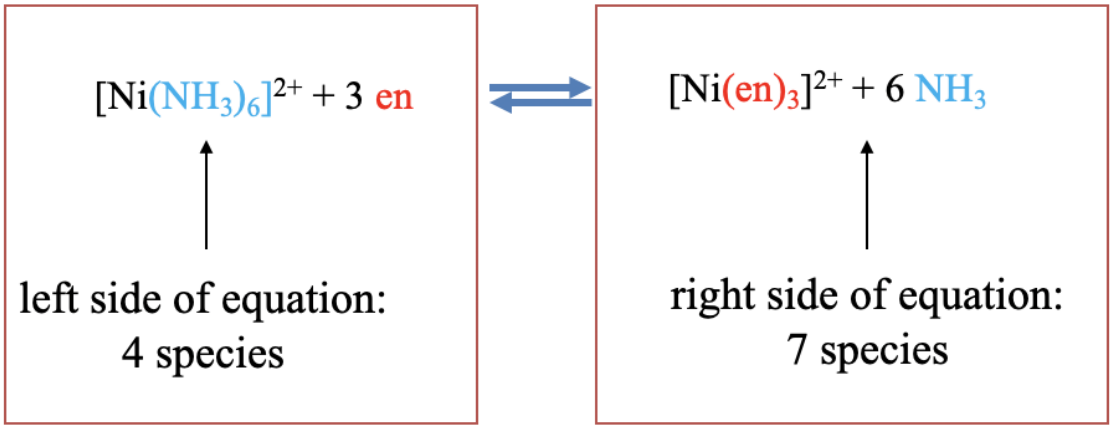


Figure 10.9.2.2.3: Example of the thermodynamic chelate effect

For example, the substitution of six ammine ligands in the hexaammine nickel (2+) complex by three ethylenediamine chelating ligands increases the number of molecules from four to seven, and hence the entropy increases, in this case by 88 J K^{-1} and mol^{-1} (Figure 10.9.2.2.3)

The Kinetic Chelate Effect

In addition to the thermodynamic chelate effect, there is the kinetic chelate effect. Chelate complexes are frequently more inert than complexes with monodentate ligands. Chelate complexes are more inert for two reasons (Figure 10.9.2.2.4).

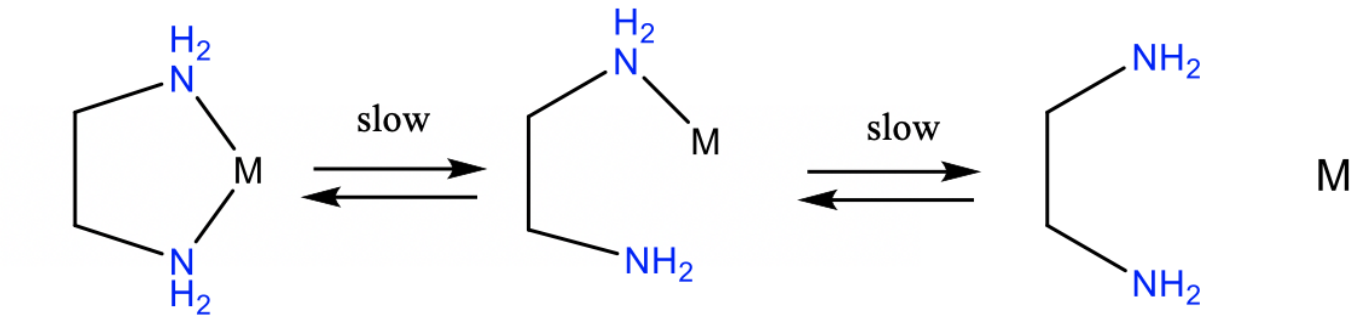


Figure 10.9.2.2.4: Illustration of the kinetic chelate effect

Firstly, the whole ligands needs to rotate and bend in order to cleave the first metal-ligand bond. This requires time and slows the kinetics of the bond cleavage. The second reason is that the detached donor atom cannot leave the proximity of the complex because the ligand is still attached via the other donor atom. This increases the probability of the re-formation of the metal-ligand bond which decreases the probability of both bonds being cleaved.

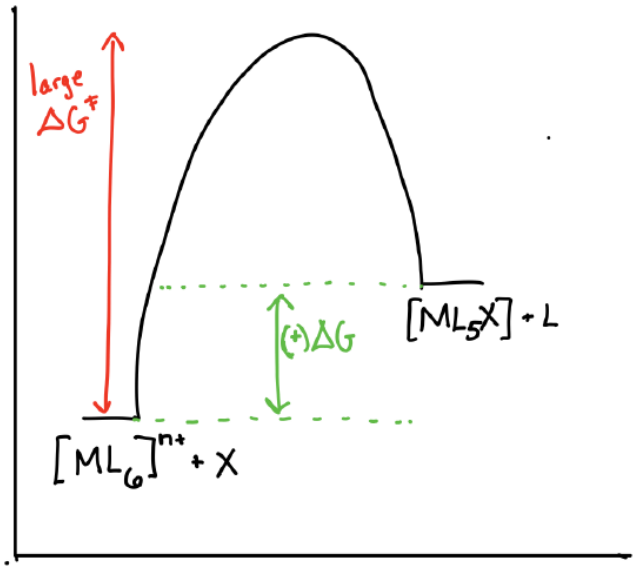
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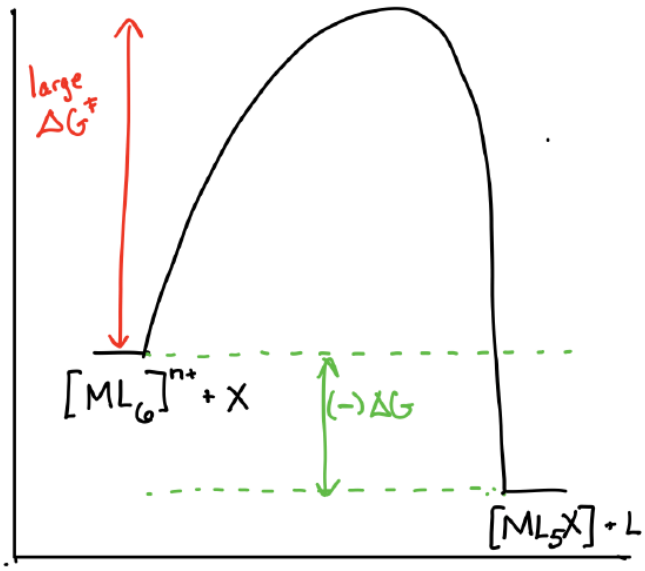
Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

Answers

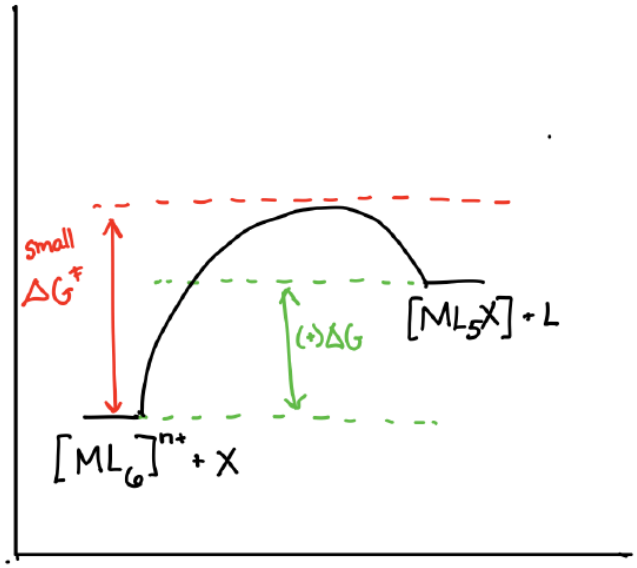
Exercise 10.9.2.2.1



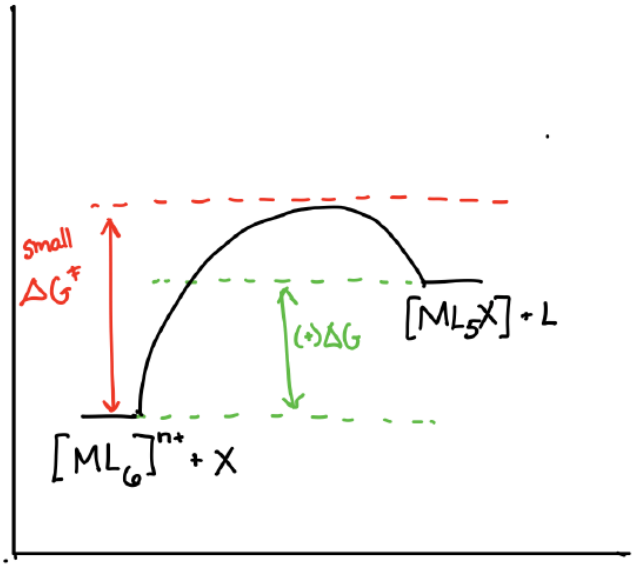
Exercise 10.9.2.2.1



Exercise 10.9.2.2.1



Exercise 10.9.2.2.1



Exercise 10.9.2.2.2

The ions in LiF are both smaller than in KBr, so the force of attraction between the ions in LiF is greater because of the smaller separation between the charges. Calcium has a 2+ charge in $CaCl_2$, whereas potassium has only a + charge, so the chloride ions are more strongly attracted to the calcium than to the potassium.

Exercise 10.9.2.2.3

	Kinetically Inert (Slow)	Kinetically Labile (Fast)
d^n electron count and ligand field strength	Octahedral configurations with empty e_g orbitals: • d^3 • low-spin d^4, d^5, d^6 Strong-field d^8 (square planar)	Octahedral configurations with occupied e_g orbitals: • d^1, d^2, d^7, d^9, d^10 • high-spin d^4, d^5, d^6 Weak-field d^8 (usually tetrahedral)

Exercise 10.9.2.2.4

Most Labile to most inert: $Na^+ > Mg^{2+} > Al^{3+}$

These are metal ions with similar size and varying charge. They are in order of increasing charge and increasing density from left to right.

Exercise 10.9.2.2.4

Most labile to most inert: $Sr^{2+} > Ca^{2+} > Mg^{2+}$

These metal ions have the same charge, and vary in size. They are in order of decreasing charge and increasing charge density from left to right.

Exercise 10.9.2.2.5

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Exercise 10.9.2.2.6

labile (electrons in higher energy d orbital set)
not labile (all electrons in lower energy d orbitals)
not labile (all electrons in lower energy d orbitals)
labile (electrons in higher energy d orbital set)
labile (electrons in higher energy d orbital set)

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- 9.1: Substitution Reactions and their Mechanisms by Kai Landskron is licensed CC BY 4.0.

10.9.2.3: Mechanistic Possibilities

A mechanism is the sequence of elementary steps by which a reaction proceeds. There are two aspects that describe the mechanism of a substitution reaction. One is called the **stoichiometric mechanism**, and the other one is called the **intimate mechanism**. The *stoichiometric* part of the mechanism is defined by the identity of the intermediate, or lack thereof. The *intimate* part of the mechanism is defined by the rate limiting step, and how the rate is dependent on the identity of the incoming ligand.

Stoichiometric Mechanisms

The *stoichiometric* part of the mechanism is **defined by the identity of the intermediate, or lack thereof**. There are three classes of stoichiometric mechanisms based on the type of intermediates that can be characterized. If the intermediate can be isolated it is either an Associative (higher-coordination number intermediate) or Dissociative (lower-coordination number intermediate) reaction. On the other hand, if the intermediate cannot be isolated because it is short-lived (or does not exist) the reaction is classified as Interchange.

Associative (A) Mechanism

Associative (A) mechanisms involve a first step where the incoming ligand bonds to the metal ion, creating **an intermediate with a higher coordination number**. The leaving group leaves in a second step to form the product. The generic reaction below illustrates the steps of an associative mechanism. Note that the intermediate, $\mathrm{ML_nXY}$, has a higher coordination number than that of the reactant, $\mathrm{ML_nX}$.

$$\begin{aligned} \text{Overall Reaction:} &\quad \mathrm{ML_nX + Y \rightleftharpoons ML_nY + X} \\ \text{Step 1 (Association):} &\quad \mathrm{ML_nX + Y \rightleftharpoons ML_nXY} \\ \text{Step 2 (Dissociation):} &\quad \mathrm{ML_nXY \rightleftharpoons ML_nY + X} \end{aligned}$$

Associative mechanisms are typical of square planar, d^8 complexes. The important features that distinguish this mechanism from others is that the **intermediate is long-lived** enough that it is detectable, and that the intermediate has a **higher coordination number** than the reactant complex.

Dissociative (D) Mechanism

Dissociative (D) mechanisms involve a first step where a bond between the metal ion and the leaving group breaks, creating **an intermediate with a lower coordination number.** The entering group enters in a second step to form the product. The generic reaction below illustrates the steps of a dissociative mechanism. Note that the intermediate, $\mathrm{ML_n}$, has a lower coordination number than that of the reactant, $\mathrm{ML_nX}$.

$$\begin{aligned} \text{Overall Reaction:} &\quad \mathrm{ML_nX + Y \rightleftharpoons ML_nY + X} \\ \text{Step 1 (Dissociation):} &\quad \mathrm{ML_nX \rightleftharpoons ML_n + X} \\ \text{Step 2 (Association):} &\quad \mathrm{ML_n + Y \rightleftharpoons ML_nY} \end{aligned}$$

The important features that distinguish this mechanism from others is that the **intermediate is long-lived** enough that it is detectable, and that the intermediate has a **lower coordination number** than the reactant complex.

Interchange (I) Mechanism

Interchange (I) Mechanisms take place in one concerted step where the entering group enters as the leaving group leaves. Bond formation and bond breaking occur simultaneously. In the case of an interchange mechanism, no intermediate is detectable. This means that either there is no intermediate, or that the intermediate is too high-energy and short-lived to be detected. The generic reaction below illustrates the single step of an interchange mechanism. Note that the species, $\mathrm{[Y\cdots ML_n\cdots X]^{\ddagger}}$, can be defined as either a transition state or a very short-lived intermediate. The distinction between these two possibilities is difficult; *when the intermediate is undetectable it is not considered a true intermediate.*

$$\text{Overall Reaction:} \qquad \mathrm{ML_nX + Y \rightleftharpoons ML_nY + X}$$
$$\text{Step 1 (Concerted):} \quad \mathrm{ML_nX + Y \rightleftharpoons [Y{\cdots}ML_n{\cdots}X]^{\ddagger} + \rightleftharpoons ML_nY + X}$$

The interchange mechanism is common for many six-coordinate (octahedral) metal complexes. The hallmark feature that distinguishes the interchange mechanism from other possible mechanisms is the **absence of a detectable intermediate**. If an intermediate is detected, the mechanism is considered associative (A). Another piece of evidence that can indicate an interchange mechanism is stereochemical changes from reactant to product. If specific sterochemistry (ie cis or trans relationships) is changed, it may be taken as evidence that an intermediate exists long enough to allow rearrangement to occur.

Distinguishing A, D, and I Mechanisms

Figure 10.9.2.3.1 shows examples of possible reaction profiles for each of the stoichiometric mechanisms described above. The profile of A and D mechanisms can be similar; they each require an intermediate, and the primary difference between A and D is the sequence of steps. An I mechanism lacks a true intermediate. These three cases can be difficult to distinguish experimentally, and especially if characterization of an intermediate is difficult. Notice that the reaction coordinate diagram for A and D pathways, shown in Figure 10.9.2.3.1, are similar. The only necessary difference between them is in the identity of the intermediate species.

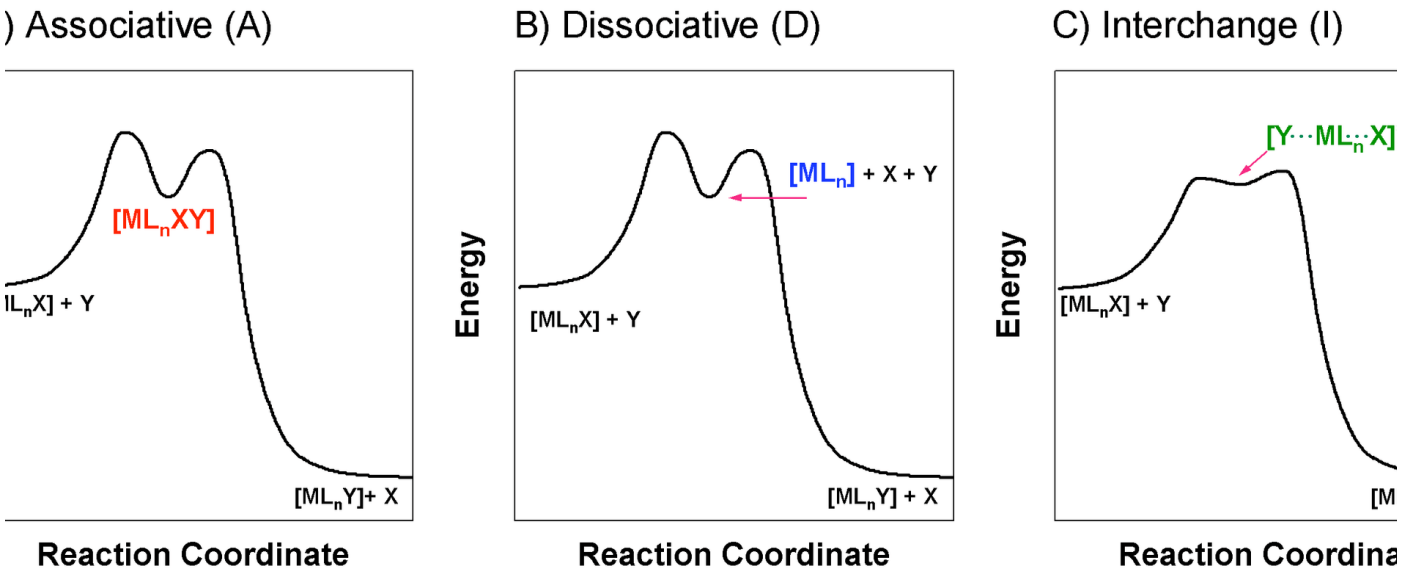


Figure 10.9.2.3.1: Example reaction coordinate diagrams for generic reactions that proceed through associative, dissociative, or interchange mechanisms. (Panel A) A reaction proceeds through an Associative pathway if it forms an intermediate with higher coordination number than its reactant complex. Here, an exergonic reaction is shown, where intermediate Extra close brace or missing open brace has a higher coordination number than reactant Extra close brace or missing open brace. (Panel B) A reaction proceeds through a Dissociative pathway if it forms an intermediate of lower coordination number than its reactant. Here, an exergonic reaction is shown where intermediate, Extra close brace or missing open brace, has lower coordination number than the reactant complex, Extra close brace or missing open brace. (Panel C) A reaction proceeds through an Interchange pathway if there is no true intermediate and the reaction proceeds in one step where bonds are broken and formed simultaneously. Shown here is an exergonic reaction where there is a high-energy species that is too unstable to be isolated; thus it is not a true intermediate and is considered equivalent to a transition state. (CC-BY-SA; Kathryn Haas).

Intimate Mechanisms

The intimate mechanism is defined by characteristics of the rate-limiting step. The reaction is classified as associatively-activated (using a subscript, a) if the rate changes by more than 10-fold as the entering group is varied. The reaction is classified as dissociatively-activated (using a subscript, d) if the rate changes by less than 10-fold as the entering group is varied.

Associatively-Activated Mechanisms

The rate-limiting step of an associatively activated pathway is formation of a bond between the entering group and the central metal ion. These reactions also require formation of an encounter complex in a pre-equilibrium step prior to bond forming or bond breaking steps discussed here (see Eigen-Wilkins Mechanism).

Associatively-activated A and I (A_a and I_a)

In the case of an associatively-activated associative pathway ($\mathrm{A_a}$) or an associatively-activated interchange pathway ($\mathrm{I_a}$), the rate-limiting step is the association of the entering group (Y) with the reactant, $\mathrm{ML}_n\mathrm{X}$. In the case of the A_a pathway, it is the first step (bolded) below.

A_a Mechanism

$$\textbf{Step 1 (Association):}\quad \mathrm{ML_nX + Y} \underset{\blacksquare}{\overset{\mathrm{k_1}}{\rightleftharpoons}} \mathrm{ML_nXY} \quad \Longleftarrow \textbf{RATE LIMITING ASSOCIATION}$$

$$\text{Step 2 (Dissociation):}\quad \mathrm{ML}_n\mathrm{XY} \underset{\blacksquare}{\overset{\mathrm{k_2}}{\rightleftharpoons}} \mathrm{ML}_n\mathrm{Y + X}$$

In the case of A_a, the first step shown above is slower than the second step ($k_1 < k_2$). In this case, an intermediate may not be detected because its steady state concentration is close to zero (ie it reacts as soon as it forms). Thus, distinguishing between A_a and I_a mechanisms is often impossible.

Associatively-activated D (D_a)

In the case of an associatively-activated dissociative reaction ($\mathrm{D_a}$), the rate limiting step is the association of the entering group (Y) with the intermediate ML_n; the second step (bolded) in the mechanism shown below:

D_a Mechanism

$$\text{Step 1 (Dissociation):}\quad \mathrm{ML}_n\mathrm{X} \underset{\blacksquare}{\overset{\mathrm{k_1}}{\rightleftharpoons}} \mathrm{ML}_n + \mathrm{X}$$

$$\textbf{Step 2 (Association):}\quad \mathrm{ML_nX + Y} \underset{\blacksquare}{\overset{\mathrm{k_2}}{\rightleftharpoons}} \mathrm{ML_nY} \quad \Longleftarrow \textbf{RATE LIMITING ASSOCIATION}$$

In this case, the intermediate concentration should be measurable since the second step is slower than the first ($k_1 > k_2$).

Exercise 10.9.2.3.1

Draw the reaction coordinate diagrams (aka reaction profiles) of reactions that proceed through A_a, I_a, and D_a pathways. Use these diagrams to explain why it is impossible to distinguish between A_a and I_a.

Hint available at the end of this section.

Answer available at the end of this section.

Dissociatively-Activated Mechanisms

When the rate-determining step is the breaking of a bond between the central metal ion and the leaving group, it is considered a dissociatively-activated (subscript d) mechanism. The rates of these reactions are largely independent of the identity of the incoming ligand.

Dissociatively-activated A (A_d)

In the case of a dissociatively-activated associative pathway ($\mathrm{A_d}$), the rate-limiting step is the dissociation of the leaving group (X) from the intermediate, $\mathrm{ML}_n\mathrm{XY}$; the second step (bolded) below.

A_d Mechanism

$$\text{Step 1 (Association):} \quad \mathrm{ML}_n\mathrm{X} + \mathrm{Y} \underset{[redacted]}{\overset{k_1}{\rightleftharpoons}} \mathrm{ML}_n\mathrm{XY}$$

$$\textbf{Step 2 (Dissociation):} \quad \mathrm{ML_nXY} \underset{[redacted]}{\overset{k_2}{\rightleftharpoons}} \mathrm{ML_nY} + \mathrm{X} \quad \Longleftarrow \textbf{RATE LIMITING DISSOCIATION}$$

In this case, the intermediate concentration should be measurable since the second step is slower than the first ($k_1 > k_2$.

Dissociatively-activated D and I (D_a and I_a)

In the case of a dissociatively-activated dissociative reaction ($\mathrm{D_d}$), or a dissociatively-activated interchange pathway ($\mathrm{I_d}$), the rate limiting step is the dissociation of the leaving group (X) from the reactant, $\mathrm{ML}_n\mathrm{X}$. For D_d the rate limiting step is the first step (bolded) in the mechanism shown below:

D_d Mechanism

$$\textbf{Step 1 (Dissociation):} \quad \mathrm{ML_nX} \underset{[redacted]}{\overset{k_1}{\rightleftharpoons}} \mathrm{ML_n} + \mathrm{X} \quad \Longleftarrow \textbf{RATE LIMITING DISSOCIATION}$$

$$\text{Step 2 (Association):} \quad \mathrm{ML}_n\mathrm{X} + \mathrm{Y} \underset{[redacted]}{\overset{k_2}{\rightleftharpoons}} \mathrm{ML}_n\mathrm{Y}$$

In the case of D_d, the first step shown above is slower than the second step ($k_1 < k_2$ and an intermediate may not be detected because its steady state concentration is close to zero (ie it reacts as soon as it forms). Thus, distinguishing between D_d and I_d mechanisms is often impossible.

Exercise 10.9.2.3.2

You should complete Excercise 10.9.2.3.1 before attempting this excercise.
Draw the reaction coordinate diagrams (aka reaction profiles) of reactions that proceed through A_d, I_d, and D_d pathways.

Answer available at the end of this section.

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Answers

Exercise 10.9.2.3.1

Notice that the reaction coordinate diagrams for A and D pathways, shown in Figure 10.9.2.3.1, are similar. The only necessary difference between them is the identity of the intermediate. These diagrams can be modified to represent associatively-activated pathways by altering the relative energy of the transition state for the associative step; the energy barrier for the associative step must be greater than that of the dissociative step. In other words, the difference between A_a, D_a is in the relative energies of the first and second transition states. In the case of I_a, the diagram could be similar to the I profile shown in Figure 10.9.2.3.1, with the exception that the energy barrier for making the M-Y bond is greater than the energy barrier for breaking the M-X bond.

Exercise 10.9.2.3.1

The three reaction coordinate diagrams shown in the figure below represent A_a, I_a, and D_a mechanisms respectively. If your diagram does not match this perfectly, that may be OK. The important features are:

- A_a: This reaction profile should show an intermediate with higher coordination number than the reactant. The intermediate should be relatively stable. The energy barrier for formation of this intermediate is the associative step, and therefore it should also be the rate-limiting step for an A_a mechanism; in other words, the first step should have the highest energy barrier.
- I_a: This reaction profile should lack a stable intermediate. The energy barrier for creating of the M-Y bond must be rater-limiting. The diagram shown below is an acceptable solution, but a diagram like shown in Panel C of Figure 10.9.2.3.1 is also correct. It is not clear from the diagram alone whether bond breaking or bond making are rate-limiting; this nuance would lie primarily in the identity of the transition state, and whether the M-Y bond is stronger or weaker than the M-X bond in the transition state.
- D_a: This reaction profile should show an intermediate with lower coordination number than the reactant. The intermediate should be relatively stable. The energy barrier for association of the entering group with the intermediate (the second step) must be rate-limiting in a D_a mechanism. In other words, the second step should have the highest energy barrier.

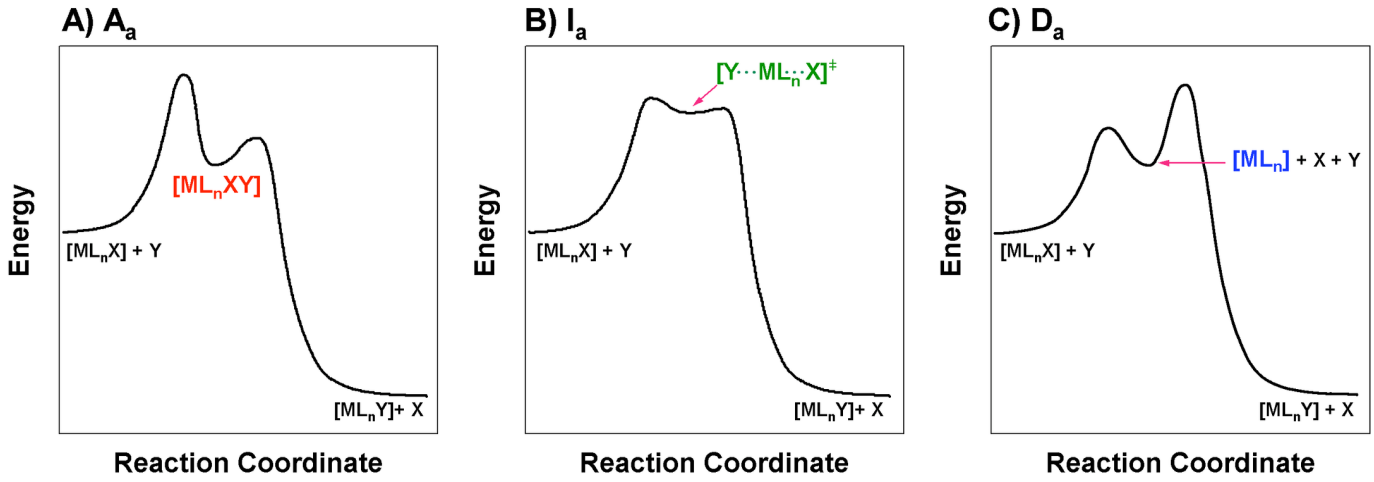


Figure for Excercise 10.9.2.3.1: Reaction coordinate diagrams for associatively-activated mechanisms. (A) Associatively-activated associative, A_a. (B) Associatively-activated interchange, I_a. (C) Associatively-activated dissociative, D_a. (CC-BY-SA; Kathryn Haas)

The A_a and I_a mechanisms have different reaction profiles while still the rate-limiting step is the initial association of the incoming ligand to the metal center. These two types of mechanisms are difficult to distinguish because in the case of A_a, there is a relatively small energy barrier for reaction of the intermediate to form product; thus this intermediate is not long-lived and would be difficult to detect. Experimental distinction between A_a and I_a lies in the detection and characterization of this intermediate, and since it may be elusive in A_a, it is difficult to unambiguously determine whether an associatively-activated mechanism is A_a or I_a.

Exercise 10.9.2.3.2

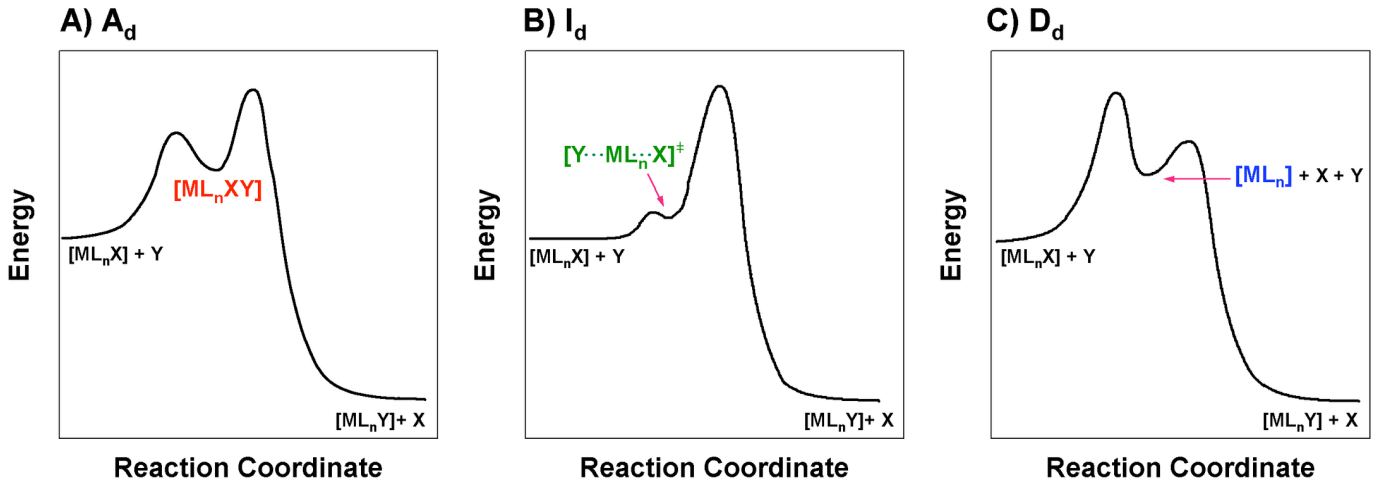


Figure for Excercise 10.9.2.3.2: Reaction coordinate diagrams for dissociatively-activated mechanisms. (A) Dissociatively-activated associative, A_d. (B) Dissociatively-activated interchange, I_d. (C) Dissociatively-activated dissociative, D_d. (CC-BY-SA; Kathryn Haas)

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10.9.3: KINETICS HINT AT THE REACTION MECHANISM

Since the different mechanisms have different rate-limiting steps, there are kinetic consequences for each type of mechanism. We can used kinetic data, therefore, to help distinguish the mechanism of a reaction. However, the information gleaned from rate laws alone can be ambiguous. For example, what does it mean if a reaction depends on on the concentration of incoming ligand? How can we distinguish between an associative mechanism (A), and an associatively-activated dissociative mechanism (D_a?

10.9.3.1: Rate Law for Dissociative Mechanisms

10.9.3.2: Rate Laws for Interchange Mechanisms

10.9.3.3: Rate Law for Associative Mechanisms

10.9.3.4: Preassociation Complexes

10.9.3.5: Activation Parameters

10.9.3.6: Some Reasons for Differing Mechanisms

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10.9.3.1: Rate Law for Dissociative Mechanisms

Derrivation of the Rate Law

A Dissociative (D) mechanism is two steps in which the first step is the dissociation of a ligand. The intermediate, ML_n, has a lower coordination number than that of the reactant, $\mathrm{ML}_n\mathrm{X}$.

$$\text{Step 1 (Dissociation):} \quad \mathrm{ML}_n\mathrm{X} \underset{[redacted]}{\overset{k_1}{\rightleftharpoons}} \mathrm{ML}_n + \mathrm{X}$$

$$\text{Step 2 (Association):} \quad \mathrm{ML}_n + \mathrm{Y} \underset{[redacted]}{\overset{k_2}{\rightleftharpoons}} \mathrm{ML}_n\mathrm{Y}$$

$$\text{Overall Reaction:} \quad \mathrm{ML}_n\mathrm{X} + \mathrm{Y} \rightleftharpoons \mathrm{ML}_n\mathrm{Y} + \mathrm{X}$$

If we assume that \(k_{-2}<

$$\frac{d\left[\mathrm{ML}_n\right]}{dt} = k_2[\mathrm{ML}_n][\mathrm{Y}]$$

We can assume that the concentration of the intermediate is small enough that it would be difficult or impossible to measure its concentration. Here, we can evoke the steady-state approximation and assume that the concentration, $[\mathrm{ML}_n]$, is approximately unchanging over the course of reaction. The $[\mathrm{ML}_n]$ depends on k_1, k_{-1} and k_2. These assumption are expressed mathematically as follows.

$$\frac{d\left[\mathrm{ML}_n\right]}{dt} = k_1\left[\mathrm{ML}_n\mathrm{X}\right] - k_{-1}\left[\mathrm{ML}_n\right]\left[\mathrm{X}\right] - k_2\left[\mathrm{ML}_n\right]\left[\mathrm{Y}\right] = 0$$

We can then use the equation above to solve for $[\mathrm{ML}_n]$.

$$\mathrm{ML}_n = \frac{k_1\left[\mathrm{ML}_n\mathrm{X}\right]}{k_{-1}[\mathrm{X}] + k_2[\mathrm{Y}]}$$

Then substitution this into the rate law given above for the second step of the mechanism. This would yield a rate law that depends only on species with measurable concentrations.

$$\frac{d\left[\mathrm{ML}_n\mathrm{Y}\right]}{dt} = \frac{k_2k_1\left[\mathrm{ML}_n\mathrm{X}\right]\left[\mathrm{Y}\right]}{k_{-1}[\mathrm{X}] + k_2[\mathrm{Y}]}$$

The rate law above suggests that the rate of product formation has an inverse relationship to the concentration of the outgoing ligand, X. This is one piece of evidence that can be used to distinguish a Dissociative mechanism; that is if the rate of reaction decreases as [X] in solution is increased it is evidence of a D mechanism. This rate law also suggests that ther is a complicated dependence of the reaction rate on the concentration of incoming ligand, Y. The importance of [Y] compared to [X] depends mathmatically on the weight of the two values in the demoninator of the rate law. If [X] >> [Y], then a valid approximation is to assume that the $k_2[\mathrm{Y}]$ term is relatively small and simplify the rate law by dropping it out completely.

$$\text{If } \mathrm{X} >> \mathrm{Y}\text{, then simplify: } \frac{d\left[\mathrm{ML}_n\mathrm{Y}\right]}{dt} = \frac{k_2k_1\left[\mathrm{ML}_n\mathrm{X}\right]\left[\mathrm{Y}\right]}{k_{-1}[\mathrm{X}]}$$

The resulting rate law (above) has a simpler dependence on [Y]; that is when [X] is large, the reaction rate is directly related to [Y].

The opposite extreme is under conditions of high [Y]. This yields a rate law that is first order in its dependence on the reactant metal complex. When [Y] is large, and the $k_{-1}[\mathrm{X}]$ term is relatively insignificant, the rate law can be simplified to the pseudo-first order rate law as follows.

$$\text{If } \mathrm{Y} >> \mathrm{X}\text{, then simplify: } \frac{d\left[\mathrm{ML}_n\mathrm{Y}\right]}{dt} = k_1[\mathrm{ML}_n\mathrm{X}]$$

The best type of experimental evidence to determine a dissociative mechanism would be a systematic study of the dependence

of rate on both [X] and [Y]. However, the dissociative reaction is unique in that it displays this type of saturation kinetics at high concnetration of the incoming ligand, and so the study of how a reaction rate behaves under high [Y] is common.

First-order reactions

Under conditions of high [Y], the a reaction following a D mechanism is said to follow "first order" kinetics. This type of reaction is sometimes called a first order reaction. That means the rate law depends on only one concentration term.

Why does the dissociative mechanism depend on concentrations in this specific way?

The rate depends on one molecule losing a ligand. Once it does so, a second ligand can replace the one that left. However, losing a ligand may be harder to do than gaining a new one. To lose a ligand, a bond must be broken, which costs energy. To gain a new ligand, a bond is made, releasing energy. That first step is harder to do, so it takes longer. It is a bottleneck that slows the reaction down. It is called the rate-determining step.

- The rate-determining step is the slow step of the reaction.
- The rate-determining step controls the rate of the overall reaction; everything else has to wait for that step to happen.
- Once the rate-determining step has occurred, everything else follows very quickly.

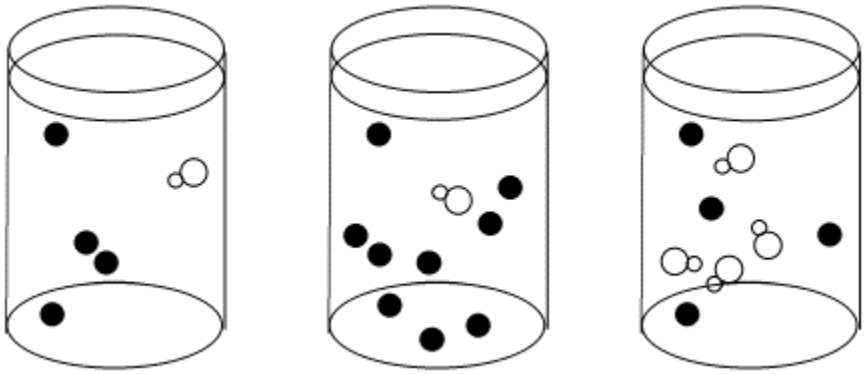


Figure 10.9.3.1.1: A bottleneck in a reaction. If the reaction must wait for the white molecule to dissociate, it doesn't matter how many black molecules there are; the reaction still goes just as slow. However, the more white molecules there are, the more frequently they will be able to react with the black molecules as dissociation occurs.

No collision is necessary for the metal complex to lose a ligand. Instead, a bond in the metal complex has to break. That just takes time and energy. As a result, concentration of the incoming ligand matters very little.

We should think a little more about energy requirements, available energy and reaction rate. It takes a certain amount of energy to break a bond. Over any given period of time, a specific amount of energy is available in the surroundings to use. That energy is not available uniformly. Some molecules will get more energy from their surroundings and others will get less. There will be a statistical distribution, like a bell curve, of energy available in different molecules. That means bond-breaking events are governed by statistics.

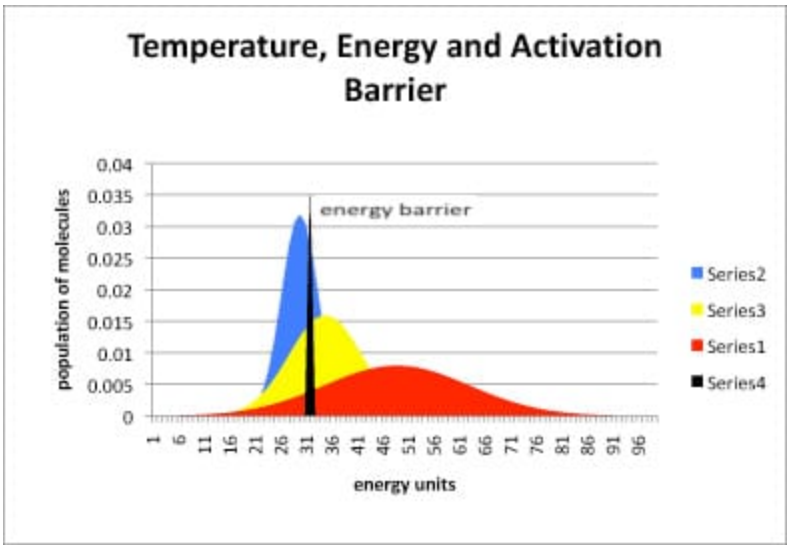


Figure 10.9.3.1.2: The relationship between temperature, energy available, and energy barrier. The black line represents energy needed to start the reaction, also called the energy barrier or the activation barrier. The blue curve is the distribution of available energy in a group of molecules at a cooler temperature. The yellow curve is for a group of molecules that is a little warmer, and the red curve even warmer.

In figure 10.9.3.1.2, most of the molecules at the low temperature (blue) do not have enough energy to begin the reaction. A small portion do, and so the reaction will proceed, but very slowly. In the yellow curve, there is more energy available, and so a large fraction of molecules have the energy necessary to begin the reaction. In the red curve, the vast majority have sufficient energy to react. Thus, one of the factors governing how quickly a reaction will happen is the energy needed, or activation barrier. A second factor is the energy available, as indicated by the temperature.

Of course, even if there is enough energy for the reaction, the reaction might not occur yet. Energy is necessary but not sufficient to start a reaction. There are also statistical factors in terms of whether a molecule has its energy allotted into the right places, or in some cases, whether two molecules that need to react together are oriented properly.

Suppose at a given temperature it takes a specific amount of time for half the molecules to gain enough energy so that they can undergo the reaction. That amount of time is called the half life of the reaction. After one half life, half the molecules have reacted and half remain. After a second half life, half the remaining molecules (another quarter, for three quarters of the original material in all) have also reacted, and a quarter still remain. After a third half life, half the remaining ones (another eighth, making it seven eighths reacted in total) will have reacted, leaving an eighth of the original material behind.

- Exponential decay is based on a statistical distribution of energy availability.
- The concept of half life is related to exponential decay.
- It takes a fixed period of time for a half of the metal complex obtain enough energy to dissociate.

Thus, the time it takes for the reaction to happen does not really depend on the concentration of anything.

However, the change in *concentration* over time -- the quantity that we can usually measure most easily -- depends on the original concentration, and for that reason the concentration of the metal complex appears in the rate law.

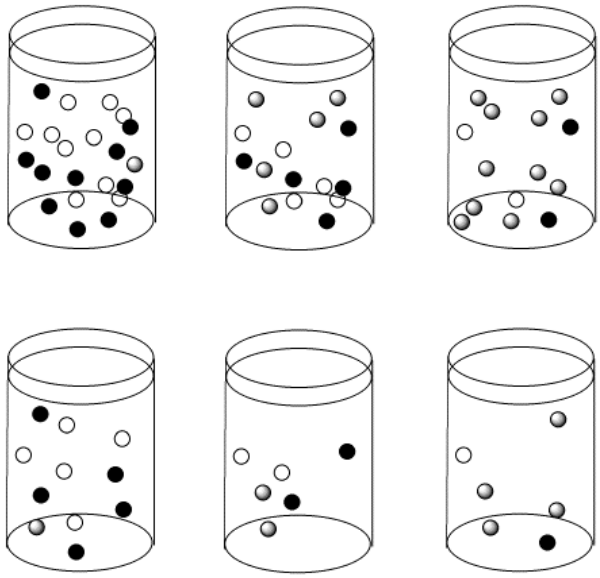


Figure 10.9.3.1.3: The reactions in the top row and bottom row are proceeding with the same half-life as we move from left to right. However, the top row starts out more concentrated than the bottom row. As a result, the *concentrations* in the top row are changing more quickly than in the bottom row.

Suppose the half life for a particular case of ligand substitution is one second. After a half life, a 1 M solution becomes 0.5 M, so the rate of change in concentration per time is 0.5M/s. But after the same half life, a 0.5 M solution becomes 0.25 M, so the change in concentration is 0.25 M/s.

Exercise 10.9.3.1.1

If a first order reaction has a half-life of 120 seconds, how much of the original material is left after

a) four minutes? b) six minutes? c) eight minutes? d) ten minutes?

Answer a available at the end of this section.

Exercise 10.9.3.1.2

Given the first-order dissociative rate law above, what would happen to the reaction rate for substitution in each of the following cases?

a. the concentration of ligand is doubled, and the concentration of metal complex is doubled
b. the concentration of ligand is tripled, and the concentration of metal complex is halved
c. the concentration of ligand is doubled, and the concentration of metal complex is tripled
d. the concentration of ligand is halved, and the concentration of metal complex is halved

Answer a available at the end of this section.

Exercise 10.9.3.1.3

Plot graphs of initial rate vs concentration to show what you would see in dissociative substitution.

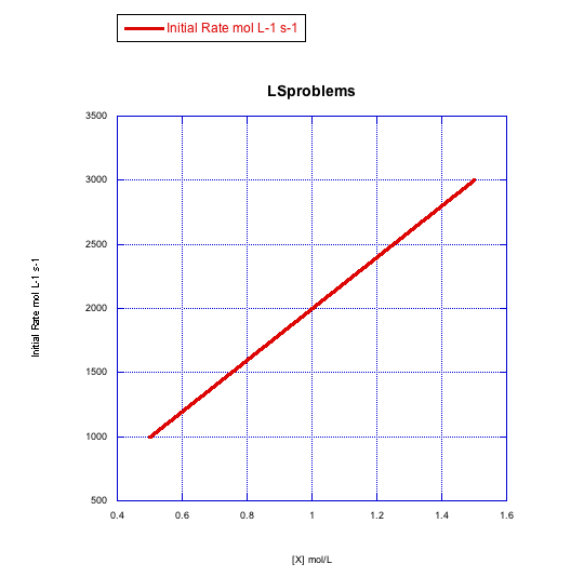
a) The concentration of metal complex, $[ML_n]$, is held constant at 0.1 mol/L and the concentration of ligand is changed from 0.5 mol/L to 1 mol/L and then to 1.5 mol/L.

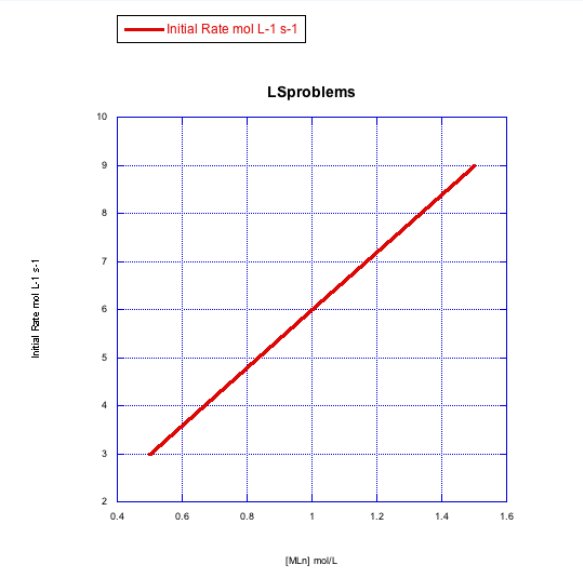
b) The concentration of new ligand, [X], is held constant at 0.1 mol/L and the concentration of metal complex is changed from 0.5 mol/L to 1 mol/L and then to 1.5 mol/L

Exercise 10.9.3.1.4

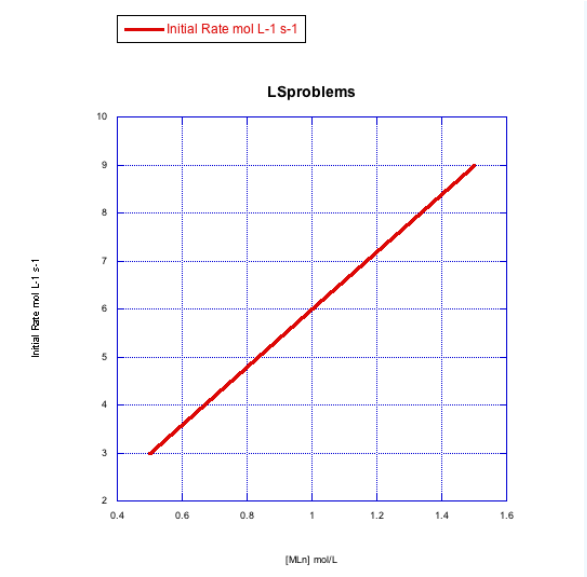
Given the following sets of initial rate data, determine whether each case represents a dissociative substitution. [MLn] = concentration of the coordination complex; [X] = concentration of incoming ligand.

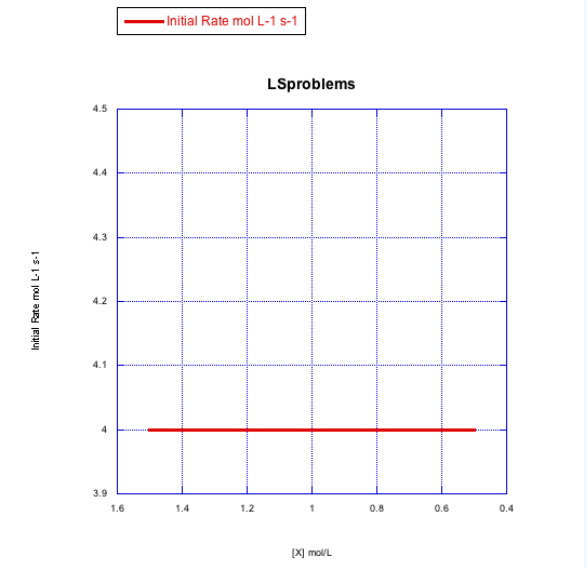
a)





b)

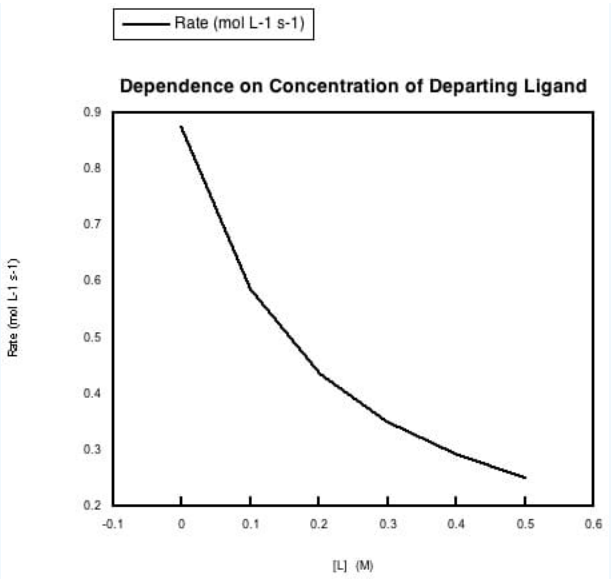




Answer a available at the end of this section.

Exercise 10.9.3.1.5

In the following data, the concentration of the metal complex and the incoming ligand were held constant, but more of the departing ligand was added to the solution.



a) Explain what the data says about rate dependence on this concentration.

b) Explain this rate dependence in terms of the reaction.

Answer a available at the end of this section.

Exercise 10.9.3.1.6

In certain solvents, such as THF, acetonitrile and pyridine, the rate law for substitution often appears to be Rate = $k_1[ML_n]$ + $k_2[ML_n][X]$, in which X is the incoming ligand and ML_n is the metal complex.

a) What do these solvents have in common?

b) What is a possible explanation for this rate law?

c) This rate law has been shown to be consistent with an entirely associative mechanism. How is that possible?

Answer a available at the end of this section.

Answers

Exercise 10.9.3.1.1

4 minutes = 240 seconds = 2 x 120 second = 2 half lives.
Material left = 50% x 50% = 0.5 x 0.5 = 0.25 = 25% left
6 minutes = 360 seconds = 3 x 120 second = 3 half lives.
Material left = 0.5 x 0.5 x 0.5 = 0.125 = 12.5% left
8 minutes = 480 seconds = 4 x 120 second = 4 half lives.
Material left = 0.5 x 0.5 x 0.5 x 0.5 = 0.0625 = 6.25% left
10 minutes = 600 seconds = 5 x 120 second = 5 half lives.
Material left = 0.5 x 0.5 x 0.5 x 0.5 x 0.5 = 0.03125 = 3.125% left

Exercise 10.9.3.1.2

Dissociative Rate Law: Rate = $[ML_n]$, if ML_n is the complex. There is no dependence on [X], if X is the new ligand.

Rate will double: Rate = 2 x $[ML_n]_0$, if $[ML_n]_0$ is the original concentration.
Rate will be halved: Rate = 0.5 x $[ML_n]_0$.
Rate will triple: Rate = 3 x $[ML_n]_0$.

Rate will be halved: Rate = 0.5 x $[ML_n]_0$.

Exercise 10.9.3.1.4

The rate increases with both concentration of metal complex and incoming ligand. This looks like an associative mechanism.

The rate depends on concentration of the metal complex, but not the incoming ligand. This looks like a dissociative mechanism.

The rate depends on the concentration of incoming ligand, but not the metal complex. Whatever is going on here, it isn't a simple dissociative mechanism.

Exercise 10.9.3.1.5

The rate of the reaction is depressed when the concentration of the departing ligand is increased.

This dependence could indicate an equilibrium in the dissociative step. The more departing ligand is added, the more the equilibrium is pushed back towards the original metal complex. With less dissociated metal complex around, the entering ligand cannot form the new complex as quickly.

Exercise 10.9.3.1.6

These solvents all have lone pairs. They could be Lewis bases or nucleophiles.

It looks like two competing mechanisms. On term suggests a dissociative mechanism, whereas the other term suggests a dissociative mechanism. They could be happening in competition with each other.

On the other hand, it could be that there is one mechanism with two different nucleophiles. If the incoming ligand is the nucleophile, the term on the right shows up in the rate law. If the solvent is the nucleophile, forming a third complex, the term on the left shows up in the rate law. That's because we would typically change the amount of metal complex and the amount of ligand that we add to the solution in order to determine the rate law, but we wouldn't normally be able to change the concentration of the solvent, so it would be a constant. (How could you confirm this explanation in an experiment?)

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10.9.3.2: Rate Laws for Interchange Mechanisms

Interchange (I) Mechanisms take place in one concerted step where there is no intermediate, or the intermediate is elusive. The reactio nessentially occurs in once step in which bond forming and bond breaking is concerted, as shown below. The species, $[\mathrm{Y}\cdots\mathrm{ML}_n\cdots\mathrm{X}]^{\ddagger}$, can be defined as either a transition state or a very short-lived intermediate.

$$\text{Step 1 (Concerted):} \quad \mathrm{ML}_n\mathrm{X} + \mathrm{Y} \rightleftharpoons [\mathrm{Y}\cdots\mathrm{ML}_n\cdots\mathrm{X}]^{\ddagger} + \overset{k_1}{\rightleftharpoons} \mathrm{ML}_n\mathrm{Y} + \mathrm{X}$$

The rate law of this one-step reaction depends on whether the relative rates of the forward and reverse reactions. When the reaction is practically irreversible, then the rate depends only on the formation of product, and not its reaction to re-form product. In this case, the rate law is a simple second-order rate law.

$$\frac{d[\mathrm{ML}_n\mathrm{Y}]}{dt} = k_1[\mathrm{ML}_n\mathrm{X}][\mathrm{Y}]$$

On the other hand, if the rate of re-formation of reactant is significant, then the rates of forward and reverse reactions must be considered in the rate law.

$$\frac{d[\mathrm{ML}_n\mathrm{Y}]}{dt} = k_1[\mathrm{ML}_n\mathrm{X}][\mathrm{Y}] - k_{-1}[\mathrm{ML}_n\mathrm{X}][\mathrm{X}]$$

In the latter case where there is a dependence of rate on both [X] and [Y], an effective strategy is to employ the condition where solution concentration of both [X] and [Y] are simultaneously high so that the reaction is effectively a competition of two pseudo-first order reactions that depend primarily on the metal complex concentrations. In such a case as this, another helpful piece of information is the equilibrium constant for the reaction ($K = \frac{k_1}{k_{-1}}$). The rate law is written below.

$$\text{When [X] and [Y] are very high:} \ \frac{d[\mathrm{ML}_n\mathrm{Y}]}{dt} = k_1[\mathrm{ML}_n\mathrm{Y}] - k_{-1}[\mathrm{ML}_n\mathrm{X}] = -\frac{d[\mathrm{ML}_n\mathrm{X}]}{dt}$$

One distinguishing feature of an I mechanism compared to a D mechanism can be determined from such an experiment under high concentration of X and Y. In the case of a D mechanism and sufficiently high concentration of incoming ligand, [Y], the reaction demonstrations saturation kinetics to give a pseudo-first order rate law depending only on the concentration of reactant metal complex. In the case of I, the reaction rate is not a simple first order rate law because even under high [Y] and [X], there is a dependence of rate on concentration of the product complex.

Reactions that are I_a or I_d are distinguished by the relative strength of the M-X and M-Y bond in the transition state. These reactions can be distinguished by varying the Identities of X and Y to determine how the reaction rate depends on identity of X and Y. If there is a large dependence on the incoming ligand, and less so on the outgoing ligand, it could be classified as an I_a mechanisms. The opposite is also true.

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10.9.3.3: Rate Law for Associative Mechanisms

Associative (A) mechanisms involve a first step where the incoming ligand bonds to the metal ion, creating an intermediate, $\mathrm{ML}_n\mathrm{XY}$, with a higher coordination number than that of the reactant, $\mathrm{ML}_n\mathrm{X}$.

$$\text{Step 1 (Association):} \quad \mathrm{ML}_n\mathrm{X} + \mathrm{Y} \underset{[redacted]}{\overset{k_1}{\rightleftharpoons}} \mathrm{ML}_n\mathrm{XY}$$

$$\text{Step 2 (Dissociation):} \quad \mathrm{ML}_n\mathrm{XY} \underset{[redacted]}{\overset{k_2}{\rightleftharpoons}} \mathrm{ML}_n\mathrm{Y} + \mathrm{X}$$

$$\text{Overall Reaction:} \quad \mathrm{ML}_n\mathrm{X} + \mathrm{Y} \rightleftharpoons \mathrm{ML}_n\mathrm{Y} + \mathrm{X}$$

To determine the rate law, we can use a similar process as we followed for D mechanisms, which are also two steps. Assuming that $k_2 >> k_{-2}$, the rate of formation of product from the second step is:

$$\frac{d[\mathrm{ML}_n\mathrm{Y}]}{dt} = k_2[\mathrm{ML}_n\mathrm{XY}]$$

The steady state approximation allows us to assume that the intermediate is in low concentration (too low to be reliably measured) and that it is unchanging. We can use the rate law for the first step to find $[\mathrm{ML}_n\mathrm{XY}]$ in terms of species that can be reliably measured.

$$\frac{d[\mathrm{ML}_n\mathrm{XY}]}{dt} = k_1[\mathrm{ML}_n\mathrm{X}][\mathrm{Y}] - k_{-1}[\mathrm{ML}_n\mathrm{XY}] - k_2[\mathrm{ML}_n\mathrm{XY}] = 0$$

...solving this first-step rate law for $[\mathrm{ML}_n\mathrm{XY}]$ gives $[\mathrm{ML}_n\mathrm{XY}] = \dfrac{k_1[\mathrm{ML}_n\mathrm{X}][\mathrm{Y}]}{k_{-1} + k_2}$

And then substitution $[\mathrm{ML}_n\mathrm{XY}]$ into the rate law for the second step, and let $k = \frac{k_1 k_2}{k_{-1}+k_2}$ to gives the overall rate law below.

$$\frac{d[\mathrm{ML}_n\mathrm{Y}]}{dt} = \frac{k_1 k_2[\mathrm{ML}_n\mathrm{X}][\mathrm{Y}]}{k_{-1} + k_2} = k[\mathrm{ML}_n\mathrm{X}][\mathrm{Y}]$$

This overall rate law is second order, and first order with respect to each of the reactants. This means that there is a direct (linear) relationship between concentration of either reactant and the rate of reaction.

Why does the associative mechanism depend on concentrations in this specific way?

This is a case of two molecules coming together. If both compounds are dissolved in solution, they must “swim around” or travel through the solution until they bump into each other and react. The more concentrated the solution is, or the more crowded it is with molecules, the more likely are the reactants to bump into each other. If we double the amount of new ligand in solution, an encounter between ligand and complex becomes twice as likely. If we double the amount of metal complex in solution, an encounter also becomes twice as likely.

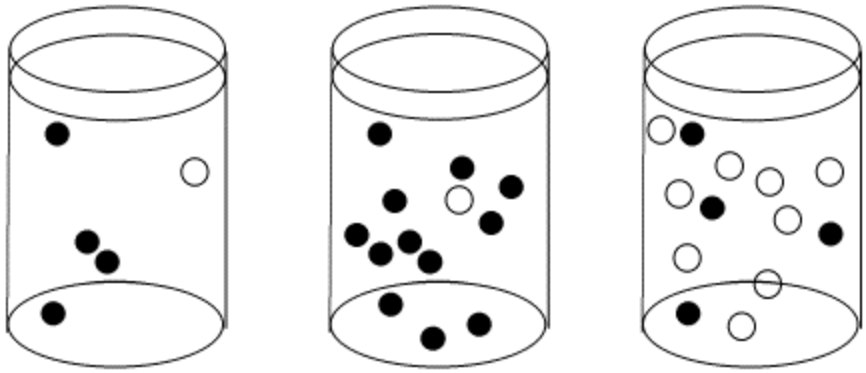


Figure 10.9.3.3.1: The effect of concentration on collision probability. In the first beaker, there is a chance that a black molecule and white molecule will meet and react together. The chance of a meeting is much higher in both the second beaker, where there are lots more black molecules, and in the third beaker, where there are many more white molecules.

Exercise 10.9.3.3.1

Given the associative rate law above, what would happen to the reaction rate for an associative substitution in the following cases?

a. the concentration of ligand is doubled, and the concentration of metal complex is doubled
b. the concentration of ligand is tripled, and the concentration of metal complex is doubled
c. the concentration of ligand is tripled, and the concentration of metal complex is tripled
d. the concentration of ligand is halved, and the concentration of metal complex is doubled

Answer a available at the end of this section.

Exercise 10.9.3.3.2

Plot graphs of initial rate vs. concentration to show what you would see in associative substitution.

a) The concentration of new ligand, [X], is held constant at 0.1 mol/L and the concentration of metal complex is changed from 0.5 mol/L to 1 mol/L and then to 1.5 mol/L.

b) The concentration of metal complex, [ML_n], is held constant at 0.1 mol/L and the concentration of ligand is changed from 0.5 mol/L to 1 mol/L and then to 1.5 mol/L.

Answer available at the end of this section.

Exercise 10.9.3.3.3

In the previous problem, the experiment was run in a particular way for particular reasons.

a) Why was one concentration held constant while the other one was changed? Why not change both?

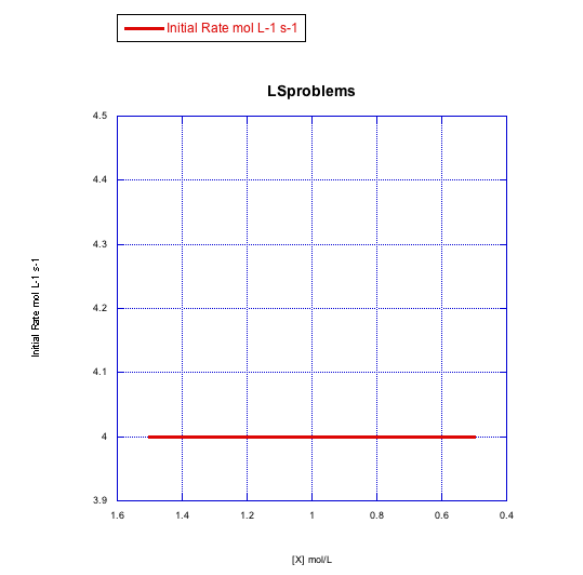
b) Why does the graph report "initial rate" -- just the rate at the very beginning of the reaction?

Answer a available at the end of this section.

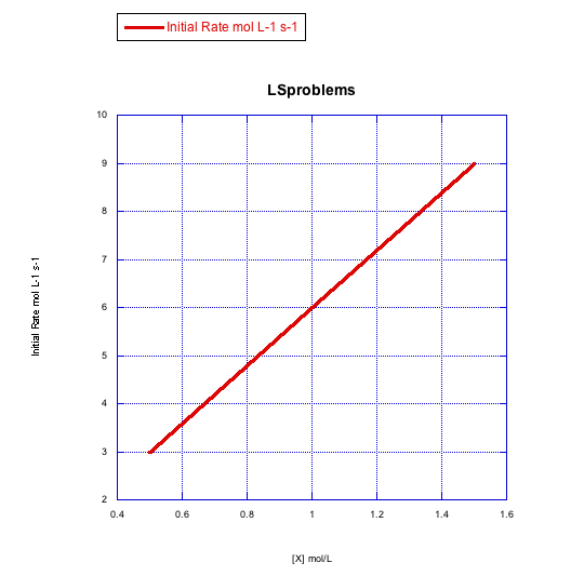
Exercise 10.9.3.3.4

Given the following sets of initial rate data (rates measured at the beginning of a reaction), determine whether each case represents an associative substitution.

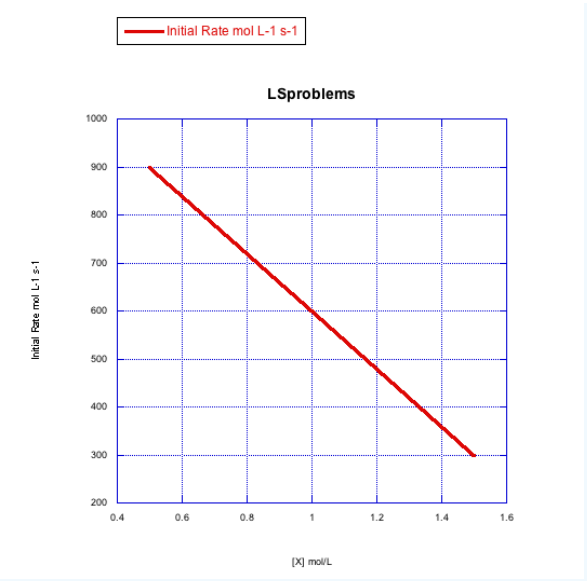
a)



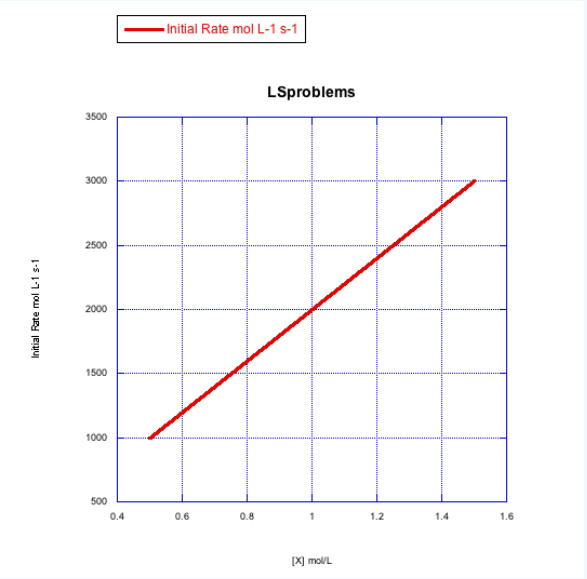
b)



c)



d)



Answer a available at the end of this section.

Exercise 10.9.3.3.5

What information can be gained from the slopes of lines in Exercise 10.9.3.3.4 ?

Answer available at the end of this section.

Note that the rate law for an A mechanism, and a reversible I mechanism are of the same form: they are each first order with respect to each reactant. Thus, an unambiguous determination between the two is difficult because it would require detection of the intermediate, which exists only at a very low concentration.

Answers

Exercise 10.9.3.3.1

Associative Rate Law: $Rate = [ML_n][X]$, if ML_n is the complex and X is the new ligand.

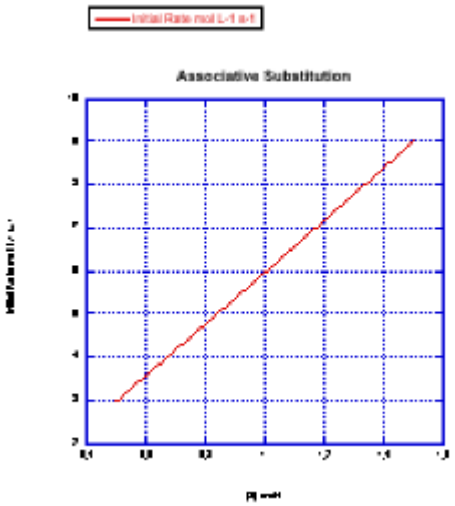
Rate will quadruple: $Rate = (2 \times [ML_n]_0) \times (2 \times [X]_0) = 4 \times [ML_n]_0[X]_0$, if $[X]_0$ and $[ML_n]_0$ are the original concentrations.

Rate will sextuple: $Rate = (3 \times [ML_n]_0) \times (2 \times [X]_0) = 6 \times [ML_n]_0[X]_0$.

Rate will nonuple: $Rate = (3 \times [ML_n]_0) \times (3 \times [X]_0) = 9 \times [ML_n]_0[X]_0$.

Rate will stay the same: $Rate = (0.5 \times [ML_n]_0) \times (2 \times [X]_0) = 1 \times [ML_n]_0[X]_0$.

Exercise 10.9.3.3.2



Exercise 10.9.3.3.3

Changing both concentrations at once would leave some doubt about whether one concentration had affected the rate, or the other concentration, or both. In practice, one concentration is usually held constant while the other is kept in excess and varied.

Rate changes over time because the concentrations of reactants change as they are consumed. By reporting only the initial rate (usually meaning less than 5% or 10% complete, but possibly even less than that if a lot of data can be gathered very quickly), the concentrations are still about what you started with. That means you can report a rate that corresponds to a given concentration with confidence.

Exercise 10.9.3.3.4

The rate would change with the ligand concentration if associative. This rate is constant over a range of ligand concentrations, so the reaction is not associative.

The rate increases linearly with ligand concentration. This reaction proceeds via an associative mechanism.

The rate changes over the concentration range, but it decreases. This is the opposite of what should happen. This reaction does not follow a simple associative pathway.

The rate increases linearly with ligand concentration. This reaction proceeds via an associative mechanism.

Exercise 10.9.3.3.5

Because $Rate = k[ML_n][L]$ is held constant while [L] is varied, then the slope of the line is k $[ML_n]$. Since you would know the value of $[ML_n]$, you could obtain the rate constant from the quantity (slope/ $[ML_n]$).

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10.9.3.4: Preassociation Complexes

Most octahedral complexes react through either an associative or dissociative interchange mechanism (I_a or I_d). Although the rate laws should be different for these two cases, it is difficult to distinguish between them. The difficulty lies in the seemingly conflicting observations from experiments performed under limiting conditions of the incoming ligand. For example, in the case of the reaction of hexaaquochromium(III) ($[Cr(H_2O)_6]$) with ammonia (NH_3), the rate laws determined at high and low concentrations of the incoming ligand give different apparent rate laws. Under most conditions, the rate law appears to indicate a dissociative mechanism (ie rate is independent of the $[NH_3]$). But, at very high $[NH_3]$, the rate law appears to indicate an associative mechanism (ie the rate depends on $[NH_3]$).

This information might seem contradictory. However, it can be explained by the formation of a transient ion pair, usually called an encounter complex, in a step prerequisite to the rate-determining step(s). The Eigen-Wilkins Mechanism is based on this idea.

The Eigen-Wilkins mechanism

The Eigen-Wilkins *mechanism* is also a rate law, and it governs the reactions of octahedral metal complexes. This mechanism does not define the rate-limiting step; rather, it defines the existence of a pre-equilibrium step (ie an initial step that is *not rate-determining*) that results in formation of an encounter complex. The encounter complex is a short-lived ion pair of the metal complex and the incoming ligand; it is an intermediate formed through Coulomb interactions. For the conversion of a generic metal complex, where X is the leaving group and Y is the entering group, the overall reaction, pre-equilibrium step, and formation of products from the encounter complex are shown below:

	CHEMICAL EQUATION	EQUILIBRIUM EXPRESSION
Formation of Encounter Complex	$ML_5X + Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (ML_5X \cdot Y)$	$K_E = \frac{[(ML_5X \cdot Y)]}{[ML_5X][Y]}$
Formation of Products:	$(ML_5X \cdot Y) \xrightarrow{k_2} ML_5Y + X$	$K_2 = \frac{[ML_5Y][X]}{[(ML_5X \cdot Y)]}$
Overall Reaction:	$ML_5X + Y \rightleftharpoons ML_5Y + X$	$K = \frac{[ML_5Y][X]}{[ML_5X][Y]}$

Fast pre-association

One possibility (that is most common) is that k_1 and $k{-}1$ are much larger than k_2. In this case, the encounter complex forms quickly, and once it forms, it also can quickly fall apart to re-form the reactant complex. When k_2 is relatively small then reaction of the encounter complex to form the product is the rate-determining step, and sometimes the concentration of encounter complex can be experimentally determined. However, it is rare that this is the case. A second, more common scenario iis that k_2 is also relatively large. Assuming that the formation of the encounter complex is still a fast step, then the rate still depends on the reaction of that encounter complex to form product. In either case, one path for deriving the rate laws is given below. The rate of formation of the product is defined by the second step:

$$\text{Rate} = \frac{d[ML_5Y]}{dt} = k_2[(ML_5X \cdot Y)]$$

Although the encounter complex may exist in high enough concentration to be detected, that is rare and technically difficult. Rather, the concentration of the encounter complex can be determined by manipulation of the equilibrium constant expression and some helpful assumptions. The equilibrium constant for formation of the encounter complex is:

$$K_E = \frac{[(ML_5X \cdot Y)]}{[ML_5X][Y]}$$

This can be rearranged to solve for concentration of the encounter complex.

$$[(ML_5X \cdot Y)] = K_E[ML_5X][Y] \tag{10.9.3.4.1}$$

...and we can re-write the rate experssion to remove the encounter complex from the expression. But by doing so, we remove the problem of the unmeasurable encounter complex being in the expression, but add the problem of the reactant metal complex

being part of the expression:

$$\text{Rate} = k_2 K_E [\text{ML}_5\text{X}][\text{Y}]$$

The problem is that we don't precisely know what the value of $[\text{ML}_5\text{X}]$. We only know the total amount we initially added. But, we assume that k_1 is large, and so the initial concentration of the metal complex may change immediately to produce some of the encounter complex. As long as k_2 is relatively small, we can assume that the initial total concentration of metal complex at the start of reaction consists primarily of the reactant complex plus the encounter complex:

$$[\text{M}]_{\text{total}} = [\text{ML}_5\text{X}] + [(\text{ML}_5\text{X} \cdot \text{Y})]$$

We can substitute XXX into XXX to remove the encounter complex from the expression, then rearrange to solve for the reactant metal ion concentration, $[\text{ML}_5\text{X}]$:

$$\begin{aligned} [\text{M}]_{\text{total}} &= [\text{ML}_5\text{X}] + K_E[\text{ML}_5\text{X}][\text{Y}] \\ &= [\text{ML}_5\text{X}](1 + K_E[\text{Y}]) \\ [\text{ML}_5\text{X}] &= \tfrac{[\text{M}]_{\text{total}}}{1+K_E[\text{Y}]} \end{aligned}$$

Now this allows us to do one more substitution into the rate expression to get the rate into terms of constants and solution concentrations that are known:

$$\text{Rate} = k_2 K_E \frac{[\text{M}]_{\text{total}}[\text{Y}]}{1 + K_E[\text{Y}]}$$

This rate expression is complex, but can be simplified under extremely high or low concentrations of the incoming ligand, [Y].

High [Y]: If the recation proceeds at high concentration of Y, then the denominator, $1 + K_E[\text{Y}]$ becomes approximately $K_E[\text{Y}]$. The expression is simplified to a first-order rate law under high [Y]:

$$\text{Rate} = k_2 K_E \frac{[\text{M}]_{\text{total}}[\text{Y}]}{K_E[\text{Y}]} = k_2[\text{M}]_{\text{total}}$$

This would allow determination of k_2 because the rate could be directly observed by varying the concentration of $[\text{M}]_{\text{total}}$ at high [Y].

Low [Y]: If the reaction is run at very low [Y], then the denominator, $1 + K_E[\text{Y}]$ becomes approximately 1. We can let the observed rate constant, $k_{obs} = k_2 K_E$ to get a simplified second-order rate law under very low [Y]:

$$\text{Rate} = k_2 K_E \frac{[\text{M}]_{\text{total}}[\text{Y}]}{K_E[\text{Y}]} = \frac{d[\text{ML}_5\text{Y}]}{dt} = k_{obs}[\text{M}]_{\text{total}}[Y]$$

The observed rate constant can be measured experimentally, and K_E can be determined theoretically ($k_{obs} = k_2 K_E$)

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10.9.3.5: Activation Parameters

The rate law shows how the rate of a reaction depends on concentrations of different species in solution. The proportionality constant, k, is called the rate constant. It contains other information about the energetic requirements of the reaction.

All reactions must overcome activation barriers in order to occur. The activation barrier is the sum of the energy that must be expended to get the reaction going. An activation barrier is often thought of, cartoonishly, as a hill the molecule has to climb over during the reaction. Once, there, it can just slide down the other side of the hill to become products. At the top of the hill, the molecule exists in what is called the "transition state". At the transition state, the structure is somewhere between its original form and the structure of the products.

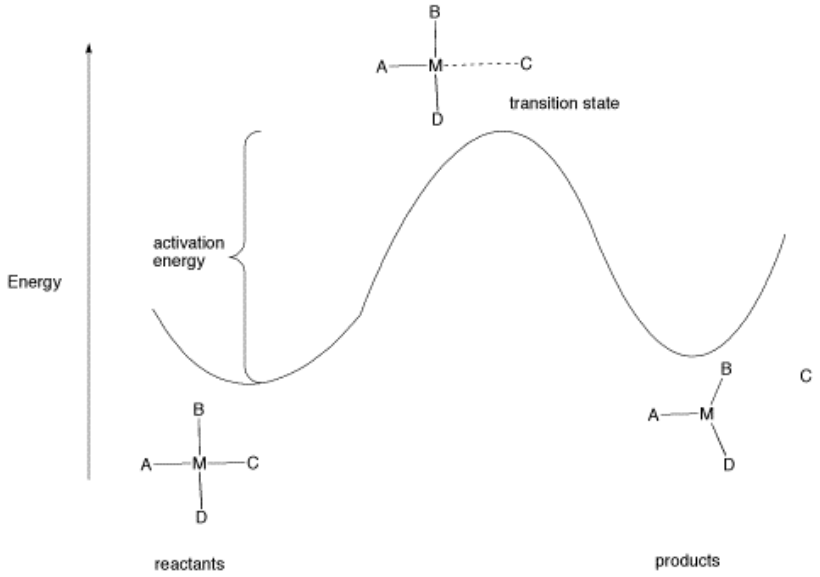


Figure 10.9.3.5.1: The activation barrier for a ligand dissociation step.

The type of diagram shown in figure LS6.1 is sometimes called a "reaction progress diagram". It shows energy changes in the system as a reaction proceeds. One or more activation barriers may occur along the reaction pathways, as various elementary steps occur in the reaction. In the above case, it is easy to imagine the source of the energy barrier, because some energy must be expended to break the bond to ligand C.

However, after that barrier is passed, energy is lowered again. This can happen for several reasons. Once C has separated from the metal complex, it is free to vibrate, tumble, roll and zip around all on its own. That means it can put its energy into any of those modes, independently of the metal complex. As a result, the entropy of the system increases. That lowers the overall "free energy" of the system. In addition, there may be some relief of crowding as the molecule changes from a four-coordinate complex to a three-coordinate complex, so strain energy is also lowered.

Exercise 10.9.3.5.1

Make drawings depicting the relationship between reaction progress and energy for the following cases:

a) a new ligand binds to a four-coordinate complex, forming a five coordinate complex.

b) a two-step process in which a new ligand binds to a four-coordinate complex, forming a five coordinate complex, and then an old ligand dissociates to form a new, four-coordinate complex.

The rate constant gives direct insight into what is happening at the transition state, because it gives us the energy difference between the reactants and the transition state. Based on that information, we get some ideas of what is happening on the way to the transition state.

The rate constant can be broken down into pieces. Mathematically, it is often expressed as

$$k = (\frac{RT}{Nh})e^{-\frac{\Delta G^{\ddagger}}{RT}}$$

In which R = the ideal gas constant, T = temperature, N = Avogadro's number, h = Planck's constant and $\Delta G^{\ddagger}$ = the free energy of activation.

The ideal gas constant, Planck's constant and Avogadro's number are all typical constants used in modeling the behaviour of molecules or large groups of molecules. The free energy of activation is essentially the energy requirement to get a molecule (or a mole of them) to undergo the reaction.

Note that k depends on just two variables:

- $\Delta G^{\ddagger}$ or the energy required for the reaction
- T or the temperature of the surroundings, which is an index of the available energy

The ratio of activation free energy to temperature compares the energy needs to the energy available. The more energy available compared to the energy needed, the lower this ratio becomes. As a result, the exponential part of the function becomes larger (since the power has a minus sign). That makes the rate constant bigger, and the reaction becomes faster.

The activation free energy is constant for a given reaction. It can be broken down in turn to:

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

in which $\Delta H^{\ddagger}$ = activation enthalpy and $\Delta S^{\ddagger}$ = activation entropy.

The activation enthalpy is the energy required for the reaction. The activation entropy deals with how the energy within the molecule must be redistributed for the reaction to occur. These two parameters can be useful in understanding events leading to the transition state.

For example, in ligand substitution, an associative pathway is marked by low enthalpy of activation but a negative entropy of activation. The low enthalpy of activation results because bonds don't need to be broken before the transition state, so it doesn't cost much to get there. That's favorable and makes the reaction easier. However, a decrease in entropy means that energy must be partitioned into fewer states. That's not favorable and makes the reaction harder. The reason the energy must be redistributed this way is that two molecules (the metal complex and the new ligand) are coming together to make one bigger molecule. They can no longer move independently of each other, and all of their combined energy must be reapportioned together, with a more limited range of vibrational, rotational and translational states to use for that purpose.

- Associative pathway: more bond making than bond breaking; lower enthalpy needs
- Associative pathway: two molecules must be aligned and come together; fewer degrees of freedom for energy distribution; decrease in entropy

On the other hand, the dissociative pathway is marked by a higher enthalpy of activation but a positive entropy of activation. The higher enthalpy of activation results because a bond must be broken in the rate determining step. That's not favorable. However, the molecule breaks into two molecules in the rate determining step. these two molecules have more degrees of freedom in which to partition their energy than they did as one molecule. That's favorable.

- Dissociative pathway: more bond breaking in rate determining step, higher enthalpy needs
- Dissociative pathway: one molecule converts to two molecules in rate determining step, greater degrees of freedom in two independently moving molecules, entropy increases

Thus, looking at the activation parameters can reveal a lot about what is going on in the transition state.

Exercise 10.9.3.5.2

What factor(s) other than entropy might raise the free energy of the transition state going into an associative step between a metal complex and an incoming ligand? (What factor might make the first, associative step slower than the second, dissociative step?)

Answer available at the end of this section.

Exercise 10.9.3.5.3

Other mechanisms for ligand substitution are also possible. The following case is referred to as an associative interchange (I_A).



a) Describe in words what happens in an associative interchange.

b) Predict the rate law for the reaction.

c) Qualitatively predict the activation entropy and enthalpy, compared with

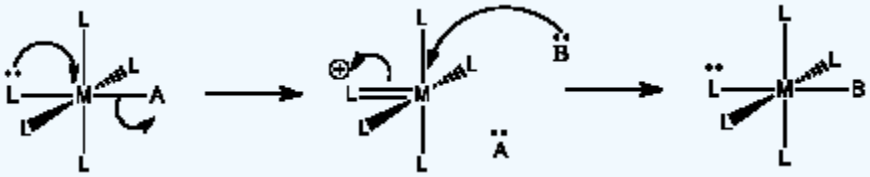
i) an associative mechanism and

ii) a dissociative mechanism.

Answer a available at the end of this section.

Exercise 10.9.3.5.4

For the following mechanism:



a) Describe in words what is happening.

b) Predict the rate determining step.

c) Predict the rate law for the reaction.

d) Qualitatively predict the activation entropy and enthalpy, compared with

i) both an associative mechanism and

ii) a dissociative mechanism.

e) Suggest some ligands that may be able to make this mechanism occur.

Answer a available at the end of this section.

Answers

Exercise $10.9.3.5.2$

The metal centre is becoming more crowded as the new ligand arrives, so an increase in energy owing to steric hindrance may also play a role in the transition state energetics.

Exercise $10.9.3.5.3$

The new ligand, B, is arriving at the same time as the old ligand, A, is departing. We might also describe it as new ligand B pushing old ligand A out of the complex.

$Rate = k[ML_5A][B]$, which looks like an associative rate law.

This is a thought-provoking question without a definite answer. Associative mechanisms typically have lower activation enthalpy than dissociative mechanisms, because there has also been some bond-making prior to the bond-breaking in the rate determining step. The associative interchange would be a little more like the associative mechanism than dissociative. The mix of bond-making and bond-breaking at the transition state would make the enthalpy of activation relatively low.

Associative mechanisms have negative activation entropies, whereas dissociative mechanisms have positive activation entropies. The associative interchange could be in between the two, given that the elementary step would be close to entropically neutral overall. What happens at the transition state is a little harder to imagine, but it might reflect the small changes in entropy through the course of the reaction, producing a small entropy of activation. On the other hand, if the incoming ligand is forced to adopt some specific approach as it comes into the molecule (to stay out of the way of the departing ligand, for example) then that restriction could show up as a small negative activation entropy.

Exercise $10.9.3.5.4$

The lone pair donation from one ligand appears to push another ligand out.

The first step is probably rate determining, because of the bond breaking involved.

If the first step is rate determining, $Rate = k[ML_5A]$.

Another question without a very clear answer. Compared with an associative mechanism, the activation entropy is probably much more positive, because additional degrees of freedom are being gained as the molecule heads over the activation barrier and one of the ligands separates to be on its own. However, the activation entropy may be less positive than in a regular dissociation, because in this case the breaking of one bond has to be coordinated with the formation of another.

The enthalpy of activation has both a bond-making and bond-breaking component, a little like in an associative mechanism. However, the amount of bond making here is probably less important, because pi bonds are typically not as strong as sigma bonds. The activation enthalpy is probably higher than an associative pathway but not as high as a dissociative one.

The donor ligand must have a lone pair. Oxygen donors would be good candidates, because even if one lone pair is already donating in a sigma bond, an additional lone pair may be available for pi donation. The same thing is true for halogen donors. It would also be true for anionic nitrogen donors but not for neutral nitrogen donors, because a neutral nitrogen has only one lone pair.

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10.9.3.6: Some Reasons for Differing Mechanisms

We usually look for physical reasons why a given compound might undergo a reaction via one mechanism and not another. That ability adds to our understanding of chemistry. If we can take information and give it predictive value, then we may be able to make educated decisions about what is probably happening with new reactions.

Why might a reaction undergo a dissociative reaction rather than an associative one? What factors might prevent an associative pathway?

One reason may be that there is not enough room. In an associative step, an additional ligand comes in and binds to the metal. If it is already crowded, that may be difficult.

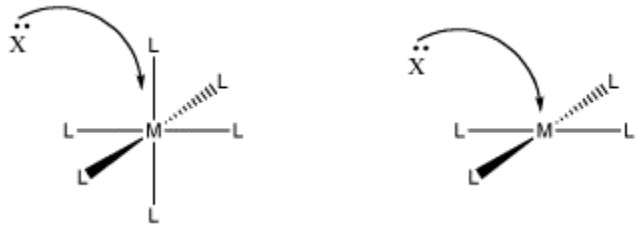


Figure 10.9.3.6.1: The role of steric crowding in ligand substitution. In one of these cases, the associative mechanism is less favored because of crowding that will occur in the transition state.

- Steric crowding may lead to a dissociative, rather than associative, mechanism.

Another reason has to do with electronics. Maybe the compound cannot easily accept an additional bonding pair. That may be the case if the compound already has eighteen electrons.

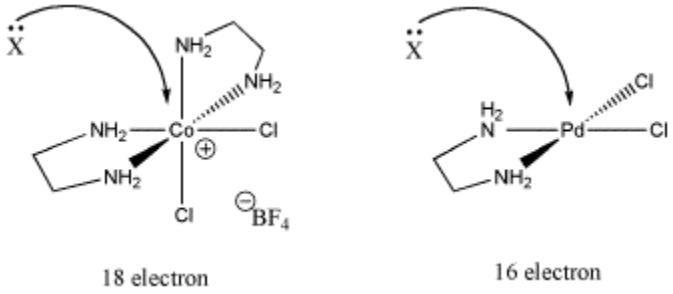


Figure 10.9.3.6.2: The role of electron count in ligand substitution. In one of these cases, the associative mechanism is less favored because the metal is already electronically saturated.

- Electronic saturation may lead to a dissociative, rather than associative, mechanism.

However, if there is less crowding, and more electrons can be accommodated, an associative pathway may result.

Exercise 10.9.3.6.1

i) Draw structures for the following reactions. Pay attention to geometry.

ii) Predict whether each of the substitutions would occur through associative or dissociative mechanisms.

a) $AuCl_3py + Na\ N_3 \rightarrow Na^+\ [AuCl_3N_3]^-$ + py

b) $Rh(C_2H_4)_2(acac) + C_2D_4 \rightarrow Rh(C_2D_4)_2(acac) + C_2H_4$

c) $[Co(NH_3)_5Cl]^{2+} + H_2O \rightarrow [Co(NH_3)_5(OH_2)]^{2+} + Cl^-$

d) *trans*-$(Et_3P)_2PtCl_2 + {}^-SCN \rightarrow$ *trans*-$(Et_3P)_2PtCl(SCN) + Cl^-$

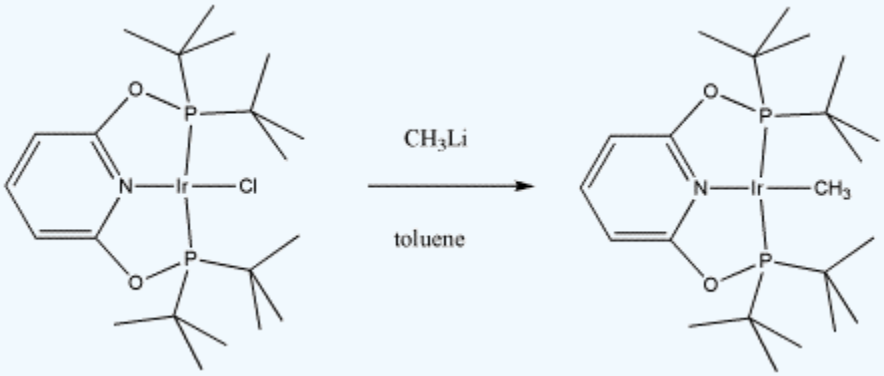
e) $Rh(NH_3)_4Cl_2^+ + {}^-CN \rightarrow Rh(NH_3)_4Cl(CN)^+ + Cl^-$

f) *trans*-$[Cr(en)_2Br_2]^+ + {}^-SCN \rightarrow$ *cis*- and *trans*-$[Cr(en)_2Br(SCN)]^+ + Br^-$

Answer available at the end of this section.

Exercise 10.9.3.6.2

Maurice Brookhart of UNC, Chapel Hill, makes organometallic compounds in order to study fundamental questions about reactivity. In this case, he has reported making a new compound capable of "C-H activation", a reaction in which unreactive C-H bonds can be forced to break. This process holds the future promise of converting coal and natural gas into important commodities currently obtained from petroleum.



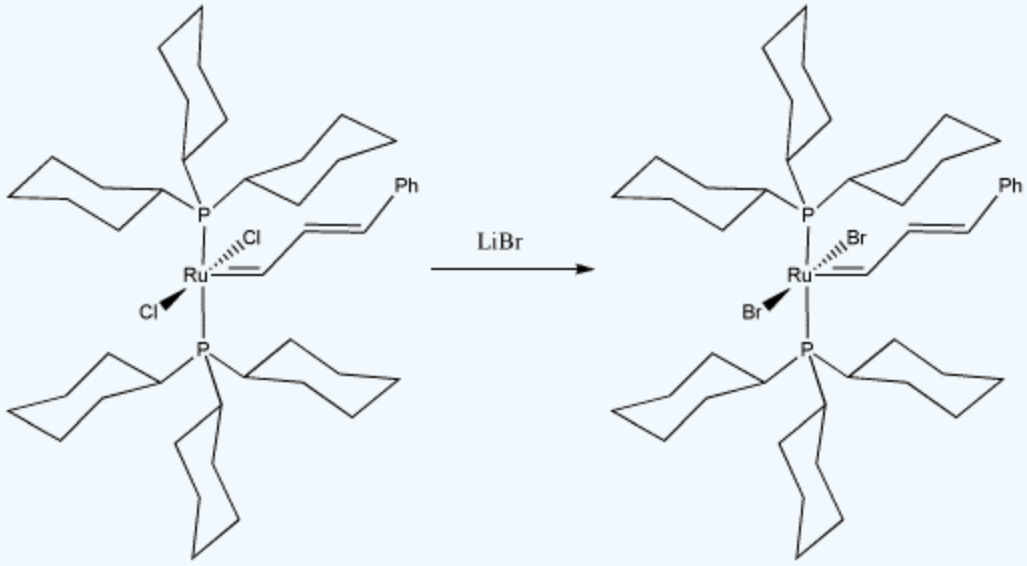
a) Draw, with curved arrows, a mechanism for the ligand substitution in the synthesis of this C-H activating complex.

b) Explain your reasons for your choice of reaction mechanism.

Answer available at the end of this section.

Exercise 10.9.3.6.3

Bob Grubbs of Cal Tech was awarded the Nobel Prize in chemistry for his development of catalysts for olefin metathesis. Olefin metathesis is important both in the reforming of petroleum and in the synthesis of important commodities such as pharmaceuticals. In the following study, he replaced chlorides on a "Grubbs Generation I catalyst" to study the effect on the olefin metathesis reaction.



a) Draw, with curved arrows, a mechanism for the ligand substitution in this complex.

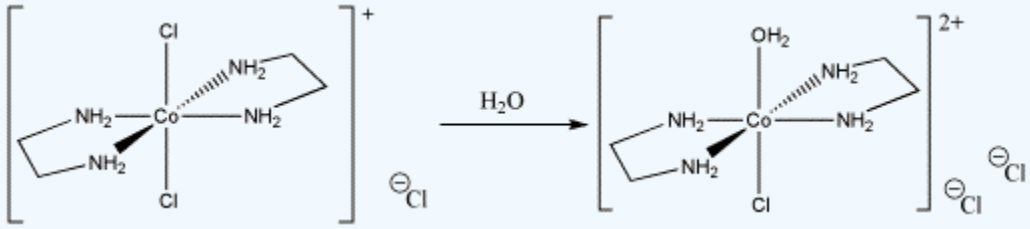
b) Explain your reasons for your choice of reaction mechanism.

c) What factor(s) do you think Grubbs hoped to study by making this substitution in the catalyst?

Answer available at the end of this section.

Exercise 10.9.3.6.4

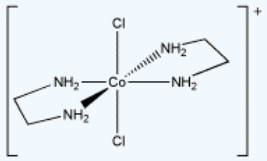
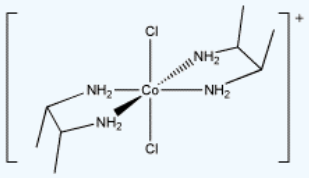
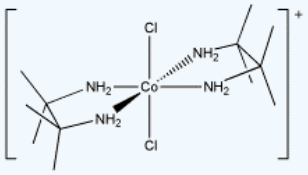
Sometimes, kinetic studies can give insight into a reaction if controlled changes in the reaction produce measurable results.



a) Draw, with curved arrows, a mechanism for the ligand substitution in this reaction.

b) Explain your reasons for your choice of reaction mechanism.

c) Explain the following kinetic data.

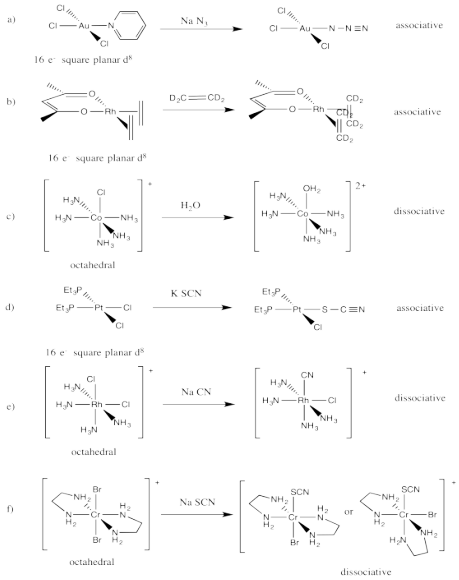
complex	substitution rate constant
	$3.2 \times 10^{-5}\ s^{-1}$
	$4.1 \times 10^{-3}\ s^{-1}$
	too fast to measure easily

Exercise 10.9.3.6.5

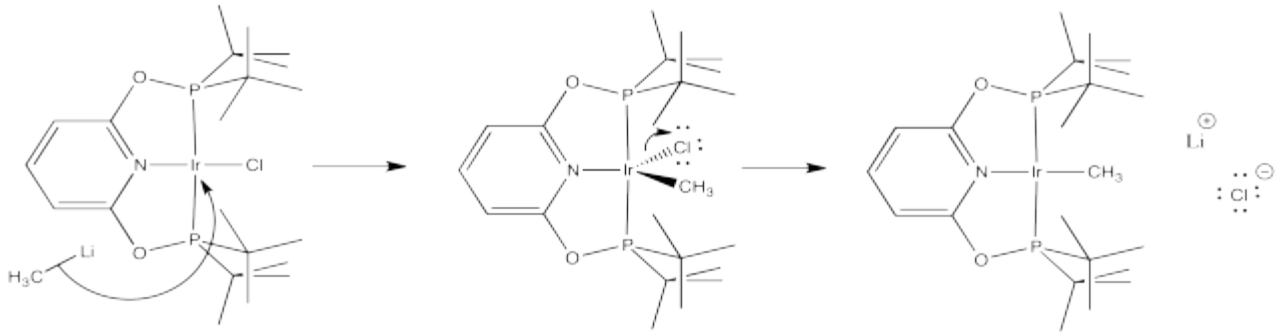
Several different structures were proposed for $Ni(cysteine)_2^{2-}$. Kinetic studies of substitution in this complex showed the rate was dependent in the concentration of both the metal complex and the incoming ligand. Which structure do you think is correct? Why?

Answers

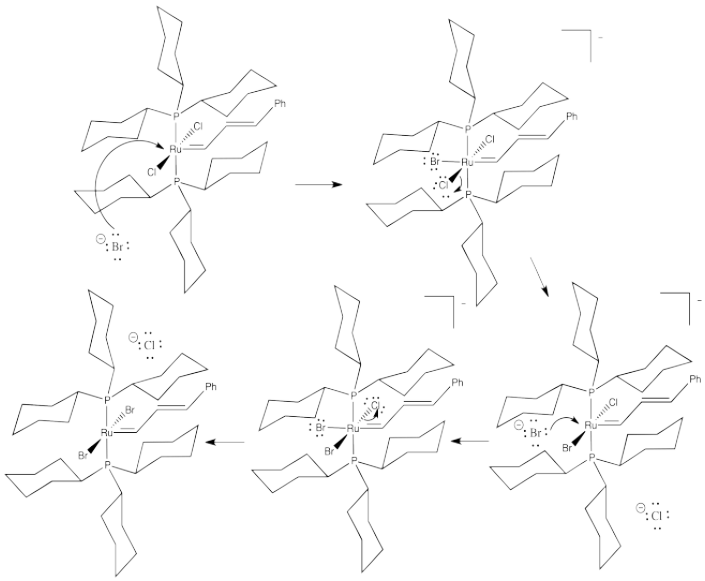
Exercise 10.9.3.6.1



Exercise 10.9.3.6.2



Exercise 10.9.3.6.3



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10.9.4: Experimental Evidence in Octahedral Substitutions

This section will review some of the common experiments that can provide evidence supporting different mechanisms, with a focus on the reactions of octahedral complexes.

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10.9.4.1: Dissociation

Consider what must happen for the simplest case of a purely dissociative (D) reaction mechanism for an octahedral metal complex. The first step, and the rate-limiting step must be dissociation of one ligand to form an intermediate with a lower coordination number. Such a situation, where an octahedral complex looses a ligand, X, to become a square pyramidal intermediate is shown below in Figure 10.9.4.1.1.

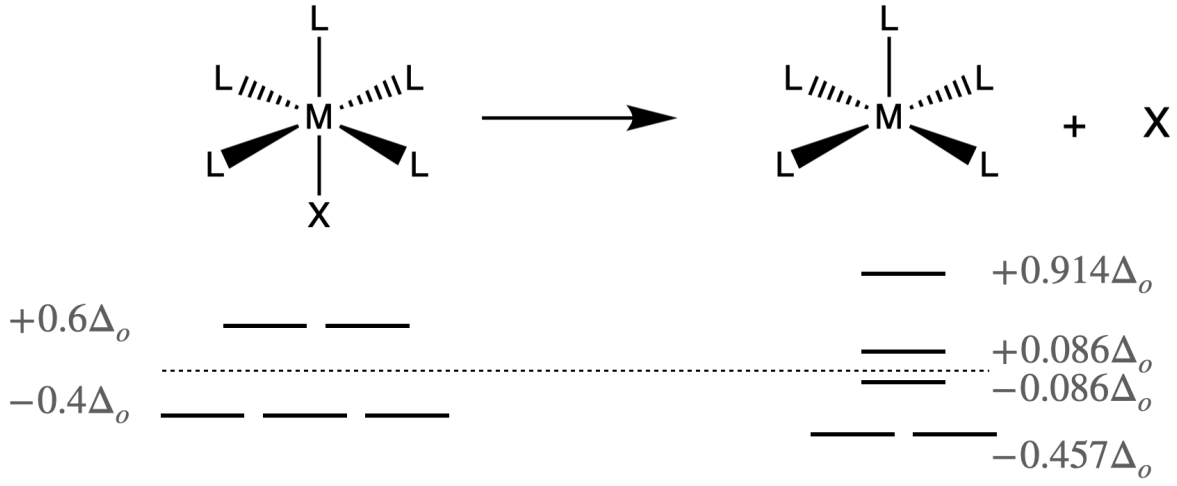


Figure 10.9.4.1.1: Dissociation of a ligand to form a square pyramidal intermediate. This would be the first step of a dissociative (D) reaction mechanism. The Ligand Field Activation Energy (LFAE) can be calculated from the splitting energies of the octahedron compared to the square planar intermediate. (CC-BY-SA; Kathryn Haas)

If the dissociation of a ligand is rate-determining, factors that lower the energy of the transition state or intermediate structures will speed the reaction rate. Here we could consider the differences in ligand-field stabilization energy (LFSE). The difference between the LFSE of the octahedral reactant and that of the intermediate is defined as the ligand field activation energy (LFAE). The LFAE can be calculated for a given d-electron count for an octahedral reactant and a square pyramidal intermediate using the information provided in Figure 10.9.4.1.1. Metal ions with particularly low (more negative) LFAE values tend to be more labile, while those with particularly high (less negative) values tend to be more inert. However, most octahedral complexes are expected to react through dissociative mechanisms due to the unfavorable steric crowding that must occur during an associative pathway.

The ease by which the M-X bond is broken will also influence rate of a dissociative reaction, and this can be probed experimentally. The following experiments can give evidence that support the argument that a reaction occurs by a dissociative pathway, or that it is dissociatively activated.

Experimental evidence that supports dissociative mechanism

1. Identity of the entering ligand has little effect on reaction rate.

If dissociation is the rate-determining step, the identity of the entering ligand, Y, should have little effect on the reaction rate. Therefore, an experiment that varies Y while holding X constant can indicate whether or not Y is involved in the rate-determining step. If the identity of Y has little effect on rate, then it must not be involved in the rate-determining step. Such experimental evidence can be taken as evidence of a dissociative mechanism. For example, the rate constants for reaction of Extra close brace or missing open brace with different incoming ligands, shown below, has rate constants of similar magnitude (they are approximately within one order of magnitude), indicating a dissociatively activated mechanism. In this case, other lines of evidence suggest this is a reaction with a I_d mechanism.

$$[\mathrm{Cr(NH_3)_5H_2O}]^{3+} + \mathrm{Y^-} \rightleftharpoons [\mathrm{Cr(NH_3)_5Y}]^{2+} + \mathrm{H_2O}$$

Table 10.9.4.1.1: Rate Constants for Exchange of Aquo Ligand of pentaammineaquo chromium(III) ion by incoming ligand, Y (chemical equation shown above). There is little effect of the identity of the incoming ligand on the rate constant. This data was sourced from Miessler, Fischer and Tarr's Inorganic Chemistry, 5th edition, pg 449.

Entering Ligand, Y^-	Rate Constant, k_1 $(10^{-4}M^{-1}s^{-1})$
NCS^-	4.2
Cl^-	0.7
Br^-	3.7
$CF_3CO_2^-$	1.4

2. Steric Crowding of the Metal Complex

Steric crowding of the metal complex would inhibit a dissociative pathway through steric crowding of the entering ligand. However, steric crowding can increase the stability of the intermediate after dissociation of the ligand from the crowded octahedral complex. If the reaction rate increases with steric crowding of the reactant complex, this is taken as evidence to support a dissociative mechanism.

3. Volume of Activation

One molecule generally takes up less space than two sperate molecules. This usually holds true in solution. Measurement of a rate constant's dependence on pressure can be used to determine the volume of activation (ΔV_{act}) and give insight into the mechanism of that reaction. In a dissociation mechanism, the dissociation causes one metal complex to become two separate molecules. Thus, the intermediate should, in principle, take up more space than the reactant complex. In a situation like this, we expect that the rate of reaction should decrease with increasing pressure, giving a positive value for ΔV_{act}. However, solvation of ions can influence volume, and this should be considered in interpretation of pressure-dependence data.

4. Increased coulombic attraction with the leaving group decreases reaction rate.

Couloubic (electrostatic) attraction between the dissociating ligand, X, and the metal complex should slow ligand dissociation. Coulombic attraction increases with increased magnitude of charges and with decreased distance. If the reaction rate slows with increased charge of the metal ion or the ligand itself, this is taken as evidence of a dissociative mechanism. Likewise, if rate decreases as the radius of the central metal ion is decreased, this is evidence to support a dissociative mechanism.

5. Increased strength of the M-X bond decreases reaction rate.

Free energy relationships between the formation constant of M-X and the kinetic rate constant of the reaction can provide evidence to support a dissociative mechanism (Discussed in the next section).

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10.9.4.2: Linear Free Energy Relationships

The Linear Free Energy Relation (LFER) is a tool that can indicate the importance of bond breakage or bond formation in the rate-determining step. In the case of a dissociative mechanism, for example, bond breaking is critical for reaction progress. Therefore, the strength of the M-X bond influences not only the extent to which the reaction will happen, but also the rate. Although thermodynamic stability of a complex does not necessarily indicate the kinetic rate at which it will react, there is a relationship between bond stability and the rate of reaction *if the breaking or formation of that bond is involved in the rate-determining step*. The relationship can be stated as follows:

$$ln\ k = ln\ K + c$$

And this relationship can be justified using the Arrhenius equation and equation for the temperature-dependence of the equilibrium constant.

$$\ln k = \ln A - \frac{E_A}{RT} \quad \text{and} \quad \ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

In an experiment designed to test the Linear Free Energy Relationship, several reactions would be conducted under nearly identical conditions, where only the identity of the leaving group, X, is varied. In these experiment, the temperature would be constant and the same in each case. If we assume that the pre-exponential factor, A is the same for each reaction condition (and it should be at identical temperatures for analogous reactions), then the $\ln K$ term of the Arrhenius equation becomes proportional to the activation energy, E_a (and proportional to Gibb's energy of activation, $\Delta G^\ddagger$, and Gibb's energy ΔG). And since the Gibb's energy is related to the equilibrium constant, K, by $\Delta G = RT \ln K$, the value of K and k should be correlated. Likewise, if T is constant over the reaction conditions and ΔS° is similar across the analogous reactions (which it should be), then $\ln K$ becomes proportional to enthalpy, ΔH°, which is proportional to Gibb's free energy of reaction ΔG°.

If a Linear Free Energy Relation plot of $\ln K$ vs $\ln k$ is linear, but with a slope less than one, it indicates a dissociative mechanism with some degree of associative character (for example, an I_d mechanism or a mechanism involving the formation of preassociation complex). If the plot of $\log K$ vs $\log k$ for the reactions is linear, this is evidence that the reaction is dissociative. An example for a linear free energy plot is shown in Figure $10.9.4.2.1$ for the hydrolysis of $[Co(NH_3)_5X]_2^+$ (this is the substitution of X^- with H_2O).

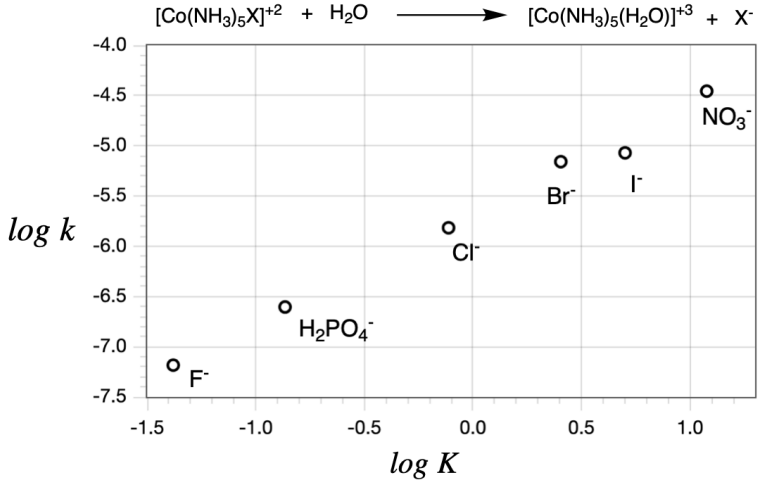


Figure $10.9.4.2.1$: Linear Free Energy relationship lot for $[Co(NH_3)_5X]_2^+$ where $X^- = F^-, H_2PO_4^-, Cl^-, Br^-, I^-, NO_3^-$. This is summarized in Cooper H. Langford, *Inorganic Chemistry* **1965** *4* (2), 265-266, DOI: 10.1021/ic50024a041. (CC-BY-SA; Kathryn Haas)

When the slope is approximately 1, as it is in the case of $[Co(NH_3)_5X]_2^+$ in Figure $10.9.4.2.1$, it indicates that the variation of the X^- leaving group has a similar effect on the magnitude of both ΔG (thermodynamic, related to K) and $\Delta G^\ddagger$ (kintetic, related to k). In other words, a slope close to 1 indicates a purely dissociative pathway (D). This data shown in Figure $10.9.4.2.1$, for example,

is evidence of a dissociative mechanism for $[Co(NH_3)_5X]^{+}_{2}$.

The argument that a reaction is dissociative can also be supported by evidence showing little effect of the incoming ligand on reaction rate. For example, data supporting the argument that $[Co(NH_3)_5H_2O]^{+}_{3}$ reacts by a dissociative pathway is shown below. The data show that variation of the identity of the incoming ligand, Y^{-}, has little effect on the rate constant (they are approximately within one order of magnitude).

$$\text{For the reaction: } [Co(NH_3)_5H_2O]^{3+} + Y^{m-} \rightleftharpoons [Co(NH_3)_5Y]^{(3-m)+} + H_2O$$

Table 10.9.4.2.1*: Rate Constants for Exchange of Aquo Ligand of pentaammineaquo cobalt(III) ion by incoming ligand, Y (chemical equation shown above). There is little effect of the identity of the incoming ligand on the rate constant. This data was sourced from Miessler, Fischer and Tarr's Inorganic Chemistry, 5th edition, pg 448.*

Entering Ligand, Y^{-}	**Rate Constant,** k_1 $(10^{-6}s^{-1})$ **(pseudo-first order with excess** $[Y^{-}]$**)**
H_2O	100
$N_3{}^{-}$	100
$SO_4{}^{2-}$	24
Cl^{-}	21
NCS^{-}	16

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10.9.4.3: Associative Mechanisms

Associative mechanisms tend to be less common for octahedral complexes as a result of steric hindrance of the metal ion by six ligands. However, reactions of octahedral complexes with associative character are more likely if the ligands have low steric bulk and/or the central metal ion is larger with longer bonds (as in the case of $4d$ and $5d$ metal ions). Reactions of octahedrons have also been observed in cases of low d-electron count or low electron density around the central ion, presumably making nucleophilic reaction more favorable. If an octahdral complex is determined to have associative character, in most cases it is associatively-active interchange (I_a).

The evidence that supports arguments for associative mechanisms is somewhat the opposite as that which would support dissociative character. One typical piece of evidence that supports an associative pathway is **a large effect of the incoming ligand on the reaction rate constant**. For example, in the reaction of hexaaquo chromium (III) ion (Extra close brace or missing open brace) with various incoming ligands (shown below), rate constants vary by several orders of magnitude. This data is evidence of an associative mechanism (I_a). In contrast, the reaction of pentaamineaquo chromium (III) ion (Extra close brace or missing open brace) occurs by an associative mechanism (data shown in Section 12.4.1). The difference in reaction mechanisms for different chromium (III) complexes can be justified by the different electron densities around their metal ion center. The ammine ligand is a stronger sigma donor and thus the metal center is more electron rich in the case of Extra close brace or missing open brace . Nucleophilic reaction by an incoming ligand is thus more likely in the case of Extra close brace or missing open brace , which has a more electrophilic center.

$$[\mathrm{Cr(H_2O)_6}]^{3+} + \mathrm{Y^-} \rightleftharpoons [\mathrm{Cr(H_2O)_5Y}]^{2+} + \mathrm{H_2O}$$

Table 10.9.4.3.1*: Rate Constants for Exchange of Aquo Ligand of hexaaquo chromium(III) ion by incoming ligand, Y (chemical equation shown above). There is little effect of the identity of the incoming ligand on the rate constant. This data was sourced from Miessler, Fischer and Tarr's Inorganic Chemistry, 5th edition, pg 449.*

Entering Ligand, $\mathrm{Y^-}$	**Rate Constant,** k_1 $(10^{-4}M^{-1}s^{-1})$
$\mathrm{NCS^-}$	180
$\mathrm{NO_3{}^-}$	73
$\mathrm{Cl^-}$	2.9
$\mathrm{Br^-}$	0.9
$\mathrm{I^-}$	0.08

Another piece of evidence that can support associative mechanisms is the temperature-dependence of the rate law, which in turn can yield the entropy of activation (represented as $\Delta S^{\ddagger}$ or ΔS_{act}). When an incoming ligand associates with a metal complex and two molecules beome one, there would be a negative change in the entropi (entropy decreases). A negative value for the entropy of activation indicates an associative pathway. An example of this is in the substitution of the aquo ligand in $[\mathrm{Ru(EDTA)(H_2O)}]^-$, which has a negative value of $\Delta S^{\ddagger}$, indicating an I_a mechanism.

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10.9.4.4: The conjugate base mechanism

The substitution reaction of acidic octahedral complexes (with ligands that can donate a proton) can be catalyzed in the presence of hydroxide ion ($\mathrm{OH^-}$. Through an initial acid-base reaction, the metal complex can be deprotonated to its conjugate base. The deprotonation increases electron density on the metal center, facilitating the loss of the leaving group ligand, especially when the leaving ligand is trans to the deprotonation site. This mechanism is referred to as the **conjugate-base mechanism** or the $\mathrm{S_N1CB}$ (**S**ubstitution, **N**ucleophilic, first-order in the **C**onjugate **B**ase mechanism) mechanism. Although it involves a dissociative rate-limiting step, the rate law is consistent with the second-order kinetics because the rate also depends on the initial reaction of the base with the metal complex. In this mechanism, the first step is formation of the conjugate base of the metal complex by deprotonation of one of its ligands. This is a case where numerous lines of evidence are necessary to establish the mechanism.

Cobalt pentammine complexes, $\mathrm{Co(NH_3)_5X^{n+}}$, have been studied extensively and are found to react through the conjugate-base mechanism. The way in which the actual mechanism was determined, and how other possible mechanism were ruled out are described below.

Evidence under acidic aqueous conditions

In acidic aqueous solutions, the reaction

$$\mathrm{[Co(NH_3)_5X]^{2+} + Y^- \longrightarrow [Co(NH_3)_5Y]^{2+} + X^-}$$

was found to proceed through an aquo complex intermediate, $\mathrm{[Co(NH_3)_5OH_2]^{3+}}$, which is also the dominant product despite the identity of the incoming ligand. In other words, to form the product of the reaction above, there are two substitution steps necessary (shown below).

$$\mathrm{[Co(NH_3)_5X]^{2+} + H_2O \rightleftharpoons [Co(NH_3)_5(OH_2)]^{3+} + X^-} \qquad \text{(step 1, form aquo intermediate)}$$

$$\mathrm{[Co(NH_3)_5(OH_2)]^{3+} + Y^- \rightleftharpoons [Co(NH_3)_5Y]^{2+} + H_2O} \qquad \text{(step 2, form final product)}$$

The first step in the reaction is the breaking of a $\mathrm{Co-X}$ bond and the formation of a $\mathrm{Co-OH_2}$ bond (step 1). Subsequently, $\mathrm{Y^-}$ can replace the aquo group (step 2).

In aqueous solution, water is always present at a much higher concentration than the various possible entering groups $\mathrm{Y^-}$, so it is reasonable that the aquo complex should be favored in the competition to form the new bond to $\mathrm{Co(III)}$. Nevertheless, the strength of the $\mathrm{Co-Y}$ bond should depend on the nucleophilicity of $\mathrm{Y^-}$ in these substitution reactions. Thus, the amount of $\mathrm{[Co(NH_3)_5Y]^{2+}}$ product should increase with increasing nucleophilicity of $\mathrm{Y^-}$. The fact that the aquo complex is the predominant reaction product despite the identity of $\mathrm{Y^-}$ strongly suggests that the the $\mathrm{Co-X}$ bond breaking is more important in the reaction outcome than formation of the new bond to the incoming $\mathrm{Y^-}$.

This evidence indicates dissociative character in the reaction. But the nature of the substitution mechanism is still unclear. For example, is the original $\mathrm{Co-X}$ bond completely broken before the new $\mathrm{Co-OH_2}$ bond has begun to form so that $\mathrm{Co(NH_3)_5}^{3+}$ is a true intermediate? Does the mechanism involve a transitory intermediate where bonds are breaking and forming in a concerted fashion?

Evidence under basic aqueous conditions

The evidence of reaction mechanism under basic conditions is seemingly contradictory to what is described above. When the entering group, Y^-, is the hydroxide ion, the reaction is

$$\mathrm{Co(NH_3)_5X^{n+} + OH^- \rightarrow Co(NH_3)_5OH^{2+} + X^{q-}}$$

Substitution by hydroxide ion is kinetically faster than by the aquo ligand in acidic solutions, and the rate is law found to be second-order:

$$\frac{d\left[\mathrm{Co(NH_3)_5OH^{2+}}\right]}{dt} = k\ \left[\mathrm{Co(NH_3)_5X^{n+}}\right]\left[\mathrm{OH^-}\right]$$

This rate law is consistent with an associative reaction involving nucleophilic attack by the hydroxide ion at the cobalt center. In an associative interchange mechanism, the $\mathrm{Co-OH}$ bond formation occurs simultaneously with breaking of the $\mathrm{Co-X}$ bond. However, just as in the case above, the hydroxo complex dominates even in the presence of $\mathrm{Y^-}$. Thus, the hydroxide ion seems to be a uniquely effective nucleophile toward cobalt(III). However, nucleophilic displacements have been investigated on many other electrophile, and in general, hydroxide is not a particularly effective nucleophile toward other electrophilic centers. So, assignment of an associative mechanism to this reaction is reasonable only if we can explain why hydroxide is uniquely reactive in this case and not in others.

The conjugate-base mechanism

An alternative mechanism, referred to as the **conjugate-base mechanism** or the $\mathrm{S_N1CB}$ (**S**ubstitution, **N**ucleophilic, first-order in the **C**onjugate **B**ase mechanism) mechanism, is also consistent with the second-order rate law. In this mechanism, the first step is formation of the conjugate base of the metal complex by deprotonation of one of its ligands. An important requirement of this mechanism is the presence of a metal-bound ligand with acidic protons (including amine, ammine, or aquo ligands). Under basic conditions the mecahnism is catalyzed by hydroxide ion.

In the case of $\mathrm{[Co(NH_3)_5OH_2]^{3+}}$ reacting under basic conditions, the hydroxide removes a proton from one of the ammine ligands to give a six-coordinate conjugate base intermediate (step 1 below). This conjugate base intermediate contains an amido ($\mathrm{NH_2^-}$) ligand which is a π-donor ligand, allowing facilitated dissociation of one of the other ligands (particulary the ligand in the trans position). This intermediate loses the leaving group X^- in the rate determining step to form a five-coordinate intermediate, $\mathrm{Co(NH_3)_4NH^{2+}}$ (step 2 below). This five-coordinate intermediate quickly picks up a water molecule from the bulk solution to give the aquo complex (step 3 below). In a series of proton transfers to (step 4) and from (step 5) the aqueous solvent, the aquo complex rearranges to the final product. The mechanism is shown below for $\mathrm{[Co(NH_3)_5OH_2]^{3+}}$ reacting with $\mathrm{Cl^-}$:

$$\mathrm{[Co(NH_3)_5Cl^{2+}OH]^- \rightleftharpoons [Co(NH_3)_4(NH_2)Cl]^+ + H_2O} \quad \text{(step 1, conjugate base)}$$

$$\mathrm{[Co(NH_3)_4(NH_2)Cl]^+ \rightleftharpoons [Co(NH_3)_4(NH2)]^{2+} + Cl^-} \quad \text{(step 2, dissociation)}$$

$$\mathrm{Co(NH_3)_4(NH2)^{2+} + H_2O \rightleftharpoons Co(NH_3)_4(NH2)(OH2)^{2+}} \quad \text{(step 3, association)}$$

$$\mathrm{Co(NH_3)_4(NH2)(OH2)^{2+} + OH^- \rightleftharpoons Co(NH_3)_4(NH2)OH^+ + H_2O} \quad \text{(step 4, proton transfer)}$$

$$\mathrm{Co(NH_3)_4(NH2)OH^+ + H_2O \rightleftharpoons Co(NH_3)_5OH^{2+} + OH^-} \quad \text{(step 5, proton transfer)}$$

The evidence in favor of the $\mathrm{S_N1CB}$ mechanism is persuasive. It requires that the ammine protons be acidic, so that they can undergo the acid–base reaction in the first step. That this reaction occurs is demonstrated by proton-exchange experiments. In basic $\mathrm{D_2O}$, the ammine protons undergo $\mathrm{H-D}$ exchange according to

$$\mathrm{[Co(NH_3)_5Cl]^{2+} + D_2O \rightleftharpoons [Co(ND_3)_5Cl]^{2+} + HDO}$$

The ammine protons are also necessary; the reaction does not occur for similar compounds, like $\mathrm{Co(2,2'-bipyridine)_2(O_2CCH_3)_2^+}$, which lack acidic protons on the nitrogen atoms that are bound to cobalt (*i.e.*, there are no $\mathrm{H-N-Co}$ moieties).

The evidence that $\mathrm{Co(NH_3)_4(NH2)^{2+}}$ is an intermediate is also persuasive. When the base hydrolysis reaction is carried out in the presence of other possible entering groups, Y^{p-}, the *rate* at which $\mathrm{[Co(NH_3)_5X]^{n+}}$ is consumed is unchanged, but the product is a mixture of $\mathrm{[Co(NH_3)_5OH]^{2+}}$ and $\mathrm{[Co(NH_3)_5Y]^{n+}}$. If this experiment is done with a variety of leaving groups, X^{q-}, the proportions of $\mathrm{[Co(NH_3)_5OH^{2+}]}$ and $\mathrm{[Co(NH_3)_5Y]^{n+}}$ are constant despite which leaving group exists in the reactant complex. These observations are consistent with the hypothesis that all reactants, $\mathrm{[Co(NH_3)_5X]^{n+}}$, give the same intermediate, $\mathrm{[Co(NH_3)_4(NH2)]^{2+}}$. The product distribution is always the same, because it is always the same species undergoing the product-forming reaction.

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10.9.4.5: The Kinetic Chelate Effect

We discussed the increased thermodynamic stability of chelating ligands in a previous section on the chelate effect (Section 10.1.1). This thermodynamic benefit is related to a change in the rate of binding and dissociation events called the kinetic chelate effect. This effect was also mentioned earlier in this chapter (Section 12.2.2).

Recall that there is a relationship between the equilibrium constant and rate constants of any chemical reaction. The relationship is demonstrated below for a general reaction.

$$aA + bB \rightleftharpoons cC + dD$$

$$\text{forward rate} = k_f[A]^a[B]^b$$

$$\text{reverse rate} = k_r[C]^c[D]^d$$

At equilibrium, the rate of the forward reactions is equal to the rate of the reverse reaction. Therefore:

$$\text{forward rate} = \text{reverse rate}$$

$$k_f[A]^a[B]^b = k_r[C]^c[D]^d$$

Rearrangement of the equation above gives:

$$\frac{k_f}{k_r} = \frac{[C]^c[D]^d}{[A]^a[B]^b} = K_{eq}$$

Because chelating ligands have larger values of K_{eq} than analogous monodentate ligands, there must also be a change in the relative rates of the forward (binding) and reverse (dissociation) reactions. In fact, there is a kinetic benefit that makes a metal bound to a polydentate ligand more inert than the analogous complex with monodentate ligands: this is called the ***kinetic chelate effect***.

The kinetic chelate effect is a result of a slower first dissociation step and faster re-association step relative to that of a monodentate ligand. The complete dissociation of a bidentate ligand, for example, would require two dissociation steps (see first reaction in figure below). It is the first dissociation step that is slower in a bidentate ligand ($k_1 < k_1'$ in the figure below). This first dissociation step is slower in part because the chelate would have to rotate to move the free ligand away from the open coordinate site on the metal ion. For the same reason, the reverse of this step (association) is faster than the association of a monodentate ligand ($k_{-1} > k_{-1}'$).

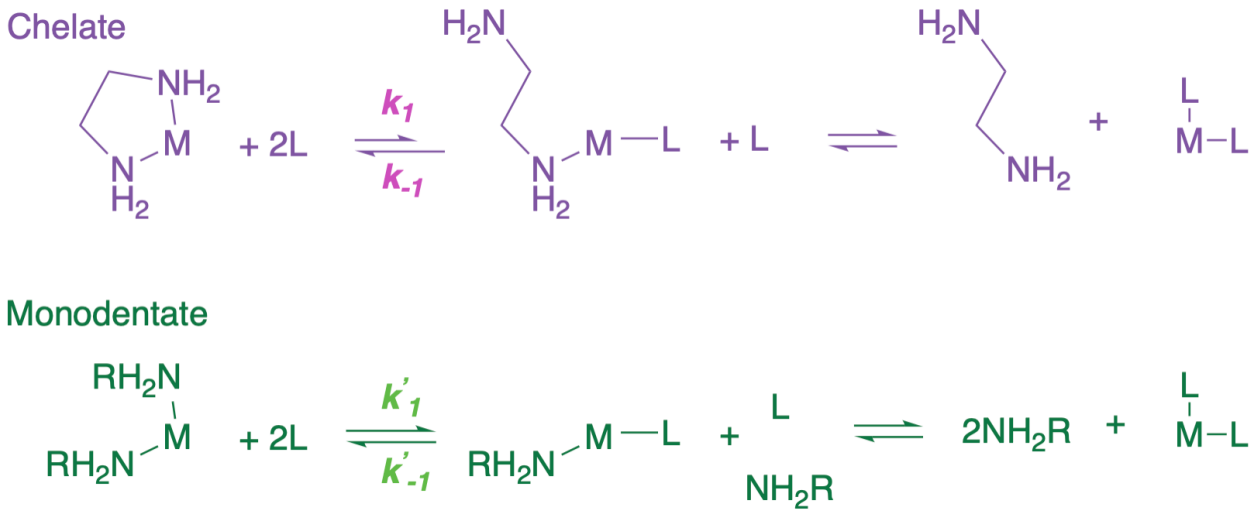


Figure 10.9.4.5.1: Step-wise dissociation of a bidentate ligand and analogous monodentate ligands. (CC-BY-SA; Kathryn Haas)

(1) Carter, M. J.; Beattie, J. K. Kinetic Chelate Effect. Chelation of Ethylenediamine on Platinum(II). Inorg. Chem.1970, 9 (5), 1233–1238. https://doi.org/10.1021/ic50087a044.

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10.9.5: Stereochemistry of Octahedral Reactions

The stereochemical outcomes of a reaction can depend on numerous factors. For simplicity, the discussion in this section will be limited to octahedral complexes that react through dissociative mechanisms, with emphasis on those that occur through the limiting case of a dissociative (D) mechanism. In light of this focus, the reactions of Co(III) complexes, particularly those with ethylenediamine ligands, provide appropriate examples of well-characterized systems.

In the purely dissociative case, the octahedral metal complex completely loses one ligand to become a five-coordinate intermediate. Therefore, the structure of the product depends primarily on the structure of the intermediate and its interaction with the entering ligand. The outcome of a D reaction should not be influenced by the identity of the leaving group. However, the identity of the entering group and the reaction conditions are appropriate considerations. For example, under basic aqueous conditions, the conjugate base mechanism can alter the stereochemical outcome compared to the same reaction under more acidic conditions.

Structure of the intermediate

When an octahedral metal complex reacts through a D mechanism, a six-coordinate metal complex forms a five-coordinate intermediate, which goes on to react with the entering group. The structure of that 5-coordinate intermediate has a major influence on the stereochemistry of the product. Recall from a previous section (Section 9.4) that 5-coordinate metal complexes can adopt either a **square pyramidal** or **trigonal bipyramidal geometry**. * In general, if the intermediate adopts a square pyramidal structure, the incoming ligand will enter at the same site where the leaving group was lost, and stereochemistry is retained from reactant to product. On the other hand, if the intermediate structure is a trigonal pyramid, at least some of the product will not retain the original configuration.

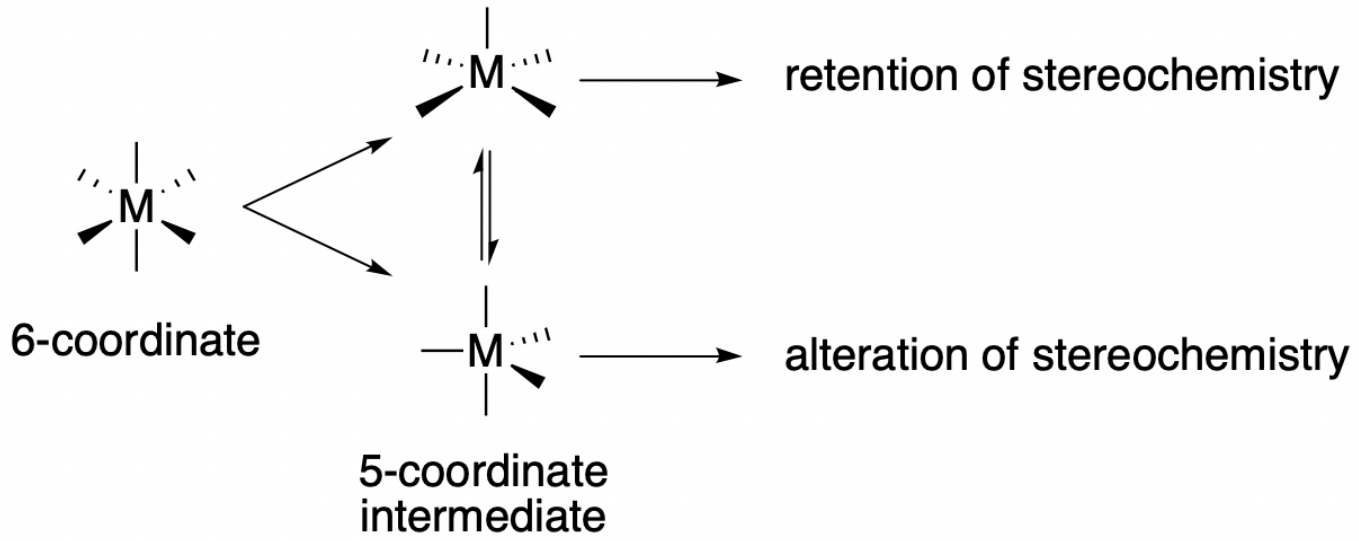


Figure 10.9.5.1: In the context of a substitution reaction, the loss of a ligand from an octahedral complex results in a five-coordinate intermediate. When the intermediate structure is a square pyramid, the new ligand enters so that the original sterochemistry is retained. The adoption of a trigonal bipyramid leads to changes in the stereochemistry of at least some of the product compared to the reactant. (CC-BY-SA; Kathryn Haas)

* Note: Recall from a previous section (Section 9.4) that square pyramid and trigonal bipyramid geometries typically have similar energies and readily interconvert through pseudorotation. However, during a D reaction, the intermediate exists for such a short moment in time, that interconversion is assumed not to occur unless there is an unusually long-lived intermediate.

Cis vs trans reactants

This section will present generalizations for the stereochemical consequences of substitution in *trans*-bisethylenediamine

(*trans*-en) and *cis*-bisethylenediamine (*cis*-en) octahedral Co(III) complexes. Cis-en complexes tend to retain a square pyramidal intermediate structure and retain the cis stereochemistry of the product, except when the conjugate base mechanism promotes isomerization. On the other hand, trans-en complexes are more likely to undergo stereochemical rearrangments through a trigonal pyramidal intermediate. However, especially in the case of trans-en complexes, the product ratios are a result of mixtures of intermediates.

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10.9.5.1: Substitution in trans-en octahedral complexes

The reaction of metal complexes of the form $[\mathrm{M(en)_2LX}]^{n+}$ have multiple possible pathways in terms of the structure of the intermediate.

When the X ligand departs from a trans complex, the most likely case is that the L ligand will remain in the axial position. In that case, there is one primary structure for the square pyramidal intermediate. Reaction of that intermediate with the incoming ligand, Y, will result in retention of trans stereochemistry.

An alternative possibility is that the intermediate adopts a trigonal bipyramidal structure. In that case, the outcome of the reaction depends on which of the possible trigonal bipyramidal structures exist and their relative amounts. There are two chemically distinguishable positions on the trigonal bipyramid; the axial and equatorial positions. The remaining L ligand can occupy either the axial position, which has a slightly longer bond, or the equatorial positions, which are slightly closer to the metal and more sterically hindered in space. To adopt either of the trigonal bipyramidal structures, rearrangement of the complex is necessary. It is more likely that the rearrangement will result in the trans ligand being in the equatorial position, since that requires less distortion of the original positions of each ligand (this is not obvious from the structures in Figure $10.9.5.1.1$). A trigonal structure with axial L requores one of the en ligand nitrogens to move by 90 degrees, while a structure with equitoral L requires only 30 degree movement from any ligand. As a result, the trigonal bipyramid with equitorial L (bottom of Figure $10.9.5.1.1$) is the dominant trigonal bipyramidal structure. That structure can produce three optical isomers from the three different angles of ligand Y entering along the equitorial plane. When Y enters trans to L, it produces the trans product. When Y enters cis to L, it produces either of the two cis optical isomers. The cis-$\Lamda$ and $cis-\Delta$ isomers are equally likely, and are produced as a racemic miture from an optically inactive starting trans reactant. The expected ratios of cis to trans are 2:1.

Regarding the trigonal bipyramidal intermediates, the identity of L influences its preference for the axial or equatorial positions. For example, π-donor ligands prefer equatorial positions due to the shorter bond lengths involved in π-donor interactions. Thus, when L is a strong π-donor, reaction products are more likely to come from the trigonal intermediate with an equatorial L. This last point is relevant to reactions where the conjugate base mechanisms is at play. The deprotonated ligand that results from the conjugate base mechanism is a stronger π-donor, and has preference for occupation of the equatorial positions of a trigonal bipyramidal intermediate. Even in cases where the square pyramid is typically preferred, the conjugate base mechanism can result in preference for a trigonal intermediate.

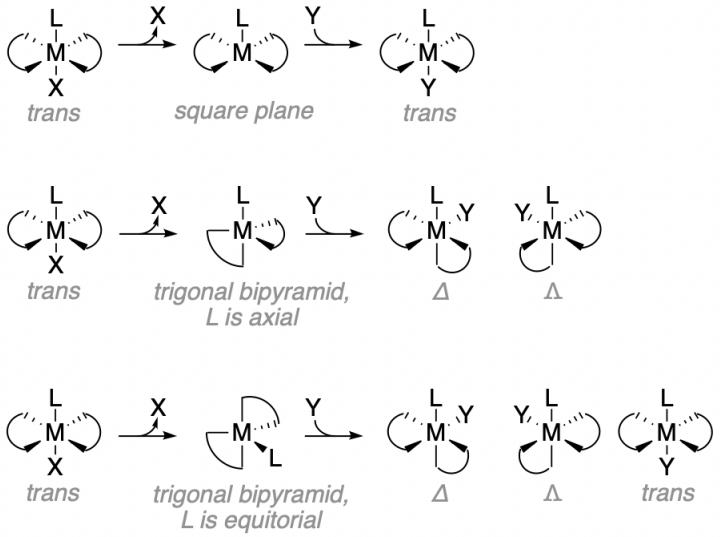


Figure $10.9.5.1.1$: Three different possibilities for the five-coordinate intermediate yield different possibilities for the stereochemistry of the product complex. The possibility of a square pyramid with basal ligand is not shown and is considered less likely than the three pathways shown because it would require a long-lived intermediate to allow time for the rearrangement of the square planar intermediate shown. (CC-BY-SA; Kathryn Haas)

The actual proportion of reaction products of a given stereochemistry depends on the extent to which each of the possible

intermediates leads to the products. However, the expected percentages of cis-trans from any single intermediate is rarely found in experimental data (See Table $10.9.5.1.1$).

Table $10.9.5.1.1$ gives the % of trans stereochemistry retained in the displacement of Cl^- by either H_2O or OH^-in a series of $trans-[Co(en)_2LCl]^+$ complexes where the identity of the *trans* ligand, L^-, is varied.

The reactions run under acidic conditions is shown below, and its data is shown in the middle column in Table $10.9.5.1.1$:

$$trans-[Co(en)_2LCl]^+ + H_2O <==> [Co(en)_2L(H_2O)]^{2+} + Cl^-$$

The reactions run under basic conditions is shown below, and its data is shown in the right column in Table $10.9.5.1.1$:

$$trans-[Co(en)_2LCl]^+ + OH^- <==> [Co(en)_2L(OH)]^+ + Cl^-$$

Table $10.9.5.1.1$: % trans product under different conditions

L^-	% trans product under acidic conditions (stereochemistry of reactant is retained)	% trans product under basic conditions (stereochemistry of reactant is retained)
OH^-	25	6
NCS^-	30-50	24
Br^-	50	100
Cl^-	65	95
$NH_3{}^-$	100	24
$NO_2{}^-$	100	94
Data from Miessler, G. L.; Fischer, P. J.; Tarr, D. A. *Inorganic Chemistry, 5th Ed.* Pearson: Boston, 2014, p. 459.		

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10.9.5.2: Substitution in cis-en octahedral complexes

The D substitution reactions of cis complexes occur through the same intermediate structures described above for trans complexes. For example, the reaction,

$$\text{cis-}[\text{M(en)}_2\text{LX}]^+ + \text{Y}^- \longrightarrow [\text{Co(en)}_2\text{LY}]^{2+} + \text{X}^-$$

can proceed through square planar or trigonal bipyramidal intermediates. Complete the exercise below.

Exercise 10.9.5.2.1

Follow the example of Figure 12.5.1.1 to sketch the possible reaction intermediates and products for $\text{cis-}[\text{M(en)}_2\text{LX}]^+ + \text{Y}^-$. Which intermediates are most likely? In the case of each trigonal bipyramid, what would be the ratios of products if ligand attack from the three angles along the trigonal plane are equally likely?

Answer available at the end of this section.

Table 10.9.5.2.1 gives the % of cis stereochemistry in the displacement of Cl^- by either H_2O or OH^- in a series of $\text{cis}-[\text{Co(en)}_2\text{LCl}]^+$ complexes where the identity of the *trans* ligand, L^-, is varied.

The reactions run under acidic conditions is shown below, and its data is shown in the middle column in Table 10.9.5.2.1 :

$$\pm\text{cis}-[\text{Co(en)}_2\text{LCl}]^+ + \text{H}_2\text{O} <==> [\text{Co(en)}_2\text{L(H}_2\text{O)}]^{2+} + \text{Cl}^-$$

The reactions run under basic conditions is shown below, and its data is shown in the right column in Table 10.9.5.2.1. Note that in all but one case, the reactions run under basic conditions were done so using optically pure starting material, and gave an optically active product.

$$\Delta-\text{cis}-[\text{Co(en)}_2\text{LCl}]^+ + \text{OH}^- <==> [\text{Co(en)}_2\text{L(OH)}]^+ + \text{Cl}^-$$

Table 10.9.5.2.1: % cis product under different conditions

L^-	% cis product under acidic conditions from racemic cis reactant (stereochemistry of reactant is retained)	% cis and trans product under basic conditions from $\Delta - cis$ starting material (stereochemistry of reactant is retained)
OH^-	100	61% $\Delta - cis$ | 36% $\Lambda - cis$ | 3% trans
NCS^-	100	56% $\Delta - cis$ | 24% $\Lambda - cis$ | 20% trans
Br^-	100	-
Cl^-	100	21% $\Delta - cis$ | 16% $\Lambda - cis$ | 63% trans
$\text{NH}_3{}^-$	-	60% $\Delta - cis$ | 24% $\Lambda - cis$ | 16% trans
$\text{NO}_2{}^-$	100	46% $\Delta - cis$ | 20% $\Lambda - cis$ | 34% trans
Data from Miessler, G. L.; Fischer, P. J.; Tarr, D. A. *Inorganic Chemistry, 5th Ed.* Pearson: Boston, 2014, p. 459.		

Under acidic conditions, and when the conjugate base mechanism is unlikely, the product specifically retains the stereochemistry of the starting material. This data (middle column above) indicates that the D reaction of the cis isomer, in contrast to trans, reacts exclusively through the square pyramidal intermediate under acidic conditions. This is because in every case, the ligand trans to the X leaving group is an amine from the en ligand, which is not a π donor. The ligand cis to the leaving group (L) has no influence on the reaction outcome under acidic conditions.

Under basic conditions, where the conjugate base mechanism is possible, cis stereochemistry is not entirely retained, and the cis products are produced in approximately a 2:1 ration of $Delta : \Lambda$ from a $Delta$ reactant.

Exercise 10.9.5.2.1

Consider the data in the right colum of Table 10.9.5.2.1. What does the presence of trans product and a 2:1 ratio of the two cis isomers indicate about the intermediates of reaction under basic conditions?

Answer available at the end of this section.

Answers

Exercise 10.9.5.2.1

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Exercise 10.9.5.2.1

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10.9.5.3: Isomerization of Chelate Rings

Recall that the stereoisomers of octahedral complexes with two and three bidentate ligands were discussed previously (Section 9.3). This page will discuss the interconversion of stereoisomers, which can occur through two primary mechanisms involving either (1) bond breaking and bond making steps, and (2) twisting.

Isomerization through dissociative substitution

One way to convert one steroisomer to another is through bond breaking and bond re-making steps. This type of structural rearrangement is essentially a substitution reaction, as described previously in this chapter, except that the leaving group and entering group are the same ligand. Evidence for this type of mechanism comes from the study of isotopically labeled amibidentate ligands (those that have different modes of coordination). For example, an acetyl group with a labeled CD_3 can be added as an "outside" group (adjacent to the coordinating groups) in a tris(acac)cobalt(III) complex. The labeled group moves to the "inside" (directly coordinated to the metal ion) during isomerization from an optically pure solution to a racemic mixture. This change can only occur through bond breaking and re-forming steps.

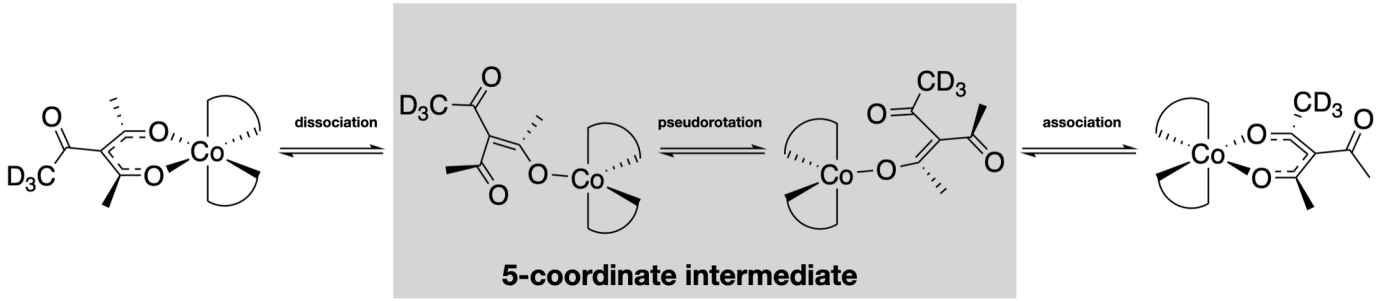


Figure 10.9.5.3.1: The rearangement of a CD_3 group from an "outer acetyl" to one directly coordinating to the metal complex of an CD_3-labeled acetyl group on acetylacetone (acac) provides evidence of isomerization through a mechanism related to dissociative substitution. (CC-BY-SA; Kathryn Haas)

Isomerism through twisting

The second pathway of isomerism is through twisting; it does not involve bond breaking or bond forming. Twisting that causes interconversion of octahedral isomers was also discussed in Chapter 9. A figure from that chapter is re-posted here for convenience.

An octahedroal coordination sphere is just a trigonal antiprism in which all edge lengths are identical. Rotation of one triangular face relative to its opposite until the two are eclipsed gives a triganal prismatic geometry. In fact, since continuation of this rotation gives another octahedral complex the trigonal prismatic geometry is an intermediate in isomerization reactions involving octahedral complexes. In tris- and bis-chelates such isomerizations are said to occur by a **Bailar twist** or a **Ray-Dutt twist**, which differ only in the relationship between the chelate rings and the faces twisted.

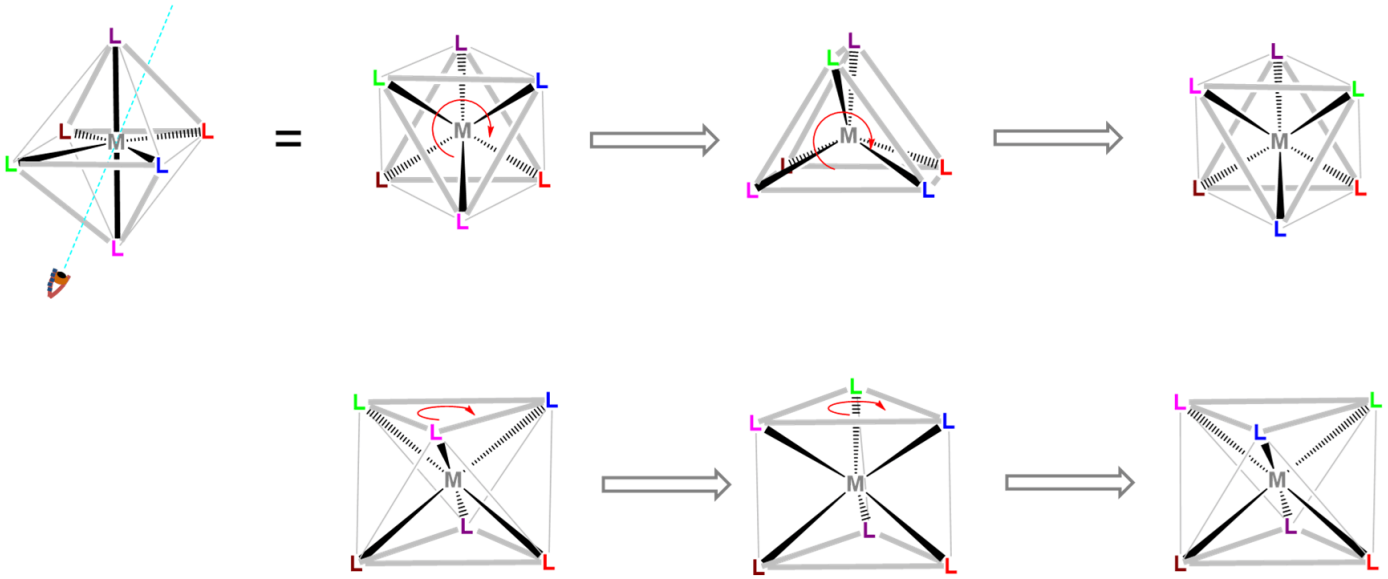


Figure 10.9.5.3.2. Since an octahedron is a trigonal antiprism a trigonal prism may be produced by rotating or "twisting" one face of the octahedron relative to its opposite. Since continuation of the rotation gives an isomer of the original octahedron, when the energy landscape for twists like these is thermally or photochemically accessible twists like these provide one pathway for isomerisation reactions involving octahedral complexes. In tris- and bis-chelates such isomerizations are said to occur by Bailar and Ray-Dutt twists, which differ only in the relationship between the chelate rings and the faces twisted. Top: View down looking down an axis bisecting a pair of opposing faces. Bottom: View perpendicular to that shown at top. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

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10.9.6: Substitutions in Square Planar Complexes

Substitutions in square planar complexes tend to occur through mechanisms with associative character, although the degree of associative character may vary (eg $A,\ I_a,\ I_d$. The outcome of square planar substitutions depend on the identities of the leaving group, the ligand trans to the leaving group, and the entering group. The reactions of Pt(II) are well studied and will serve as the primary examples in this section. Pt(II) complexes are of particular interest because of their role as effective chemotherapeutics in the treatment of several types of solid tumor cancers.

The generic chemical equation for substitution in a square planar complex is shown below, where X is the leaving group, Y is the entering group, and $[\mathrm{ML_3X}]$ is the reactant complex:

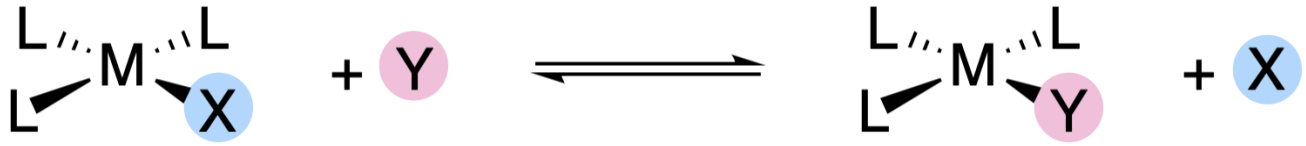


Figure 10.9.6.1: Generic form of square planar metal complex undergoing a substitution reaction. (CC-BY-SA; Kathryn Haas)

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10.9.6.1: Kinetics and Stereochemistry of Square Planar Reactions

Kinetics

In general, the reaction kinetics of square-planar associative substitution takes the form of the following rate law, which has two terms:

$$\frac{d[\mathrm{ML_3Y}]}{dT} = k_1[\mathrm{ML_3X}] + k_2[\mathrm{ML_3X}][\mathrm{Y}]$$

Each of the terms corresponds to one of the two possible reaction pathways. The term, $k_2[\mathrm{ML_3X}][\mathrm{Y}]$, is second-order, and corresponds to a simple associative pathway. The $k_1[\mathrm{ML_3X}]$ term is first-order, although it also corresponds to an associative pathway. The reason it appears to be first order is because square planar complexes can react through a solvent-assisted pathway where bulk solvent replaces the leaving group, and then is replaced by the entering group (Figure $10.9.6.1.2$). Because solvent concentration does not appreciably change as the reaction proceeds, it is not part of the rate law term even though it is involved in the rate-determining association. The step in which solvent is substituted by the entering group must happen faster than the solvent-assisted replacement of X.

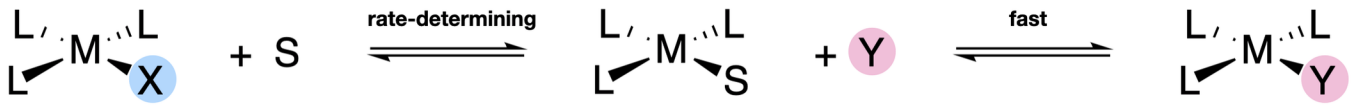


Figure $10.9.6.1.2$: Solvent-assisted substitution pathway where X is the leaving group, Y is the entering group, and S is solvent. (CC-BY-SA; Kathryn Haas)

The kinetic rate constats in square planar substitution can depend on the identities of the leaving group, the ligand trans to the leaving group, and the entering group. The ligands that are in the cis positions with respect to the leaving group do not have a significant affect on the rate, and these are referred to as spectator ligands.

Stereochemistry

Square planar complexes react to give products in which the stereochemistry of the reactant is retained. In other words, a *trans*-reactant will give a *trans*-product, and a *cis*-reactant will give a *cis*-product (Figure $10.9.6.1.3$). The identity of the trans ligand has particular importance in the outcome of square planar substitutions (discussed further in the next sections). We will designate the trans ligand generally with the symbol T to indicate its position (Figure $10.9.6.1.3$), the leaving group as X, and the entering group as Y. The spectator ligands (ligands that are cis to X) will be desginated L and L'. For the discussion that follows, the plane of the metal complex will be designated as the xy plane, while the z axis is perpendicular to the plane (Figure $10.9.6.1.3$). The x and y axes will run colinear to the bond axes, with the x axis running colinear to the T-M-X bonds (Figure $10.9.6.1.3$).

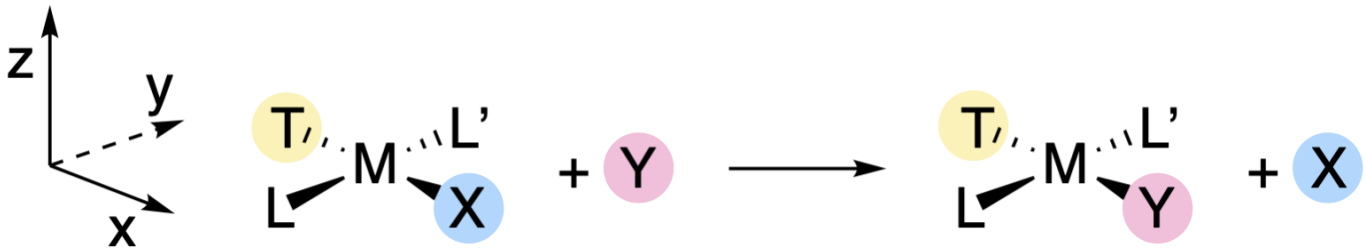


Figure $10.9.6.1.3$: Stereochemistry is strictly retained in the reactions of square planar complexes. By convention, the plane of the metal complex is the xy plane, with the x axis colinear with the T-M-X bonds. M = metal ion | X = leaving group ligand | Y = entering group ligand | T = ligand trans to the leaving/entering group. (CC-BY-SA; Kathryn Haas)

The retention of stereochemistry, and the fact that X, Y, and T can influence the rate of reaction provide hints at the nature of intermediates and/or transition states involved in these reactions. The existence of five-coordinate square pyramidal structures, like those of $[\mathrm{Ni(CN)_5}]^{3-}$ and $[\mathrm{Pt(SnCl_3)_5}]^{3-}$, suggests that five-coordinate intermediates are possible. However the substitutions of square planar complexes are generally classified as associative interchange mechanisms (I_a) because isolation of a true intermediate is rarely accomplished. In any case, the retention of stereochemistry is explained by a five-coordinate trigonal bipyramidal transition state in which X, Y, and T are each in the trigonal plane (along with the metal center). As the M-X bond is breaking, the M-Y bond is forming and Y replaces X in the position trans to T. Because T, Y and X are in the trigonal plane in the transition state, all three ligands are able to interact with the same d orbitals of the central metal ion. Thus the identities of X, Y, and T should influence the ability of the M-X bond to break and the M-Y bond to form. On the other hand, L and L' are in a perpendicular plane, and would interact with different orbitals than X and Y. This explains why spectator ligands L and L' have little effect on the reaction rate, as they are interacting with different orbitals than those involved in bond breaking and bond making.

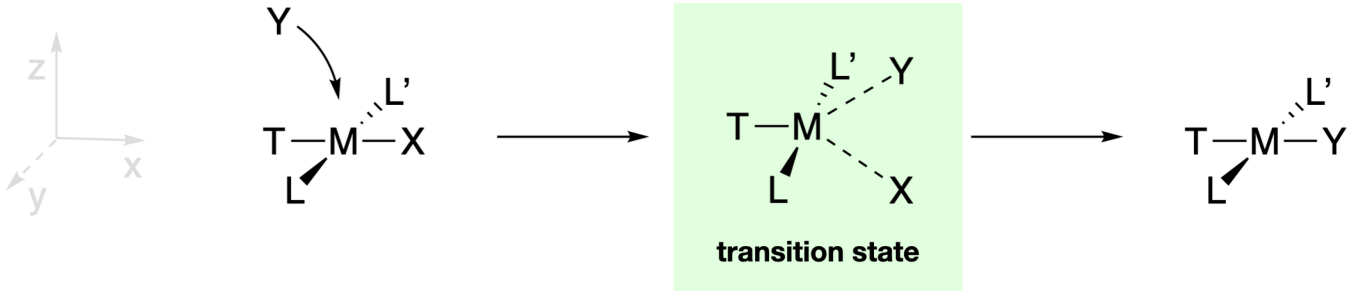


Figure $10.9.6.1.4$: Mechanism for simple I_a substitution. The structure of the transition state is trigonal bipyramidal, with T, X, and Y in the trigonal plane with M. The spectator ligands, L and L', are in a perpendicular plane and are coplanar with T and M. (CC-BY-SA; Kathryn Haas)

The solvent-assisted pathway can occur through similar transition states and mechanistic steps, except that there are additional steps involving solvent association and displacement.

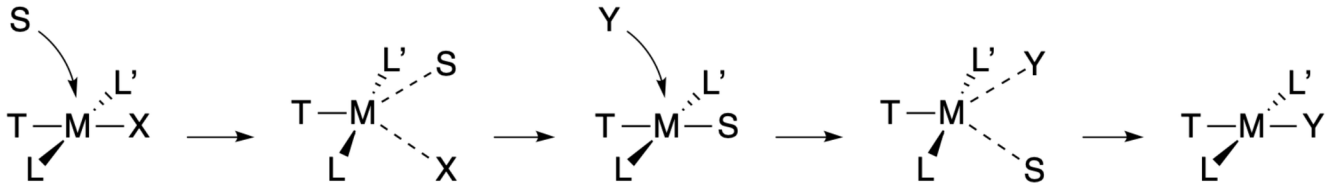


Figure $10.9.6.1.5$: Solvent-assisted I_a substitution. Compare to Figure $10.9.6.1.4$. S is solvent. (CC-BY-SA; Kathryn Haas)

Although there is general consensus that square planar complexes react through associative pathways, the characterization of intermediates and/or transition states has remained elusive, and there is still debate as to the intricate details of the reaction mechanisms involving square planar complexes. For example, there are arguments that a six-coordinate transition state may exist in the solvent-assistant pathway.

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10.9.6.2: Evidence for Associative Reactions

The reactions of Pt(II) complexes have been thoroughly investigated, and there are several lines of experimental evidence that have lead to the general conclusion that square planar complexes react through associative mechanisms. The experimental evidence is presented here.

The entering group

In the reaction of $\mathrm{trans{-}[PtL_2Cl_2]}$, the rate of reaction depends on the identity of the incoming ligand Y.

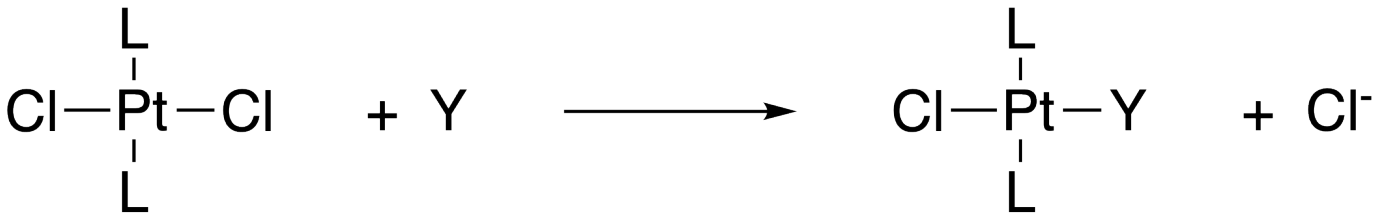


Figure 10.9.6.2.1: Substitution reaction of $\mathrm{trans{-}[PtL_2Cl_2]}$. (CC-BY-SA; KAthryn Haas)

For example, the rate of the reaction shown above depends heavily on the ligand, Y, as follows:

$$\text{most kinetically labile } \mathrm{PR_3} > \mathrm{CN^-} > \mathrm{SCN^-} > \mathrm{I^-} > \mathrm{Br^-} > \mathrm{N_3{}^-} > \mathrm{NO_2{}^-} > \mathrm{py} > \mathrm{NH_3} \quad \mathrm{Cl^-} > \mathrm{CH_3OH} \text{ most kinetically inert}$$

In general, ligands that would form the strongest bonds with Pt(II) due to their soft character or π-binding ability react fastest. The rate constants in the above series range by nearly ten orders of magnitude. This huge range of rate constants as a factor of Y demonstrates suggests that M-Y bond formation is part of the rate limiting step. This is evidence for rate-determining association A or I_a.

The leaving group

Since the leaving group occupies a similar position in the transition state as the entering group, we should expect the leaving group to have a similar effect on the rate constants as was found for Y. In fact, this is true. For the reaction of $\mathrm{[Pt(diene)X]^+}$ with pyridine, the follow trend was observed by varying the leaving group, X:

$$\text{most kinetically labile } \mathrm{NO_3{}^-} > \mathrm{Cl^-} > \mathrm{Br^-} > \mathrm{I^-} > \mathrm{N_3{}^-} > \mathrm{SCN^-} > \mathrm{NO_2{}^-} > \mathrm{CN^-} \text{ most kinetically inert}$$

The rate of reaction follows an order that is nearly opposite as that observed for Y: The softer the ligand, the slower the dissociation. The rate constants in this series span a range of approximately five orders of magnitude, illustrating that breaking of the M-X bond is part of the rate-determining step. This is evidence for a mechanism involving associative interchange character (I_a or I_d. The importance of the leaving group somewhat depends on the identity of the entering group, and vice-versus.

The trans ligand

The trans ligand also occupies a similar position to X and Y in the transition state. So, as you might expect, it too has influence on the rate of reaction. In general, the rate of substitution of X in Pt(II) complexes general follows the order given below when T is varied as:

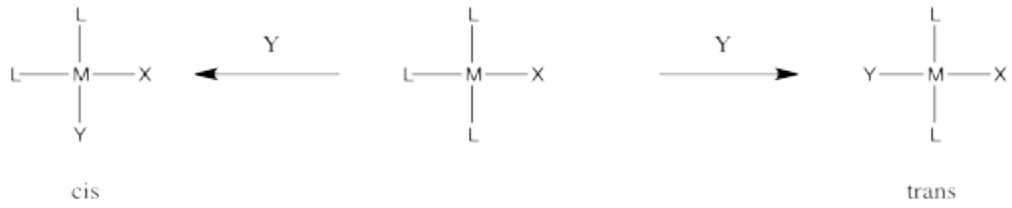
$$\text{M-X most kinetically labile } \mathrm{CN^-} \quad \mathrm{CO} \quad \mathrm{C_2H_4} > \mathrm{PH_3} \quad \mathrm{SH_2} > \mathrm{NO_2{}^-} > \mathrm{I^-} > \mathrm{Br^-} > \mathrm{py} \quad \mathrm{NH_3} > \mathrm{OH^-} > \mathrm{H_2O} \text{ M-X most kinetically i}$$

The effect of the trans ligand deserves a more through discussion, and will be addressed in the next section. It is mentioned here because it is evidence for the trigonal bipyramidal intermediate that was described earlier for associative substitution in square planar metal complexes.

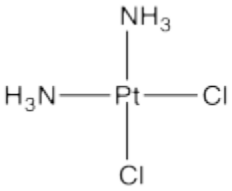
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10.9.7: The Trans Effect

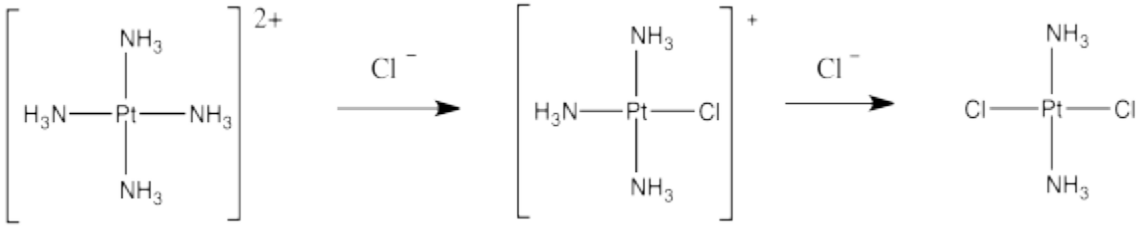
Occasionally in ligand substitution there is a situation in which there are two identical ligands that could be replaced, but two different products would result depending on which ligand left. This situation often happens in square planar complexes, for example. Replacement of one ligand would lead to a *cis* product. Replacement of the other one would lead to a *trans* product.



An important example of this issue is in the synthesis of cis-platin, an antitumour medication frequently used to treat ovarian and testicular cancer.

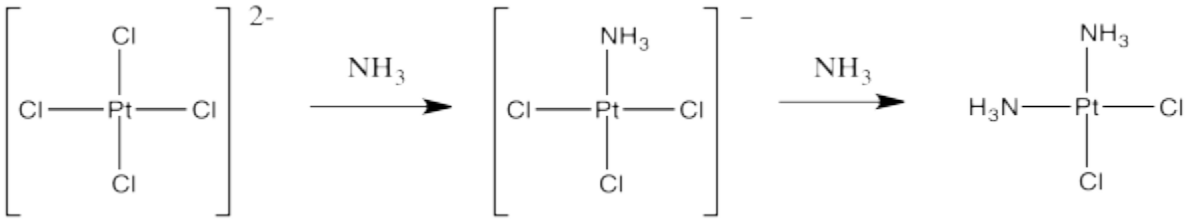


Cis-platin could be made from treatment of tetraammineplatinum(II) with chloride salts. The chloride ion could replace two of the ammonia ligands.



But that doesn't work. That synthesis results in the formation of *trans*-platin, a compound that has all of the nasty side effects of the *cis* isomer but with none of the therapeautic benefit.

If instead you were to start with tetrachloroplatinate salts and treat them with ammonia, you could replace two of the chloride ligands. That works really well, and it provides *cis*-platin, not *trans*-platin.



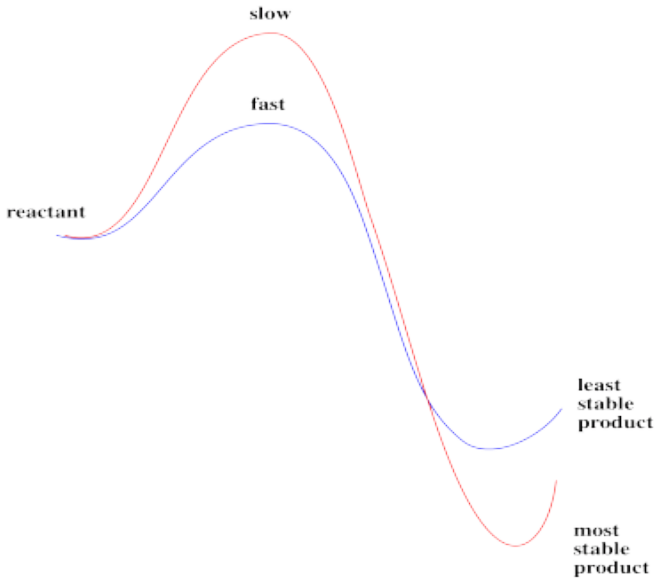
Exercise 10.9.7.1

What do you think is the mechanism of substitution of the two reactions above? Why?

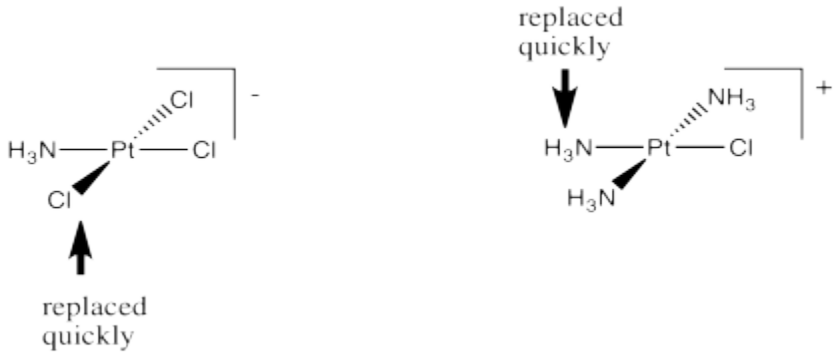
Answer available at the end of this section.

This reaction, if run under these conditions, is clearly not always under thermodynamic control. Two different products result, depending on how the reaction is done. One of those isomers is probably more stable than the other; if thermodynamics were in charge, it would form the same thing both times.

Instead, there may be an element of kinetic control for at least one of the pathways. A given product might be made, not because it is more stable, but simply because it forms more quickly than the other one.



Take another look at those two reactions. One of the things that they have in common is that the ligand that gets replaced is *trans* to a chloride. It is not *trans* to an ammonia. Maybe the other ligands in the complex can influence how quickly one ligand can leave.



Specifically, the "*trans* effect" is the role of *trans*-ligands in influencing substitution rates in square planar complexes.

The following kinetic data were obtained for substitutions on square planar platinum complexes, in the reaction:

$$trans-(PEt_3)_2PtLCl + py \rightarrow trans-(PEt_3)_2PtLpy^+ + Cl^-$$

L	k_{obs} (s^{-1})	T, °C
PMe_3	0.20	0
H^-	0.047	0
PEt_3	0.041	0
CH_3^-	6.0 x 10^{-4}	25

$C_6H_5^-$	1.2×10^{-4}	25
Cl^-	3.5×10^{-6}	25

Ref: Cooper Langford & Harry Gray, *Ligand Substitution Processes*, W.A. Benjamin, NY, 1965, p. 25.

Exercise 10.9.7.2

Draw structures for each of the complexes listed in the table.

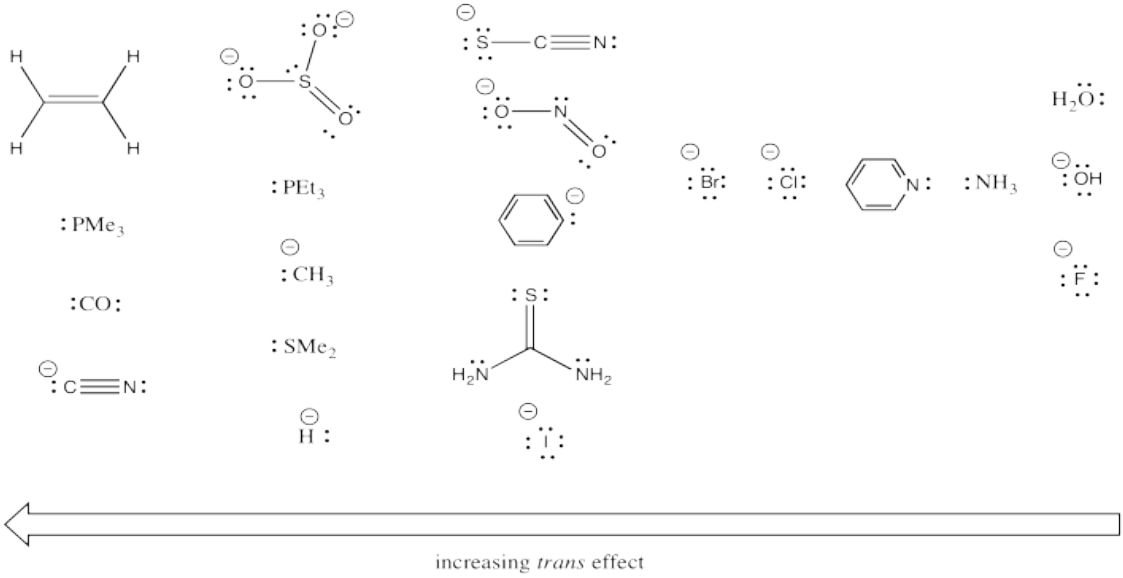
Answer available at the end of this section.

Exercise 10.9.7.3

Provide a mechanism with arrows for the reaction studied in the table.

Answer available at the end of this section.

Clearly that *trans* ligand has a dramatic effect on how quickly the chloride can be substituted in the above study. Additional studies like this one have led to some general trends. Below, the ligands on the left have strong *trans*-effects. Ligands *trans* to them are substituted very quickly. The ligands on the right have very modest *trans* effects. Ligands *trans* to them are substituted only slowly.



Exercise 10.9.7.4

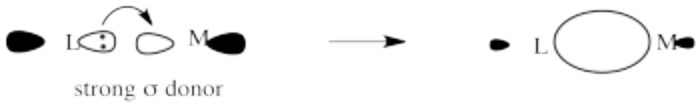
Look for empirical trends in the series of ligands above. Without trying to explain exactly why, find chemically relevant factors that may be responsible for these reactivity trends.

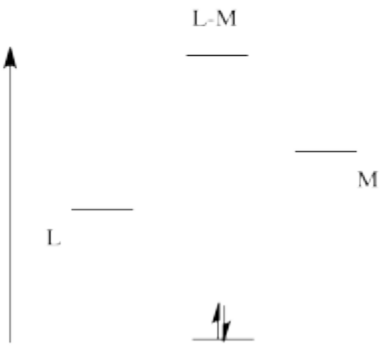
Answer available at the end of this section.

In general, explanations of the trans effect have focused on two separate types of ligands. These are strong sigma donors and strong pi acceptors.

Strong sigma donors donate electrons very effectively to the metal via a sigma bond. Because the ligand trans to this donor would

be bonding via donation to the same metal p orbital, there is a competition. The metal p orbital bonds more favorably with the strong sigma donor, and the ligand trans to it is left with a weaker bond.

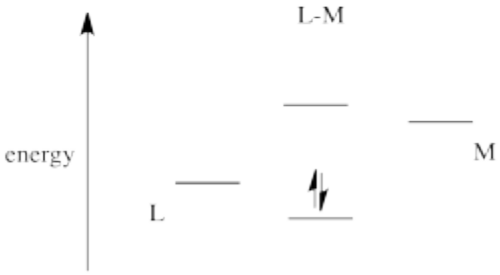




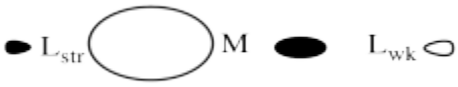
The strong sigma donor gets good overlap with the metal orbital and the resulting interaction goes down low in energy.

The weak sigma donor gets poorer overlap with the metal orbital and only weak stabilization of the donor electrons.





Place these two choices together, and the metal orbital will engage in a strong bonding interaction with the strong σ-donor. Doing so lowers the electronic energy significantly. It won't interact very much with the weak σ-donor, because doing that won't result in as much lowering of electronic energy. The result is a strong bond on one side of the metal and a weak bond on the other. That weak bond will break easily and that ligand will be replaced easily.

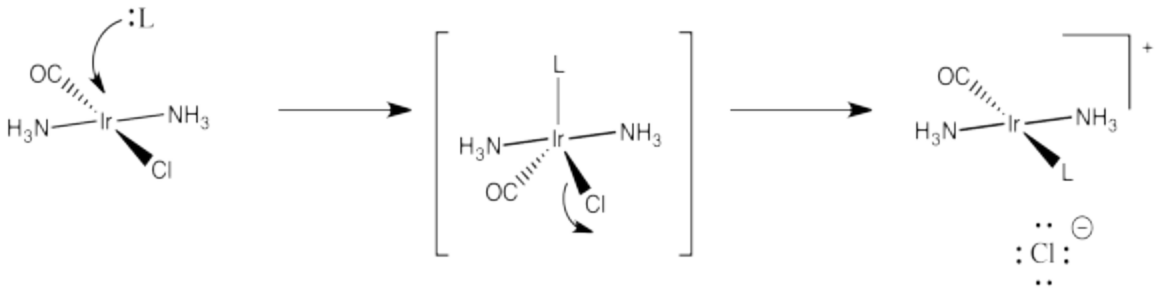


Exercise 10.9.7.5

Which of the ligands in the *trans* effect series are probably strong σ-donors? Why?

Answer available at the end of this section.

Strong pi acceptors exert their trans effect in a different way. They are thought to stabilize a particular geometry of the five-coordinate intermediate in substitution of square planar complexes. We haven't worried too much about the geometry of that intermediate, but it is probably trigonal bipyramidal. It would have three ligands in an equatorial plane and two more directly opposite each other, in the axial positions.



Essentially, the incoming ligand pushes two of the ligands down from the square plane to form this trigonal bipyramid. When it comes time for a ligand to leave, it is probably going to be one of these ligands that is already on the move. They are already on a trajectory out of the square plane, anyway.

A strong pi acceptor like CO exerts its *trans* effect by making sure it, along with the ligand opposite it, gets into that equatorial plane. It does that by a stabilizing delocalization that happens when the π-acceptor is in the electron-rich equatorial plane. In that position, it can draw electron density via π-donation from two different donors. If it were in an axial position, it could still delocalize electrons this way, but it would draw most effectively from just one donor rather than two.



favoured

So which of those two ligands is going to keep moving and leave the complex? It certainly won't be the one that is exerting a stabilizing, delocalizing effect on the complex via its strong bonding interactions. It will be the unlucky *trans* ligand that got dragged along with it.

Exercise 10.9.7.6

Which of the ligands in the *trans*-effect series are probably strong π-acceptors? Show why.

Exercise 10.9.7.7

Draw an orbital picture showing the -delocalization described in the trigonal bipyramidal intermediate. Label the orbitals, assuming the z axis is along the axis of the trigonal bipyramid (i.e. the equatorial plane is the xy plane).

Answer available at the end of this section.

Exercise 10.9.7.8

Substitution of trans ligands in μ-oxo-bis(μ-acetato)diruthenium complexes: Synthesis and kinetic studies. Hussain, Bhatt, Kumar, Thorat, Padhiyar and Shukla, *Inorganica Chemica Acta*, **2009**, *362*, 1101-1108.

Given the structure $[Ru_2O(L)_6(acetate)_2](PF_6)_2$, in which L is a neutral donor,

a) Draw the structure of the counterion, PF_6^-.

b) Provide an account of the valence electron count in the ruthenium coordination complex.

Valence electrons on metal	
Total charge on ligands	
Charge on the metal	
Revised count on metal	
Electrons donated by ligands	
Total electrons on metal in complex	

Data shows that the ligands L are *trans* to the bridging oxo ligand are labile.

c) Use orbital cartoons and words to provide an explanation for this effect.

When water is added to an acetone solution of $[Ru_2O(pyridine)_4(L)_2(acetate)_2](PF_6)_2$, then $[Ru_2O(pyridine)_4(H_2O)_2(acetate)_2](PF_6)_2$ is formed.

d) Draw the product of this reaction.

When pyridine is added to $[Ru_2O(pyridine)_4(H_2O)_2(acetate)_2](PF_6)_2$, then $[Ru_2O(pyridine)_6(acetate)_2](PF_6)_2$ is formed. The following rate constants were observed for this reaction.

[pyridine] mol L^{-1}	k_{obs} s^{-1} (x 10^{-3})
0.005	1.75
0.012	2.53
0.025	9.7
0.049	16.7
0.100	35.2

e) Use the data from this table to determine the order in pyridine. Provide an explanation for your conclusion.

f) Draw a mechanism for the reaction, consistent with the data.

g) Write a rate law for the reaction.

h) The authors studies the same reaction with different ligands instead of pyridine. They observed an increase in rate constants with increasing basicity of the incoming ligands. Provide an explanation for this observation.

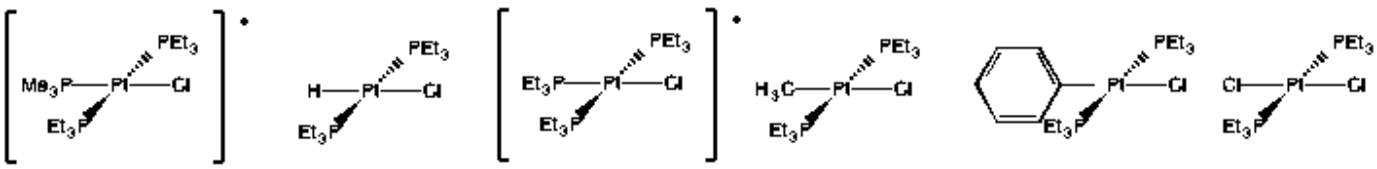
Answer a available at the end of this section.

Answers

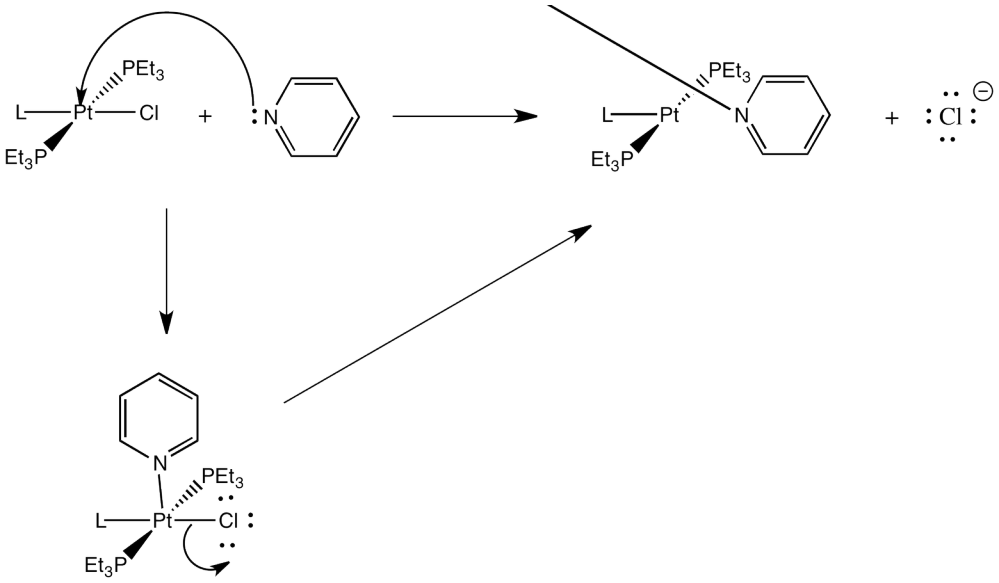
Exercise 10.9.7.1

This is probably an associative mechanism because of the square planar geometry.

Exercise 10.9.7.2



Exercise 10.9.7.3



Exercise 10.9.7.4

There is an electronegativity trend: the less electronegative, the greater the *trans* effect (see the halogens, as well as the series O,N,C and also the orders within several pairings: S,P; O,S and N,P).

Alternatively, some of the above could be described by a polarizability trend: more polarizable atom, greater *trans* effect (for example, the halogens).

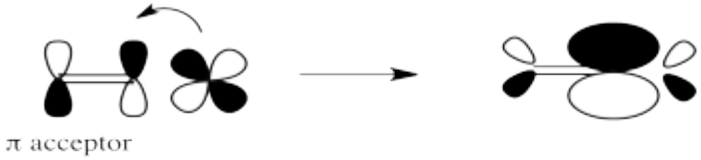
Most of the ligands containing π-bonds have strong *trans* influence (but not all).

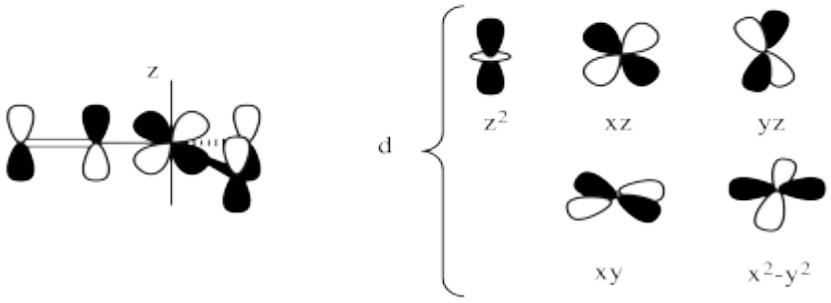
Most of the π-donors have a weaker *trans* influence. However, these ligand cover a very broad range in this series.

Exercise 10.9.7.5

The strongest σ-donors are typically those with more polarizable donor atoms (such as S, P, I) as well as those with less electronegative donor ions such as C^- and H^-.

Exercise 10.9.7.7





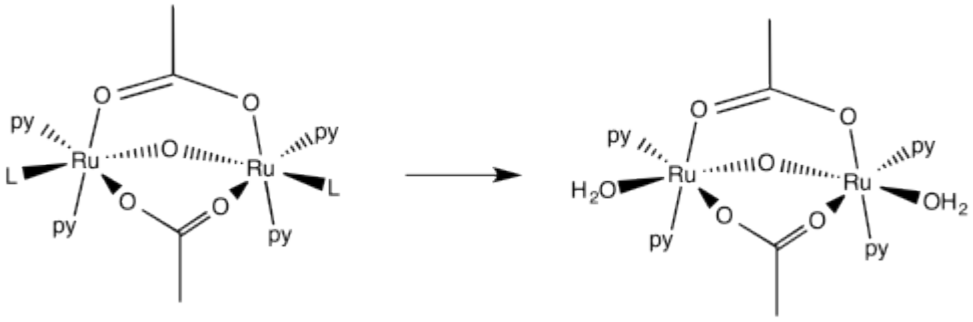
Exercise 10.9.7.8



5 valence electrons - 6 bonds - 0 nonbonding = -1

Valence electrons on metal	8
Total charge on ligands	-4 (-2 per Ru)
Charge on the metal	+2
Revised count on metal	6
Electrons donated by ligands	12
Total electrons on metal in complex	18

The oxo is a strong sigma donor and hogs the orbital with the metal thus leaving very little room for orbital bonding trans to the sigma donor.



First order. Although there is some amount of error in the data, doubling the pyridine concentration generally results in a doubling of the rate.
The mechanism you draw would have to involve a first associative step; because the complex is already 18 electrons, associative interchange is likely.

$$Rate = k[ML_n][py]$$

Basic ligands have stronger attraction to the metal thus accelerating the reaction.

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10.9.8: Redox Mechanisms

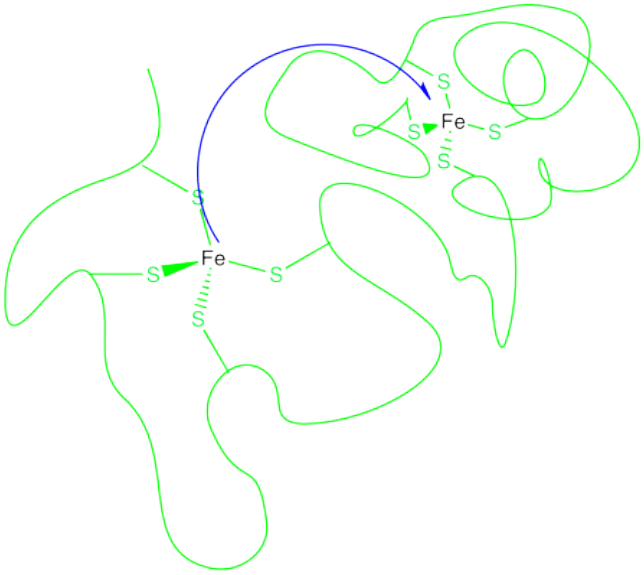
The oxidation state of a metal ion can be changed by **red**uction/**ox**idation (redox) reactions in which electrons are transferred between a metal center and another species. The other species could be another metal ion or some other redox partner. In the case of metal complexes, the electron transfer often occurs at the metal center, changing the oxidation state of the metal ion(s) involved. This section will focus on the redox reactions involving change in metal ion oxidation state.

There are two general mechanisms by which electrons can be transferred to or from a metal center. The definition of these two mechanisms depends on whether the redox partner is bound within the metal ion's inner sphere (bound directly to the metal ion), or whether it is just nearby the metal complex (in the metal ion's outer sphere). If the redox partner is bound to the metal ion itself, it is called an **inner-sphere electron transfer**. Electrons can also be transferred between two species that are close in proximity, but not bound to one another. When electrons are transferred to or from a metal through close proximity, but not through direct bonds to the metal center, it is an **outer-sphere electron transfer**.

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10.9.8.1: Outer Sphere Electron Transfer

How does an electron get from one metal to another? This might be a more difficult task than it seems. In biochemistry, an electron may need to be transfered a considerable distance. Often, when the transfer occurs between two metals, the metal ions may be constrained in particular binding sites within a protein, or even in two different proteins.



That means the electron must travel through space to reach its destination. Its ability to do so is generally limited to just a few Angstroms (remember, an Angstrom is roughly the distance of a bond). Still, it can react with something a few bond lengths away. Most things need to actually bump into a partner before they can react with it.

This long distance hop is called an outer sphere electron transfer. The two metals react without ever contacting each other, without getting into each others' coordination spheres. Of course, there are limitations to the distance involved, and the further away the metals, the less likely the reaction. But an outer sphere electron transfer seems a little magical.

Barrier to Reaction: A Qualitative Picture of Marcus Theory

So, what holds the electron back? What is the barrier to the reaction? Rudy Marcus at Caltech has developed a mathematical approach to understanding the kinetics of electron transfer, in work he did beginning in the late 1950's. We will take a very qualitative look at some of the ideas in what is referred to as "Marcus Theory". An electron is small and very fast. All those big, heavy atoms involved in the picture are lumbering and slow. The barrier to the reaction has little to do with the electron's ability to whiz around, although even that is limited by distance. Instead, it has everything to do with all of those things that are barely moving compared to the electron.

Imagine an iron(II) ion is passing an electron to an iron(III) ion. After the electron transfer, they have switched identities; the first has become an iron(III) and the second has become an iron(II) ion.

Nothing could be simpler. The trouble is, there are big differences between an iron(II) ion and an iron(III) ion. For example, in a coordination complex, they have very different bond distances. Why is that a problem? Because when the electron hops, the two iron atoms find themselves in sub-optimal coordination environments.

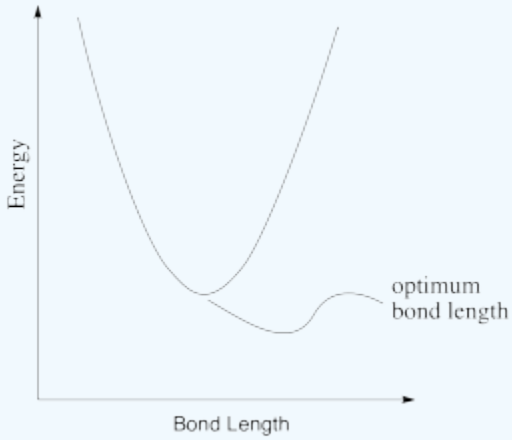
Exercise 10.9.8.1.1

Suppose an electron is transferred from an Fe(II) to a Cu(II) ion. Describe how the bond lengths might change in each case, and why. Don't worry about what the specific ligands are.

Answer available at the end of this section.

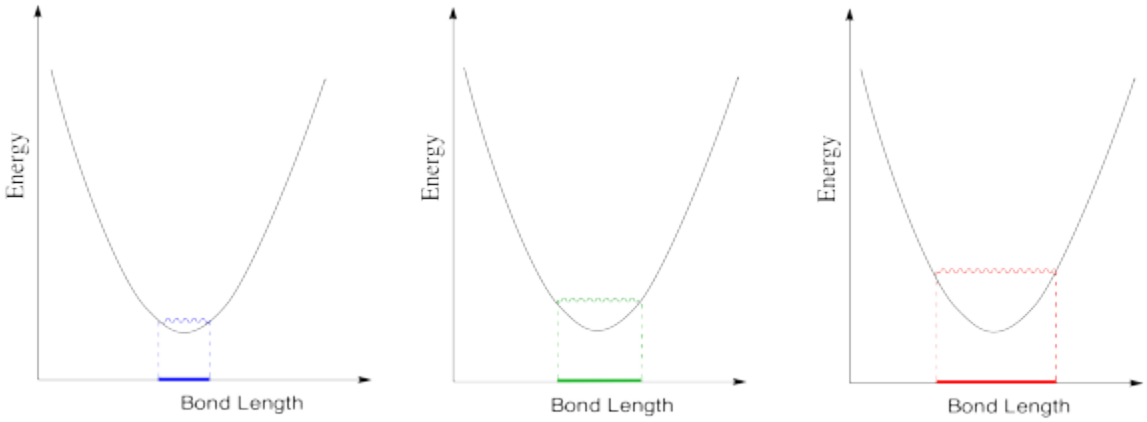
Exercise 10.9.8.1.2

In reality, a bond length is not static. If there is a little energy around, the bond can lengthen and shorten a little bit, or vibrate. A typical graph of molecular energy vs. bond length is shown below.



a. Why do you think energy increases when the bond gets shorter than optimal?
b. Why do you think energy increases when the bond gets longer than optimal?
c. In the following drawings, energy is being added as we go from left to right. Describe what is happening to the bond length as available energy increases.

Answer a available at the end of this section.



Exercise 10.9.8.1.3

The optimum C-O bond length in a carbon dioxide molecule is 1.116 Å. Draw a graph of what happens to internal energy when this bond length varies between 1.10 Å and 1.20 Å. Don't worry about quantitative labels on the energy axis.

Answer available at the end of this section.

Exercise 10.9.8.1.4

The optimum O-C-O bond angle in a carbon dioxide molecule is 180 °. Draw a graph of what happens to internal energy when this bond angle varies between 170 ° and 190 °. Don't worry about quantitative labels on the energy axis.

Answer available at the end of this section.

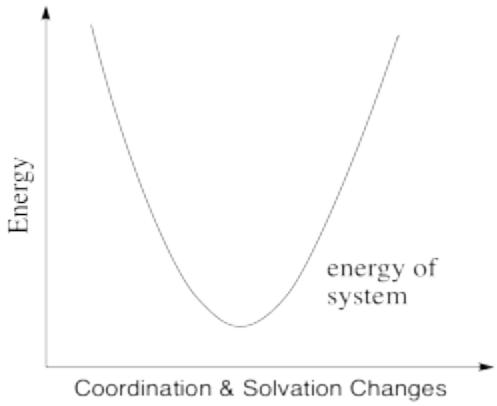
The barrier to electron transfer has to do with reorganizations of all those big atoms before the electron makes the jump. In terms of the coordination sphere, those reorganizations involve bond vibrations, and bond vibrations cost energy. Outside the coordination sphere, solvent molecules have to reorganize, too. Remember, ion stability is highly influenced by the surrounding medium.

Exercise 10.9.8.1.5

Draw a Fe(II) ion and a Cu(II) ion with three water molecules located somewhere in between them. Don't worry about the ligands on the iron or copper. Show how the water molecules might change position or orientation if an electron is transferred from iron to copper.

Answer available at the end of this section.

Thus, the energetic changes needed before electron transfer can occur involve a variety of changes, including bond lengths of several ligands, bond angles, solvent molecules, and so on. The whole system, involving both metals, has some optimum set of positions of minimum energy. Any deviations from those positions requires added energy. In the following energy diagram, the x axis no longer defines one particular parameter. Now it lumps all changes in the system onto one axis. This picture is a little more abstract than when we are just looking at one bond length or one bond angle, but the concept is similar: there is an optimum set of positions for the atoms in this system, and it would require an input of energy in order to move any of them move away from their optimum position.

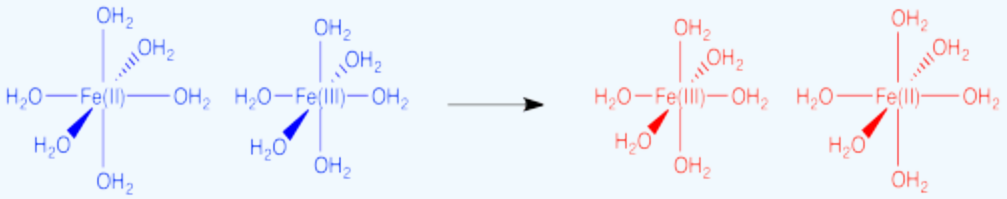


It is thought that these kinds of reorganizations -- involving solvent molecules, bond lengths, coordination geometry and so on -- actually occur prior to electron transfer. They happen via random motions of the molecules involved. However, once they have happened, there is nothing to hold the electron back. Its motion is so rapid that it can immediately find itself on the other atom before anything has a chance to move again.

Consequently, the barrier to electron transfer is just the amount of energy needed for all of those heavy atoms to get to some set of coordinates that would be accessible in the first state, before the electron is transferred, but that would also be accessible in the second state, after the electron is transfered.

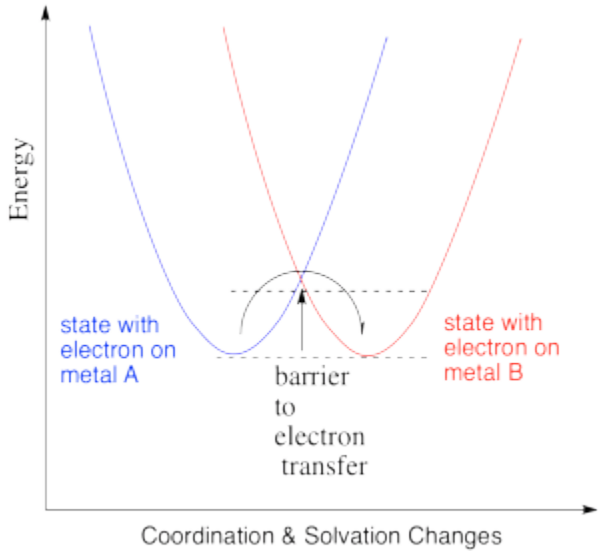
Exercise 10.9.8.1.6

Describe some of the changes that contribute to the barrier to electron transfer in the following case.

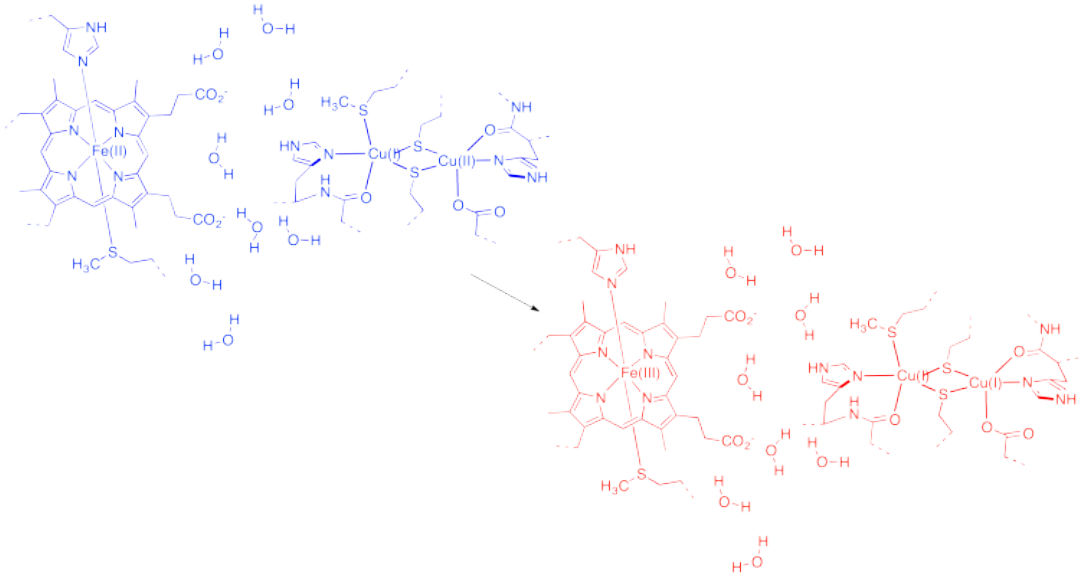


Answer available at the end of this section.

In the drawing below, an electron is transferred from one metal to another metal of the same kind, so the two are just switching oxidation states. For example, it could be an iron(II) and an iron(III), as pictured in the problem above. In the blue state, one iron has the extra electron, and in the red state it is the other iron that has the extra electron. The energy of the two states are the same, and the reduction potential involved in this transfer is zero. However, there would be some atomic reorganizations needed to get the coordination and solvation environments adjusted to the electron transfer. The ligand atoms and solvent molecules have shifted in the change from one state to another, and so our energy surfaces have shifted along the x axis to reflect that reorganization.



That example isn't very interesting, because we don't form anything new on the product side. Instead, let's picture an electron transfer from one metal to a very different one. For example, maybe the electron is transferred from cytochrome c to the "copper A" center in cytochrome c oxidase, an important protein involved in respiratory electron transfer.



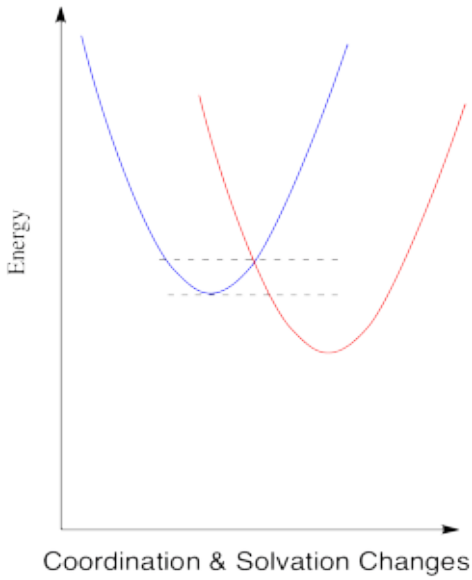
Exercise 10.9.8.1.7

In the drawing above, some water molecules are included between the two metal centres.

a. Explain what happens to the water molecules in order to allow electron transfer to occur, and why.
b. Suppose there were a different solvent, other than water, between the complexes. How might that affect the barrier to the reaction?

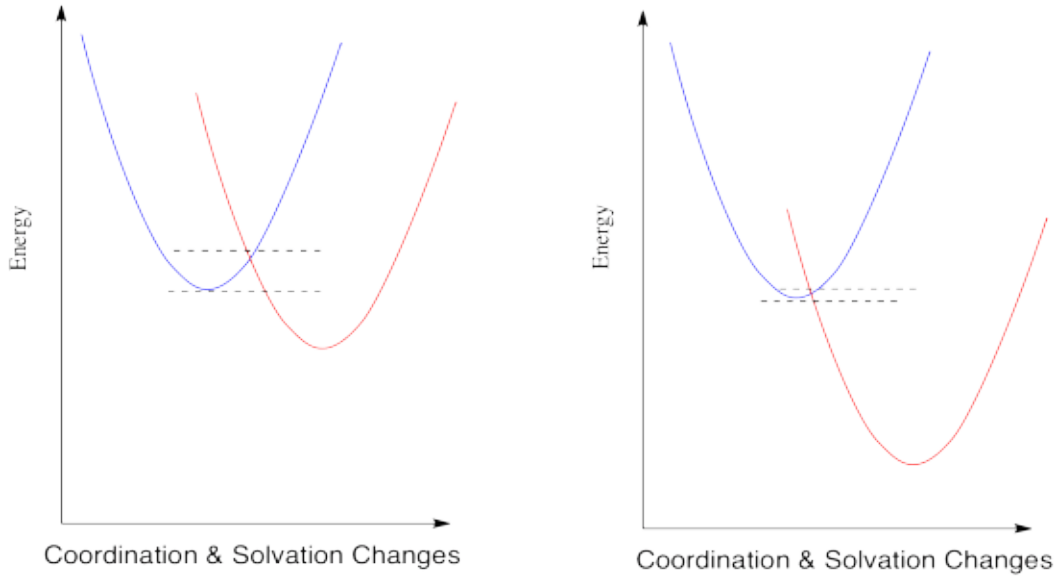
Answer a available at the end of this section.

The energy diagram for the case involving two different metals is very similar, except that now there is a difference in energy between the two states. The reduction potential is no longer zero. We'll assume the reduction potential is positive, and so the free energy change is negative. Energy goes down upon electron transfer.



Compare this picture to the one for the degenerate case, when the electron is just transferred to a new metal of the same type. A positive reduction potential (or a negative free energy change) has the effect of sliding the energy surface for the red state downwards. As a result, the intersection point between the two surfaces also slides downwards. Since that is the point at which the electron can slide from one state to the other, the barrier to the reaction decreases.

What would happen if the reduction potential were even more positive? Let's see in the picture below.



The trend continues. According to this interpretation of the kinetics of electron transfer, the more exothermic the reaction, the lower its barrier will be. It isn't always the case that kinetics tracks along with thermodynamics, but this might be one of them.

But is all of this really true? We should take a look at some experimental data and see whether it truly works this way.

Oxidant	E°	k ($M^{-1}s^{-1}$) (margin of error shown in parentheses)
$Co(diene)(NH_3)_2^{3+}$	0.12	3.0(4)
$Co(diene)H_2O)NCS^{2+}$	0.38	11(1)
$Co(diene)(H_2O)_2^{3+}$	0.53	800(100)
Co(EDTA)	0.60	6000(1000)

As the reduction potential becomes more positive, free energy gets more negative, and the rate of the reaction dramatically increases. So far, Marcus theory seems to get things right.

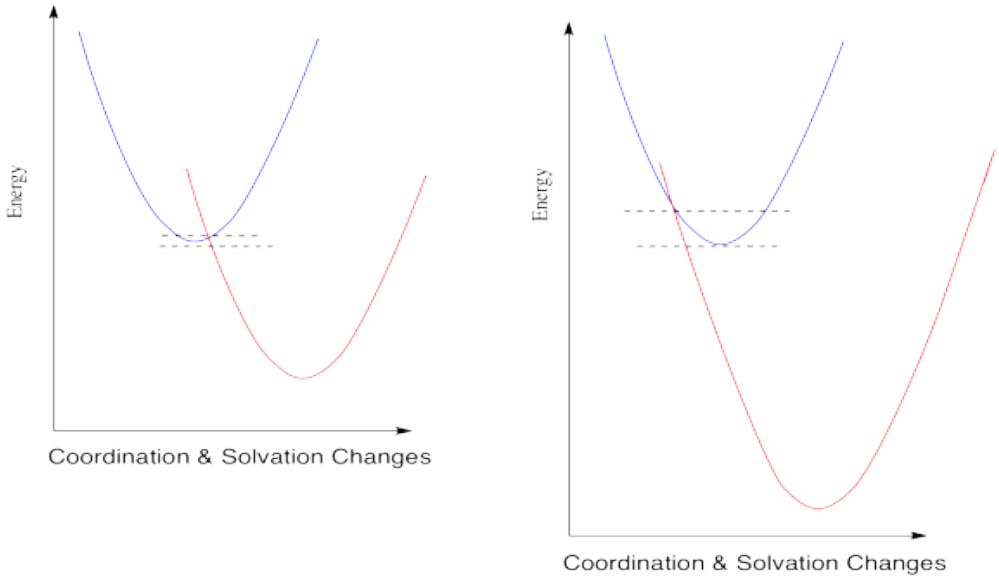
Exercise 10.9.8.1.8

a. Plot the data in the above table.
b. How would you describe the relationship? Is it linear? Is it exponential? Is it direct? Is it inverse?
c. Plot rate constant versus free energy change. How does this graph compare to the first one?

Answer a available at the end of this section.

Marcus Inverted Region

When you look a little closer at Marcus theory, though, things get a little strange. Suppose we make one more change and see what happens when the reduction potential becomes *even more* positive.

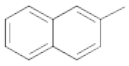
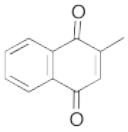
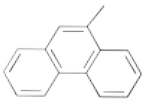
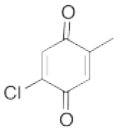
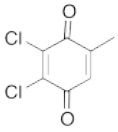


So, if Marcus is correct, at some point as the reduction potential continues to get more positive, reactions start to slow down again. They don't just reach a maximum rate and hold steady at that plateau; the barrier gets higher and higher and the reactions get slower and slower. If you feel a little skeptical about that, you're in good company.

Marcus always maintained that this phenomenon was a valid aspect of the theory, and not just some aberration that should be ignored. The fact that nobody had ever actually observed such a trend didn't bother him. The reason we didn't see this kind of thing, he said, was that we just hadn't developed technology that was good enough to measure these kind of rates accurately.

But technology did catch up. Just take a look at the following data (from Miller, *J. Am.Chem. Soc.* **1984**, *3047*).



Acceptor	ΔG	k	Acceptor	ΔG	k
	-0.05	2×10^6		-1.9	6×10^8
	-0.2	2×10^7		-2.2	1×10^8
	-0.5	1×10^9		-2.4	6×10^7

Don't worry that there are no metals involved anymore. An electron transfer is an electron transfer. Here, an electron is sent from the aromatic substructure on the right to the substructure on the left. By varying the part on the left, we can adjust the reduction potential (or the free energy change, as reported here.

Exercise 10.9.8.1.9

a. Plot the data in the above table.

b. How would you describe the relationship?

Answer a available at the end of this section.

As the reaction becomes more exergonic, the rate increases, but then it hits a maximum and decreases again. Data like this means that the "Marcus Inverted Region" is a real phenomenon. Are you convinced? So were other people. In 1992, Marcus was awarded the Nobel Prize in Chemistry for this work.

Exercise 10.9.8.1.10

Take a look at the donor/acceptor molecule used in Williams' study, above. a) Why do you suppose the free energy change is pretty small for the first three compounds in the table? b) Why does the free energy change continue to get bigger over the last three compounds in the table?

Answer available at the end of this section.

Exercise 10.9.8.1.11

The rates of electron transfer between cobalt complexes of the bidentate bipyridyl ligand, $Co(bipy)_3^{n+}$, are strongly dependent upon oxidation state in the redox pair. Electron transfer between Co(I)/Co(II) occurs with a rate constant of about 10^9 $M^{-1}s^{-1}$, whereas the reaction between Co(II)/Co(III) species proceeds with k = 18 $M^{-1}s^{-1}$.

a. What geometry is adopted by these complexes?
b. Are these species high spin or low spin?
c. Draw d orbital splitting diagrams for each complex.
d. Explain why electron transfer is so much more facile for the Co(I)/Co(II) pair than for the Co(II)/Co(III) pair.

Answer a available at the end of this section.

Answers

Exercise 10.9.8.1.1

The bonds to iron would contract because the increased charge on the iron would attract the ligand donor electrons more strongly. The bonds to copper would lengthen because of the lower charge on the copper.

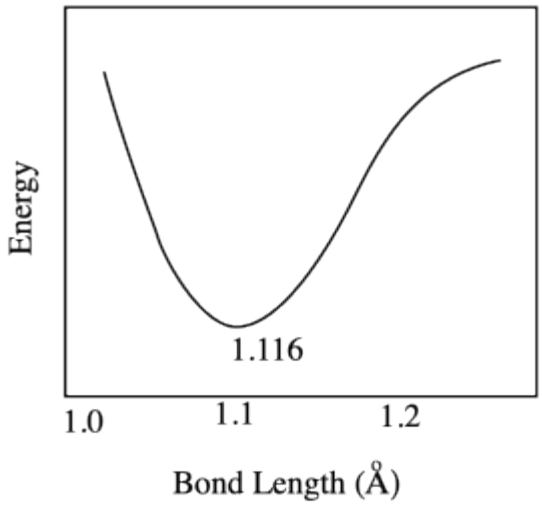
Exercise 10.9.8.1.2

a) Most likely there are repulsive forces between ligands if the bonds get too short.

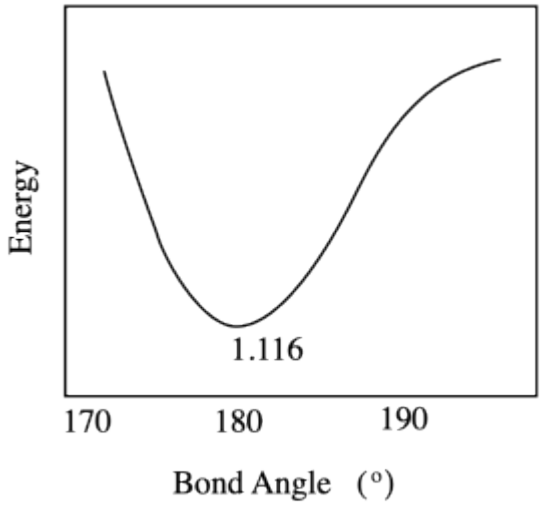
b) Insufficient overlap between metal and ligand orbitals would weaken the bond and raise the energy.

c) The range of possible bond lengths gets broader as energy is increased. The bond has more latitude, with both longer and shorter bonds allowed at higher energy.

Exercise 10.9.8.1.3

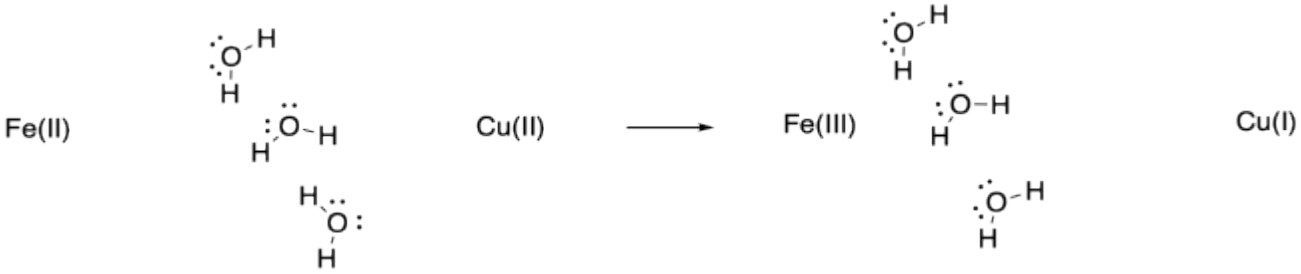


Exercise 10.9.8.1.4



Exercise 10.9.8.1.5

The water molecules may pivot toward the more highly charged Fe(III), or they may shift closer to it because of the attraction between the ion and the dipole of the water molecule.



Keep in mind that such adjustments would happen in non-polar solvents, too, although they would involve weaker IMFs such as ion - induced dipole interactions.

Exercise 10.9.8.1.6

The reactants and products are very similar in this case. However, the Fe(III) complex has shorter bonds than the Fe(II) complex because of greater electrostatic interaction between the metal ion and the ligands. These changes in bond length needed in order to get ready to change from Fe(III) to Fe(II) (or the reverse) pose a major barrier to the reaction.

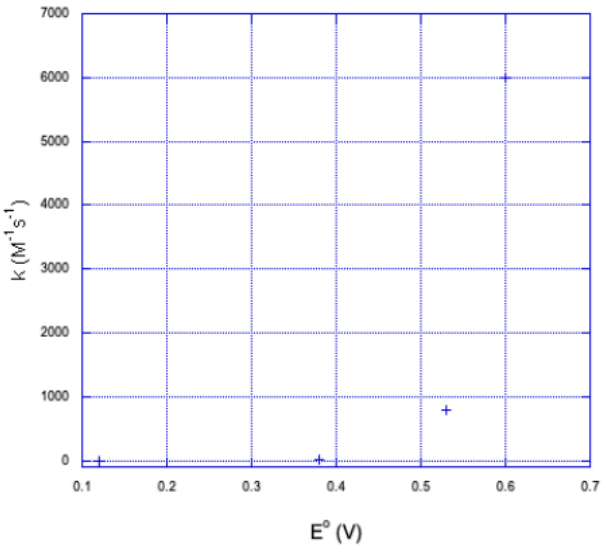
Exercise 10.9.8.1.7

a) The drawing is an oversimplification, but in general the water molecules are shown reorienting after the electron transfer because of ion-dipole interactions. In this case, the waters are shown orienting to present their negative ends to the more positive iron atom after the electron transfer. In reality, in a protein there are lots of other charges (including charges on the ligand) that may take part in additional ion-dipole interactions.

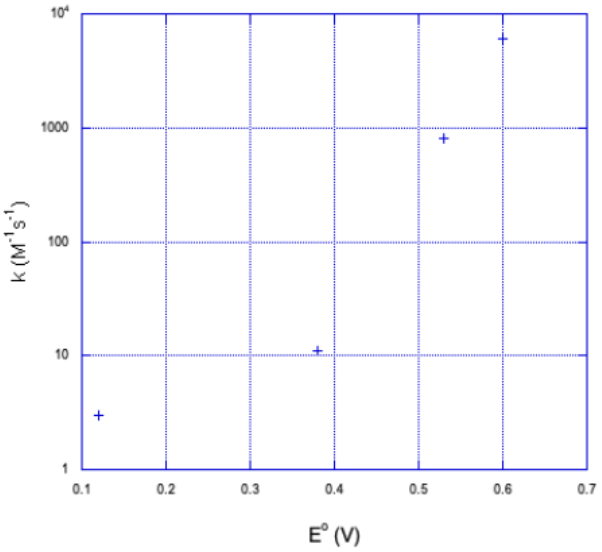
b) Because electron transfer is so fast, atomic and molecular reorganisations are actually thought to happen before the electron transfer. The water molecules would happen to shift into a position that would provide the greatest possible stabilisation for the ions and then the electron would be transferred. A less polar solvent than water would be less able to stabilize ions and the electron would be slower to transfer as a result. In addition, a less polar solvent than water would be a poor medium to transmit an electron, which is charged and therefore stabilized by interactions with polar solvents.

Exercise 10.9.8.1.8

a) Here is a plot of the data.

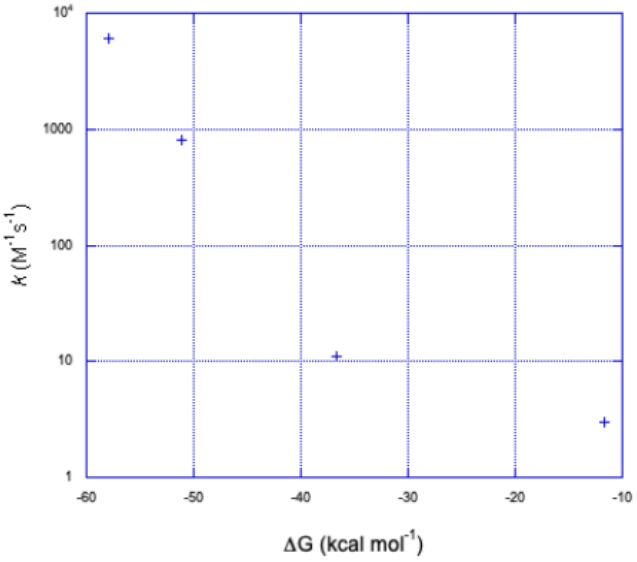


b) It doesn't look linear. If we plot the y axis on a log scale, things become a little more linear.



It looks closer to a logarithmic relationship than a linear one.

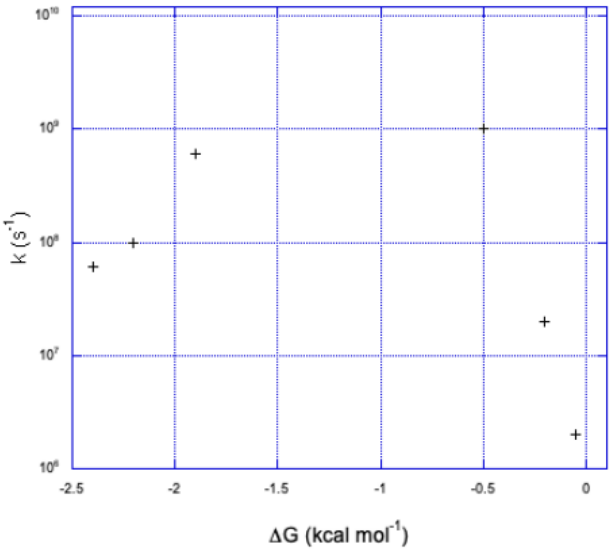
c) Assuming one electron transfer:



The graph takes the same form but in the opposite direction along the x axis.

Exercise 10.9.8.1.9

a)



b) We can see two sides of an inverted curve. The reaction gets much faster as the free energy becomes more negative, but at some point the rate begins to decrease again.

Exercise 10.9.8.1.10

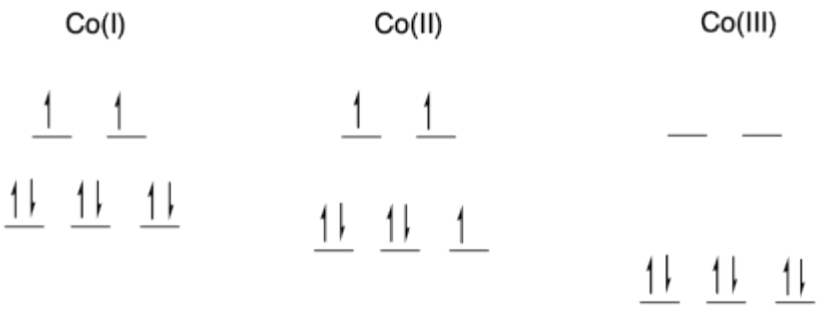
The acceptor compound becomes an anion when it accepts an electron. The first three compounds do not appear to be strongly electrophilic; they can accept electrons simply because of resonance stability of the resulting anion. The last three have electron withdrawing groups (chlorines and oxygens) that would stabilize the anion even further.

Exercise 10.9.8.1.11

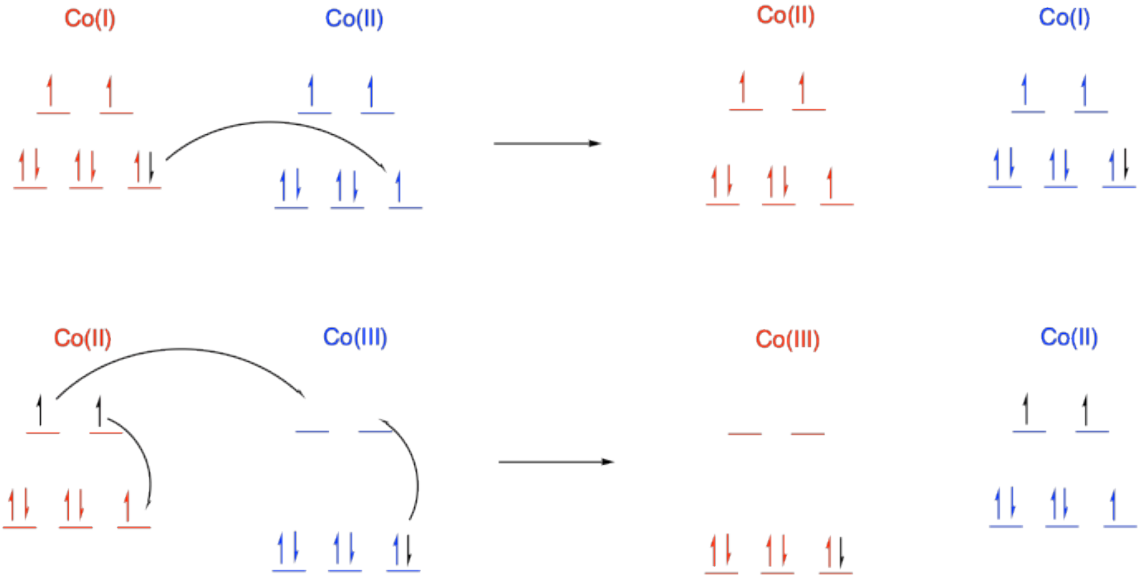
a) octahedral; bpy is a bidentate ligand.

b) Co is first row; Co(I) and Co(II) have relatively low charge. Usually we would expect them to be high spin. Co(III) is at a cut-off point in the first row; it is just electronegative enough that it is usually low spin.

c)



d) In a transfer from Co(II) to Co(III), there is additional reorganization needed because the metal changes between high and low spin. Not only does one electron have to move from one metal to another metal, but additional electrons have to shuffle from one orbital to another on the same metal to accommodate the change. These reorganizations have a barrier, slowing the reaction.



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10.9.8.2: Inner Sphere Electron Transfer

In some cases, electron transfers occur much more quickly in the presence of certain ligands. For example, compare the rate constants for the following two electron transfer reactions, involving almost exactly the same complexes:

$$Co(NH_3)_6{}^{3+} + Cr^{2+} \longrightarrow Co^{2+} + Cr^{3+} + 6\,NH_3 \;\; k = 10^{-4} M^{-1} s^{-1}$$

$$Co(NH_3)_5Cl^{2+} + Cr^{2+} \longrightarrow Co^{2+} + CrCl^{2+} + 6\,NH_3 \;\; k = 6 \times 10^{5} M^{-1} s^{-1}$$

(Note: aqua ligands are omitted for simplicity. Ions, unless noted otherwise, are aqua complexes.)

Notice two things: first, when there is a chloride ligand involved, the reaction is much faster. Second, after the reaction, the chloride ligand has been transferred to the chromium ion. Possibly, those two events are part of the same phenomenon.

Similar rate enhancements have been reported for reactions in which other halide ligands are involved in the coordination sphere of one of the metals.

In the 1960's, Henry Taube of Stanford University proposed that halides (and other ligands) may promote electron transfer via bridging effects. What he meant was that the chloride ion could use one of its additional lone pairs to bind to the chromium ion. It would then be bound to both metals at the same time, forming a bridge between them. Perhaps the chloride could act as a conduit for electron transfer. The chloride might then remain attached to the chromium, to which it had already formed a bond, leaving the cobalt behind.

Electron transfers that occur via ligands shared by the two metals undergoing oxidation and reduction are termed "inner sphere" electron transfers. Taube was awarded the Nobel Prize in chemistry in 1983; the award was based on his work on the mechanism of electron transfer reactions.

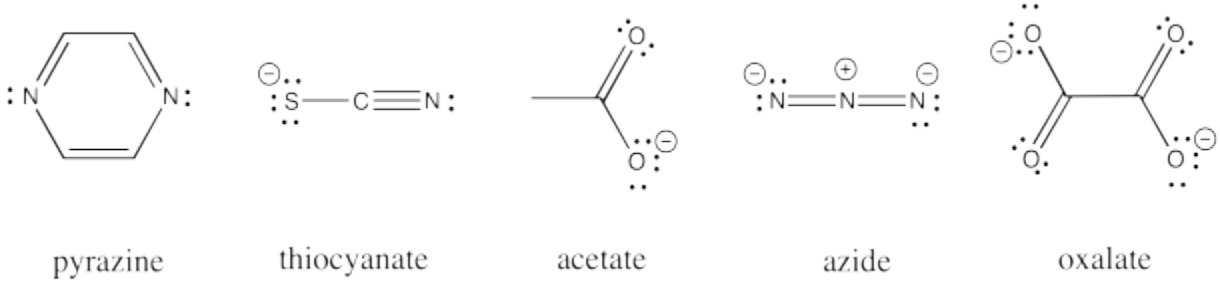
Exercise 10.9.8.2.1

Take another look at the two electron transfer reactions involving the cobalt and chromium ion, above.

a. What geometry is adopted by these complexes?
b. Are these species high spin or low spin?
c. Draw d orbital splitting diagrams for each complex.
d. Explain why electron transfer is accompanied by loss of the ammonia ligands from the cobalt complex.
e. The chloride is lost from the cobalt complex after electron transfer. Why does it remain on the chromium?

Answer a available at the end of this section.

Other ligands can be involved in inner sphere electron transfers. These ligands include carboxylates, oxalate, azide, thiocyanate, and pyrazine ligands. All of these ligands have additional lone pairs with which to bind a second metal ion.



pyrazine thiocyanate acetate azide oxalate

Exercise 10.9.8.2.2

Draw an example of each of the ligands listed above bridging between a cobalt(III) and chromium(II) aqua complex.

Answer available at the end of this section.

Exercise 10.9.8.2.3

Explain, with structures and d orbital splitting diagrams, how the products are formed in the following reaction, in aqueous solution.

$$\mathrm{Fe(OH_2)_6}^{2+} + \mathrm{(SCN)Co(NH_3)_5}^{2+} \longrightarrow \mathrm{(NCS)Fe(OH_2)_5}^{2+} + \mathrm{Co(OH_2)_6}^{2+} + 5\,\mathrm{NH_3}$$

Answer available at the end of this section.

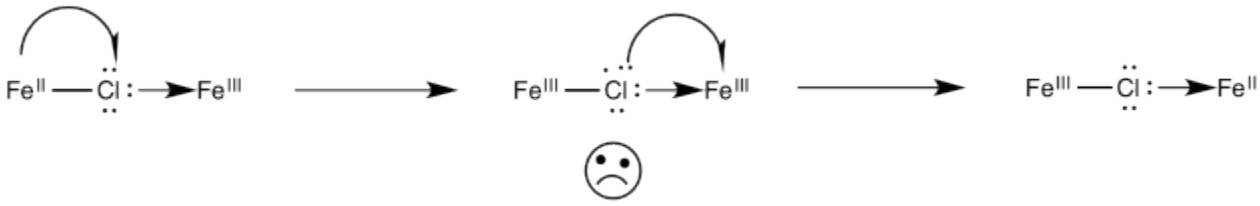
How does the electron travel over the bridge?

Once the bridge is in place, the electron transfer may take place via either of two mechanisms. Suppose the bridging ligand is a chloride. The first step might actually involve an electron transfer from chlorine to the metal; that is, the chloride could donate one electron from one of its idle lone pairs. This electron could subsequently be replaced by an electron transfer from metal to chlorine.



Sometimes, we talk about the place where an electron *used to be*, describing it as a "hole". In this mechanism, the electron donated from the bridging chloride ligand leaves behind a hole. The hole is then filled with an electron donated from the other metal.

Alternatively, an electron might first be transferred from metal to chlorine, which subsequently passes an electron along to the other metal. In the case of chlorine, this idea may be unsatisfactory, because chlorine already has a full octet. Nevertheless, some of the other bridging ligands may have low-lying unoccupied molecular orbitals that could be populated by this extra electron, temporarily.



Exercise 10.9.8.2.4

For the iron / cobalt electron transfer in problem Exercise 10.9.8.2.3 (RO9.3.), show

a. an electron transfer mechanism via a hole migration along the bridge
b. an electron transfer mechanism via an electron migration along the bridge

Answer a available at the end of this section.

Exercise 10.9.8.2.5

One of the many contributions to the barrier for electron transfer between metal ions is internal electronic reorganization.

a) Draw d orbital splitting diagrams for each of the following metal ions in an octahedral environment.

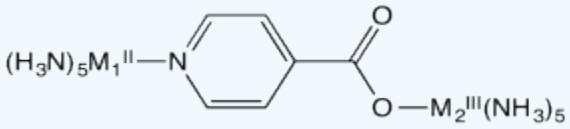
Ru(II) or Os(II)

Ru(III) or Os(III)

Co(II)

Co(III)

Flash photolysis is a method in which an electron can be moved instantly "uphill" from one metal to another (e.g. from M_2^{II} to M_1^{III}, below); the electron transfer rate can then be measured as the electron "drops" back from M_1^{II} to M_2^{III}.



b) Explain the relative rates of electron transfer reaction in this system, as measured by flash photolysis in the table below.

M_1^{II}	M_2^{III}	k_{obs} s^{-1}
Os	Ru	$> 5 \times 10^9$
Os	Co	1.9×10^5

c) Does the reaction above probably occur via an inner sphere or by an outer sphere pathway? Why?

Answer a available at the end of this section.

Exercise 10.9.8.2.6

Outer sphere electron transfer rates depend on the free energy change of the reaction (ΔG°) and the distance between oxidant and reductant (d) according to the relation

Rate constant = $k = Ae^{(-\Delta G)}e^{-d}$

a) What happens to the rate of the reaction as distance increases between reactants?

One potential problem in measuring rates of intramolecular electron transfer (i.e. *within* a molecule) is competition from intermolecular electron transfer (*between* molecules).

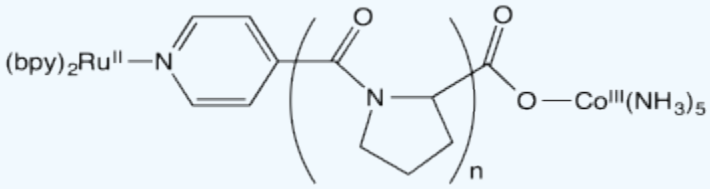
b) What would you do in the flash photolysis experiment above to discourage intermolecular electron transfer?

c) How could you confirm whether you were successful in discouraging intermolecular reaction?

Answer a available at the end of this section.

Exercise 10.9.8.2.7

Stephan Isied and coworkers at Rutgers measured the following electron transfer rates between metal centers separated by a peptide. (*Chem Rev* **1992**, *92*, 381-394)



a. The proline repeating unit is crucial in ensuring a steady increase in distance between metal centers with increased repeat units, n. Why?
b. An inner sphere pathway in this case is expected to be somewhat slow because of the lack of conjugation in the polyproline bridge. Explain why.
c. Plot the data below, with log*k* on the y axis (range from 4-9) and d on the x axis (12-24 Angstroms).

n	d (Å)	k_{obs} (s^{-1})
1	12.2	5×10^{8}
2	14.8	1.6×10^{7}
3	18.1	2.3×10^{5}
4	21.3	5.1×10^{4}
5	24.1	1.8×10^{4}

d) A linear relationship is in agreement with Marcus theory; log*k* = - c x d. Is your plot linear?

Isied offers a number of possible explanations for the data, all of which involve two competing reaction pathways.

e) Suggest one explanation for the data.

Answer a

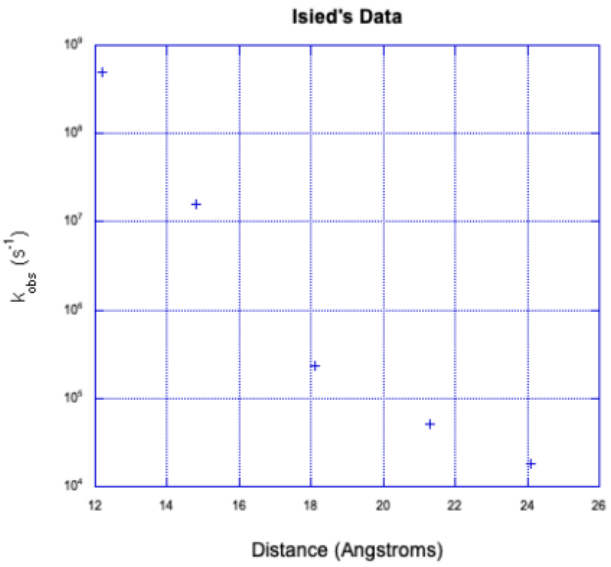
a) Rings are frequently used to introduce conformational rigidity (or decrease conformational flexibility), limiting the range of potential shapes a molecule could adopt. If the molecule can't wiggle around as much, then the distance between the ends of the molecule should be more constant.

Answer b

b) Although the ligand is bridging, it would be difficult to picture either an electron or hole mechanism of inner sphere electron transfer. There are few pi bonds or lone pairs to use as places to put electrons or temporarily remove electrons from, shuttling the electrons from place to place along the ligand. A conjugated system would be much more likely to carry out inner sphere electron transfer.

Answer c

c)



Answer d

d) The data is not linear.

Answer e

e) The data appear to show two lines that cross. That's a classic symptom of two competing mechanisms. The faster mechanism, to the left, is probably an intramolecular electron transfer. The slower mechanism, to the right, may be an intermolecular electron transfer.

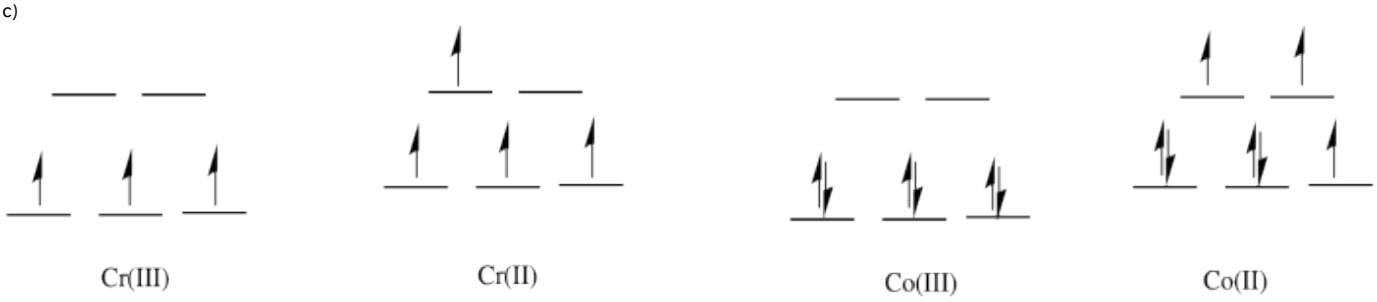
Answers

Exercise 10.9.8.2.1

a) octahedral

b) In the first row, 2^+ complexes are almost always high spin. However, 3^+ complexes are sometimes low spin.

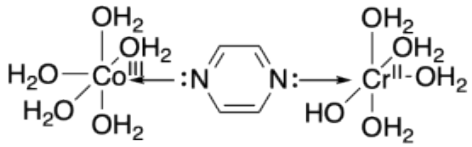
c)

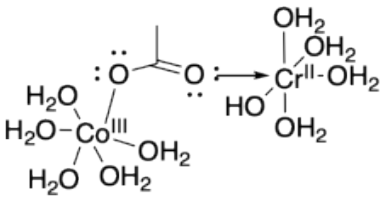


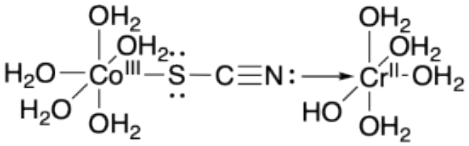
d) The Co(II) complex is high spin and labile. The ligands are easily replaced by water.

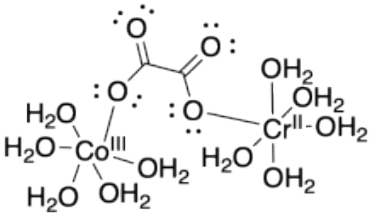
e) The Cr(III) complex is only d^3; it is inert.

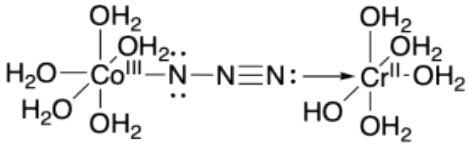
Exercise 10.9.8.2.2



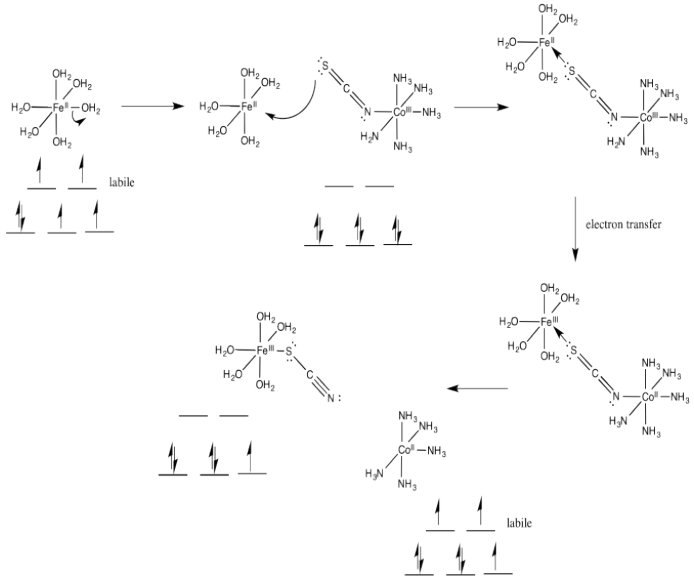




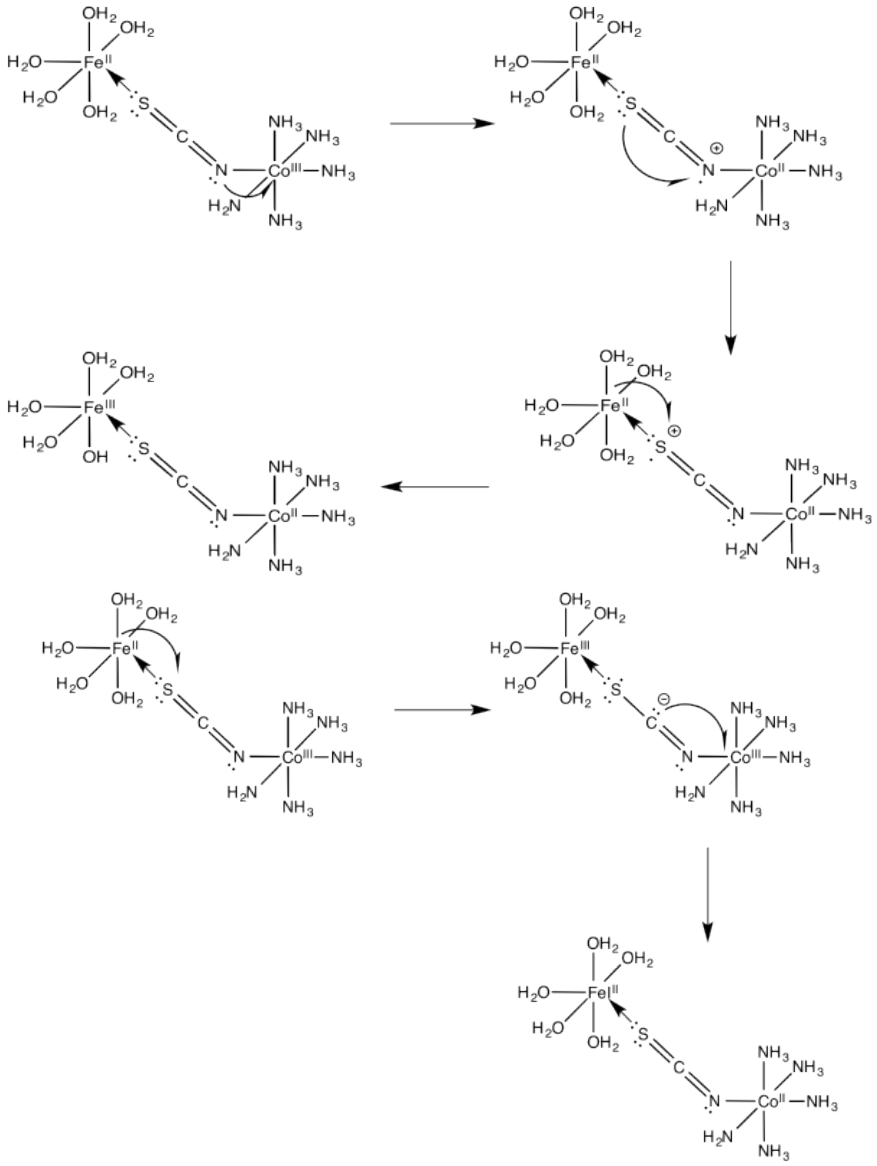




Exercise 10.9.8.2.3

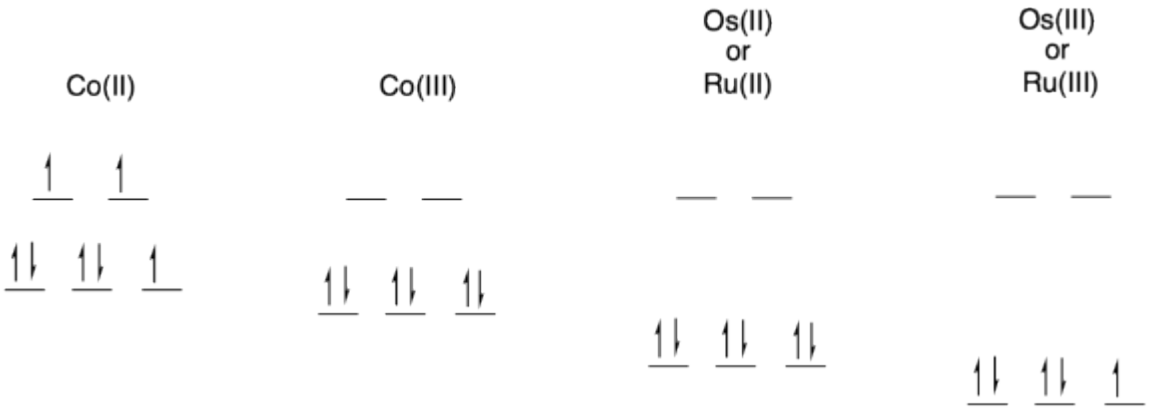


Exercise 10.9.8.2.4



Exercise 10.9.8.2.5

a)



b) The electron transfer between Os(II) and Ru(III) will not involve any electron reorganization because both are low spin to begin with. However, the electron transfer between Os(II) and Co(III) will result in cobalt changing from low spin to high spin. The need to move electrons between different d orbitals on the cobalt will add to the barrier, slowing down the reaction.

c) The pathway is probably inner sphere because of the bridging ligand. Furthermore, the conjugation in the bridging ligand would help in conducting an electron from one end of the ligand to the other, either through an electron mechanism or a hole mechanism.

Exercise 10.9.8.2.6

a) The rate decreases exponentially as distance increases.

b) You might keep the concentration low in order to increase the distance between molecules, reducing the likely hood of an outer-sphere electron transfer.

c) If you ran the experiment at a series of dilutions, intramolecular electron transfer would be unaffected but outer sphere electron transfer would not. If the rates were the same across a number of different concentrations, the reaction would probably be intramolecular.

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10.9.9: Reactions of Coordinated Ligands

So far, our coverage of the reactions of metal complexes has focused only on the reactions that occur at the metal center. However, there are also reactions that can occur to the ligands bound at the metal center. When a ligand binds to an electropositive metal center, bonds within the ligand can be polarized in new ways, leading to new or enhanced reactivity. Some of these reactions are covered in the chapters on organometallic chemistry, and there are many examples of how biology employs metal ions at enzyme active sites to catalyze biological transformations. This section will briefly describe some of the most common types of reactions that can be catalyzed by metal ion binding.

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10.9.9.1: Metal-catalyzed Hydrolysis

Transition metal ions (but not alkali metal ions) act as Lewis acids in metal-ligand interactions. As a consequence of the metal ion interacting with the ligand, the electronic structure of the ligand is altered. In some cases, the metal-ligand interaction causes changes in the strength and reactivity of other bonds within the ligand itself. For example, when a ligand has an acidic proton, interactions with a metal ion will make that acidic proton more acidic. In other words, interaction with the metal ion can cause a decrease in the ligand's pK_a. The metal-ligand complex itself can act as a stronger Bronsted acid (giving off a proton) compared to the "free" ligand. We can see this type of alteration in the pK_a of water when it is "free" compared to when it is bound to a metal ion.

Example: Water meets a transition metal ion[1]

In biology, the solvent is water. Water is also a ligand that binds to metal ions, according to the equation shown below.

$$n\,\mathrm{H_2O} + \mathrm{M}^{x+} \rightleftharpoons [\mathrm{M(H_2O)}_n]^{x+}$$

There is a LOT of water around in biological systems. Consequently, the reaction shown above is shifted far to the right (toward the aquo metal complex, $[\mathrm{M(H_2O)}_n]^{x+}$) in aqueous solution. Consequently, when metals are dissolved in aqueous solution, the "free" ion does not exist, and rather the metal is in complex with water. This is generally true unless there are other ligands present that have stronger affinity for the metal ion.

Consider the two equilibrium reactions shown below. The autoionization of water is shown on the left. This reaction has a very small equilibrium constant ($K_W = 10^{-14}$) and thus the pK_a for dissociation of a proton from water is $pK_a = 14$. On the left is the dissociation of a proton from a water molecule bound to Zn^{2+} ion (other water ligands are not drawn for simplicity). The bond between $\mathrm{H_2O}$ and Zn is considered to be covalent.

$$\mathrm{H_2O} \rightleftharpoons \mathrm{H}^+ + \mathrm{OH}^- \qquad \text{vs.} \qquad [\mathrm{Zn(H_2O)}]^{2+} \rightleftharpoons \mathrm{H}^+ + [\mathrm{Zn(OH)}]^+$$

Exercise 10.9.9.1.1

Predict which reaction above is more favorable. In other words, in which case is water a better acid; when water is "free", or when it is bound to a transition metal ion like Zn^{2+}? Defend your prediction.[1]

Hint available at the end of this section.

Answer available at the end of this section.

Exercise 10.9.9.1.2

Water has a pK_a of 14. When water is bound to a Zn^{2+} ion in aqueous solution, its pK_a is lowered to 10. Calculate the pH of pure water and the pH of a solution of 0.1 M $ZnSO_4$.

Hint available at the end of this section.

Answer available at the end of this section.

Exercise 10.9.9.1.3

Transition metals dramatically decrease solution pH compared to pure water. On the other hand, alkali metals do not significantly affect pH.

a) Based on this information, what can you conclude about the relative covalent nature of water's interactions with transition metals compared to alkali metals?

b) Rationalize this based on the element's position on the periodic table and their consequent electron configurations.

Answer available at the end of this section.

Exercise 10.9.9.1.4

When a transition metal binds to a Cys side chain, it usually binds to the thiolate anion form of this side chain. Explain why the Cys loses its proton when a metal ion binds. Use drawings to describe what happens to the pK_a of the thiol hydrogen.

Hint available at the end of this section.

Answer available at the end of this section.

Biological hydrolysis[2]

Above you learned how metals can act as Lewis Acids to increase the acidity of a bound water molecule (or other ligand). This modulation of water's pK_a can be really useful to catalyze reactions in which hydroxide ion is a reactant. The enzyme **carbonic anhydrase (CA)** is a prime example of how biology uses this property to catalyze an important biological acid/base reaction. CA is the enzyme that converts CO_2 into bicarbonate (HCO_3^-) very quickly. This is important in the blood to get to CO_2 to the lungs to be exhaled. Conversion of CO_2 to bicarbonate is also important in production of the aqueous fluid of eye and other secretions; and CA is an important drug target for treatment of glaucoma.

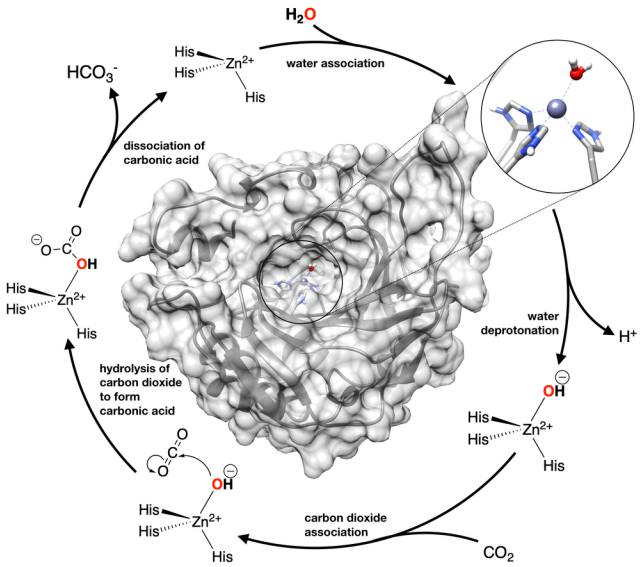


Figure 10.9.9.1.4: Formation of carbonic acid from carbon dioxide catalyzed by human carbonic anhydraze IV. The structure of protein and acitve site were created from PDB 1znc. (CC-BY-SA; Kathryn Haas)

The figure shows the structure of human carbonic anhydrase IV (from PDB 1znc), with a blow up of the Zn active site where Zn is bound to 3 histidine side chains (His). The mechanism for this enzyme is shown in the chemical equations circling the structure in Figure 10.9.9.1.4. As we discused above, binding water to a metal ion can change its pK_a, and make its protons more acidic by

stabilizing the hydroxide ion. When hydroxide is needed to carry out hydrolysis reactions, acidic metal ions, like Zn^{2+} are often used to stabilize the hydroxide nucleophile in order to catalyze the reaction (lower the activation energy). The pK_a of "free" water is 14. For water in $[Zn(H_2O)_6]^{2+}$ in aqueous solution, the pK_a is 10. But, in the active site of carbonic anhydrase, the pK_a of water is lowered even more, to 7, by the protein environment around the Zn active site. The active site of this protein has the "power" to lower the pKa of water even more than in the case of aqueous Zn as a virtue of the hydrophobic pocket of the active site that makes charge separation more unstable compared to bulk water where charges can be better solubilize by bulk water.

Look carefully at the catalytic cycle shown in Figure $10.9.9.1.4$ and identify the step in which water looses a proton (the step labeled "water deprotonation". This step would be nearly impossible under biological conditions at pH 7.4. In other words, it would happen too infrequently to be useful in biological systems. But, when the pKa is lowered to 7, which is below the pH, that step becomes so favorable, that it would happen spontaneously in solution.

Carbonic anhydrase is just one example of how metal ions can be useful for catalyzing hydrolysis reactions. There are several more examples of catalytic enzymes and small molecule metal complexes that use metals (Cu, Co, Ni, Mn, Ca, and Mg) to catalyze hydrolysis of esters (eg hydrolysis of fats), amides (eg hydrolysis of peptide bonds with water), phosphate esters (eg hydrolysis of DNA and RNA) using mechanisms simlar to that shown above for hydrolysis of carbon dioxide.

Sources

1. Inspired by or taken directly from *Metals in Acid Base Chemistry*, an in-class activity created by Sheila Smith, University of Michigan- Dearborn (sheilars@umd.umich.edu) and posted on VIPEr (www.ionicviper.org) on October 17, 2009. Copyright Sheila Smith 2009. This work is licensed under the Creative Commons Attribution Non-commercial Share Alike License. To view a copy of this license visit http://creativecommons.org/about/license/.

2. From *Metals in Biological Systems - Who? How? and Why?*, a 5 slides about learning object created by Adam R. Johnson, Harvey Mudd College (adam_johnson@hmc.edu), Hilary Eppley, DePauw Univeristy (), and Sheila Smith, University of Michigan-Dearborn (sheilars@umd.umich.edu) and posted on VIPEr (www.ionicviper.org) on January 20, 2010. Copyright Sheila Smith 2009. This work is licensed under the Creative Commons Attribution Non-commercial Share Alike License. To view a copy of this license visit http://creativecommons.org/about/license/.

Answers

Exercise $10.9.9.1.1$

Consider these two things:

(1) In which case is the hydroxide ion more stable: when it is a free ion or when it is bound to Zn? How will this effect one case relative to the other?

(2) Consider separation of charge in each equilibrium. Is the localization of positive and negative charge more energetically favorable in the reactands or in the products in each case? How will this effect one case relative to the other?

Exercise $10.9.9.1.1$

Water is a better acid when it has a covalent bond to a metal ion. The metal-ligand interaction weakens the H-O bond and stabilizes the conjugate base that forms after deprotonation.

Exercise $10.9.9.1.2$

You will need the chemical equations above and you will need to recall the definitions of K_a and pK_a, as well as pH to complete this task. Recall that $pK_a = -\log K_a$ and $pH = -\log[H^+]$. The K_a is the equilibrium constant for the chemical equation. Use an I.C.E. table to calculate the amount of hydrogen ion at equilibrium.

Exercise $10.9.9.1.2$

The pH of pure water is 7. The pH of 0.1 M $ZnSO_4$ depends only on the concentration of the Zn aquo complex that forms after dissociation of $ZnSO_4$ to Zn^{2+} and $SO_4{}^{2-}$. We can use the I.C.E method to determine that the concentration of hydrogen ion at equilibrium is approximately 3.2×10^{-6} after 0.1M Zn^{2+} is initially added to water. This gives approximately $pH = 5.5$.

Exercise $10.9.9.1.3$

a) transition metals form more covalent bonds with water, while alkali metal's interactions are more electrostatic in character.

b) transition metals have partially-filled d subshells, while alkali metals have the electron configurations of the nobel gases. Perhaps the nobel gas electron configuration makes covalent bonding unfavorable, while partially filled d-orbitals enables productive bonding interactions with ligands.

Exercise $10.9.9.1.4$

A cystein side chain has a thiol (R-SH) group. Recall that thiols behave similarly to alcohols, but thiols are more acidic than alcohols.

Exercise $10.9.9.1.4$

Bonding of a cystein S to a metal ion would weaken the S-H bond and increase the acidity of that proton (it's pKa would decrease). In bilogical conditions, near neutral pH, this bonding could decrease the pKa of the thiol group so much that the H is lost to give the conjugate base thiolate bound to the metal.

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10.9.9.2: Template Reactions

A template reaction is one in which a metal ion acts as a template to bring reactive sites in close proximity. In the absence of the metal ion, the same reaction would proceed to form a different product. An example of the template effect is the dialykation of nickel dithiolate (Figure 10.9.9.2.1). The same dialkylation in the absence of the Ni template creates a polymer.

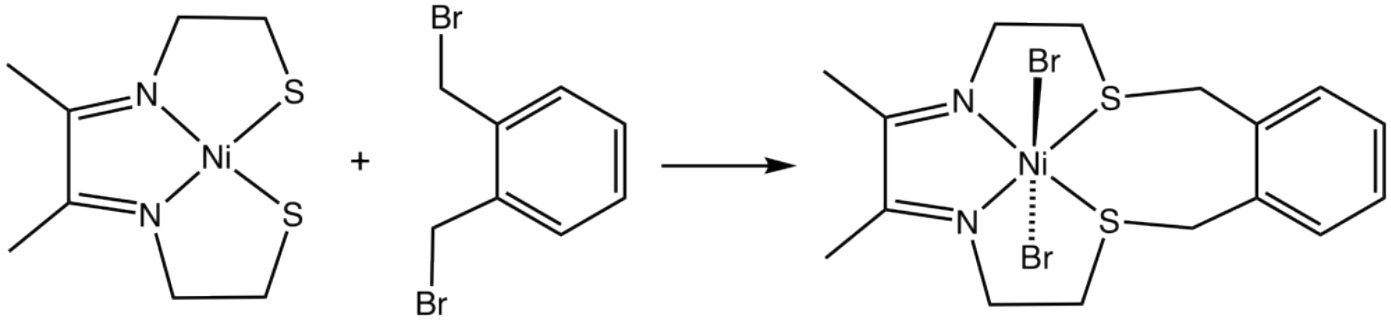


Figure 10.9.9.2.1: The Dialkylation of nickle dithiolate. (Public Domain; Smokefoot)

Another example of a template reaction is in the synthesis of crown ethers from dialkylations that are templated by metal ions. Again, the same reaction carried out without the template metal would form a polymer.

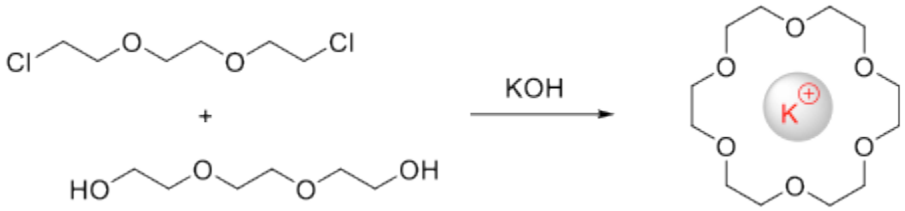


Figure 10.9.9.2.1: 18-Corwn-6 can be synthesized by the Williamson ether synthesis using potassium ion as the template cation. (Carolineneil, 18-crown-6 was synthesized using potassium ion as the template cation, CC BY-SA 4.0)

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10.9.9.3: Electrophilic Substitutions

We have seen how metal ion binding can alter the pKa of a bound ligand by polarizing bonds. In a similar fashion, binding of a ligand to a metal ion can alter the location of electron density so that positions on the ligand take on new reactivity. This can be seen in the case of acetylacetone (acac) complexes (most recently discussed in section 12.5.3). The metal coordination to the acac ligand induces enol tautomerization, placing electron density at the central alpha carbon and causing it to become a potent nucleophile. Reactions occur at that nucleophilic carbon in similar manner to the electrophilic aromatic substitution reactions that you may have learned about in an Organic Chemistry course.

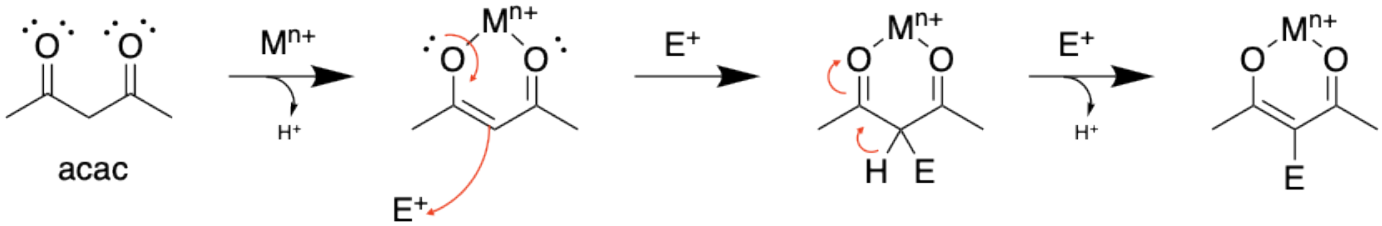


Figure 10.9.9.3.1: Electrophilic substitution of the acac ligand. E^+ = electrophile. (CC-BY-SA; Kathryn Haas)

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10.P: Problems

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11: COORDINATION CHEMISTRY III - ELECTRONIC SPECTRA

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11.1: Absorption of Light

Introduction

The d-orbital splitting in coordination complexes results in a gap (Δ) that happens to be just the right magnitude to absorb visible light. Because metal complexes can absorb visible light, they display an array of colors. Not only is the color attractive to the eye, it is an indication of the chemical and physical properties of the metal complex. The color (like the magnitude of Δ) depends on the identity of the metal ion, the coordination geometry, and the ligand identity. Chemists don't just "look" at color, though - we measure it using electronic absorption spectroscopy. This is usually done in a lab using a UV-visible spectrophotometer.

An example of such a measurement is shown below in Figure 11.1.1 for a Cu(II) complex. The sample appears a pink color to the eye, and when it is measured using a UV-visible spectrometer, it is shown to absorb visible light at approximately 530 nm. The absorption spectrum can indicate the oxidation state of Cu, the ligands bound to the Cu(II) ion, and the coordination geometry. The color of the solution in Figure 11.1.1 is a shade of pink.

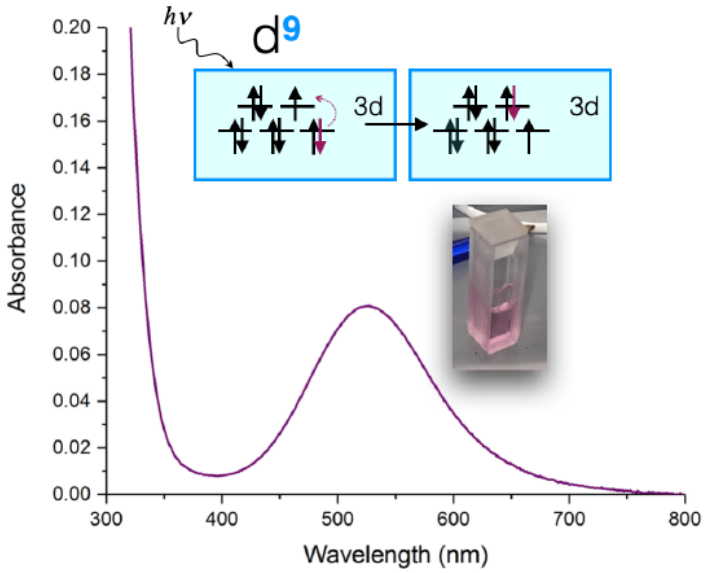


Figure 11.1.1: A UV-visible spectrum of a Cu(II)-peptide complex. A photo of the sample shows its pink color. The splitting diagram for its approximation as an octahdral complex is shown, where an electronic transition from t_{2g} to e_g is shown. (CC-BY-NC-SA; Kathryn Haas)

We observe the complementary color of light absorbed

The absorption spectrum shown above in Figure 11.1.1 is a simple case in which only one absorption band is observed in the visible region of the spectrum. In a simple case like this, the color of a complex can be predicted as the complementary color of the light absorbed by the solution. When a solution or object absorbs a certain wavelength, we see the complementary color; or the color opposite to the absorbed wavelength on the color wheel in Figure 11.1.2. In the case of the Cu(II) complex spectrum shown in Figure 11.1.1, the color of the light absorbed at 530 nm is green, and the predicted color observed is pink.

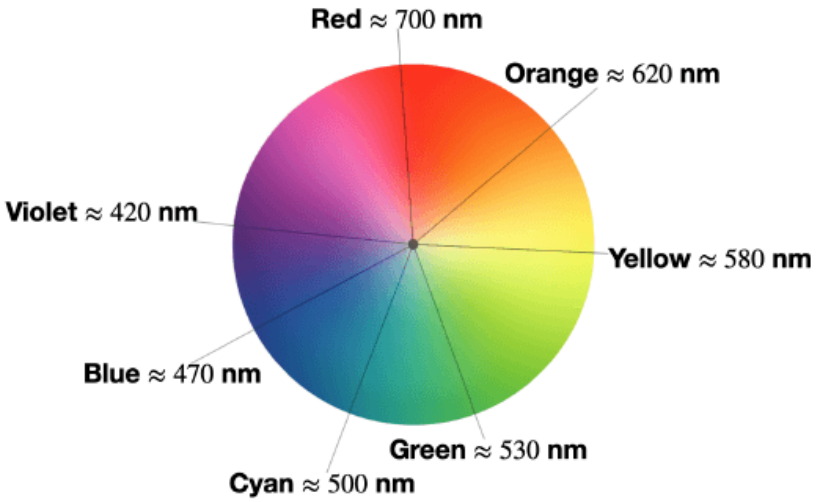


Figure 11.1.2: Color wheel with approximate wavelengths of colors. (CC-BY-NC-SA; Kathryn Haas)

The table below lists the approximate colors of absorption corresponding to wavelengths of light absorbed, and gives similar information to that deduced from Figure 11.1.2.

*Table 11.1.1: Approximate wavelengths of absorption and their complementary colors observed. * This prediction is limited to simple cases where there is only one absorption band in the visible spectrum.*

λ absorbed	E (cm^{-1})	E (eV)	Approximate color absorbed	Predicted color observed (by eye)
> 700 nm	$< 14,000 \frac{1}{cm}$	< 1.77 eV	Infrared	not observable
$\approx 700 - 635$ nm	$\approx 14,300 - 16,000 \frac{1}{cm}$	$\approx 1.77 - 1.95$ eV	Red	Green
$\approx 635 - 590$ nm	$\approx 15,700 - 16,900 \frac{1}{cm}$	$\approx 1.95 - 2.10$ eV	Orange	Blue
$\approx 590 - 560$ nm	$\approx 16,900 - 17,900 \frac{1}{cm}$	$\approx 2.10 - 2.21$ eV	Yellow	Violet
$\approx 560 - 520$ nm	$\approx 17,900 - 19,200 \frac{1}{cm}$	$\approx 2.21 - 2.38$ eV	Green	Red
$\approx 520 - 490$ nm	$\approx 19,200 - 20,400 \frac{1}{cm}$	$\approx 2.38 - 2.53$ eV	Cyan	Red-Orange
$\approx 490 - 450$ nm	$\approx 20,400 - 22,200 \frac{1}{cm}$	$\approx 2.53 - 2.76$ eV	Blue	Orange
$400 - 450$ nm	$\approx 22,200 - 25,000 \frac{1}{cm}$	$\approx 2.76 - 3.10$ eV	Violet	Yellow
<400 nm	$> 25,000 \frac{1}{cm}$	> 3.10 eV	Ultraviolet (UV)	not observable

Energy of electronic absorption

The absorption spectrum of a metal complex can be used to calculate the splitting energy, Δ, when the absorption corresponds to a $d \rightarrow d$ transition. Let's use the d^9 Cu(II) complex (discussed above) as an example. A d^9 metal ion has only one visible-light $d \rightarrow d$ transition. Let's assume that the coordination geometry is *approximately* octahedral (although it is actually a Jahn-Teller distorted octahedron, and more like a square plane). If we assume it's octahedral, then the d-orbital splitting diagram (see Figure 11.1.1) leads us to expect one electronic transition: an electron is excited from the t_{2g} to e_g. The energy absorbed is equal to the energy of the Δ.

Many cases are not as simple as a d^9 octahedral case because there are multiple possible electronic transitions, and also multiple absorption bands in the UV-vis spectrum. In these more complex cases, the actual energy of the transition are affected by differences in electron-electron repulsion energies in the ground state and the excited states. We will learn how to account for multiple possible excited states and electron-electron repulsions using Tanabe-Sugano diagrams later in this chapter.

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11.1.1: Beer-Lambert Absorption Law

When light passes through a solution that absorbs light, it enters the solution with an initial intensity (I_o) at a given wavelength, and it emerges with an intensity, I.

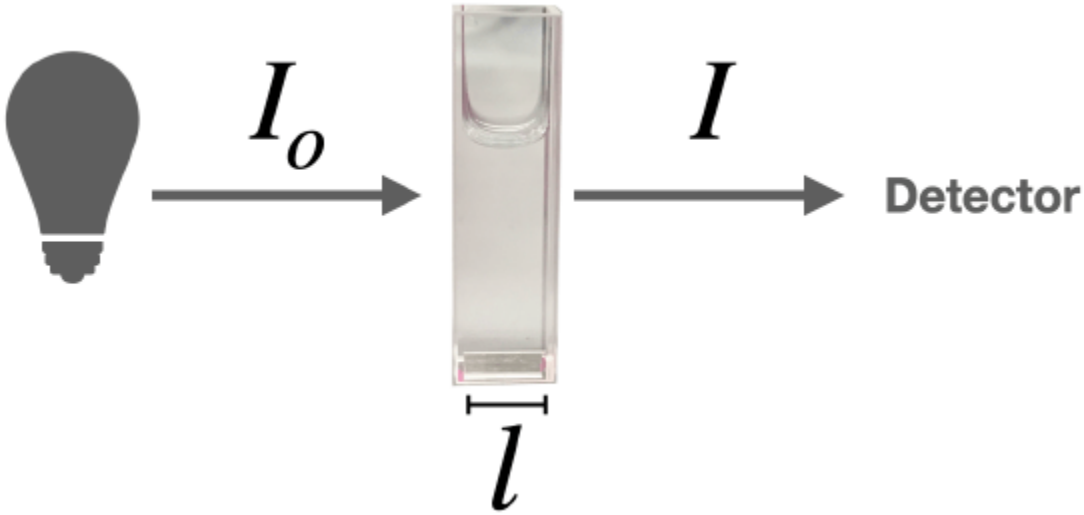


Figure 11.1.1.1: Initial intensity (I_o) of light passes through a solution and emerges as intensity, I. The path length is l. (CC-BY; Kathryn Haas)

The Beer-Lambert Law defines the relationship between absorbance at a given wavelength and the concentration of the solution.

$$\log\left(\frac{I_o}{I}\right) = A = \varepsilon lc \tag{11.1.1.1}$$

The absorbance (A) is a unitless number because $\frac{I_o}{I}$ is unitless. The absorbance depends on the concentration (c) and the path length (l). The concentration of the sample solution is measured in molarity (M) and the length of the light path in centimeters (cm). The Greek letter epsilon (ε) in these equations is called the **molar absorptivity** (also called the **molar absorption coefficient**). The units of ε are $\frac{L}{mol \times cm}$ or $L \times mol^{-1} \times cm^{-1}$.

Chemists most often measure and report absorbed light in terms of wavelength (λ) in units of nanometers (nm). But the wavelength scale is inconvenient for measuring energy because it is inversely proportional to both frequency and energy. In other disciplines, like physics for example, absorption spectra are more often reported in terms of frequency (ν) using units of inverse centimeters (cm^{-1}). The relationships between energy (E), ν, and λ are given by the equation below:

$$E = h\nu = \frac{hc}{\lambda} = hc\left(\frac{1}{\lambda}\right) = hc\bar{\nu} \tag{11.1.1.2}$$

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11.2: Quantum Numbers of Multielectron Atoms

Note

The quantum numbers of atoms (and ions) correspond to quantized energy states, called microstates, that depend on the electron configuration. Electrons within a subshell or orbital can adopt different configurations of their electrons, with different individual quantum numbers. These different electron configurations are **microstates**, and they can be grouped into **terms** and ordered according to their relative energies. Since electronic transitions occur between terms of different energies, knowledge of the terms for a given atom or ion can aid in the interpretation of electronic spectra.

Introduction

Transition metal ions can give rise to a spectrum of beautifully colored colored complexes. The colors are often caused by absorption of visible light due to electronic transitions involving metal d-orbitals. These electronic transitions are not only attractive to the eye, they are useful spectroscopic signals because the transitions occur between quantized electronic energy states, called microstates. Spectroscopy, coupled with knowledge of the possible microstates and their energies can yield clues about molecular structure.

To learn what a microstate is, let's use the simple example of a carbon atom with a $1s^2 2s^2 2p^2$ electron configuration. The s subshell is full, and there is only one way to put two electrons into an s subshell. Both electrons must occupy the orbital having $m_l = 0$, and each must have opposite spins, ($m_s = +\frac{1}{2}$), and ($m_s = -\frac{1}{2}$). On the other hand, the p subshell of carbon has two electrons that can occupy any of three orbitals (Figure 11.2.1). This leaves room for different orientations of the electrons within the p subshell. Each different electron configuration is a **microstate**, and each has an energy that can be distinguished using electronic spectroscopy (UV-vis for example). In the case of a carbon atom with a two p electrons, there are 15 different possible microstates, as illustrated in Figure 11.2.1.

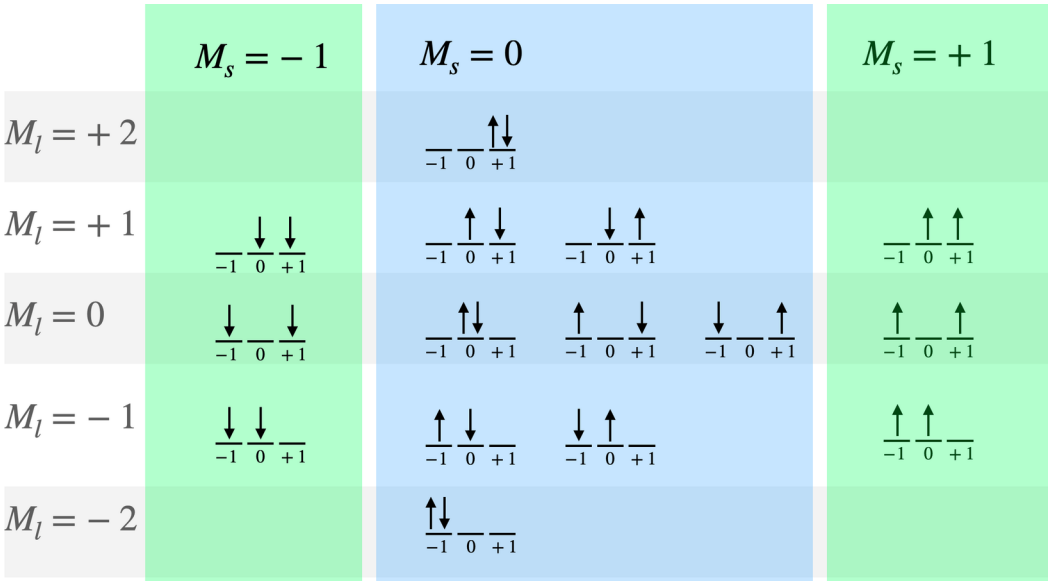


Figure 11.2.1: Fifteen possible microstates for two electrons in a p subshell. These microstates are organized according to their total spin (M_s) and total magnetic (M_l) quantum numbers. Arrows pointing upward represent electrons with $m_s = +\frac{1}{2}$, and those pointing downward represnt $m_s = -\frac{1}{2}$. Each horizontal line represents a p orbital, and m_l values are indicated under each orbital. (CC-BY-NC; Kathryn Haas)

Just as individual electrons have quantum numbers (n, l, m_l, m_s), the electronic states of atoms have quantum numbers (L, M_l, M_s, S, J). Each individual microstate in Figure 11.2.1 can be described by quantum numbers M_l and M_s. The values of total angular momentum (L), and total intrinsic spin (S) arise from sets of microstates, and are related to quantum numbers M_l and M_s for individual microstates. The relative energies of the terms for 3d metals and other light atoms can be predicted (roughly) by Hund's Rules, according to values of S and L. These atomic quantum numbers and Hund's rules are described below.

A closer look at electronic spectra

Let us take a closer look at optical absorption spectra, also called electronic spectra, of coordination compounds. We have previously argued that ligand field theory can predict and explain the electronic spectra. However, ligand field theory (LFT) is sufficient to explain the spectra in only a few cases. For example the $[\mathrm{Ni(H_2O)_6}]^{2+}$ ion is an octahedral d^8-complex ion. According to LFT, the metal d-orbitals in an octahedral field are the t_{2g} and the e_g–orbitals (Figure $11.2.2$). Six electrons are in the t_{2g} orbitals, and two electrons are in the e_g orbitals (Figure $11.2.2$). Ligand field theory (LFT) would predict that there is one electron transition possible, namely the promotion of an electron from a t_{2g} into an e_g orbital. This process would be triggered by the absorption of light whereby the wavelength of the light would depend on the Δ_o between the t_{2g} and the e_g orbitals. Overall, this should lead to a single absorption band in the absorption spectrum of the complex. We can check this prediction by experimentally recording the absorption spectrum of the complex (Figure $11.2.2$).

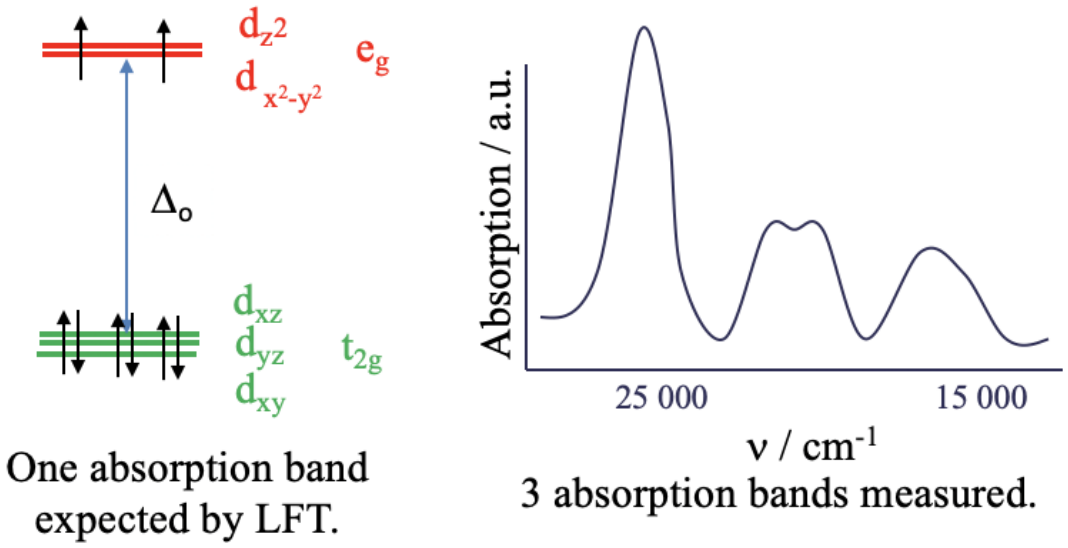


Figure $11.2.2$. Electron transition according to LFT and actual absorption spectrum of the $[\mathrm{Ni(H_2O)_6}]^{2+}$ complex ion. Attribution: E.R. Schofield.

What we find is that the absorption spectrum is far more complex than expected. Instead of just a single absorption band there are multiple ones. Obviously, LFT is unable to explain this spectrum. The question is: why? The answer is: LFT assumes that there are no electron-electron interactions. However, in reality there is repulsion between electron in d-orbitals and this has an effect on their energy. And, electrons within the d-subshell, for example, repel each other to different extents depending on the relative orientations of their orbitals in space.

To illustrate how electrons in different orbitals might have different interactions, let's consider the case of a d^2 excited state in an octahedral ligand field (Figure $11.2.3$).

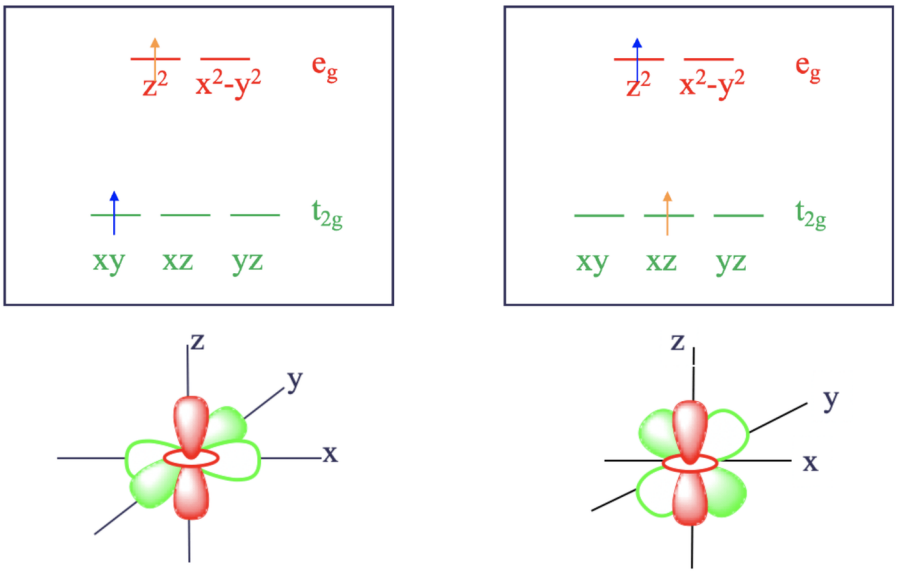


Figure 11.2.3: Two microstates with different energies for a d^2 ion in an octahedral ligand field. Electron configurations of two different microstates are shown on the top, and the orbitals associated with each shown underneath each configuration. Left: An excited microstate with one electron in the d_{xy} orbital (shown in green) and one electron in the d_{z^2} (shown in red). Right: An excited microstate with one electron in the d_{xz} orbital (shown in green) and one electron in the d_{z^2} (shown in red).

According to LFT, both electrons would be in the t_{2g} orbitals in the ground state. For instance, they could be in the microstate where one electron is in d_{xy}, and the other is in the d_{xz} orbital (not pictured). This configuration is called a microstate of a state because there are other combinations of orbitals possible. For example, the ground state would also be realized by a microstate in which the electrons were in the d_{xz} and the d_{yz} orbitals. Upon absorption of light, the electron in the d_{xy} orbital could be excited into one of the higher-energy e_g orbitals. That excited electron could occupy either the d_{z^2} or the $d_{x^2-y^2}$ orbitals. Those two possibilities reflect two different microstates associated with the excited state. For a moment, let's assume that the excited electron goes into the d_{z^2} orbital. In this microstate one electron would be in the d_{xz} orbital and the other one in the d_{z^2} orbital (Figure 11.2.3, right). There is another possibility for how to excite an electron from the ground state. We could assume that instead of the d_{xy} electron being promoted, the d_{xz} electron gets promoted. In this case, we would realize a microstate in which one electron in the d_{xy} orbital and the other one in the d_{z^2} orbital (Figure 11.2.3, left).

Now let us compare the two cases shown in Figure 11.2.3. Ligand field theory would argue that both excited microstates have the same energy. However, in fact they do not. Why? It is because the electrons in the first excited microstate interact differently than those of the second excited microstate. This difference becomes plausible when considering the orbital shapes and orientations (Figure 11.2.3, bottom). The d_{xz} orbital has electron density on the z-axis, while the d_{xy} orbital is perpendicular to d_{z^2}. The different relative orientations of d_{xy} and d_{xz} with respect to d_{z^2} cause electrons in the d_{z^2} orbital to interact differently with an electron in a d_{xy} than in a d_{xz}. As a result, the two excited microstates do not have the same energy. In other words, to achieve either of these different excited microstates from the ground state, we need different amounts of energy. Thus, the complex would absorb light with different energies (or wavelengths). This is in contrast to what LFT predicts.

If LFT cannot predict the number of electronic transitions, then how can we correctly predict how many absorption bands we get? The answer is, we must find all possible microstates for the d^2 electron configuration and group together those with the same energy. A group of microstates with the same energy is called a **term**. *The number of electron transitions can then be predicted from the number of terms.*

Quantum Numbers

The table below summarizes the quantum numbers of atoms (individual microstates and sets of microstates). You may wish to review the quantum numbers for individual electrons and then refer to this table as you read this and the next sections. Recall the meanings of the quantum numbers for individual electrons (n, l, m_l, m_s that were described in a previous section (Section 2.2.2).

Symbol	Name	Allowed Range	Comment
L	Total Orbital Angular Momentum	$\|l_1 + l_2\|, \|l_1 + l_2\text{-}1\|, \ldots, \|l_1\text{-}l_2\|$	Total *orbital* angular momentum of a *collection of microstates*, designated as S, P, D, F..etc
S	Total Intrinsic Spin	$\|m_{s1} + m_{s2}\|, \|m_{s1} + m_{s2}\text{-}1\|, \ldots, \|m_{s1}\text{-}m_{s2}\|$	Total spin of a *collection of microstates*
M_l	Magnetic Quantum Number	$L, L-1, L-2, \ldots, -L$	Direction of total angular momentum for an individual microstate
M_s	Spin Magnetic Quantum Number	$S, S-1, S-2, \ldots -S$	Total spin of electrons for an individual microstate
J	Total Angular Momentum	$L+S, \ldots, \|L-S\|$	Total angular momentum

Quantum Numbers S and L for sets of microstates

The quantum numbers S and L represent sets of microstates. Once these values are found, they can be ordered in terms of relative energies, first according to the value of S, then L.

Total Orbital Angular Momentum Quantum Number: L

L gives the total sum of orbital angular momentum vectors in a multielectron atom. The possible values of L can be found from the values of l for individual electrons in the system. For example, in a system with two electrons with values of m_{l_1} and m_{l_2}, the possible values of L are:

$$L = \sum_i^n m_{l_i} = |m_{l_1} + m_{l_2}|, |m_{l_1} + m_{l_2}\text{-}1|, \ldots, |m_{l_1}\text{-}m_{l_2}| \tag{11.2.1}$$

The absolute value symbols indicate that L cannot be a negative value. The values of L correspond to different energy levels for groups of microstates. Microstates with values of $L = 0, 1, 2, 3\ldots$ correspond to symbols $S, P, D, F\ldots$ respectively. This is analogous to the relationship between the electron quantum number, l, and the $s, p, d, f..$ orbital subshells. However, the capital letters used for microstates do not indicate orbital or subshell assignments for the electrons.

The Total Intrinsic Spin Quantum Number: S

The sum total of the spin vectors of all of the electrons is called S. The values of S are computed from m_s in a manner very similar to how L is computed from m_l. Because S measures the magnitude of a vector, it cannot be negative. For a system with two electrons, each with spin m_{s1}, and m_{s2}, the possible values of S are given below.

$$S = \sum_i^n m_{si} = |m_{s1} + m_{s2}|, |m_{s1} + m_{s2}\text{-}1|, \ldots, |m_{s1}\text{-}m_{s2}| \tag{11.2.2}$$

The possible values of S fall into a series that depend on whether there are an odd or even number of electrons.

- Odd number of electrons: $S = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots$
- Even number of electrons: $S = 0, 1, 2, 3, \ldots$

Example 11.2.1 : Total Orbital Angular Momentum of Carbon

What are the possible L values for the electrons in the $1s^2 2s^2 2p^2$ configuration of carbon?

Solution

Both electrons (i.e., the 2p electrons) are $l = 1$. The possible combinations are 0, 1, and 2 corresponding to symbols S, P, and D, respectively.

Example 11.2.2 : Total Orbital Angular Momentum of Unknown Species

What are the possible L values for the electrons in the $[Xe]6s^2 4f^1 5d^1$?

Solution

We can ignore the electrons in the $[Xe]$ core and the electrons in the $6s$ block. So all we have to consider is the lone f electron ($l = 3$) and the lone d electron ($l = 2$).

The two extremes for possible L values are $3 + 2 = 5$ and $3\text{-}2 = 1$.

Thus, possible values of L for this Xe atom are 5(H), 4(G), 3(F), 2(D), and 1(P).

Example 11.2.5 : The Hydrogen Ground State

Find S for $1s^1$.

Solution

S must be $\frac{1}{2}$, since that's the spin of a single electron and there's only one electron.

Example 11.2.6 : The Beryllium Excited State

Find S for $1s^2 2s^1 2p^1$.

Solution

$S = 1, 0$

Example 11.2.7 : The Carbon Ground State

Find S for carbon atoms with the $1s^2 2s^2 2p^2$ electron configuration.

Solution

$S = 1, 0$ This is the same as the previous problem. Notice that S is not affected by which orbitals are occupied by electrons. S depends only on the number of unpaired electrons. These are usually the electrons in partially-filled subshells (i.e., unpaired electrons in open shells).

Example 11.2.8 : The Nitrogen Ground State

Find S for nitrogen atoms with the $1s^2 2s^2 2p^3$ electron configuration.

Solution

S can be $S = \frac{3}{2}, \frac{1}{2}$.

Quantum numbers M_l and M_s for individual microstates

Once S and L are found, the allowed values of M_l and M_s can be calculated.

The Total Magnetic Quantum Number: M_l

The Total Magnetic Quantum Number M_l is the total z-component of all of the relevant electrons' orbital momentum. While L describes the total angular momentum in the system, M_l tells you which direction it is pointing. L can be assigned to a collection of microstates, but M_l is unique to a specific microstate in that group. Unlike L, M_l is allowed to have negative values. The possible values of M_l are integer values ranging from the largest positive sum to the most negative sum of possible m_l values:

$$M_l = L, L-1, L-2, ..., -L \tag{11.2.3}$$

For the p^2 case, the m_l values of p orbitals are $-1, 0, +1$. The largest value of M_l would come from a state where both electrons occupy $m_l = +1$, thus the maximum is $M_l = L = 2$. Likewise, the minimum value of M_l comes from both electrons occupying $m_l = -1$ to give $M_l = -L = -2$. The possible M_l values for p^2 are the series of integer values $+2, +1, 0, -1, -2$.

It is worth noting that there are values of M_l that are forbidden due to the Pauli exclusion principle. For example, the value of $M_l = +3$ could only come from three electrons occupying the $m_l = +1$ orbital. That is impossible because more than one electron would possess the same set of electron quantum numbers.

The Total Spin Magnetic Quantum Number: M_s

M_s is the sum total of the z-components of the electrons' inherent spin in an individual microstate. The difference between S and M_s is subtle, but important. M_s indicates the total z-component of the electrons' spins, while S indicates the entire resultant vector. It is also distinct from M_l, which is the sum total of the z-component of the *orbital angular momentum*. M_s can be computed from S, as shown below. Note that while S must be positive, M_s can have negative values.

$$M_s = S, S-1, S-2, ... -S \tag{11.2.4}$$

For the p^2 case, the possible values of M_s are $M_s = +1, 0, -1$. The value $M_s = +1$ comes from the sum of two electrons with spin "up", $m_s = +\frac{1}{2}$. The value $M_s = -1$ comes from the sum of two electrons with spin "down", $m_s = -\frac{1}{2}$. And the value $M_s = 0$ comes from the sum of one electron with $m_s = +\frac{1}{2}$ and the other with $m_s = -\frac{1}{2}$.

There are some values of M_s that will be forbidden, but not in the case of p^2. However in the case of a p^4, for example, the value M_s =2 is forbidden because there is no way to put four "up" electrons in three orbitals without violating the Pauli exclusion principle.

Example 11.2.3 : Total Magnetic Quantum Number of the Zirconium Ground State

What are the possible values M_l of a zirconium atom with the $[Kr]5s^24d^2$ electron configuration?

Solution

Both open-shell electrons (i.e., the 4d electrons) are $l = 2$, so the values are 4, 3, 2, 1, 0, -1, -2, -3, -4.

Example 11.2.4 : Total Spin Magnetic Quantum Number of the Carbon Ground State

What are the M_s values for $1s^22s^22p^2$?

Solution

This system is paramagnetic, with two unpaired electrons in the $2p$ orbital. The three p orbitals have values of $m_s = -1, 0, 1$. The maximum value of $M_s = +1$ would come from the two electrons occupying $m_{s_1} = +1$ and $m_{s_2} = 0$. The minimum value, $M_s = -1$ would come from the two electrons occupying $m_{s_1} = -1$ and $m_{s_2} = 0$. Thus, the possible values for the total spin magnetic quantum number are $M_s = 1, 0,$ -1, where the value of $M_s = 0$ comes from a configuration where, for example, $m_{s_1} = +1$ and $m_{s_2} = -1$.

Example 11.2.4 : Total Spin Magnetic Quantum Number of the Nitrogen Ground State

What are the M_s values for $1s^2 2s^2 2p^3$?

Solution

$M_s = +\frac{3}{2},\ +\frac{1}{2},\ -\frac{1}{2},\ -\frac{3}{2}$

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11.2.1: Finding Microstates and Term Symbols

Constructing "Free Ion" Term Symbols and their Relative Energies

The different electronic states of an atom or ion are described by L and S in the form of a **term symbol** (Figure $11.2.1.1$). Keep in mind that M_l is related to L, and M_s is related to S, and in some cases their values are equal.

One term symbol can describe one or more microstates with the same energy. The free ion terms are useful in the interpretation of electronic spectra. These term symbols are also commonly called *free ion terms (*or *Russell-Saunders terms*) because they describe the atomic or ionic state, free of any ligands. The term symbol indicates the total orbital angular momentum of the atom, (L), and the multiplicity, $(2S+1)$, of the state. The multiplicity can be found with the formula, $(2S+1)$, but it is also equal to the number of unpaired electrons plus one.

Misplaced '#'

The generic form of a free ion term symbol is shown in Figure $11.2.1.1$. Recall that $L = 0, 1, 2, 3...$ is denoted by a capital letter $S, P, D, F...$, respectively. The latter designation for L is used in the term symbol.

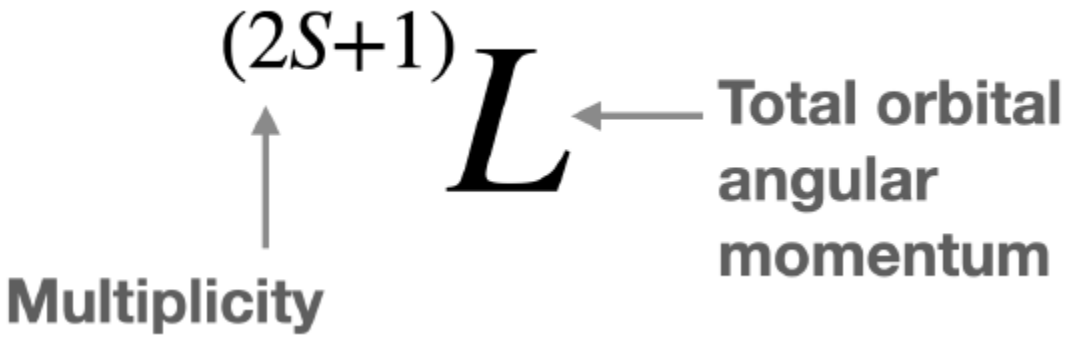


Figure $11.2.1.1$: A term symbol of the free ion takes the form ${}^{(2S+1)}L$, where L is the total orbital angular momentum quantum number, and S is the total intrinsic spin quantum number. The value $2S+1$ is called the multiplicity. (CC-BY-NC; Kathryn Haas)

Example 11.2.1.1 : Hydrogen Ground State

What is the free ion term symbol of an H atom in the ground state ($1s^1$)? How many microstates are there for the ground state hydrogen atom? Comment on the degeneracy and multiplicity of the state.

Solution

There is only one electron in a s orbital. That electron must have $l = 0$, and s could be either $+\frac{1}{2}$ or $-\frac{1}{2}$. This is two possible microstates, one with spin "up" and one with spin "down". In either case there is only one value of the total intrinsic spin quantum number, $S = +\frac{1}{2}$. Therefore, the only possible value of spin multiplicity is Multiplicity $= 2 \times (+\frac{1}{2}) + 1 = 2$. The s orbital corresponds to $l = 0$, so $L = 0$, or S. Thus the term symbol is ${}^2S$.

There are two possible microstates of the ground state (both represented by the ground state term). One microstate has $m_s = +\frac{1}{2}$ and the other has $m_s = -\frac{1}{2}$.

The question about degeneracy specifically asks about degeneracy of *the state*. Let's give the most complete answer possible. In terms of energy levels (the ground state in this case), there are two microstates with approximately equal (degenerate) energy, thus the degeneracy of the state is two (2) and is the same as the multiplicity $(2S + 1 = 2)$. However, sometimes we also refer to the "degeneracy" of electron configurations. It is important to recognize that ground state electron

configuration with $M_s = m_s = +\frac{1}{2}$ is singly degenerate, and the same is true for $M_s = m_s = -\frac{1}{2}$. Recognising degeneracy of electron configurations will be useful later in this chapter because the degeneracy of an electron configuration can be helpful for interpreting term symbols in an octahedral field.

Exercise 11.2.1.1

Find the term symbols for the following cases:

a. $L = 0,\ S = 0$
b. $L = 0,\ S = \frac{1}{2}$
c. $L = 1,\ S = 1$
d. $L = 2,\ S = \frac{3}{2}$
e. $L = 3,\ S = 2$

Answer available at the end of this section.

Finding all possible microstates for an atom or ion

What are the possible microstates and the overall number of microstates for a free ion with d^2-electron configuration? We can express this in a so-called microstate table (11.2.1.2).

M_s \ M_L	-4	-3	-2	-1	0	+1	+2	+3	+4
-1	Not possible (Pauli principle)	$-2^{-}\ -1^{-}$	$-2^{-}\ 0^{-}$	$-2^{-}\ 1^{-}$ $-1^{-}\ 0^{-}$	$-2^{-}\ 2^{-}$ $-1^{-}\ 1^{-}$	$-1^{-}\ 2^{-}$ $0^{-}\ 1^{-}$	$0^{-}\ 2^{-}$	$1^{-}2^{-}$	Not possible (Pauli principle)
0	$-2^{-}\ -2^{+}$	$-2^{-}\ -1^{+}$ $-2^{+}\ -1^{-}$	$-2^{-}\ 0^{+}$ $-2^{+}\ 0^{-}$ $-1^{-}\ -1^{+}$	$-2^{-}\ 1^{+}$ $-2^{+}\ 1^{-}$ $-1^{-}\ 0^{+}$ $-1^{+}\ 0^{-}$	$-2^{-}\ 2^{+}$ $-2^{+}\ 2^{-}$ $-1^{-}\ 1^{+}$ $-1^{+}\ 1^{-}$ $0^{-}\ 0^{+}$	$-1^{-}\ 2^{+}$ $-1^{+}\ 2^{-}$ $0^{-}\ 1^{+}$ $0^{+}\ 1^{-}$	$0^{-}\ 2^{+}$ $0^{+}\ 2^{-}$ $1^{-}\ 1^{+}$	$1^{-}2^{+}$ $1^{+}2^{-}$	$2^{-}\ 2^{+}$
+1	Not possible (Pauli principle)	$-2^{+}\ -1^{+}$	$-2^{+}\ 0^{+}$	$-2^{+}\ 1^{+}$ $-1^{+}\ 0^{+}$	$-2^{+}\ 2^{+}$ $-1^{+}\ 1^{+}$	$-1^{+}\ 2^{+}$ $0^{+}\ 1^{+}$	$0^{+}\ 2^{+}$	$1^{+}2^{+}$	Not possible (Pauli principle)

Figure 11.2.1.2. d^2 electron configuration microstate table. This table is organized with M_l values increasing horizontally and M_s values decreasing vertically. You may see different ways to organize a microstate table, and there is no wrong orientation to use, as long as you can use it to correctly find and organize microstates. Each microstate is indicating using notion $(m_l)^{m_s}$, where only the sign of m_s is indicated for simplicity. For example, an electron in $m_l = -2$ with $m_s = +\frac{1}{2}$ is notated -2^{+}.

You can see the microstate table for the d^2 electron configuration depicted above. Each column represents a possible value M_l. For the d^2 configuration, M_l can adopt values from -4 to +4, hence there there are 9 columns. Each row represents possible M_s value. For the d^2 electron configuration, M_s can vary between +1 and -1. $M_s = +1$ means both electrons have the spin $+\frac{1}{2}$, $M_s = 0$ means one electron has the spin $+\frac{1}{2}$ and the other one has the spin $-\frac{1}{2}$. The $M_s = -1$ value is adopted when both electrons have the spin $-\frac{1}{2}$. Now we can combine each M_s value with each M_l value, which defines a particular field in the table. You can see that some fields are empty due to the Pauli principle. For example, the field for $M_l = -4$ and $M_s = -1$ is not filled because in this case both electrons would have the same quantum numbers, namely $m_l = 2$, and $m_s = -\frac{1}{2}$. We can further see that for some fields only one combination of electrons is possible, while for others there are multiple possible microstates. For example, for the field with $M_l = 4$ and $M_s = 0$ there is only one combination of electrons possible. You can see the notation "$2^{-}2^{+}$" in this field. This means that the first electron has an m_l value of 2 and a spin of $-\frac{1}{2}$ and the second electron also has an m_l value of 2 and an m_s value of $+\frac{1}{2}$. The most populated field is the field for $M_l = 0$ and $M_s = 0$; there are overall five microstates with that

combination of M_l and M_s values. If we count the overall number of microstates in the table then we arrive at the number 45. This is consistent with what we would expect according to the following formula.

Misplaced '#'

In our example L=4 and S = 1, and thus the number of microstates is: $((2x4)+1)((2x1)+1)=45$. **In general for a d^n electron configuration with n d-electrons, the number of microstates is $(10!)/((10-n)!n!)$.**

One useful property of a microstate table is that we can derive all possible terms and term symbols for a particular electron configuration from it. For simplification's sake, we indicate a possible microstate in the table in Figure $11.2.1.5$ just by an "x". Then we draw the largest possible rectangular box into the microstate table that contains only fields with at least one possible electron combination (Figure $11.2.1.5$).

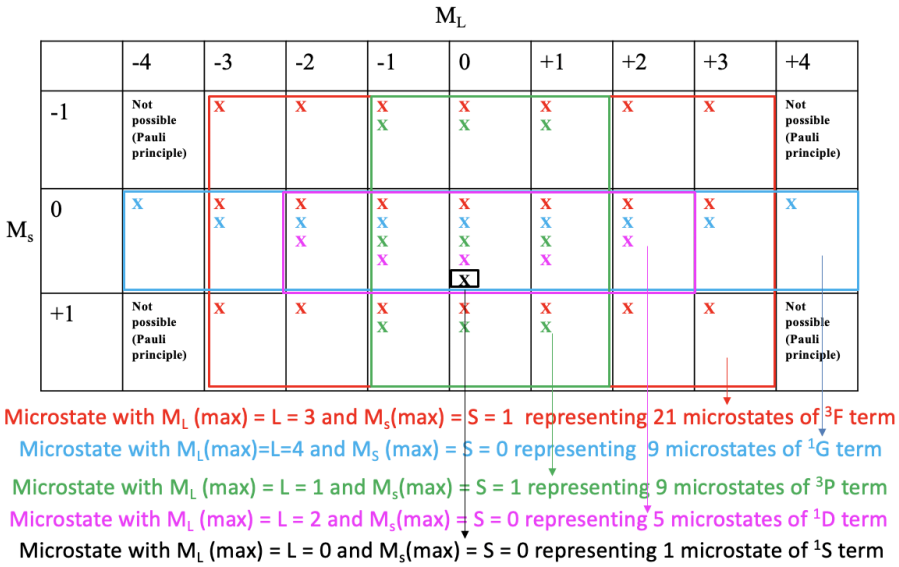


Figure $11.2.1.5$. Deriving the terms and term symbols for the d^2 electron configuration from the microstate table

You can see that the largest possible box is the red box drawn (Figure $11.2.1.5$). This box contains the microstates that belong to the first term of the electron configuration d^2. The number of microstates is equal to the number of fields within the red box. That makes $7 \times 3 = 21$ microstates. What is the term symbol for this term? In order to answer this question we need to find the microstate in the red box that has the highest M_l and the highest M_s value. You can see that it is the one with $M_l = 3$ and $M_s = 2$. Thus, L=3 and S=1. This defines the term as a ^{3}F term because 2S+1 = 3, and L=3 corresponds to the term symbol F. This term is a triplet term. Note that a triplet term also includes microstates with opposite spins. Overall seven of the 21 microstates have $M_s = 0$.

Next, we look what is the next-largest rectangular box we can draw, and which contains microstates we did not consider yet. We can see that the blue box contains nine fields equaling nine microstates. The microstate within this box that has the highest M_l and M_s values is the one with $M_l = 4$ and $M_s = 0$. This defines a ^{1}G term. This is a singlet term. Note that a singlet term ONLY has microstates with paired spins (M_S=0).

There is another rectangular box which also contains nine microstates. It is the green one. The microstate with the highest M_l and M_s values is the one with $M_l = 1$ and $M_s = 1$. Thus, $L = 1$, and $2S + 1 = 3$, which defines a ^3P term. Note that despite this being a triplet term, which indicates two unpaired electrons (\S=1\), the term also contains three microstates that have opposite spins with a total $M_s = 0$.

The next-largest box is the purple one containing five fields and five microstates. What is the term with the highest M_l and M_s values? It is the one with $M_l = 2$ and $M_s = 0$. This means that L=2 and S=0, which defines a ^{1}D term, a singlet term with only microstates with paired spins. There is one microstate left that we did not consider thus far, the one with $M_l = 0$ and $M_s = 0$. These are the highest M_l and M_s values because there is no other microstate. Thus, this term contains only one microstate and the term symbol is ^1S. Now we have found all the terms and term symbols.

Example 11.2.1.2 : Boron

What are the possible term symbols for $1s^2 2s^2 2p^1$ electronic configuration of boron? Which is the ground state?

Solution

We only need to consider the one electron in the $2p$ orbital, since that is the only open shell electron. For one electron, there is only one value of $S = ½$, so multiplicity must be $2S + 1 = 2$. The possible values of L for one electron in a p orbital are $L = 0, 1$ (or S, and P terms). This gives the free ion term symbols ^2P and ^2S. Both of these terms have multiplicity of 2, so the ground state would be the one with the highest value for L. The ground state term is ^2P.

Example 11.2.1.3 : Beryllium Excited State

What are the term symbols for the $1s^2 2s^1 2p^1$ excited-state electronic configuration of Beryllium?

Solution

The term symbols will be of the form ^1P and ^3P. For the ^1P state, $L = 1$ and $S = 0$, so the total angular momentum $J = 1$. For the second state, $L = 1$ and $S = 1$, so the possible values of $J = 2, 1, 0$. There are four microstates for this configuration with term symbols of $^1P_1$ and $^3P_2$, $^3P_1$, and $^3P_0$.

Finding The Ground State Term

...from a list of microstates

Each term symbol represents an atomic state with an associated energy level. If you have found all the possible microstates using a microstate table, and have identified their terms, then the term with the lowest energy (ie the ground state) can be found using Hund's first two rules. In abbreviated form, Hund's rules state...

1. The lowest energy electron configuration has the maximum multiplicity (the maximum number of unpaired electrons).
2. For a given multiplicity, the configuration with the largest total orbital angular momentum (L) value has the lowest energy.

In the case of the p^2 carbon atom (see Figure $11.2.1.1$), the lowest energy state would have a multiplicity of 3 (two unpaired electrons). Of the states with a multiplicity of 3, the largest value of L is 1 (and thus, P). Thus, the ground state term for carbon is ^3P. These rules are reliable for identifying the ground state term for any atom, but have limited use for ordering relative energies outside of the ground state for 3d metal ions and other light atoms. For heavier atoms (e.g., 4d metals) another type of interaction, called jj coupling must be considered, but this is outside the scope of this discussion. **Tip:** There is a deep symmetry that connects different electronic configurations. It turns out that a p^1 configuration has the same term symbols as a p^5. Similarly, $p^2 = p^4$. A similar relationship can be used to figure out high electron number term symbols for the d and f orbitals.

...if you just want the find Ground State term

To assign transitions in an electronic spectrum, we should know the ground state term, as well as all other terms and their relative energies for a given atom or ion. However, the identification of all possible terms becomes tedious with more than one or two electrons in the d orbitals. Fortunately, there are tools (like correlation diagrams) that can help us find all terms for an atom or ion, as long as the ground state term can be identified. Here is a quick shortcut for finding the ground state term for transition metal complex with partially-filled d shell.

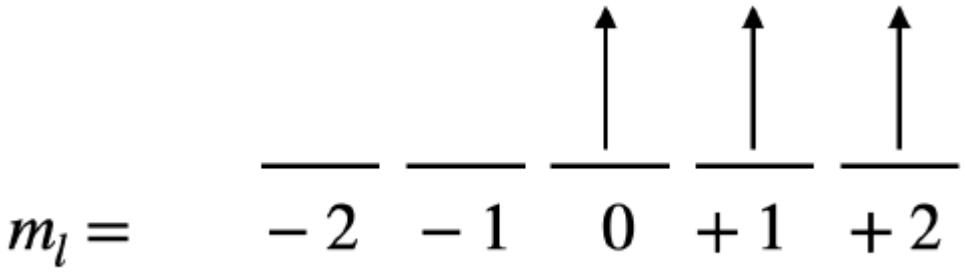
Quickly find the ground state free ion tern

In this case, we'll focus on transition metal d-orbitals. To begin, you'll need to know the metal ion identity and its oxidation state. These instructions assume that the d orbital is the only shell that is partially filled.

1. Determine the number of d-electrons.
2. Then fill these electrons into an electron orbital diagram of five degenerate orbitals, putting electrons into the highest value of m_l first, and filling orbitals with single electrons before pairing them (just as you may have done in an introductory chemistry course).
3. Calcuate the total intrinsic spin (\S\) and spin multiplicity using the diagram drawn in #2.
4. Calculate L using the diagram drawn from #2.
5. Write the term symbol for the ground state.

Let's use the example of the $[\mathrm{Cr(NH_3)_6}]^{3+}$ complex ion, and determine its ground state term following the shortcut described above.

1. Determine the number of d-electrons.
   $[\mathrm{Cr(NH_3)_6}]^{3+}$ contains Cr^{3+}, which is a d^3 metal ion. There are three d electrons.
2. Draw a diagram of five degenerate d orbitals, with m_l values labeled. Fill in the electrons to maximize m_s and m_l.



3. Calculate spin multiplicity (should be the maximum possible value!).
   $S = m_{s_1} + m_{s_2} + m_{s_3} = +\frac{1}{2} + +\frac{1}{2} + +\frac{1}{2} = \frac{3}{2}$
   Spin multiplicity = $2S + 1 = 2\frac{3}{2} + 1 = 4$
4. Calculate L (should be the maximum possible value after spin is maximized.
   $L = m_{l_1} + m_{l_2} + m_{l_3} = 2 + 1 + 0 = 3$
5. Write the ground state free ion term:
   ${}^{(2S+1)}L = {}^4F$

Exercise 11.2.1.2

Earlier on this page, you found all the terms for a d^2 metal ion. Use both of the methods (Hund's rule, and the shortcut method) described here to identify the ground state term for d^2.

Answer available at the end of this section.

Exercise 11.2.1.3

Find the ground state free ion terms for the metal ions in the following cases:

(a) $[\mathrm{Ti(H_2O)_6}]\mathrm{Cl_2}$

(b) $[\mathrm{Ti(NH_3)_6}]\mathrm{Cl_3}$

(c) $[Cu(H_2O)_6]Cl_2$

Answer available at the end of this section.

Answers

Exercise 11.2.1.1

(a) ^1S
(b) ^2S
(c) ^3P
(d) ^4D
(e) ^5F

Exercise 11.2.1.2

Using Hund's rule: The terms identified for d^2 are ^3F, ^1G, ^3P, ^1D, and ^1S. Hund's first rule tells us that either ^3F or ^3P could be the ground state because these two terms have the highest multiplicity. Hund's second rule tells us that ^3F must be the ground state because it has the largest value of L.

Using the shortcut: The drawing is shown below, with one electron in $m_l = +2$ and the second electron in $m_l = +1$. Both electrons are unpaired with $m_s = +\frac{1}{2}$. This gives $L = 3$ or an F term. And, $S = 1$ with a multiplicity of 3. The ground state term is ^3F.

Exercise 11.2.1.3

(a) Ti^{2+} is a d^2 metal ion, ^3F
(b) Ti^{3+} is a d^1 metal ion, ^2D
(c) Cu^{1+} is a d^9 metal ion, ^2D. Note that d^9 and d^1 are related by the symmetry of their electronic states.

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11.2.2: Spin-Orbit Coupling

The magnetic fields created by S and L are not isolated from one another; they interact through **spin-orbit coupling** *(aka Russell-Saunders coupling)*. We will consider only this simple form of coupling in this text. Its application is limited to the elements with $z < 40$, including the first row of the transition elements. In the case of heavier elements, we must also consider jj coupling; however, we will not discuss the latter here.

In the Russell-Saunders spin-orbit coupling scheme, the interaction between S and L is expressed by an additional quantum number, the total angular momentum quantum number (J). The possible values of J are values between $L + S$ and $|L - S|$.

$$J = L + S,\ L + S - 1,\ L + S - 2,\ ...,\ |L - S| \tag{11.2.2.1}$$

A value of J must be positive or zero for a multielectron system. J values can fall into series $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, ...$ or $0, 1, 2, ...$ The quantum number J is added to the term symbol as a subscript to the right of the letter describing the term. A full term symbol is as follows:

$$^{(2S+1)}L_J \tag{11.2.2.2}$$

The result of spin-orbit coupling is that a term for the free ion is split into states of different energies. For example, a ^3P state of a carbon atom with a p^2 electron configuration would be split into three different energy states (according to the three possible J values 0, 1, and 2): $^3P_0$,$^3P_1$,$^3P_2$.

The relative energies of the states can be predicted from Hund's Third Rule.

Hund's third Rule:

- For subshells that are less than half-filled, the lowest energy state has the lowest J value.
- For subshells that are exactly half-filled, there is only one J value, thus it is the lowest energy.
- For subshells that are more than half-filled, the lowest energy state has the largest J value.

Thus, in this case where the p subshell is less than half full, the lowest energy state from the ^3P free ion term would be that with $J = 0$, $^3P_0$, followed by $J = 1$ and $J = 2$. The splitting and relative energies are depicted in Figure 11.2.2.1. Spin-orbit coupling and the splitting of the free ion terms have important implications for electronic spectra because they affect the energies of electronic transitions.

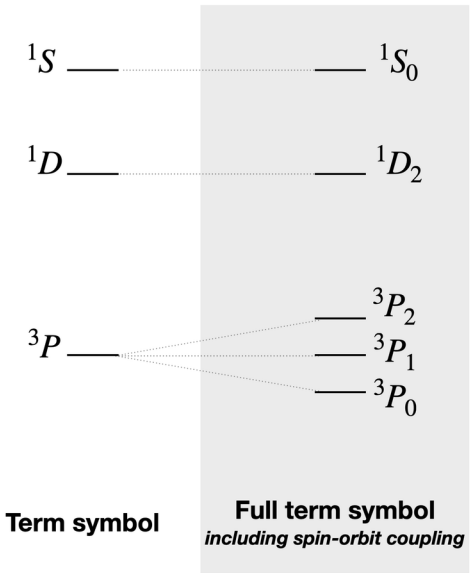


Figure 11.2.2.1: The effects of spin-orbit (Russell-Sauders) coupling on the "free ion" term symbols for. Energy splitting not shown to scale. (CC-BY-NC; Kathryn Haas)

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11.3: ELECTRONIC SPECTRA OF COORDINATION COMPOUNDS

Types of transitions related to the metal ion:

1. **d-d transitions**: d-d transitions are electronic transitions that occur between the molecular orbitals (MOs) that are mostly metal in character: specifically, the orbitals that we think of as the d-orbitals of a transition metal complex. These transitions are useful in determining the energy of splitting and can be used to indicate coordination chemistry (geometry and ligand sets). In octahedral complexes, d-d transitions occur between the t_{2g} and e_g orbitals (across Δ). These transitions cannot occur in metal complexes where the d-orbital is completely empty (d^0) or completely full (d^{10}). In other words, a d-d transition is only possible in $d^1 - d^9$ metal ions. In a UV-visible absorption spectrum, d-d transitions appear as relatively weak absorptions with extinction coefficients (ε) less than 1,000.
2. **Charge transfer (CT) transitions**: Charge transfer transitions occur between MOs that are mostly metal in character and those that are mostly ligand in character. These transitions depend on the type of ligand: they occur only when the metal is bound to ligands that are π-donors or π-acceptors. And there are two types of CT transitions. If the metal is bound to a π-donor ligand, electrons from lower-energy MO's that are mostly ligand in character can become excited to MO's that are mostly metal in character. These are **ligand to metal charge transfers (LMCT) transitions** (Figure 11.3.1, left diagram). If the the metal is bound to ligands that are π-acceptors, electrons from the MO's that are mostly metal in character can become excited to higher-energy orbitals that are mostly ligand in character. These are **metal to ligand charge transfer (MLCT)** transitions (Figure 11.3.1, right diagram). In a UV-visible absorption spectrum, CT transitions appear as relatively intense absorptions with extinction coefficients (ε) much greater than 1,000.

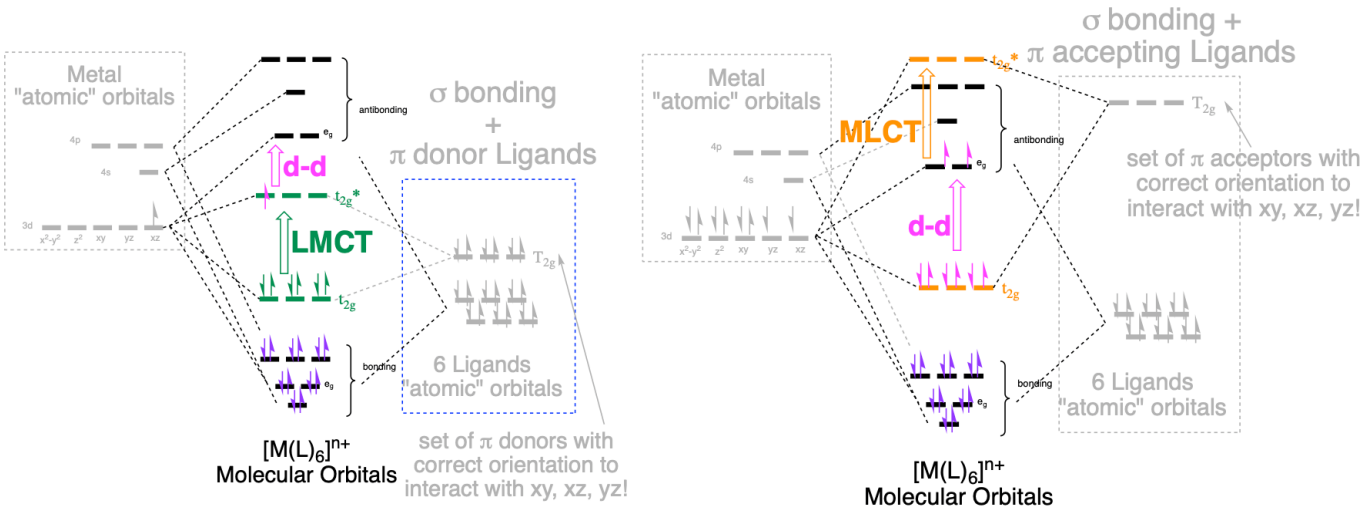


Figure 11.3.1: Abbreviated and annotated MO diagrams for example cases of metal ions in octahdral geometry with sets of π-donor and π-acceptor lignads. In both example MO diagrams, d-d transitions are shown (pink, open arrow from t_{2g} to e_g). **Left:** LMCT transitions are possible with π-donor ligands when electrons are excited from MOs that are mostly ligand in character to MOs that are mostly metal in character. An example of LMCT is shown (green, open arrow from t_{2g} to $t*_{2g}$). **Right:** MLCT transitions are possible with π-acceptor ligands when electrons from MOs that are mostly metal in character are excited to orbitals that are mostly ligand in character (the π^* orbitals from ligands). An example MLCT is shown ((orange, open arrow from e_g to $t*_{2g}$).

11.3.1: Selection Rules
11.3.2: Correlation Diagrams
11.3.3: Tanabe-Sugano Diagrams
11.3.4: Symmetry labels for split terms
11.3.5: Applications of Tanabe-Sugano Diagrams
11.3.6: Tetrahedral Complexes
11.3.7: Charge-Transfer Spectra
11.3.8: Applications of Charge-Transfer

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11.3.1: Selection Rules

Electronic transitions between states of different energies give rise to electronic spectra. However, some transitions are more probable, and thus more intense, than others. In UV-vis spectroscopy, for example, the transitions that are "allowed" can give rise to absorption bands that are much more intense than transitions that are "forbidden". To be clear, "forbidden" transitions are still possible, and are sometimes observable, but are less intense because they happen less frequently than "allowed" transition when the molecules are exposed to electromagnetic radiation.

Selection Rules that govern Electronic Transitions

The Selection Rules governing transitions between electronic energy levels (including microstates and terms) are:

1. **The Spin Selection Rule**, $\Delta S = 0$.
2. **The Laporte (or orbital) Selection Rule**, for centrosymmetric molecules $g \rightarrow u$ or $u \rightarrow g$, or $\Delta l = \pm 1$.

Selection rules that govern electronic transitions

Spin selection rule

The Spin Selection Rule forbids transitions between states with different total spin, and thus different spin multiplicity. This rule allows transitions only between states with the same total intrinsic spin ($\Delta S = 0$), and thus the same spin multiplicity value in the term symbol. In other words, the direction of the promoted electron's spin should not change. Just in case it is not obvious yet, the spin multiplicity is the left superscript in the term symbol, so this rule allows transitions between terms with the same superscript. For example, this rule would allow a transition from a ${}^3T$ term to a ${}^3A$ term, but not from ${}^3T$ to ${}^2D$.

Laporte (orbital) Selection Rule

The Laporte Selection Rule applies to molecules that have a center of symmetry (aka center of inversion, centrosymmetric). This rule forbids transitions between states with the same parity (symmetry) with respect to an inversion center (i). Parity is indicated on molecular orbitals and on term symbols with subscripts g (gerade, or even) and u (ungerade, or uneven). Transitions between u and g terms are allowed (eg $T_{2g} \rightarrow T_{1u}$ is allowed), but those between two g or two u terms are forbidden (eg $T_{2g} \rightarrow T_{1g}$ is forbidden). Because different types of orbitals have different symmetries with respect to i, this rule is sometimes referred to as the "orbital selection rule". It forbids transitions within one type of orbital subshell. For example, p orbitals are antisymmetric with respect to i, while both s and d orbitals are symmetric with respect to i. This rule forbids $s \rightarrow s$, $p \rightarrow p$, $d \rightarrow d$, and $d \rightarrow s$ transitions, but allows transition between $d \rightarrow p$ and $d \rightarrow s$ orbitals. This rule is important in transition metal complexes because it fobids $d - d$ transitions in centrosymmetric geometries, including octahedral and linear coordination geometries.

Despite these selection rules, $d \rightarrow d$ transitions are a hallmark feature of octahedral transition metal complexes, and are often responsible for their brilliant colors. These $d \rightarrow d$ transtions, and other forbidden transitions may still occur, primarily through relaxation of these rules in specific cases.

Breaking the rules!

Relaxation of the Laporte and Spin Selection Rules rules can occur through:

- **Vibronic coupling:** the bonds of metal complexes vibrate and may cause temporary distortions in molecular symmetry. These distortions can cause temporary loss in symmetry (as well as some orbital mixing), and thus allow $d \rightarrow d$ transitions in those moments of distortion. Despite being forbidden by the Laporte Selection rule, the $d \rightarrow d$ transitions in octahedral complexes appear, but are weak (of low intensity) with molar absorptivities $\leq 100\ M^{-1}cm^{-1}$.

- **Orbital Mixing**: In the case of octahedral complexes, π-acceptor and π-donor ligands can mix with the d-orbitals so that transitions are no longer purely $d \rightarrow d$ (but these are usually considered "charge transfer" transitions, not $d \rightarrow d$). In the case of tetrahedral complexes, the molecule has no center of symmetry (thus no u or g subscripts on the terms). In the valence orbital model, a tetrahedral molecule is said to have sp^3 and sd^3 hybridized orbitals, while MO theory predicts MO's with mixtures of some s, p, and d character - this mixing of orbital types can allow transitions between "mixed" orbitals that would otherwise be forbidden in "pure" orbitals. A similar phenomenon would occur in octahedrons with significant distortion, or in other coordination geometries that provide potential for orbital mixing.
- **Spin-Orbit coupling**: This gives rise to spin-forbidden bands of low intensity, usually with very weak molar absorptivities approximately $\leq 1 M^{-1} cm^{-1}$. This phenomenon is usually more important for transition metals of the second row $4d$ and beyond.

Exercise 11.3.1.1

Consider the d^2 case presented in a previous section. The free ion terms for d^2 were found to be ^3F, ^1G, ^3P, ^1D, ^1S. First, identify the ground state term. Then identify the Spin-Allowed excitations starting from the ground state.

Answer available at the end of this section.

Answers

Exercise 11.3.1.1

The ground state is ^3F. There is only one spin-allowed transition: $^3F \rightarrow ^3P$.

The spin-forbidden transitions from ^3F include $^3F \rightarrow ^1D$, $^3F \rightarrow ^1G$, and $^3F \rightarrow ^1S$.

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- Selection Rules for Electronic Spectra of Transition Metal Complexes by Robert J. Lancashire is licensed CC BY 4.0.

11.3.2: Correlation Diagrams

Splitting of Terms in an Octahedral Field

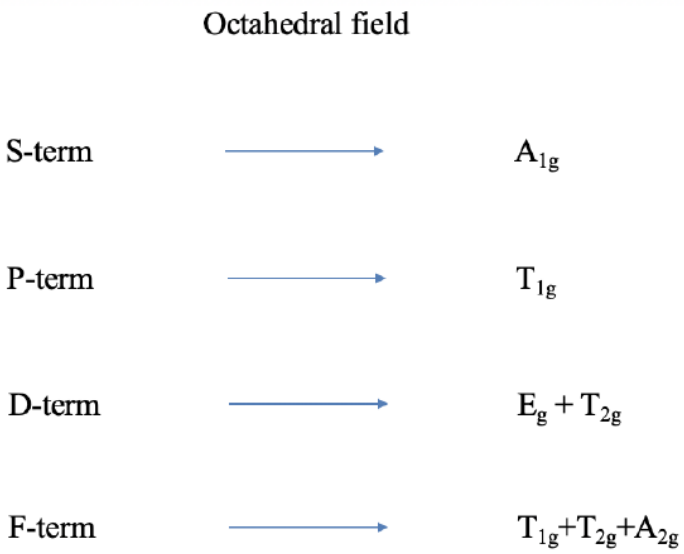


Figure 11.3.2.1: Octahedral field term splitting

Thus far we have only considered free ion terms, which means terms without the presence of a ligand field. Let us think next about the influence of an octahedral field on a term. Terms are wavefunctions, just like orbitals, and therefore they behave like orbitals in a ligand field. For example, the d-orbitals split into $t_{2g}$and e_g orbitals in an octahedral ligand field. A D-term behaves similarly. It splits into T_{2g} and E_g terms (note the capital letters that describe term, and the lower-case letters that describe orbitals!). \The p-orbitals are triple-degenerate, having T_{1g} symmetry in the O_h (octahedral) point group, and do not split in energy: they give the t_{1g} orbitals under an octahedral field. Similarly, the P-terms have the same symmetry and also do not split. The P-term becomes a T_{1g} term in an octahedral field.

Following analogous arguments, S terms become A_{1g} terms. F terms do split in energy like f-orbitals and become T_{1g}, T_{2g}, and A_{2g} terms. Overall, the presence of the octahedral field increases the number of terms from four to seven (Figure 11.3.2.1). It is easy to see that the ligand field leads to many states, and many potential electron transitions. Thus, we would expect quite complicated spectra. For other ligand fields, the terms also behave analogously to orbitals. For, instance in a tetrahedral field D-terms split into E and T_2 terms, and so forth.

Term Splitting for octahedral d^2 metal complexes

Now let us think about how the term energies of our free d^2-ion changes when placed in an octahedral ligand field, depending on the ligand field strength. We can express this by a correlation diagram (Figure 11.3.2.2). In a correlation diagram, we plot the energies of the terms relative to the field strength.

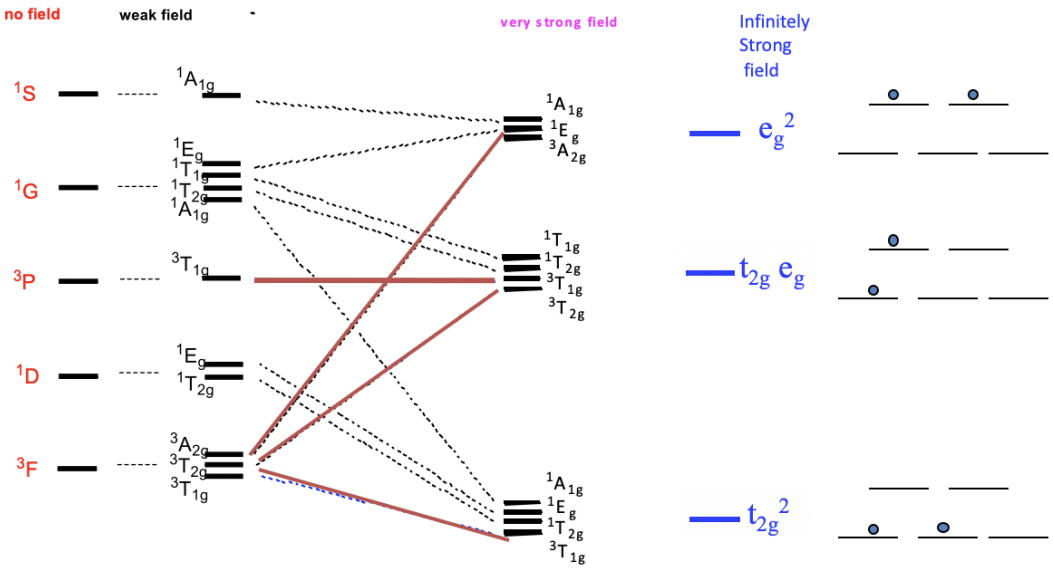


Figure 11.3.2.2: Correlation diagram

On the left side we plot the terms without any field according to their energies. In the case of a d^2 ion, the energies are

$$^3\mathrm{F} < {}^1\mathrm{D} < {}^3\mathrm{P} < {}^1\mathrm{G} < {}^1\mathrm{S}.$$

Next, we plot the relative energies in a weak octahedral ligand field, and label the terms according to their symmetry. We can see that the D, F, and G terms split in energy, while the S and P terms do not. Because of the weak field, energy differences are very small. Now let us increase the ligand field strength continuously, until we have reached a very strong ligand field. We see that some of the terms move up in energy, while other terms move down as the ligand field increases. For example, two of the three terms resulting from the F-terms increase in energy while one decreases. It is also possible that a term does not change its energy. For example, the $^3T_{1g}$ term from the ^3P term does not change its energy. In very strong ligand field there are three groups of terms that have similar energy. In the hypothetical case of an infinitely strong ligand field, the terms that belong to a particular group become identical in energy. In this case, there are only three states for the electrons possible. The field is considered so strong that the energy associated with electron-electron interactions become negligible compared to the energy of the field. The electrons behave as though there were no electron-electron interactions. Therefore, we can call the lowest energy state the t_{2g}^2 state. It is equivalent to the state of the two electrons being in the t_{2g} orbitals. The second state is called the $t_{2g}e_g$ state. It is equivalent to the state of one electron being in the t_{2g} and one electron being in the e_g orbitals. The third state is called the e_g^2 state, which is equivalent to the state with both electrons in the e_g^2-orbitals.

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- 8.2: Term splitting in ligand fields, selection rules, Tanabe-Sugano diagrams. Metal to ligand, and ligand to metal transitions by Kai Landskron is licensed CC BY 4.0.

11.3.3: Tanabe-Sugano Diagrams

Tanabe-Sugano diagrams are modified forms of correlation diagrams. The modification is simply that the energies of terms are plotted in terms of transition energy and Δ divided by a constant, B, called the Racha parameter. Terms are plotted relative to the lowest-energy term; in other words, the ground state term is plotted as the horizontal axis (x-axis). The Tanabe-Sugano diagram of a d^2 transition metal complex is shown below in Figure $11.3.3.1$. Tanabe-Sugano diagrams for other d-electron counts are available in the Reference Section of LibreTexts.

Tanabe-Sugano diagram of a d^2 octahedral complex

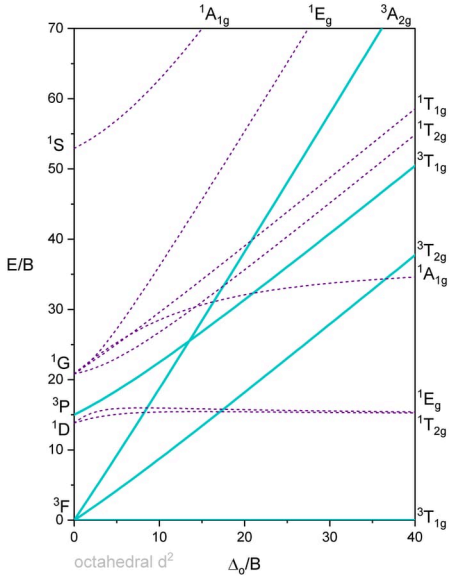


Figure $11.3.3.2$: d^3: Tanabe-Sugano Diagram for octahedral metal complex with two d electrons. For convenience, terms that can accommodate spin-allowed transitions from the ground state are indicated by solid lines. Terms that have different multiplicity than the ground state are shown in dashed lines. (CC-BY-SA; Kathryn Haas)

The difference between the diagram shown in Figure $11.3.3.1$ and the previously-discussed correlation diagram for a d^2 metal ion is that the energy of the ground state is plotted horizontally, and the energy of all other terms are plotted relative to that. In the case of the d^2 electron configuration, the $^3T_{1g}$ term is the ground term and is plotted as a horizontal line. We can see that the ligand field strength on the x-axis is given in units of B (specifically as $\frac{\Delta}{B}$), and the energy of the terms is also given in units of B (specifically $\frac{E}{B}$. B is a so-called Racah parameter, which is a quantum-mechanical energy unit for the electromagnetic interactions between the electrons. It is chosen because it provides “handy” numbers.

You can see that some lines in Figure $11.3.3.1$ are bent (eg the two $^1A_{1g}$ terms), and some are straight. Bending of lines occurs when two terms interact with each other because they are close in energy and have the same symmetry. This is again an analogy to orbitals. Just as orbitals interact when they have the same symmetry type and similar energy, terms also interact when they have the same symmetry and similar energy. Without taking their interactions into account, their energies can cross when the energy of term A declines and the energy of term B increases with increasing field strength (Figure $11.3.3.2$). The closer the terms come to the point where they cross, the stronger their interactions, because their energies become more and more similar. These interactions lead to the "bending away" of the terms from each other, leading to bent curves. This means that curves for two terms of the same symmetry type will bend away in a Tanabe-Sugano diagram and never cross. For example the terms for the two $^1A_{1g}$ terms bend away from each other and do not cross.

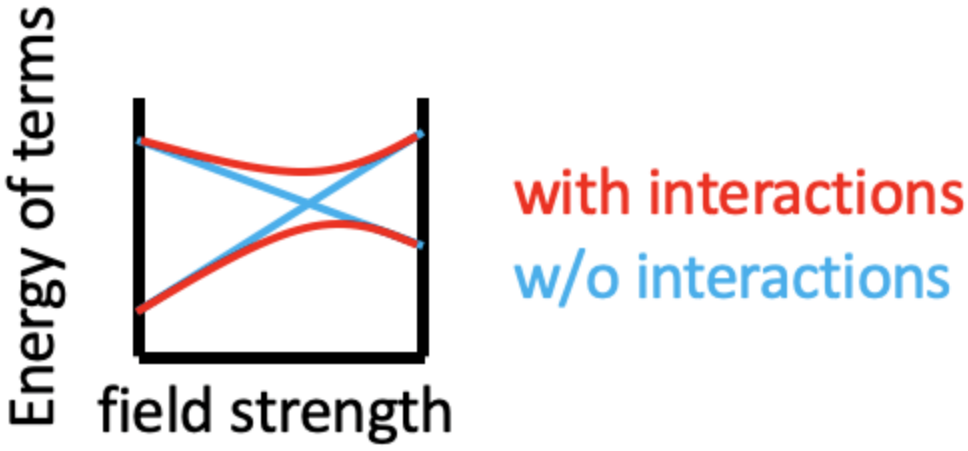


Figure 11.3.3.2: Origin of line-bending in Tanabe-Sugano diagrams.

Next, let us think about which electron transitions would be allowed by considering spin selection and the Laporte rule. First, notice that all the terms in Figure 11.3.3.1 have "gerade" symmetry and are labeled with a "g" subscript. In fact, this is the case for the terms of any octahedral complex. What does this mean for the allowance of electron transitions? It means that no electron transition would be allowed by the Laporte Rule, and that would imply that the complex could not absorb light. The Laporte selection rule, however, does not hold strictly. It only says that the probability of the electron-transition is reduced - but not forbidden. This means that an absorption band that disobeys the Laporte rule will have lower intensity compared to one that follows the Laporte rule, but it can still be observed. The spin-selection rule, however, holds strictly, and transitions between terms of different spin multiplicity are strictly forbidden, meaning that they have near zero probability to occur. Overall, we can therefore excite an electron from the $^3T_1$ ground state to other triplet terms, namely the $^3T_2$ term, and the $^3A_2$ term (Figure 11.3.3.1).

Tanabe-Sugano diagram of d^3 octahedral complexes

Now, let us have a look at the Tanabe-Sugano diagram of a d^3 ion in an octahedral ligand field (Figure 11.3.3.3). What is the ground term? We can see that the term designation on the horizontal line reads "$^4A_{2g}$", therefore this term is the ground term. How many electron transitions from the ground state should we expect? To answer this question we need to count the number of other quartet terms. There is the $^4T_{2g}$, the $^4T_{1g}$, and another $^4T_{1g}$. Thus, there are overall three electron transitions possible.

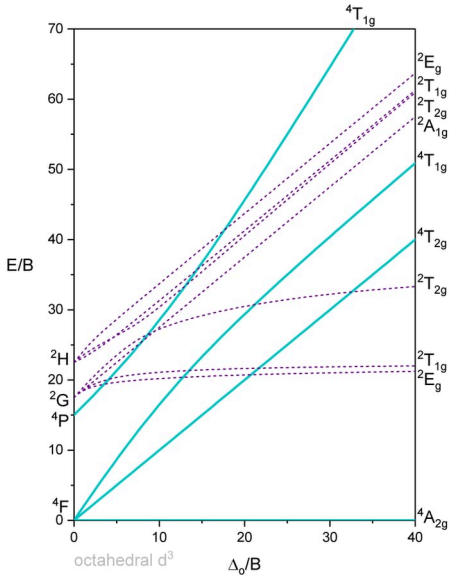


Figure 11.3.3.3: d^3: Tanabe-Sugano Diagram for octahedral metal complex with three d electrons. For convenience, terms that can accommodate spin-allowed transitions from the ground state are indicated by solid lines. Terms that have different multiplicity than the ground state are shown in dashed lines. (CC-BY-SA; Kathryn Haas)

Can we understand why the ground state is a quartet term? It helps to consider how we would fill the electrons into the d-orbitals for the electron configuration d^3. All three electrons would be filled spin-up in the t_{2g} orbital following Hund's rule (Figure 11.3.3.4). Because each electron has the spin +1/2 the total spin of all three electrons is 3x1/2=3/2. Thus, the spin multiplicity is ((2x3/2)+1)=4. Note that the microstate we have drawn is actually only one of the (2L+1)(2S+1) microstates. S=3x1/2=3/2, but what is L? You can see on the left side of the diagram that the $^4A_2$ term originated from a ^4F term. This means L=3, and (2L+1)((2S+1)=7x4=28. This means that there are actually 27 other microstates that have the same energy as the microstate that we drew. Why did we draw this microstate in favor of the others? This is because this microstate is the state with the maximum M_L (=L) and M_S (=S) values determining the term symbol.

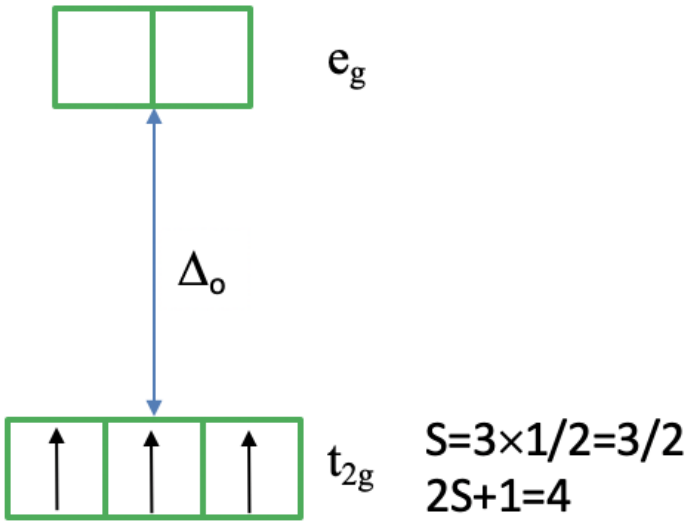


Figure 11.3.3.4: d-orbitals in an octahedral ligand field for the electron configuration d^3

Tanabe-Sugano diagram of d^4 octahedral complexes

Now let us look at the Tanabe-Sugano diagram of a d^4 octahedral complex (Figure 11.3.3.5). You can see that this diagram is separated into two parts separated by a vertical line. The line indicates the ligand field strength at which the complex changes from a high spin complex to a low spin complex. At lower ligand field strengths, the ground term is a ^5E_g term (solid turquoise line). At higher field strength the ground term is a $^3T_{1g}$ term (dashed purple line).

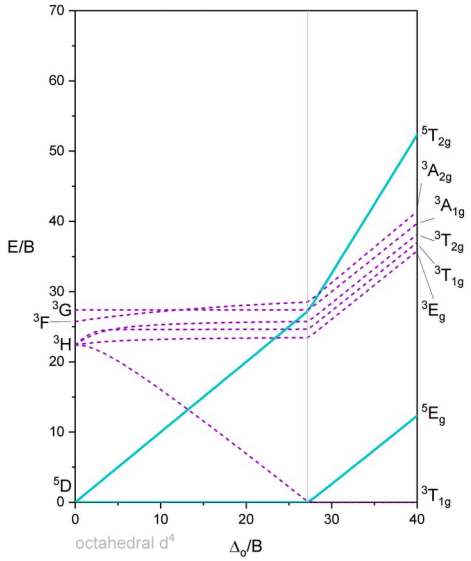
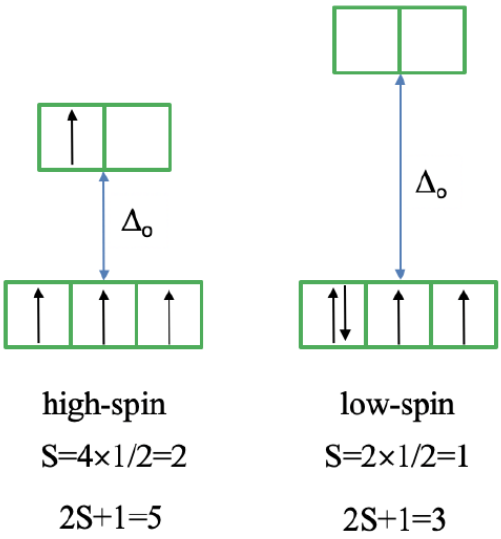


Figure 11.3.3.5: d^4, simplified: Tanabe-Sugano Diagram for octahedral metal complex with four d electrons. A grey vertical line at 27.2 $\frac{\Delta_o}{B}$ divides high spin from low spin cases. For convenience, terms that can accommodate spin-allowed transitions from the pentet ground state in high spin (left of grey line) are indicated by heavy solid lines. Terms that can accommodate spin-allowed transitions from the low spin triplet ground state are shown in heavy dashed lines. This version of the d^4 Tanabe Sugano Diagram is abbreviated in that it shows only the spin-allowed terms that are most relevant for interpreting UV-visible spectra. For the full version of a d^4 diagram, see the Resources section. (CC-BY-SA; Kathryn Haas)

We can rationalize this again by drawing the orbital box representation of the d-orbitals in the octahedral ligand field. In the high spin state, there are four unpaired electrons, thus S=4x1/2=2, and 2S+1=5. In the low spin state, there are two unpaired electrons, and thus S=2x1/2=1, and 2S+1=3. This explains the quintet and the triplet nature of the high and low spin ground terms. Note again, that the two microstates represented by the orbital box diagrams (11.3.3.6) are not the only microstates that have the respective energy. They are only the "representative" microstates because they have the maximum M_L and M_S values.



11.3.3.6: d-orbitals in the octahedral ligand field for the electron configuration d^4.

How many electron transitions are possible from the ground term? For a high spin complex there is only one because the is only one other quintet term, namely the $^5T_{2g}$ term. For the low spin complex, there are five transitions because there are five other triplet terms.

Tananbe-Sugano diagram of d^5 octahedral complexes

The Tanabe-Sugano diagram of a d^5 octahedral complex is also divided into two parts separated by a vertical line (Figure 11.3.3.7). The left part reflects the high spin and the right part the low spin complex.

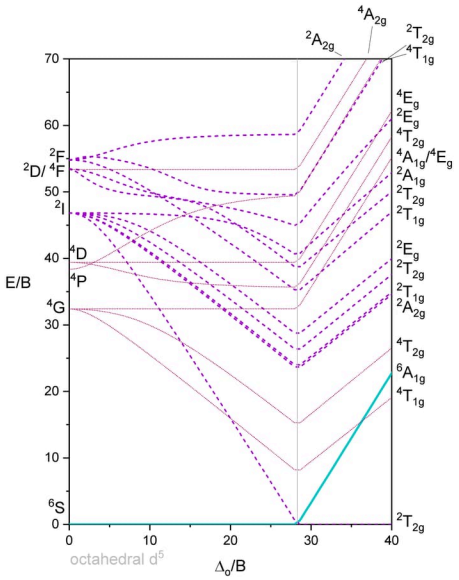


Figure 11.3.3.7: d^5, simple: Tanabe-Sugano Diagram for octahedral metal complex with five d electrons. A grey vertical line at 27.3 $\frac{\Delta_o}{B}$ divides high spin from low spin cases. For convenience, terms that can accommodate spin-allowed transitions from the sextet ground state in low spin (right of grey line) are indicated by heavy solid lines. Terms that can accommodate spin-allowed transitions from the low spin doublet ground state are shown in heavy dashed lines. Terms that have different multiplicity than ground states are shown in lighter dotted lines. This version of the d^5 Tanabe Sugano Diagram is abbreviated for simplicity and for the purpose of interpreting UV-visible spectra. For the full version of a d^5 diagram, see the Resources section. (CC-BY-SA; Kathryn Haas)

The high spin ground state is a sextet term, and the low spin ground state is a doublet term. We can understand the sextet and doublet nature of the terms when considering that the associated electron box diagrams have five and one unpaired electrons respectively. S=5x1/2=5/2 and 2S+1=6 for the high spin term, and S=1x1/2=1/2 and 2S+1=2 for the low spin term. What are the possible electron transitions from the ground state? For the high-spin complex there is no other sextet term, meaning that there is no electron transition possible. Hence, high-spin octahedral d^5-complexes are colorless. An example is the hexaaqua manganese (2+) complex. A solution of this complex is near colorless, only very slightly pinkish. The slight color is because also spin-forbidden transitions can occur, albeit at a very low probability. For a d^5-low spin complex there are three additional doublet states, and thus there are three electron transitions possible.

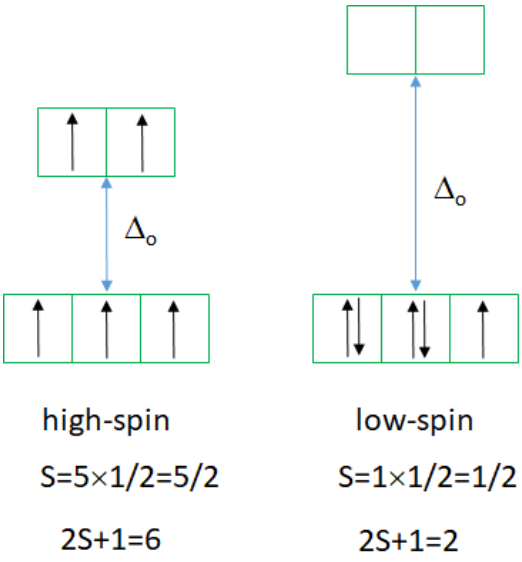


Figure 11.3.3.8: d-orbitals in the octahedral ligand field for the electron configuration d^5

Tanabe-Sugano diagram of d^6 octahedral complexes

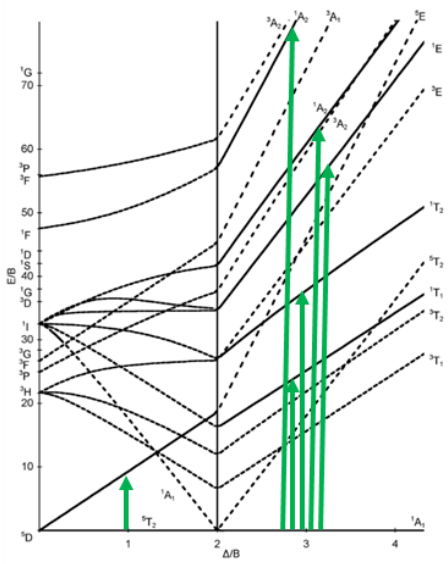


Figure 8.2.13 Tanabe-Sugano diagram of the d^6 octahedral complex (Chem507f091 / Public domain https://commons.wikimedia.org/wiki/F...no_diagram.png)

The next diagram is the one for the d^6 electron configuration (Fig. 8.2.13). Again, the diagram is separated into parts for high and low spin complexes. The dashed lines in the diagram indicate the terms that have a different spin multiplicity than the ground term. This way we can more easily see how many electron transitions are allowed.

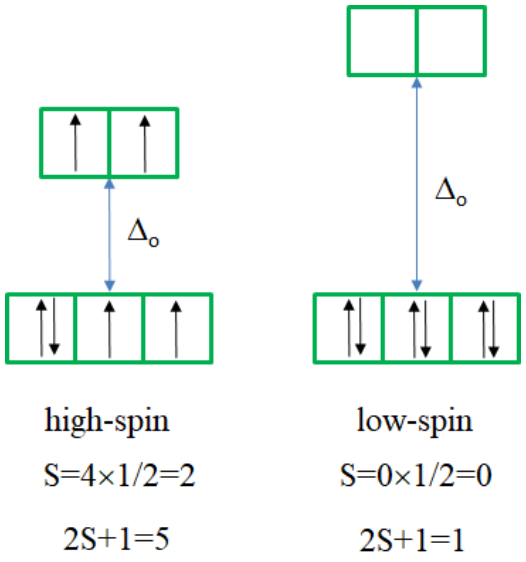


Figure 8.2.14 d-orbitals in the octahedral ligand field for the electron configuration d^6

The ground term for the high-spin complex is the quintet $^5T_2$ term. It is a quintet term because four electrons in the d-orbitals are unpaired, and two are paired. The value for S is thus 4x1/2=2, and the spin multiplicity is 2S+1=5. The ground term for the low spin complex is a $^1A_1$ term. It is a singlet term because all electrons are paired, and thus S=0, and 2S+1=1. How many electron transitions are there for the high-spin complex? There is only one because the ^5E term is the only other quintet term. There are five transitions possible for the low-spin case because there are five additional singlet terms.

Tanabe-Sugano diagram of d^7 octahedral complexes

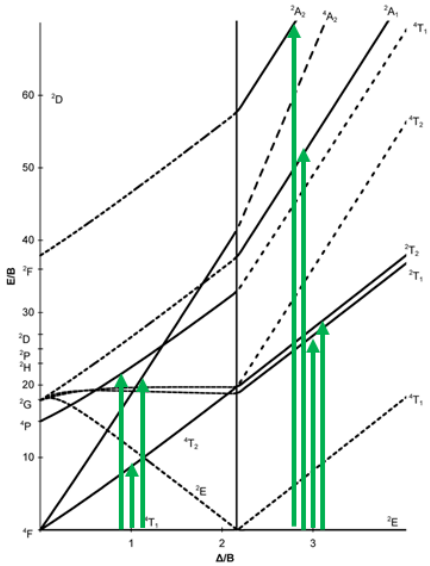


Figure 8.2.15 Tanabe-Sugano diagram of the d^7 octahedral complex (Attribution: Chem507f091 / Public domain https://commons.wikimedia.org/wiki/F...no_diagram.png)

Next, let us look at the Tanabe-Sugano diagram of a d^7 octahedral complex (Fig. 8.2.15). In this case, the high spin complex has a $^4T_1$ ground term, and the low spin complex has a ^2E ground term.

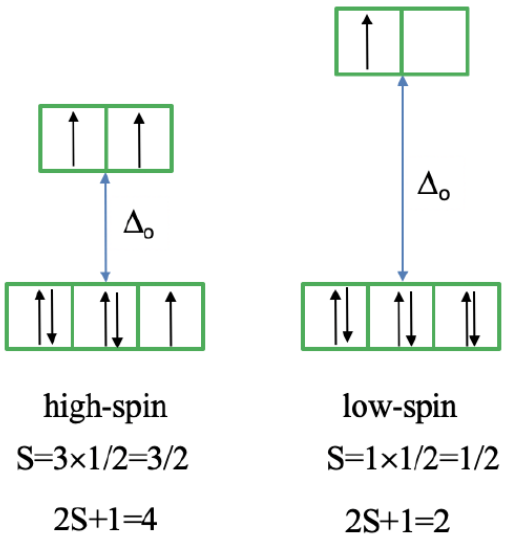


Figure 8.2.16 d-orbitals in the octahedral ligand field for the electron configuration d^7

The microstate that "represents" the high spin ground term has three unpaired electrons, hence the spin quantum number S=3/2 and the spin multiplicity is 2S+1=4. The microstate that represents the low spin ground term has one unpaired electron, an S value of ½, and a spin multiplicity of 2. There are three other quartet terms, and four other doublet terms, hence there are three electron transitions for the high-spin complex, and four for the low spin complex.

Tanabe-Sugano diagram of d^8 octahedral complexes

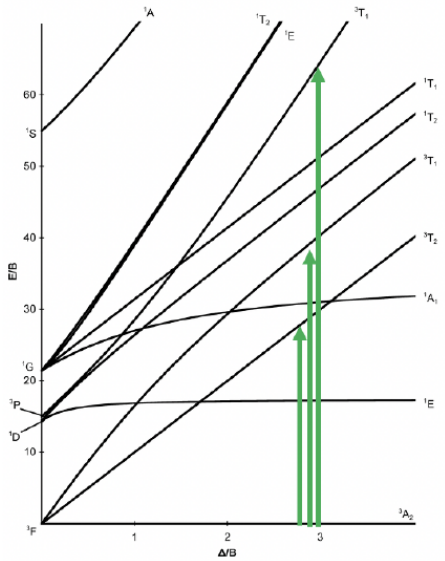


Figure 8.2.17 Tanabe-Sugano diagram of the d^8 octahedral complex (Attribution: Chem507f091 / Public domain https://commons.wikimedia.org/wiki/F...no_diagram.png)

Now let us look at an octahedral complex with d^8 electron configuration. For this electron configuration, there are no high and low spin complexes possible, therefore, the Tanabe-Sugano diagram is no longer divided into two parts (Fig. 8.2.17).

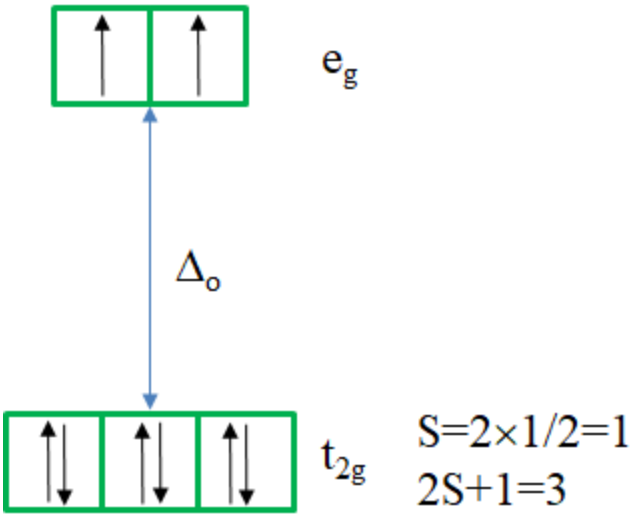


Figure 8.2.18 d-orbitals in the octahedral ligand field for the electron configuration d^8

There is a single ground term of the type $^3A_2$. It is a triplet state because the microstate representing the term has two unpaired electrons in the e_g orbitals (Fig. 8.2.18). Thus, S=2x1/2=1, and the spin multiplicity is 2S+1=2. How many electron transitions would you expect? There are three other triplet states, namely the $^3T_2$ and two $^3T_1$ terms. Therefore, there are three electron transitions possible.

Unnecessary diagrams for $d^1,\ \ d^9,\ \ d^10$

We could also ask: Are there Tanabe-Sugano diagrams for d^1, d^9, and d^{10}? For, d^1 there are no electron-electron interactions, thus the simple orbital picture is sufficient. The ^2D term splits into T_{2g} and E_g terms, and there is only one electron transition possible. The d^9 electron configuration is the “hole-analog” of the d^1 electron configuration. It has also just one ^2D term which splits into a T_{2g} and an E_g term in the octahedral ligand field. Therefore, also in this case there is only one electron transition from the T_{2g} into the E_g term possible. In the case of d^{10} all microstates are filled with orbitals, and there is only the ^1S term which does not split in an octahedral ligand field. Therefore, there are no electron transitions in this case.

Jahn-Teller distortions and other geometries

Some of the electron configurations discussed above are ones that are particularly susceptible to Jahn-Teller distortion. The Jahn-Teller theorem predicts that electron configurations with asymmetrically populated orbitals (i.e., those that have spin multiplicity of a doublet or greater), will distort. Distortions affect the electronic spectra of coordination complexes, and in practice Jahn-Teller distortions are significant only in the cases where the e_g orbitals are asymmetrically populated (e.g., octahedral d^9 and high spin d^4).

Finally, it should be mentioned that it is also possible to construct Tanabe-Sugano diagrams for other shapes such as the tetrahedral shape, but we will not discuss these further here.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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- 8.2: Term splitting in ligand fields, selection rules, Tanabe-Sugano diagrams. Metal to ligand, and ligand to metal transitions by Kai Landskron is licensed CC BY 4.0.

11.3.4: Symmetry labels for split terms

While the free ion terms symbols are derived using Russell-Saunders terms, we only briefly discussed how the term symbols may be found from a character table upon ligand-field splitting. The symmetry labels (called Mulliken Labels) that are used in character tables to describe the symmetry of wavefunctions were described in a previous section (Section 4.3.3). Just as orbitals are wavefunctions that are described by the irreducible representations that are part of a character table, so are the terms. When we are discussing the terms of an octahedral complex, we can apply what we already know about octahedral symmetry and symmetry labels to understand how the terms labels are assigned.

Upon close inspection of any of the Tanabe-Sugano diagrams shown previously, or in the Resources Section, you may notice that each free ion term (listed at the right of the diagram) splits into a term or set of terms that retain the same multiplicity (the left superscript). Under an octahedral field, all terms have symbols A, B, E or T because they are singly, doubly, or triply degenerate. While some of these terms have subscripts "1" or "2", all the terms also have "g" subscripts due to the symmetry of the d orbitals. Some of the symbols might also look familiar, as they are similar to the labels you know for splitting of d orbitals, like E_g and T_{2g}.

It is useful to know that under an octahedral field, the D, F, G, H, I terms split, but the terms S, P do not split. From inspection of the O_h character table, we find that free ion terms will split as follows:



The term symbols under an octahedral field have symmetry that matches symmetry of other elements within the molecule, including the d-orbitals. A reminder of their symmetry meanings is below (see also Section 4.3.3).

Review of Mulliken Labels

Each wavefunction (including terms) can be described by a Mulliken label (symmetry label). The labels used for terms in an octahedral ligand field are listed in the table below.

Mulliken Labels	**meaning**
A or B	singly degenerate
E	doubly degenerate
T	triply degenerate
Subscripts	**meaning**
1	symmetric to σ_v or perpendicular C_2
2	anti-symmetric to σ_v or perpendicular C_2
g	symmetric to inversion center
u	anti-symmetric to inversion center

We can use our knowledge of symmetry to derive the term labels for a given electron configuration under an octahedral field. Let's focus only on the capital letter that is assigned as the term symbol. Assignment of the octahedral term subscripts will not be described here, but are similar to assignment of these same subscripts to orbitals with matching symmetry.

For example, the d^1 electron configuration has a free ion ground state term of ^2D. According to the table shown above, these terms will split into E_g and T_{2g} terms. Which would be its ground state term under an octahedral field? And which is the excited state term? To answer these questions we need to look at the electron configurations of the ground and excited states in an octahedral field. It is convenient to know that the term symbol under an octahedral field indicates the *degeneracies of the related*

electron configurations.

Let's take a look at the electron configurations of the split d-orbitals to determine which term is the ground state. In the ground state of a d^1 under an octahedral ligand field, there would be one electron in the t_{2g} orbitals, thus the electron configuration is $t_{2g}^1 e_g^0$. For simplicity we can consider only the cases where m_s values are $+\frac{1}{2}$. There are three ways to put the electron in t_{2g} therefore, the ground state is triply degenerate, with a symbol "T". This is illustrated in the left panel of Figure 11.3.4.1.

In the excited state of a d^1 under an octahedral ligand field, there would be one electron in the e_g orbitals, or a configuration of $t_2g^0 e_g^1$. There are two ways to arrange the electron with $m_s = +\frac{1}{2}$ in the e_g orbitals (Figure 11.3.4.1, left). Therefore, the excited state is doubly degenerate, with a symbol "E".

In summary, the ^2D free ion term for d^1 splits into a lower-energy $^2T_{2g}$ and a higher-energy ^2E_g term under an octahedral field (Figure 11.3.4.1, left).

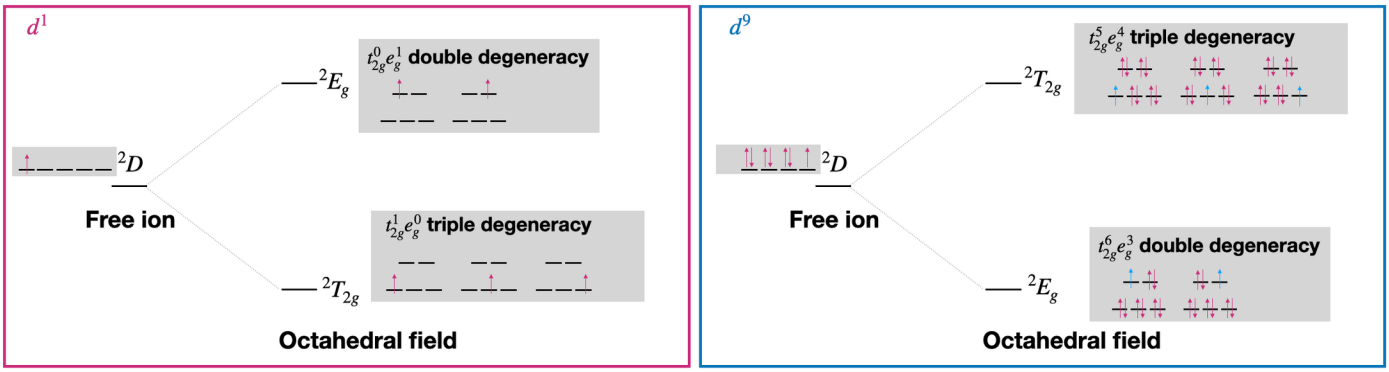


Figure 11.3.4.1: Term splitting of d^1 and d^9 free ion terms in an octahedral field. The symbols of the octahedral terms match the degeneracies of the electron configurations. (CC-BY-SA; Kathryn Haas)

We could use a similar treatment to derive the relative energies and terms of a d^9 ion in an octahedral field. The ground state term of d^9 is the same as for d^1: it is ^2D. If we look at the ground state and excited state electron configurations of a d^9 ion, we find that the ground state configuration is $t_{2g}^6 e_g^3$, which is doubly degenerate. On the other hand, the excited state has an electron configuration of $t_{2g}^5 e_g^4$, and has triple degeneracy. In summary, in the case of d^9, the ^2D free ion term splits into a lower energy ^2E_g term and a higher-energy $^2T_{2g}$ term. *This is exactly the opposite of d^1!*

The d^1 and d^9 cases are opposite because they are related by what is said to be a "positive hole" concept. The d^9 configuration could be derived from a d^{10} configuration with one positive "hole" (an electron removed). The positive hole is similar to the lone electron in d^1 except that in the ground state, the hole is in e_g, while the electron in d^1 is in t_{2g}; thus the two situations are exact opposites.

Just as d^1 and d^9 are related by the hole concept, so are d^4 and d^6. If you consider that d^1 is the addition of one electron to the totally symmetric d^0 case, then perhaps you can see how d^6 is similar in that it is the addition of one electron to the totally symmetric d^5 case. Thus, d^1 and d^6 have similar splittings under the octahedral field. Similarly, d^9 is created by removing one electron from the totally symmetric case of d^{10} and d^4 is created by removing one electron from d^5. Thus d^4 and d^9 have identical splittings for their ground state free ion terms, which in these cases are a D term.

Due to the relationships between d^1, d^4, d^6, and d^9, the same Orgel Diagram is used to show term splitting for these cases (Figure 11.3.4.2). Orgel diagrams are yet another form of correlation diagrams.

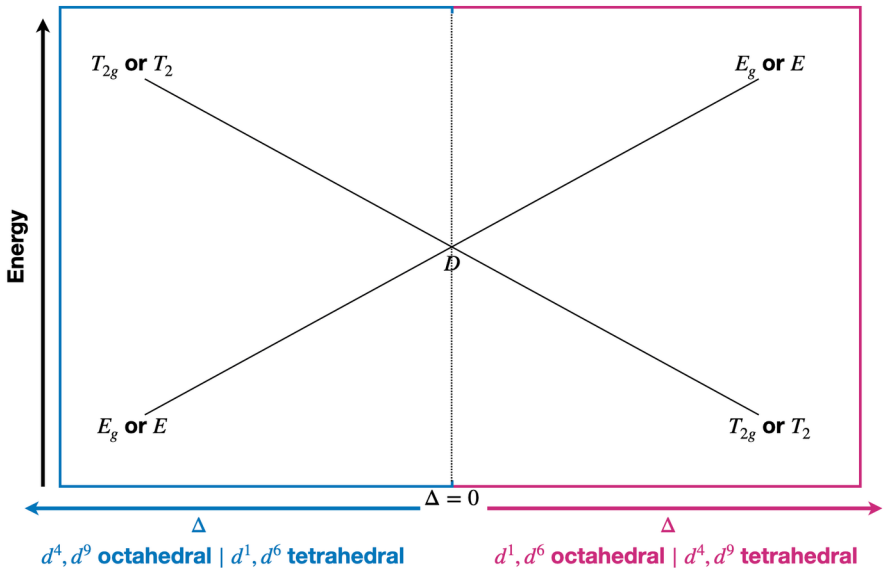


Figure 11.3.4.2: Orgel diagram for splitting of the ground state D term of d^1, d^4, d^6, and d^9 ions in an tetrahedral or octahedral field. (CC-BY-SA; Kathryn Haas)

Just as there are relationships between d^1, d^4, d^6, and d^9, there are similar relationships between d^2, d^3, d^7, and d^8, and there is an Orgel diagram that can represent the splitting of their relevant free-ion terms.

Tetrahedral splitting

Because tetrahedral field splitting has the opposite pattern to octahedral field splitting of the d-orbitals, there are relationships between tetrahedral and octahedral terms. In general, for a tetrahedral field with d^n electrons, the Tanabe-Sugano diagram of an octahedral diagram for d^{10-n} can be used to interpret the tetrahedral case. The Orgel diagrams are labeled in general terms for this reason. They can be applied to both tetrahedral and octahedral cases.

Jahn-Teller distortions

We can also see what would happen to the terms in the case of Jahn-Teller distortion. In the case of a Jahn-Teller distortion (most common for d^9 and high-spin d^4 where the e_g orbitals are asymmetrically occupied), we can use the degeneracy of orbital electron configurations to identify term labels. Let's walk through an example using the most simple case: a d^1 metal ion (Figure 11.3.4.3).

Jahn-teller usually causes a tetragonal distortion of an octahedron. This would be a change from O_h to D_{4h} symmetry.

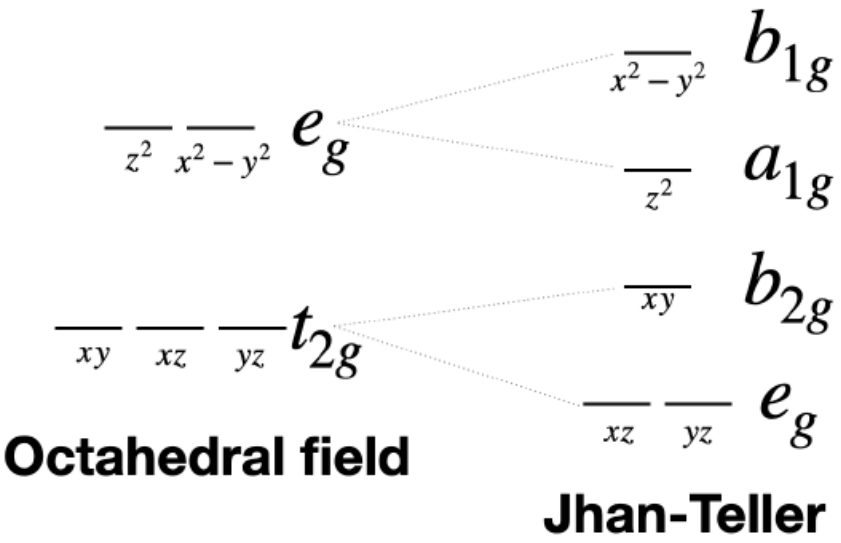


Figure 11.3.4.3: Splitting of d-orbitals from O_h to D_{4h} symmetry by Jahn-Teller distortion. (CC-BY-SA; Kathryn Haas)

The t_{2g} orbitals (the set d_{xy}, d_{xz}, d_{yz} are split into e_g (d_{xz}, d_{yz}) and b_{2g} (d_{xy}) by this symmetry change. Thus, we can expect any T_{2g} terms to be split similarly into E_g and B_{2g} terms by Jahn-Teller distortion. The e_g orbitals under O_h are split into a_1g (d^{z^2}) and b_1g ($d_{x^2-y^2}$) under D_{4h}. Thus, we can expect E_g terms to be split into B_{1g} and A_{1g} terms by Jahn-Teller distortion (Figure 11.3.4.4).

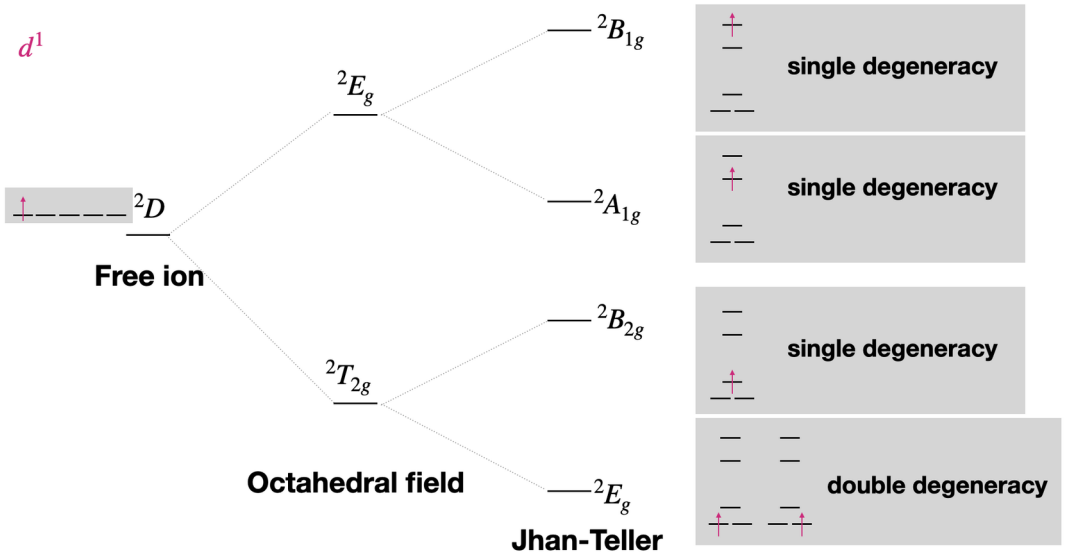


Figure 11.3.4.4: Splitting of d^1 from an octahedral field to D_{4h} by Jhan-Teller tetragonal distortion. (CC-BY-SA; Kathryn Haas)

Just as d^1 and d^9 gave opposite order of their terms under an octahedral field, they also give opposite order of terms in the Jahn-Teller distortion.

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- 4.3.3: Character Tables by Kathryn Haas is licensed CC BY-NC-SA 4.0.

11.3.5: Applications of Tanabe-Sugano Diagrams

The Tanabe-Sugano diagrams can be used to interpret absorption spectra and gain insight into the properties of a coordination complex. For example, you could use the appropriate diagram to predict the number of transitions, assign the identity of a specific transition, or calculate the value of Δ for a specific metal complex.

How to use the Tanabe-Sugano Diagrams

1. Determine the d-electron count of the metal ion of interest.
2. Choose the appropriate Tanabe-Sugano diagram: this is the one matching the d-electron count of the metal ion. There is a full list of Tanabe-Sugano diagrams in the Resources Section.
3. Acquire an electronic spectrum of the metal complex and identify λ_{max} for spin-allowed (strong intensity) and spin forbidden (weak intensity) transitions.
4. Convert wavelength (λ_{max}) to energy (E) in wavenumbers (cm^{-1}) and generate energy ratios relative to the lowest-energy allowed transition. (i.e. $\frac{E_2}{E_1}$ and $\frac{E_3}{E_1}$).
5. Using a ruler, slide it across the printed Tanabe-Sugano diagram until the E/*B* ratios between lines is equivalent to the ratios found in step 4.
6. Solve for *B* using the E/*B* values (y-axis, step 4) and Δ_{oct}/B (x-axis, step 5) to yield the ligand field splitting energy, $Delta$ (Sometimes this is labeled as $10D_q$, and it is useful to know that $\Delta = 10D_q$).

Example 11.3.5.1: Chromium Splitting

A Cr^{3+} metal complex has strong transitions and λ_{max} at

- 431.03 nm,
- 781.25 nm, and
- 1,250 nm.

Determine the Δ_{oct} for this complex.

Solution

1. Cr has 6 electrons. Cr^{3+} has three electrons, so it has a d-configuration of d^3
2. Locate the d^3 Tanabe-Sugano diagram
3. Convert to wavenumbers:

$$\frac{10^7(nm/cm)}{1250\ nm} = 8,000\ cm^{-1} \tag{11.3.5.1}$$

$$\frac{10^7(nm/cm)}{781.25\ nm} = 13,600\ cm^{-1} \tag{11.3.5.2}$$

$$\frac{10^7(nm/cm)}{431.03\ nm} = 23,200\ cm^{-1} \tag{11.3.5.3}$$

4. Allowed transitions are ${}^4T_{1g} \leftarrow {}^4A_{2g}$, ${}^4T_{1g} \leftarrow {}^4A_{2g}$ and ${}^4T_{2g} \leftarrow {}^4A_{2g}$.

Transition	Energy cm^{-1}	Ratios to lowest
${}^4T_{1g} \leftarrow {}^4A_{2g}$	23,200	2.9
${}^4T_{1g} \leftarrow {}^4A_{2g}$	13,600	1.7
${}^4T_{2g} \leftarrow {}^4A_{2g}$	8,000	1

5. Sliding the ruler perpendicular to the x-axis of the d^3 diagram yields the following values:

Δ_{oct}/B	10	20	30	40
Height $E(\nu_3)/B$	29	45	64	84
Height $E(\nu_2)/B$	17	30	40	51
Height $E(\nu_1)/B$	10	20	30	40
Ratio $E(\nu_3)/E(\nu_1)$	2.9	2.25	2.13	2.1
Ratio $E(\nu_2)/E(\nu_1)$	1.7	1.5	1.33	1.275

6. Based on the two tables above it should be assessed that the Δ_{oct}/B value is 10. B is found by dividing E by the height.

Energy cm^{-1}	Height	B
23,200	29	800
13,600	17	800
8,000	10	800

7. Next multiply Δ_{oct}/B by B to yield the Δ_{oct} energy.

$$10 \times 800 = 8000\ cm^{-1} = \Delta_{oct} \tag{11.3.5.4}$$

Each problem is of varying complexity as several steps may be needed to find the correct Δ_{oct}/B values that yield the proper energy ratios.

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11.3.6: Tetrahedral Complexes

Transitions in tetrahedral complexes are Laporte-allowed

Tetrahedral metal complexes often have more intense electronic transitions than their octahedral counterparts. This is due to the fact that the $d-d$ transitions in a tetrahedron are allowed by the Laporte selection rule, while $d-d$ transitions in an octahedral complex are Laporte-forbidden. Recall that the Laporte selection rule applies to centrosymmetric complexes only. The Laporte rule applies to octahedral complexes but not to tetrahedral complexes because a tetrahedron does not have a center of inversion. Notice that the terms (and orbital labels) in a tetrahedron do not include the g subscripts that are present under octahedral symmetry (Figure $11.3.6.1$). The splitting pattern of a tetrahedral complex is exactly opposite to the octahedral case. In the case of a tetrahedron, however, the "g" subscripts are inappropriate because of the tetrahedron's lack of a center of inversion, and transitions between the terms in a tetrahedron do not violate the Laporte Rule.

Another way to explain this in terms of electron transitions between orbitals is through the orbital mixing required to form a tetrahedral complex. Orbital types (i.e., s, p, d) must mix to form the moleculare orbitals of a tetrahedral transition metal complex. The mixing of s and p orbitals with the d orbitals allows transitions that are forbidden in the case of pure d-orbitals.

It is also worth noting that $\Delta_t = \frac{4}{9}\Delta_o$. The smaller Δ for transition metals means that the tetrahedral complexes can absorb at a lower energy and longer wavelength relative to an analogous octahedron.

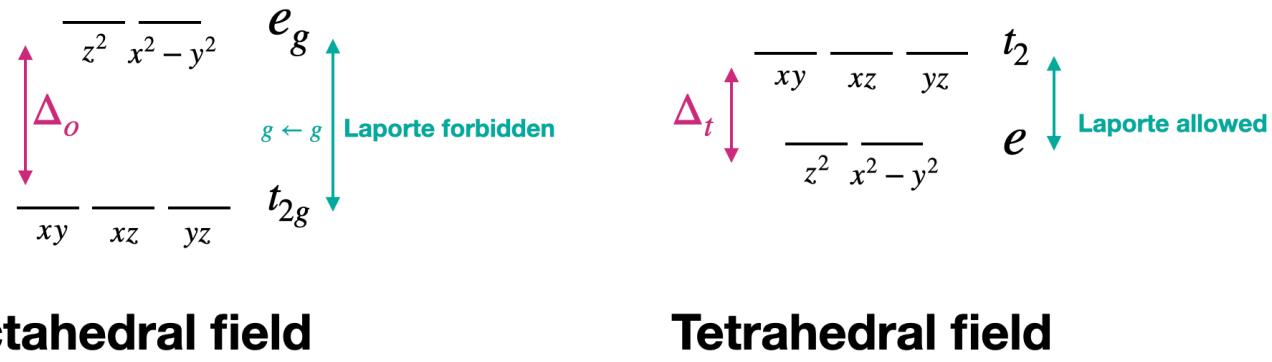


Figure $11.3.6.1$: $d-d$ transitions in octahedral complexes are Laporte-forbidden, while those in tetrahedral complexes are Laporte-allowed. (CC_BY_SA; Kathryn Haas)

Tanabe-Sugano diagrams for tetrahedral complexes

Due to the opposite splitting pattern, the transitions for a d^n tetrahedral complex are sufficiently represented by the d^{10-n} Tanabe-Sugano diagram (just drop the g subscripts from the diagrams). For example, the electronic spectrum of a d^8 tetrahedral complex (e.g., $[\mathrm{Ni(H_2O)_6}]^{2+}$) can be interpreted using the d^2 Tanabe-Sugano diagram.

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11.3.7: Charge-Transfer Spectra

Charge Transfer Transitions

Zn^{2+}		d^{10} ion	white
$[Cu(MeCN)_4]^+$	Cu(I)	d^{10} ion	colourless
$[Cu(phen)_2]^+$	Cu(I)	d^{10} ion	dark orange
TiF_4		d^0 ion	white
$TiCl_4$		d^0 ion	white
$TiBr_4$		d^0 ion	orange
TiI_4		d^0 ion	dark brown
$[MnO_4]^-$	Mn(VII)	d^0 ion	extremely purple
$[Cr_2O_7]^-$	Cr(VI)	d^0 ion	bright orange

Figure 11.3.7.1: Some examples of complexes with d^0 and d^{10} electron configurations, and their colors. Attribution: E.R. Schofield.

We are still not done with our electronic spectra. Thus far, we have only considered transitions of d-electrons between d-orbitals, and their terms. These are called d-d transitions. However, there are also so-called charge transfer transitions possible, which are not d-d transitions. We can easily see that there must be transitions other than d-d transitions when we look at the colors of d^{10} and d^0 ions. For those, there are no d-d transitions possible. Therefore, they all should be colorless. However, that is not always true. Some of these ions are indeed colorless, but some are not (Figure 11.3.7.2). For example, Zn^{2+}, a d^{10} ion, is colorless in complexes, but not Cu(I), which is also d^{10}. While tetrakis(acetonitrile)copper(+) is colorless, bis(phenanthrene) copper(+) is dark orange. d^0 ions have similar properties: While TiF_4 and $TiCl_4$ are colorless, $TiBr_4$ is orange, and TiI_4 is brown. Some d^0 species are even extremely colorful, for example, permanganate with Mn^{7+}, which is extremely purple, and dichromate with Cr(VI), which is bright orange.

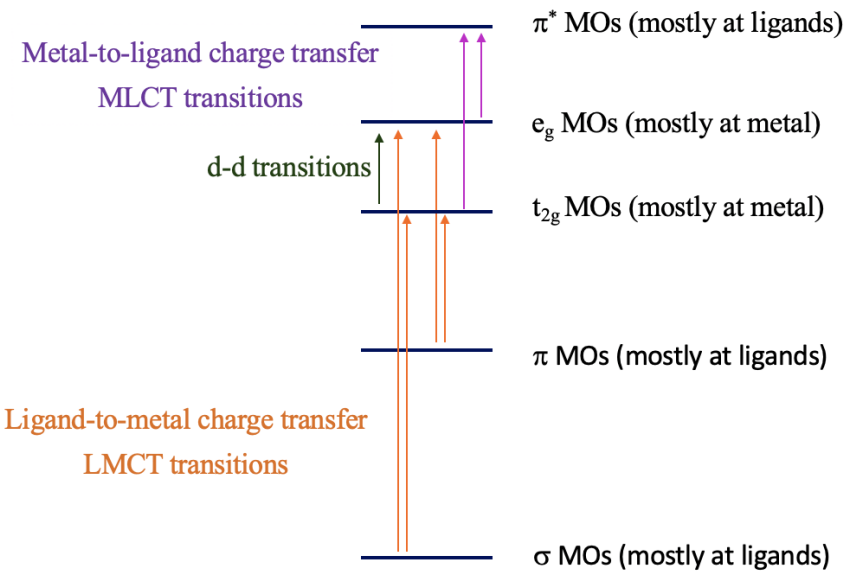


Figure 11.3.7.2: Charge-transfer transitions. Attribution: E.R. Schofield.

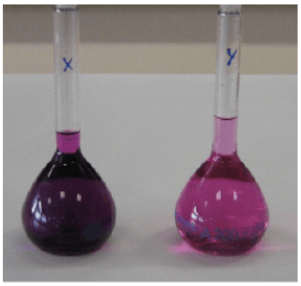
The explanation for these phenomena is charge-transfer transitions (11.3.7.2). There are two types of charge-transfer transitions: ligand-to-metal (LMCT) and metal-to-ligand (MLCT) charge transfer transitions. For the ligand-to-metal transitions, electrons from bonding σ and π-orbitals get excited into metal d-orbitals in the ligand field, for example the t_{2g} and the e_g orbitals in an octahedral complex. If the energy difference between the σ/π-orbitals and the d-orbitals is small enough, then this electron transition is associated with the absorption of visible light. The transition is called a ligand-to-metal transition because the ligand σ/π-orbitals are mostly located at the ligands, while the metal-d-orbitals in a ligand field are mostly located at the metal. Vice versa, the metal-to-ligand transition involves the transition of an electron from metal d-orbitals in a ligand field to ligand π*-orbitals. This essentially moves electron density from the metal to the ligand, hence the name ligand-to-metal-charge transfer transition. If the energy-difference between the ligand π* and the metal orbitals is small enough, then the absorption occurs in the visible range. Charge-transfer transitions are usually both spin- and Laporte allowed; hence, if they occur, the color is often very intense. How can we distinguish between d-d and charge transfer transitions? Charge transfer transitions often change in energy as the solvent polarity is varied (solvatochromic), as there is a change in polarity of the complex associated with the charge transfer transition. This can be used to distinguish between d-d transitions and charge-transfer bands.

LMCT Transitions

Can we predict when the energy windows between the bonding molecular orbitals and the metal d-orbitals are small enough for LMCT transitions in the visible to take place? Generally, it would be desirable if the energy of the metal orbitals were as low as possible and the energy of the bonding ligand orbitals were as high as possible. The energy of metal d-orbitals decreases with increasing positive charge at the metal because the effective nuclear charge on the metal increases. This means that very high metal oxidation states favor LMCT transitions. The d-orbitals should have few or no electrons, so that electrons can be promoted into the orbitals, and orbital energy decreases because electron-electron repulsion is minimized. Examples are Mn(VII), Cr(VI), and Ti(IV). The energy of MOs from bonding ligand orbitals increases when the ligand orbitals have high energy; this is typically the case for π-donor ligands with a negative charge (Fig. 8.2.21).

Ligand properties	Metal ion properties
Ligand MOs: high energy	Valence orbitals: low energy
π-donor electrons	high positive charge
Negatively charged ligands	Few or no d electrons
O^{2-}, Cl^-, Br^-, I^-	Eg. Mn(VII), Cr(VI), Ti(IV)





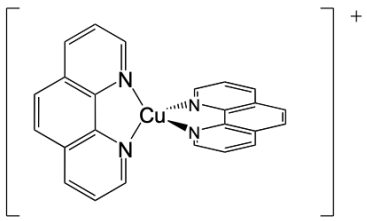
11.3.7.1: The properties of the metal ions and ligands suitable for LMCT transitions. MnO_4^- is deep purple due to LMCT transitions (Attribution: Benjah-bmm27 / Public domain https://commons.wikimedia.org/wiki/F...ate-sample.jpg) and (Attribution: Pradana Aumars / CC0 https://commons.wikimedia.org/wiki/F...entrations.jpg), respectively.

Examples of ligands are oxo- and halo ligands. This explains, for example, the LMCT transitions in permanganate. The Mn is in the very high oxidation state +7, and the ligands are oxo-ligands, which are π-donors with a 2- negative charge. The transitions are both Laporte and spin-allowed, leading to a very high intensity of light absorption, and thus color (Fig. 8.2.21).

MLCT Transitions

What are favorable metal ion and ligand properties for a metal-to-ligand transition, then? In this case we would like to keep the energy of the metal orbitals as high as possible so that the energy difference between a metal d-orbital and a π*-orbital is minimized. This is accomplished when the positive charge at the metal ion is small, and there are many d-electrons that can repel each other, thereby increasing orbital energies, for example Cu(I), Fig. 8.2.22.

Metal ion properties	Ligand properties
low metal ion charge	π-acceptor ligand with low-lying π* orbitals
many electrons	
Cu(I), d^{10} ion	1,10-phenanthroline, CN^-, CO, SCN^-



$[Cu(phen)_2]^+$, dark orange

11.3.7.3: bis(phenanthroline) copper(+). Attribution: E.R. Schofield.

The ligand should be a π-acceptor with low-lying π*-orbitals - for example, phenanthroline, CN^-, SCN^-, and CO. The bis(phenanthroline) copper(+) ion, for instance, is dark orange and has an MLCT absorption band at 458 nm. This MLCT transfer

is both spin and Laporte-allowed.

It should be mentioned that some complexes allow for both metal-to-ligand and ligand-to-metal transitions. For example, in the $Cr(CO)_6$ complex, the σ-orbitals are high enough and the π*-orbitals are low enough in energy to allow for light absorption in the visible range. Finally, intraligand bands are also possible when the ligand is a chromophore.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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- 8.2: Term splitting in ligand fields, selection rules, Tanabe-Sugano diagrams. Metal to ligand, and ligand to metal transitions by Kai Landskron is licensed CC BY 4.0.

11.3.8: Applications of Charge-Transfer

Transition metal complexes with strong π-accepting ligands have proven quite useful across many applications in industry, materials science, and medicine due to their intense absorption of light, photostability, and unique geometric, redox, and photodynamic properties. These complexes usually have low-valent metal ions (low oxidation state) with π-accepting ligands constructed of conjugated poly-aromatic rings. Intense light absorption occurs through metal-to-ligand charge transfer (MLCT), causing a formal oxidation of the metal ion and reduction of the ligand. These compounds are used as sensors, and their excited states can be used as indispensable reactants. Some examples of their applications are discussed briefly below.

Ruthenium bypyridine derivatives

Let's use the example of a simple and interesting metal complex: tris(bypyridine)ruthenium(II), or $[\mathrm{Ru(bpy)_3}]^{2+}$. This molecule is the most generic form of a family of derivatives that have this core structure in common. $[\mathrm{Ru(bpy)_3}]^{2+}$ absorbs ultraviolet light at 452 nm due to an intense MLCT. It also absorbs light at shorter wavelenghts due to ligand-centered $\pi * \leftarrow \pi$, metal-centered $d \leftarrow d$, and LMCT transitions. The ground state is a singlet state (all paired electrons), and the spin-selection rule allows formation of a singlet excited state. However, in the case of high-atomic-number d^6 metal ions, like Ru, there is intense spin-orbit coupling that favors intersystem crossing. **Intersystem crossing** is the phenomenon by which a system's spin multiplicity can change by the transition of an electron's spin without energy cost. In the case of $[\mathrm{Ru(bpy)_3}]^{2+}$, the excited singlet state transitions to an isoenergetic (or degenerate) triplet excited state. $[\mathrm{Ru(bpy)_3}]^{2+}$ has a long-lived excited state due to the fact that the transition between the triplet excited state and the singlet ground state is spin-forbidden. The excited state can relax to the singlet ground state radiatively (releasing a photon) or non-radiatively (as phonons/heat).

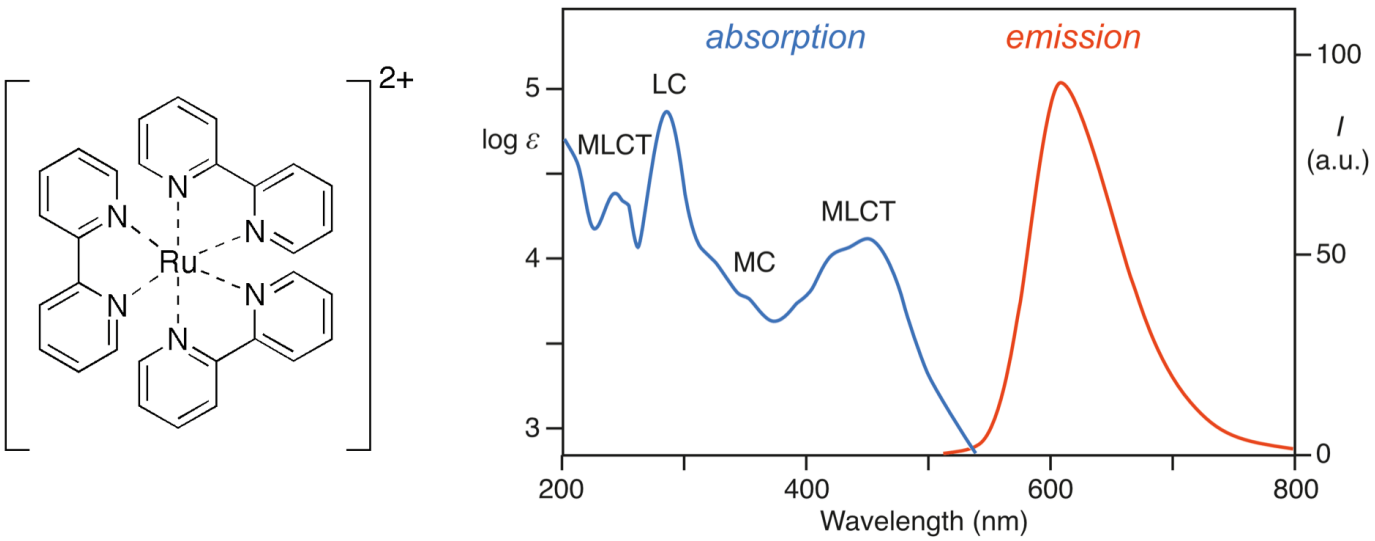


Figure 11.3.8.1: Structure of $[\mathrm{Ru(bpy)_3}]^{2+}$ (left) and its absorption and emission spectrum (right). (CC-BY-SA: Albris, Ru(bpy)32+ absorption&emission, Added structure of Ru(bpy)3 by Kathryn Haas)

Bioimaging

The $[\mathrm{Ru(bpy)_3}]^{2+}$ complex is fluorescent, with a quantum yeld of approximately 2%. Derivatives of this core structure offer a variety of interesting properties, including a tunable color of emission. Other modifications have been made to make Ru bipyridine derivatives more functional for cellular imaging. For example, these metal complexes have been modified to bind to carbohydrates, specific organelles, or specific organs for targeted biological imaging applications.

Energy and catalysis

Due to the long lifetime of the $[\mathrm{Ru(bpy)_3}]^{2+} *$ excited triplet state, this molecule has potential as a photosensitizer for the

oxidation and reduction of water (water splitting) for energy production. The MLCT excitation is essentially a removal of an electron from Ru (an oxidation of Ru) and a placement of an electron onto a bpy ligand (a reduction of the ligand). The resultant $[Ru^{3+}]$ center is a powerful oxidant, capable of oxidizing water, while the unpaired electron on reduced bpy is a powerful reductant. The power of this complex for catalyzing the splitting of water has been demonstrated using an electron mediator, methyl viologin, a Pt catalyst, and a sacrificial reductant. Once the excited $[Ru(bpy)_3]^{2+}*$ has formed, the excited electron can be captured by methyl viologen and passed to a Pt catalyst which reduces hydrogen ion (H^+) to H_2. The oxidized $[Ru(bpy)_3]^{3+}$ complex is then reduced by reaction with a sacrificial reductant like EDTA or triethanolamine to re-form $[Ru(bpy)_3]^{2+}$.

$[Ru(bpy)_3]^{2+}$ is also used as a photosensitizer for organic synthesis. Many analogues of $[Ru(bpy)_3]^{2+}$ are employed as well. These transformations exploit the redox properties of excited $[Ru(bpy)_3]^{2+}*$ and its reductively quenched derivative $[Ru(bpy)_3]^{+}$. (from Wikipedia)

Other applications

Derivatives of $[Ru(bpy)_3]^{2+}$ are numerous. Such complexes are widely discussed for applications in biodiagnostics, photovoltaics, and organic light-emitting diodes, but no derivative has been commercialized. Application of $[Ru(bpy)_3]^{2+}$ and its derivatives to fabrication of optical chemical sensors is arguably one of the most successful areas so far. (from Wikipedia)

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12: COORDINATION CHEMISTRY IV - REACTIONS AND MECHANISMS

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12.1: Introduction to Reactions of Metal Complexes

Although there are a vast array of reactions that occur at transition metal centers, we will touch on only a subset of the possibilities. This chapter will focus on the reactions of octahedral and square planar metal complexes, and the reactions will be divided into three types:

1. **Substitution reactions at the metal center**: these are reactions in which one ligand is replaced with another ligand within the metal's inner coordination sphere.
2. **Redox**: these are reactions in which the metal oxidation state formally changes by gaining or loosing electrons.
3. **Ligand reactions**: these are reactions that occur primarily on the ligands that are bound to metal ions.

Review of reaction coordinate diagrams and terms

Before we begin our discussion of reactions, let's review some of the vocabulary and models that chemists use to understand reactions.

A chemical reaction can be represented with a reaction coordinate diagram in which the total potential energy of a state is plotted in the vertical y axis, and the "**reaction coordinate**" (sometimes also referred to as "reaction progress", or "extent of reaction") is plotted on the horizontal x axis. The reaction coordinate is often drawn as the progress of a reaction from reactants (R) on the left to products (P) on the right.* Examples of reaction coordinate diagrams for a one-step and a two-step reaction are shown in Figure 12.1.1. Notice the difference in the reaction profile that depends on the number of reaction steps. A one-step reaction has one "hill" shape, while a two step reaction takes on a "saddle" shape.

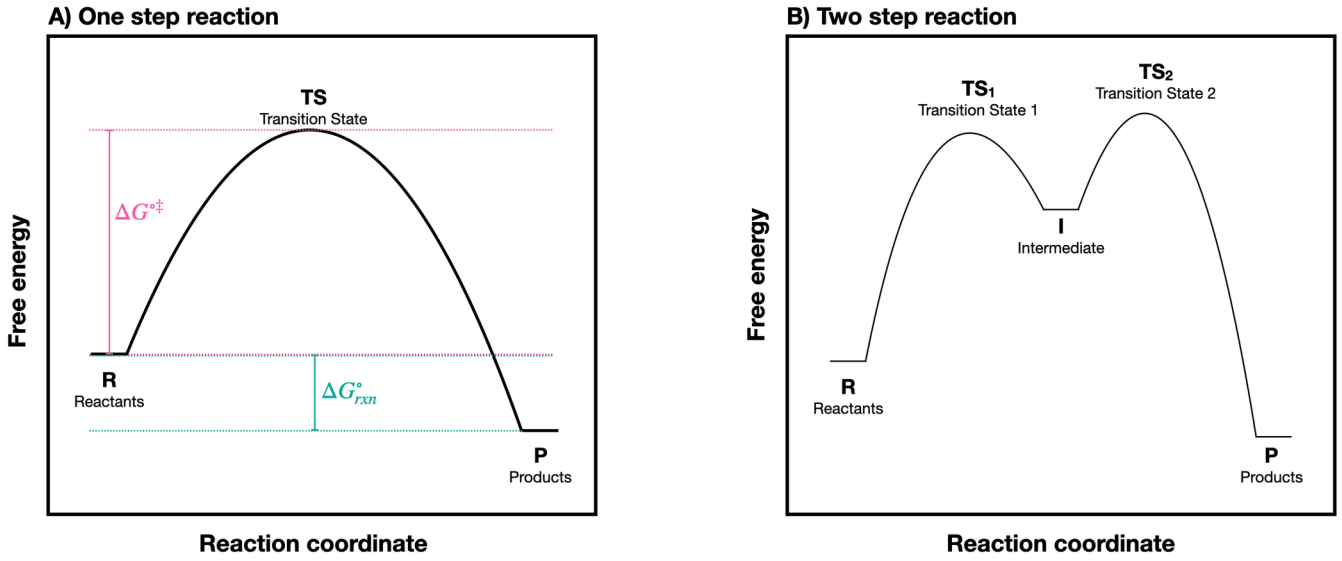


Figure 12.1.1: Examples of a reaction coordinate diagram for a one-step reaction (left), and a two-step reaction (right). (CC-BY-SA; Kathryn Haas)

*Many students find it helpful to envision the horizontal axis in an reaction coordinate diagram as being analogous to the progress bar at the bottom of a youtube video.

Thermodynamics

The difference in energy between reactants (R) and products (P) indicates whether reactants or products will dominate at thermodynamic equilibrium. At standard conditions, this difference is the standard Gibbs Free Energy of the reaction (ΔG°_{rxn} or ΔG°). The Gibbs free-energy change is a combination of enthalpy change (ΔH°) and entropy change (ΔS°):

$$\Delta G^{\circ} = \Delta H^{o} - T\Delta S^{o}$$

where

- T is the temperature in Kelvin (recall that the Kelvin temperature is simply the Celsius temperature plus 273.15).
- Enthalpy change (ΔH°) is the heat released or absorbed by the reaction.
- Entropy change (ΔS°) is the change in disorder from reactants to products. In a reaction in which one molecule cleaves into two smaller molecules, for example, disorder increases, so ΔS° is positive.

The standard Gibbs free energy change for a reaction can be related to the reaction's equilibrium constant K_{eq} by the equation:

$$\Delta G^\circ = -RT \ln K_{eq}$$

where R is the gas constant (8.314 J/mol×K) and T is the temperature in Kelvin (K).

A negative value for $\Delta \mathrm{G_{rnx}}^\circ$ (an exergonic reaction) corresponds to $\mathrm{K_{eq}}$ being greater than 1, an equilibrium constant which favors product formation. Conversely, an endergonic reaction has a positive value of $\Delta \mathrm{G}^\circ$, and a $\mathrm{K_{eq}}$ between 0 and 1.

Kinetics

The highest point between two energy minima is a transition state (TS). The difference in energies of the reactant and the highest-energy TS is the standard free energy of activation ($\Delta \mathrm{G}^{\circ\ddagger}$). The activation energy, in combination with the temperature at which the reaction is being run, determines the rate of a reaction: the higher the activation energy, the slower the reaction. The rate constant (k) is the proportionality constant relating the rate of the reaction to the concentrations of reactants. The relationship between activation energy and the rate constant, k, is given by the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}} \qquad \text{or} \qquad \ln k = \ln A - \frac{E_A}{RT}$$

A rate law is an expression showing the relationship of the reaction rate to the concentrations of each reactant. The rate is defined as the change in reactants or products over time. For example, in a reaction of two reactants (R_1 and R_2) to form product (P), a rate law could be written as follows:

$$\frac{d[\mathrm{P}]}{dT} = \mathrm{k[R_1][R_2]}$$

The rate law above is second order overall, and first order with respect to both R_1 and R_2. The order indcates the power of reactant concentrations for individual reactants or overall for the reaction.

In a one-step reaction, the product is formed in one step. There is an energy barrier to overcome so that this process can happen. At the height of that energy barrier is the TS. In a one-step reaction, there is one transition state. In contrast, in a two-step reaction, there are two transition states and an intermediate (denoted by the letter I). The first step from R to I, passes over transition state TS_1, is endergonic. The second step passing through transition state TS_2 is exergonic. The intermediate (I) is thus depicted as an energy 'valley' (a local energy minimum) situated between the two energy maxima; TS_1 and TS_2.

In Figure $12.1.1$B, notice that the energy barrier for the first step is larger than the energy barrier for the second step. This means that the first step is slower than the second. In a multi-step reaction, the slowest step - the step with the largest energy barrier - is referred to as the rate-limiting or rate-determining step. The rate-determining step can be thought of as the 'bottleneck' of the reaction: a factor which affects the rate-determining step will affect the overall rate of the reaction. Conversely, a factor which affects only a much faster step will not significantly affect the rate of the overall reaction.

Summary and Key Terms

Reaction coordinate diagrams convey some very important ideas about how the reaction can proceed, and about the thermodynamics and kinetics of the reaction. In the sections that follow, the following key terms will be used:

Description of Key Terms

Reactants (R): The molecular species that are the starting materials for a chemical reaction. These are often written at the left side of a reaction coordinate diagram.

Products (P): The molecular species that result from a chemical reaction. These are often written at the right side of a reaction coordinate diagram.

Transition State (TS): a transition state is the transient species that exists at an energy maximum. In other words, TS's are highest-energy structures along a reaction pathway. Hammond's postulate suggests that the structure of a transition state should resemble the lower-energy species (R, P, or I) adjacent to it along the reaction coordinate, and most closely resembles the structure of the species closest in energy.

Intermediate (I): an intermediate is a high-energy structure at a local minimum. Intermediates are sometimes thought of as long-lived transition states. Unlike transition states, intermediates sometimes exist long enough and in high enough concentration to be detectable experimentally.

Microscopic reversibility: if a reaction can proceed in the forward direction from R to P, then in principle, it can also proceed in the reverse direction from P to R. There may be many possibilities for how a reaction *could* happen, but the lowest-energy pathway in the forward direction is also the lowest energy pathway in the reverse direction. In other words, the reactions passes through the same lowest-energy I and TS in the forward and reverse directions.

Steady-State Approximation: the concentration of an intermediate is assumed to react as quickly as it forms. This approximation allows us to assume that concentration of an intermediate remains "steady" throughout the reaction progress. This approximation is useful for analysis of reaction kinetics.

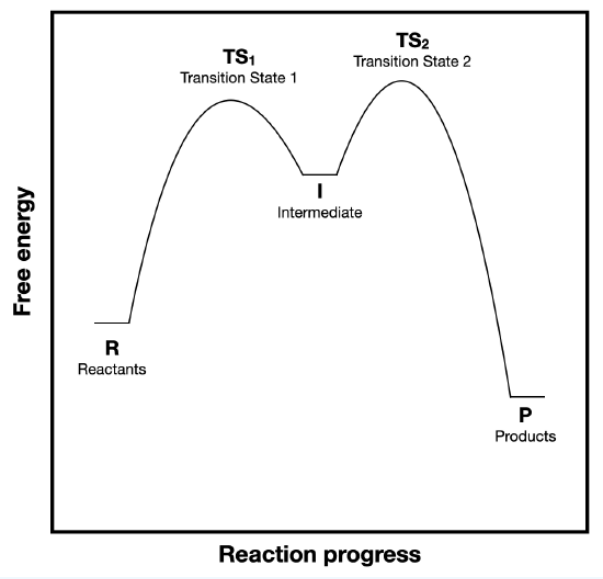
Order: The order of a reaction indicates the power of total reactant concentration in a kinetic rate law. The order of a reactant indicates that reactant's power in the rate law. For example, is a rate law that is $\mathrm{Rate} = \mathrm{k}\ [\mathrm{A}]^2[\mathrm{B}]$, the reaction is second order in A, first order in B and third order overall. If there were also a reactant, C, that was not part of the rate law, the reaction would be zero order with respect to C.

Exercise 12.1.1

Figure $12.1.1$ is replicated below for convenience. This figure shows a reaction coordinate diagram for a two-step reaction.

a. (ΔG°) and $\Delta G^{\circ\ddagger}$) are labeled on Figure $12.1.1A$, but not on Figure $12.1.1B$. Add the appropriate labels to diagram B. (copied below for convenience).

b. Consider the energy barriers for the first and second steps and explain why the steady-state approximation is a valid assumption.

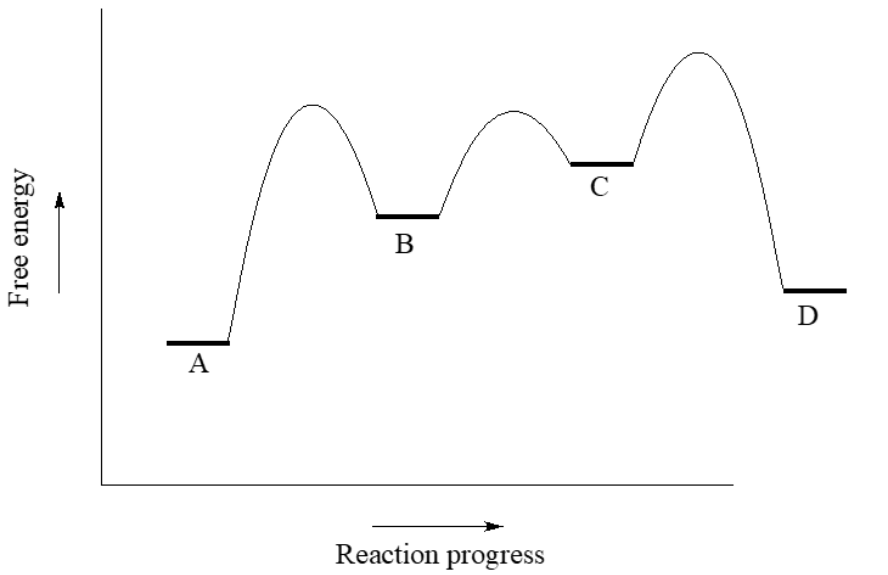


Answer available at the end of this section.

Exercise 12.1.1

Use the reaction coordinate diagram below to answer the questions.

a. Is the overall reaction endergonic or exergonic in the forward (A to D) direction?
b. How many steps does the reaction mechanism have?
c. How many intermediates does the reaction mechanism have?
d. Redraw the diagram if necessary. Add a label showing the energy barrier for the rate-determining step of the forward reaction.
e. Add a label showing ΔG°_{rxn} for the reverse reaction (D to A).
f. What is the fastest reaction step, considering both the forward and reverse directions?



Answer available at the end of this section.

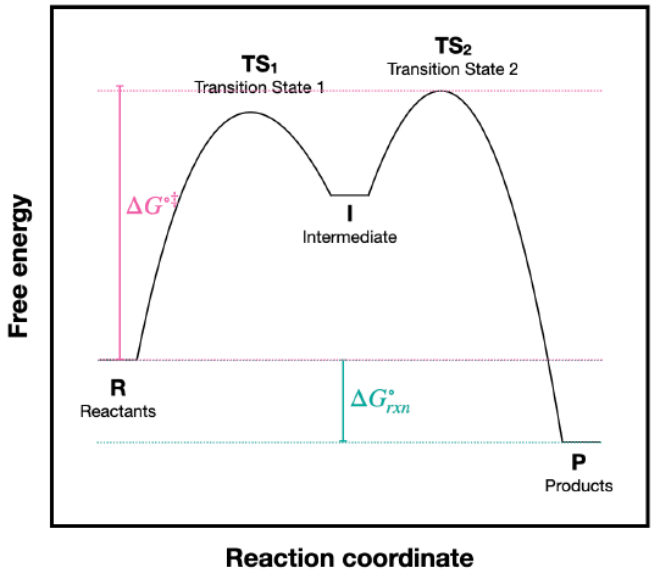
Organic Chemistry With a Biological Emphasis by Tim Soderberg (University of Minnesota, Morris)

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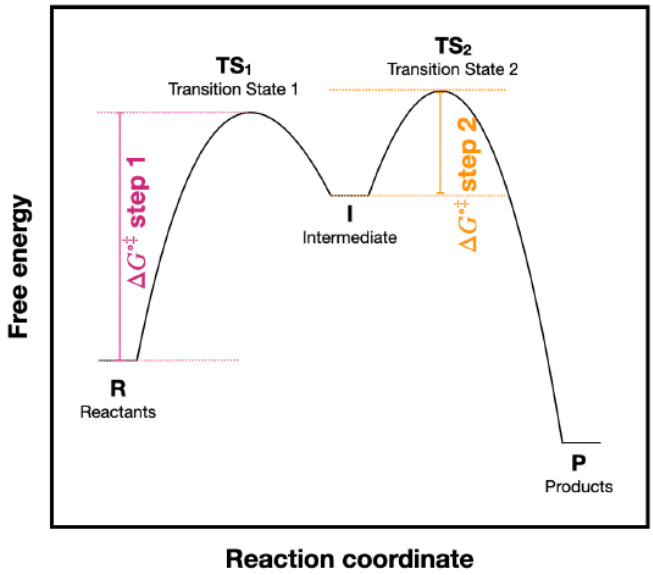
Answers

Exercise 12.1.1

a) The activation energy for this reaction is the difference between R and TS_2 because TS_2 is the highest energy along the reaction pathway.

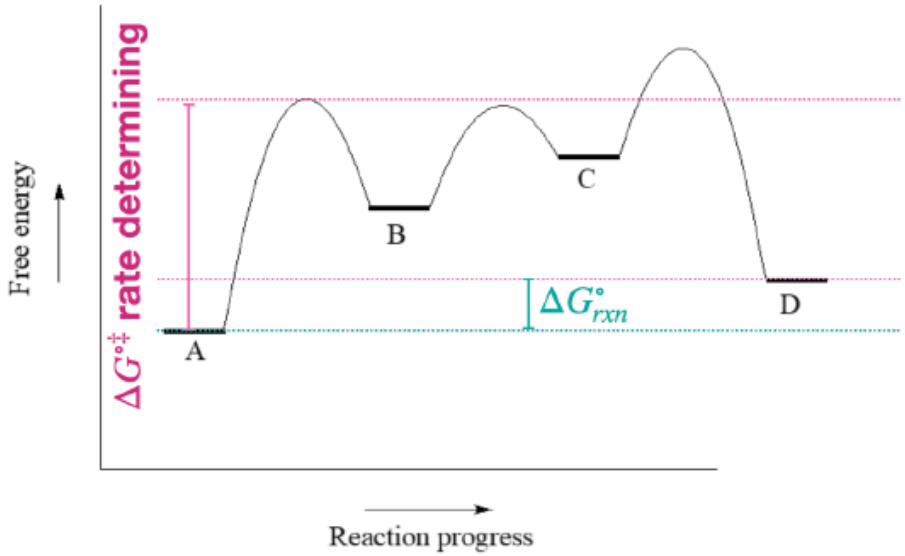


b) The activation energy for step 2 is much smaller than for step 1. This tells us that step 2 occurs faster than step 1. So, the concentration of intermediate should not increase over the course of the reaction, and it should react at least as fast as it is formed. The fact that the activation barrier for step 2 is less than for step one allows us to assume that [I] does not change over the course of the reaction. This should generally be true for all intermediates.



Exercise 12.1.1

a. D is higher energy than A, so the reaction is endergonic
b. Three steps
c. Two: B and C are intermediates.
d. The first step is rate determining since it has the largest activation barrier.
e. ΔG°_{rxn} for the reverse reaction (D to A) is the same as for the froward direction, with a reverse of its sign.



f. The fastest step has the lowest barriers: this would be the step to/from B and C.

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12.2: SUBSTITUTIONS REACTIONS

12.2.1: Introduction to Substitution Reactions
12.2.2: Inert and Labile Complexes
12.2.3: Mechanistic Possibilities

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12.2.1: Introduction to Substitution Reactions

Ligand substitution refers to the replacement of one ligand in a coordination complex with another ligand.

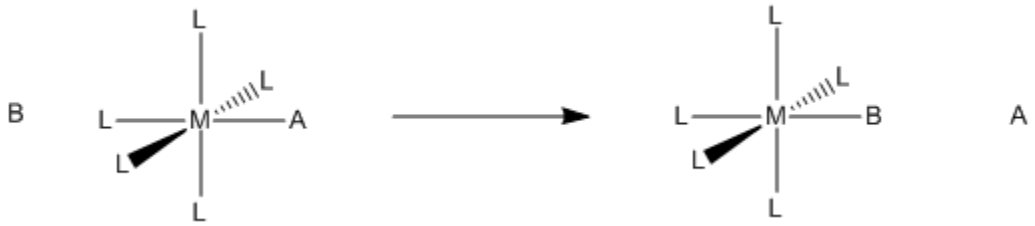


Figure 12.2.1.1: Substitution of one ligand for another in a coordination complex.

Remember, a ligand in coordination chemistry is just a Lewis base that binds to a metal atom or ion. It does so by donating a lone pair (or other pair of electrons). Generallly, this donation is reversible. The donor can always take its electrons back. Typically, there may be some balance between the metal's need for more electrons and the donor's attraction for its own electrons; donor atoms are frequently more electronegative than the metal.

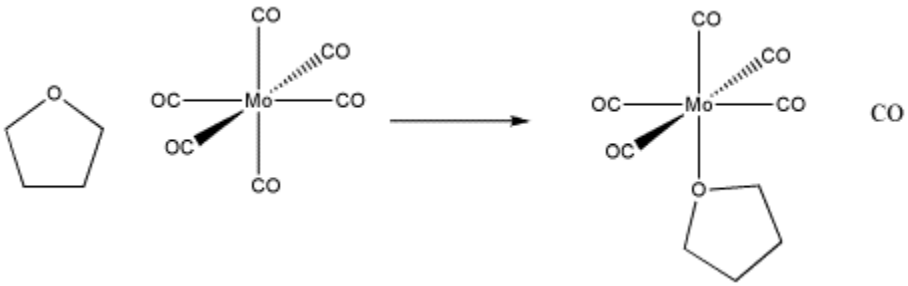


Figure 12.2.1.2: An example of ligand substitution. THF replaces a carbon monoxide in this molybdenum complex.

Even though the reaction is pretty simple, it can occur in different ways.

That is, the elementary steps involved in the reaction can occur in different orders. The elementary reactions are the individual bond-making or bond-breaking events that lead to an overall change. Sometimes the order of steps is referred to as the mechanism or the mechanistic pathway.

- The mechanism is the order of elementary reaction steps.
- Elementary reaction steps are individual bond-making and breaking steps.

You may have seen reaction mechanisms before. For example, carbonyl addition chemistry can involve lengthy mechanisms, in which a number of proton transfers and other bond-making and bond-breaking steps must occur to get from one state to another. Because ligand substitution is simpler than that, it is a good place to study mechanism in a little more depth, without getting overwhelmed by the details.

The sequence of steps in the mechanism influences how different factors will impact the reaction. For example, changing concentrations of different components in a reaction mixture can affect the time it takes for a reaction to finish.

- The mechanism can have a dramatic impact on the outcome of the reaction under different circumstances.

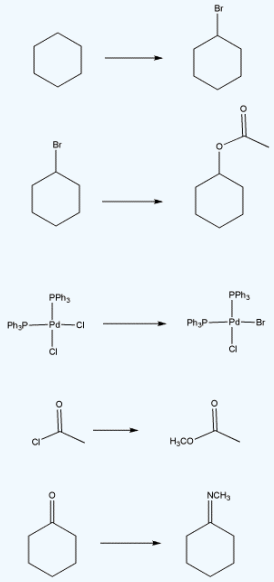
These kinds of considerations have a dramatic impact on industrial processes such as pharmaceutical production. In that setting, chemical engineers need to make decisions about how much of each reactant must be admitted to a reaction mixture and how long they should be allowed to react together. If they allow the reaction to proceed for too, long, there may be “side-reactions” that start to occur, interfering with the quality of the product, and they will waste valuable time in the production pipeline. If they don’t allow it to react long enough, the reaction may not finish, and the product will be contaminated with leftover starting materials.

In this chapter, we will look at how this simple reaction can occur in different ways. We will see some different methods that are

used to tell which way the reaction occurs (i.e. evidence of what is really happening). We will also look at some different factors that may influence whether the reaction is likely to occur one way or the other (i.e. reasons it is happening that way, or reasons we expect it will happen that way).

Exercise 12.2.1.1

Some kind of substitution occurs in each of the following reactions: an atom or group replaces another. In each case, identify what is being replaced, and what replaces it.



Answer a available at the end of this section.

Answers

Exercise 12.2.1.1

a bromine atom replaces a hydrogen atom
an acetate group (ethanoyl ester) replaces a bromine atom
a bromine atom replaces a chlorine atom (or ions)
a methoxy group replaces a chlorine atom
a methylamino group replaces an oxygen atom

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12.2.2: Inert and Labile Complexes

Kinetics of Substitution Reactions

Kinetics is a branch of chemistry that is concerned with the rates of chemical reactions. In this section, we will discuss the rates of metal-ligand (M-L) substitution reactions.

Let's start with some examples. In the table below are three examples of ligand substitution reactions of hexaaquo metal complexes to form hexaammine complexes. These reactions are nearly identical with the exception of the metal ion. The products are thermodynamically favored in all cases.

Reaction	Rate constant (k)	Labile or Inert
$[\mathrm{Ni(OH_2)}]^{2+} + 6\,\mathrm{NH_3} \rightleftharpoons [\mathrm{Ni(NH_3)_6}]^{2+}$	$k = 10^{4} s^{-1}$ (1 ns)	Labile (happens in < 1 min)
$[\mathrm{Cr(OH_2)}]^{3+} + 6\,\mathrm{NH_3} \rightleftharpoons [\mathrm{Cr(NH_3)_6}]^{3+}$	$k = 10^{-3} s^{-1}$ (6 days)	Inert (slow, takes hours)
$[\mathrm{Cu(OH_2)}]^{2+} + 6\,\mathrm{NH_3} \rightleftharpoons [\mathrm{Cu(NH_3)_6}]^{2+}$	$k = 10^{8} s^{-1}$	Very Labile (happens in seconds)

Definitions

- **Kinetically Labile** - Metal complexes that undergo "kinetically fast" substitution reactions are **kinetically labile**. Taube suggested that these are reactions in which half of the reactant is consumed in one minute or less ($t_{1/2}$ <1 min).
- **Kinetically Inert** - Metal complexes that undergo "kinetically slow" substitution reactions are **kinetically inert** or **non-labile**. Taube suggested that these are reactions in which $t_{1/2}$ >1 min.

A common pitfall is to confuse the meaning of kinetic terms, like *labile* and *inert,* with thermodynamic terms, like *stable* and *unstable*. It is important to distinguish between kinetics and thermodynamics. For example, the complex $[Fe(H_2O)Cl]^{2+}$ has a large formation constant and is thermodynamically stable; yet it is also labile. On the other hand, the complex $[Co(NH_3)_6]^{3+}$ is unstable in acidic aqueous solution and decomposes spontaneously to $[Co(H_2O)_6]^{3+}$; yet it decomposes slowly because it is inert. It is good practice to use clear terms such as "*kinetically* labile" or "*kinetically* inert" and "*thermodynamically* stable" and "*thermodynamically* unstable".

Exercise 12.2.2.1

Draw the reaction coordinate diagrams for a reaction of the form $[ML_6]^{n+} + X \rightleftharpoons [ML_5X]^{n+} + L$ in the following scenarios:

a. $[ML_6]^{n+}$ is theromdynamically stable and kinetically inert.
b. $[ML_6]^{n+}$ is theromdynamically unstable and kinetically inert.
c. $[ML_6]^{n+}$ is theromdynamically stable and kinetically labile.
d. $[ML_6]^{n+}$ is theromdynamically unstable and kinetically labile.

Answer a) available at the end of this section.

Answer b) available at the end of this section.

Answer c) available at the end of this section.

Answer d) available at the end of this section.

Factors that affect rates of substitution reactions:

Some of the factors that affect the kinetic rates of ligand substitution are the same factors that affect thermodynamic stability (see Chapter 10). The same factors that make a complex stable can also make it more inert. Why are kinetic factors related to thermodynamic stability? It is because the structure and stability of the reactant complex is related to the structure and stability of the transition state. The reactant complex must change its geometry to form an intermediate or transition state. When the reactant is particularly stable, it can result in a higher activation energy associated with moving away from the stable configuration. However, it is incorrect to assume that stability is *always* correlated with reaction rates. Kinetic and thermodynamic factors are related, yet separate.

There are three important factors that influence kinetic rate of substitution:

1. Ligand Field Stabilization Energy (LFSE): Electron configurations that place electrons in higher-energy orbitals (particularly antibonding orbitals) result in more labile complexes. As long as there are not electrons in higher-energy orbitals, the lability correlates roughly with LFSE. The more negative the LFSE, the more inert.
2. Coulombic attraction between the metal and ligand: In general, higher charge density on the metal ion or on the ligand(s) leads to stronger electrostatic attraction between metal and ligand. Stronger Coulombic attraction generally leads to slower dissociation steps and faster association steps. The effect that these have on the reaction rate depends on elementary steps that take part in the rate-determine step(s).
3. Denticity: Multi-dentate ligands create particularly inert complexes as a result of the kinetic chelate effect.

All three considerations are described in more detail below.

Exercise 12.2.2.2

In which compound from each pair would you expect the strongest ionic bonds? Why?

a) LiF vs KBr
b) $CaCl_2$ vs. KCl

Answer a available at the end of this section.

Taube's observations of metal complex substitution rates

Henry Taube (Nobel Prize, 1983) tried to understand kinetic lability by comparing the factors that govern bond strengths to observations about the rates of reaction of coordination complexes. He saw some things that were unsurprising. He also drew some new conclusions based on ligand field theory.

Taube observed that **many M^{+1} ions (M = metal) are more labile than many M^{+3} ions**, in general. That isn't too surprising, since metal ions function as electrophiles (Lewis acids) and ligands function as nucleophiles (Lewis bases) in forming coordination complexes. In other words, *metals with higher charges ought to be stronger Lewis acids, and so they should bind ligands more tightly*. However, there were exceptions to that general rule. For example, Taube also observed that Mo_5^+ compounds are more labile than Mo_3^+ compounds. So, there must be more going on here than *just* the effects of electrostatic attraction.

Another factor that governs ionic bond strengths is the *size of the ion*. Typically, **ions with smaller atomic radii form stronger bonds** than ions with larger radii. Taube observed that Al^{3+}, V^{3+}, Fe^{3+} and Ga^{3+} ions are all about the same size. All these ions exchange ligands at about the same rate. That isn't surprising, because they have the same charge and the same radius. However, Cr^{3+} is also about the same size as those ions and it also has the same charge, but it is much less labile. Once again, there are exceptions to our regular expectations based on simple electrostatic considerations. Furthermore, 4d and 5d transition metals (Y→Cd, and Ac→Hg) are much more inert than 3d transition metals (Sc→Zn). This is unexpected when we consider size; the 4d and 5d metals are much larger than the 3d metals. This unexpected behavior tells us that electrostatics alone cannot predict lability.

Taube came up with a hypothesis that could explain the seeming contradictory oservations described above: *kinetic lability must be affected by d-electron configuration*. This idea forms the basis of Taube's rules about lability.

For example, metals like Ni^{2+} and Cu^{2+} are very labile. The d orbital splitting diagrams for those compounds would have d electrons in the e_g set. Remember, the e_g set arises from interaction with the ligand donor orbitals; this set corresponds to a σ antibonding level.

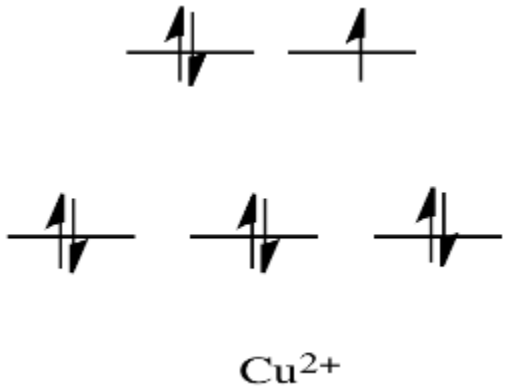


Figure 12.2.2.1: d^9-electron configuration assuming octahedral geometry.

By comparison, V^{2+} is rather inert. The d orbital splitting diagram in this case has electrons in the t_{2g} set, but none in the e_g set.

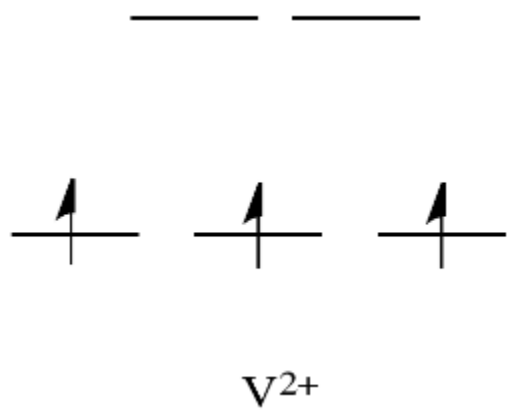


Figure 12.2.2.2: d^3-electron configuration assuming octahedral geometry.

So, having electrons in the higher energy, antibonding e_g level weakens the bond to the ligand, so the ligand can be replaced more easily. In the absence of those higher energy electrons, the bond to the ligand is stronger, and the ligand isn't replaced as easily.

On the other hand, metals like Ca^{2+}, Sc^{3+} and Ti^{4+} are pretty labile. The d orbital splitting diagrams in those cases are pretty simple: there are no d-electrons at all in these ions.

That means having no electrons in these mostly non-bonding levels leaves the complex susceptible to ligand replacement. But it's hard to see why population of an orbital that is mostly non-bonding would have an effect on ligand bond strength.

Instead, this factor probably has something to do with the part of ligand substitution that we have ignored so far. Not only does one ligand need to leave, but a second one needs to bond in its place. So, having an empty orbital for the ligand to donate electrons into (or, put another way, not having electrons in the way that may complicate donation from the ligand) makes that part of the reaction easier.

Exercise 12.2.2.3

Consider all possible electron configurations for octahedral complexes (d^0 to d^{10}, high spin and low spin cases): predict whether each case would be inert, intermediate, or labile.

Answer available at the end of this section.

Exercise 12.2.2.4

Put the metal ions in order of decreasing reaction rate (from labile to inert):

a) Al^{3+}, Na^{+}, Mg^{2+}

b) $Ca^{2+}, Mg^{2+}, Sr^{2+}$

Answer (a) available at the end of this section.

Answer (b) available at the end of this section.

Exercise 12.2.2.5

Some metals, like Mn^{2+}, can be either labile or inert, depending on whether they are high spin or low spin. Explain why using d orbital splitting diagrams.

Answer available at the end of this section.

Exercise 12.2.2.6

Predict whether the following metals, in octahedral complexes, are labile or not.

a) Co^{3+} (high spin)

b) Co^{3+} (low spin)

c) Fe^{2+} (low spin)

d) Fe^{2+} (high spin)

e) Zn^{2+}

Answer available at the end of this section.

Generalizations for how metal ion affects kinetics:

These are some generalizations about how the kinetics of substitution is affected by the metal ion identity and the d^n electron configuration.

1. s-block metals are very labile, except for those with very high charge density (eg. $Mg^{2+}\ is\ inert$)
2. d^{10} metals are labile (eg: Zn^{2+}, Cu^{+}, Hg^{2+})
3. Other ions with a full shell are labile (eg: Ln^{3+} of f-block)
4. 3d M^{2+}, *when high spin,* are generally labile (eg. $Cu^{2+}is\ very\ labile$)

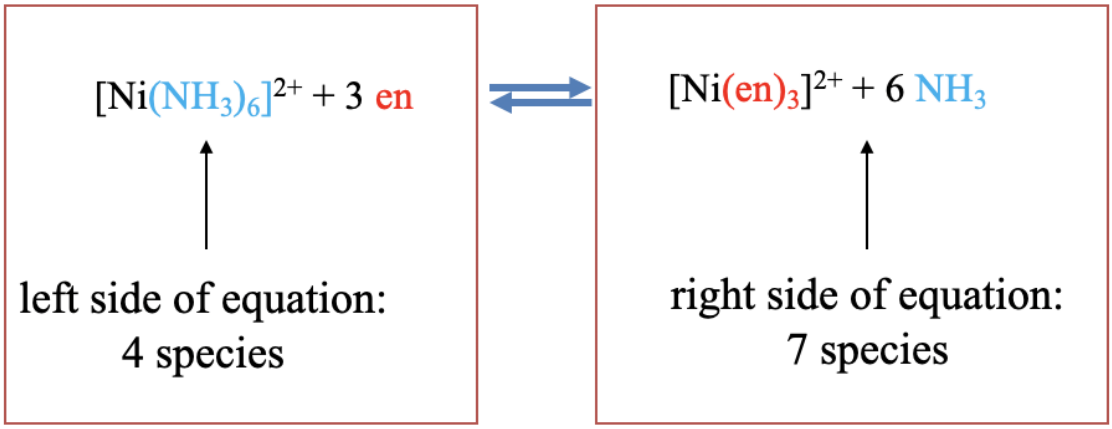
5. 4d and 5d are usually inert due to higher LFSE (low spin, high LFSE)
6. M^{2+} is more labile than the same metal as M^{3+}
7. d^3 and low spin d^6 are inert (eg. Cr^{3+}, Co^{3+}, low spin Fe^{2+})

Chelate Complexes

In addition to considering factors related to the metal ion and charge or covalent character of metal-ligand bonds, an important consideration is the effect a chelate ligand on reaction kinetics. This effect is also discussed in more detail later in this chapter (Section 12.4.5).

Recall the Thermodynamic Chelate Effect

Chelating complexes tend to be more stable than complexes with monodentate ligands. This is called the "thermodynamic chelate effect". The effect deserves an explanation. The explanation is the increase of entropy that occurs when two or more monodentate ligands are replaced by a chelating ligand. The entropy increases because the overall number of particles increases as the substitution takes place.



$$\Delta S° = +88 \text{ J K}^{-1} \text{ mol}^{-1}$$

Figure 12.2.2.3: Example of the thermodynamic chelate effect

For example, the substitution of six ammine ligands in the hexaammine nickel (2+) complex by three ethylenediamine chelating ligands increases the number of molecules from four to seven, and hence the entropy increases, in this case by 88 J K^{-1} and mol^{-1} (Figure 12.2.2.3)

The Kinetic Chelate Effect

In addition to the thermodynamic chelate effect, there is the kinetic chelate effect. Chelate complexes are frequently more inert than complexes with monodentate ligands. Chelate complexes are more inert for two reasons (Figure 12.2.2.4).

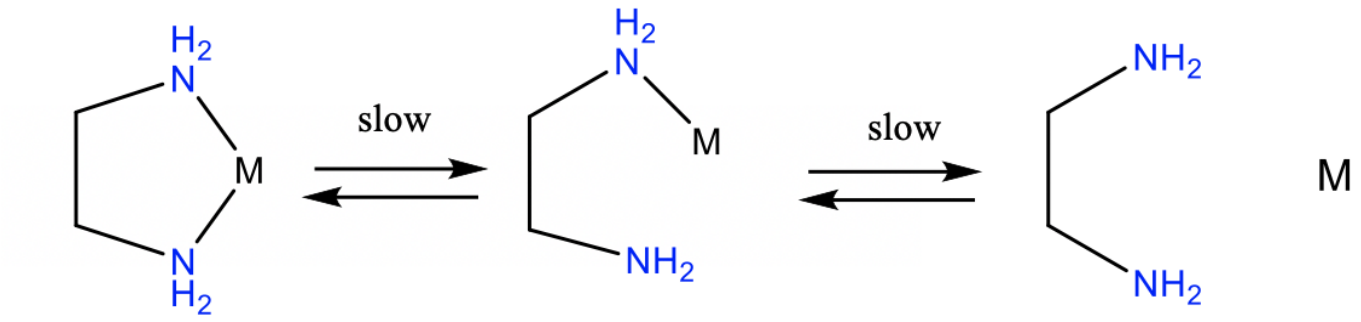


Figure 12.2.2.4: Illustration of the kinetic chelate effect

Firstly, the whole ligands needs to rotate and bend in order to cleave the first metal-ligand bond. This requires time and slows the kinetics of the bond cleavage. The second reason is that the detached donor atom cannot leave the proximity of the complex because the ligand is still attached via the other donor atom. This increases the probability of the re-formation of the metal-ligand bond which decreases the probability of both bonds being cleaved.

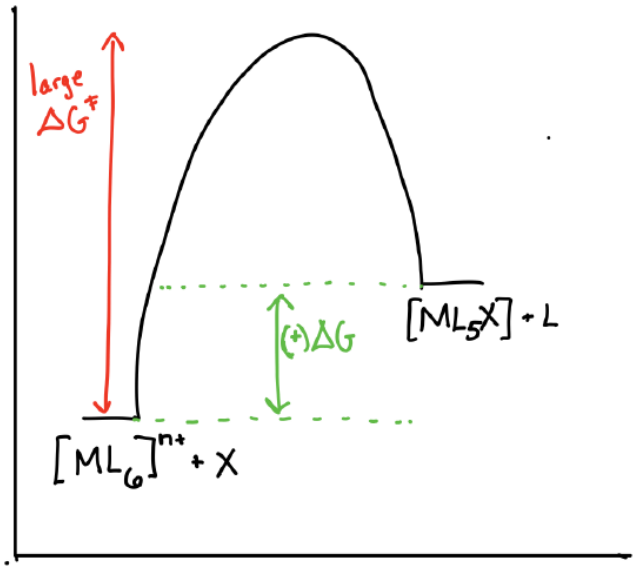
Chris P Schaller, Ph.D., (College of Saint Benedict / Saint John's University)

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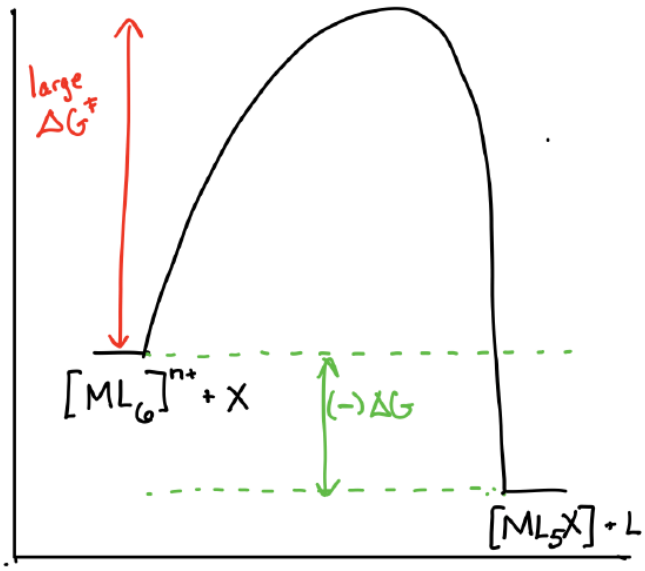
Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

Answers

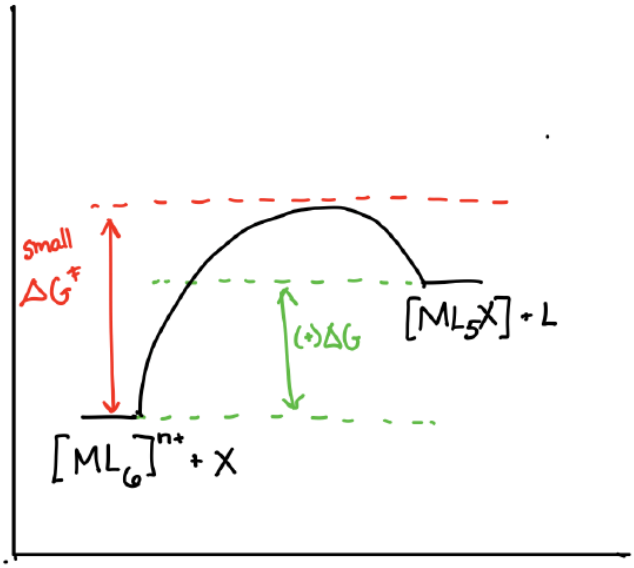
Exercise 12.2.2.1



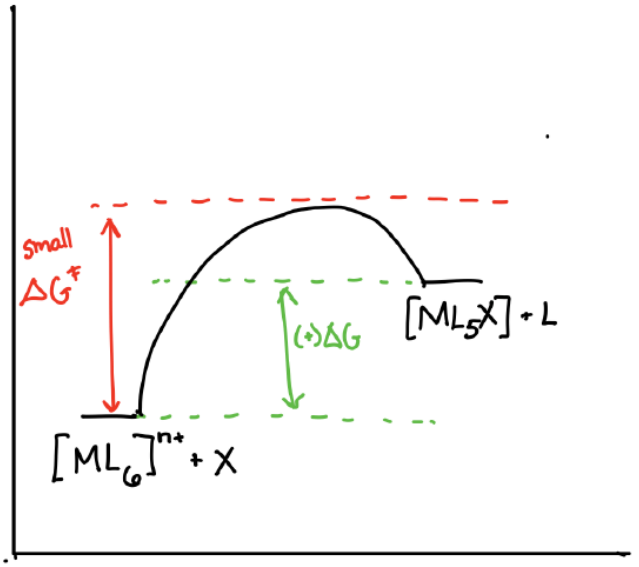
Exercise 12.2.2.1



Exercise 12.2.2.1



Exercise 12.2.2.1



Exercise 12.2.2.2

The ions in LiF are both smaller than in KBr, so the force of attraction between the ions in LiF is greater because of the smaller separation between the charges. Calcium has a 2+ charge in $CaCl_2$, whereas potassium has only a + charge, so the chloride ions are more strongly attracted to the calcium than to the potassium.

Exercise 12.2.2.3

	Kinetically Inert (Slow)	Kinetically Labile (Fast)
d^n electron count and ligand field strength	Octahedral configurations with empty e_g orbitals: • d^3 • low-spin d^4, d^5, d^6 Strong-field d^8 (square planar)	Octahedral configurations with occupied e_g orbitals: • d^1, d^2, d^7, d^9, d^10 • high-spin d^4, d^5, d^6 Weak-field d^8 (usually tetrahedral)

Exercise 12.2.2.4

Most Labile to most inert: $Na^+ > Mg^{2+} > Al^{3+}$

These are metal ions with similar size and varying charge. They are in order of increasing charge and increasing density from left to right.

Exercise 12.2.2.4

Most labile to most inert: $Sr^{2+} > Ca^{2+} > Mg^{2+}$

These metal ions have the same charge, and vary in size. They are in order of decreasing charge and increasing charge density from left to right.

Exercise 12.2.2.5

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Exercise 12.2.2.6

labile (electrons in higher energy d orbital set)
not labile (all electrons in lower energy d orbitals)
not labile (all electrons in lower energy d orbitals)
labile (electrons in higher energy d orbital set)
labile (electrons in higher energy d orbital set)

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- 9.1: Substitution Reactions and their Mechanisms by Kai Landskron is licensed CC BY 4.0.

12.2.3: Mechanistic Possibilities

A mechanism is the sequence of elementary steps by which a reaction proceeds. There are two aspects that describe the mechanism of a substitution reaction. One is called the **stoichiometric mechanism**, and the other one is called the **intimate mechanism**. The *stoichiometric* part of the mechanism is defined by the identity of the intermediate, or lack thereof. The *intimate* part of the mechanism is defined by the rate limiting step, and how the rate is dependent on the identity of the incoming ligand.

Stoichiometric Mechanisms

The *stoichiometric* part of the mechanism is **defined by the identity of the intermediate, or lack thereof**. There are three classes of stoichiometric mechanisms based on the type of intermediates that can be characterized. If the intermediate can be isolated it is either an Associative (higher-coordination number intermediate) or Dissociative (lower-coordination number intermediate) reaction. On the other hand, if the intermediate cannot be isolated because it is short-lived (or does not exist) the reaction is classified as Interchange.

Associative (A) Mechanism

Associative (A) mechanisms involve a first step where the incoming ligand bonds to the metal ion, creating **an intermediate with a higher coordination number**. The leaving group leaves in a second step to form the product. The generic reaction below illustrates the steps of an associative mechanism. Note that the intermediate, $\mathrm{ML_nXY}$, has a higher coordination number than that of the reactant, $\mathrm{ML_nX}$.

$$\begin{aligned} \text{Overall Reaction:} \quad & \mathrm{ML_nX + Y \rightleftharpoons ML_nY + X} \\ \text{Step 1 (Association):} \quad & \mathrm{ML_nX + Y \rightleftharpoons ML_nXY} \\ \text{Step 2 (Dissociation):} \quad & \mathrm{ML_nXY \rightleftharpoons ML_nY + X} \end{aligned}$$

Associative mechanisms are typical of square planar, d^8 complexes. The important features that distinguish this mechanism from others is that the **intermediate is long-lived** enough that it is detectable, and that the intermediate has a **higher coordination number** than the reactant complex.

Dissociative (D) Mechanism

Dissociative (D) mechanisms involve a first step where a bond between the metal ion and the leaving group breaks, creating **an intermediate with a lower coordination number.** The entering group enters in a second step to form the product. The generic reaction below illustrates the steps of a dissociative mechanism. Note that the intermediate, $\mathrm{ML_n}$, has a lower coordination number than that of the reactant, $\mathrm{ML_nX}$.

$$\begin{aligned} \text{Overall Reaction:} \quad & \mathrm{ML_nX + Y \rightleftharpoons ML_nY + X} \\ \text{Step 1 (Dissociation):} \quad & \mathrm{ML_nX \rightleftharpoons ML_n + X} \\ \text{Step 2 (Association):} \quad & \mathrm{ML_n + Y \rightleftharpoons ML_nY} \end{aligned}$$

The important features that distinguish this mechanism from others is that the **intermediate is long-lived** enough that it is detectable, and that the intermediate has a **lower coordination number** than the reactant complex.

Interchange (I) Mechanism

Interchange (I) Mechanisms take place in one concerted step where the entering group enters as the leaving group leaves. Bond formation and bond breaking occur simultaneously. In the case of an interchange mechanism, no intermediate is detectable. This means that either there is no intermediate, or that the intermediate is too high-energy and short-lived to be detected. The generic reaction below illustrates the single step of an interchange mechanism. Note that the species, $\mathrm{[Y\cdots ML_n\cdots X]^{\ddagger}}$, can be defined as either a transition state or a very short-lived intermediate. The distinction between these two possibilities is difficult; *when the intermediate is undetectable it is not considered a true intermediate.*

$$\text{Overall Reaction:} \qquad \mathrm{ML_nX + Y \rightleftharpoons ML_nY + X}$$
$$\text{Step 1 (Concerted):} \quad \mathrm{ML_nX + Y \rightleftharpoons [Y{\cdots}ML_n{\cdots}X]^{\ddagger} + \rightleftharpoons ML_nY + X}$$

The interchange mechanism is common for many six-coordinate (octahedral) metal complexes. The hallmark feature that distinguishes the interchange mechanism from other possible mechanisms is the **absence of a detectable intermediate**. If an intermediate is detected, the mechanism is considered associative (A). Another piece of evidence that can indicate an interchange mechanism is stereochemical changes from reactant to product. If specific sterochemistry (ie cis or trans relationships) is changed, it may be taken as evidence that an intermediate exists long enough to allow rearrangement to occur.

Distinguishing A, D, and I Mechanisms

Figure 12.2.3.1 shows examples of possible reaction profiles for each of the stoichiometric mechanisms described above. The profile of A and D mechanisms can be similar; they each require an intermediate, and the primary difference between A and D is the sequence of steps. An I mechanism lacks a true intermediate. These three cases can be difficult to distinguish experimentally, and especially if characterization of an intermediate is difficult. Notice that the reaction coordinate diagram for A and D pathways, shown in Figure 12.2.3.1, are similar. The only necessary difference between them is in the identity of the intermediate species.

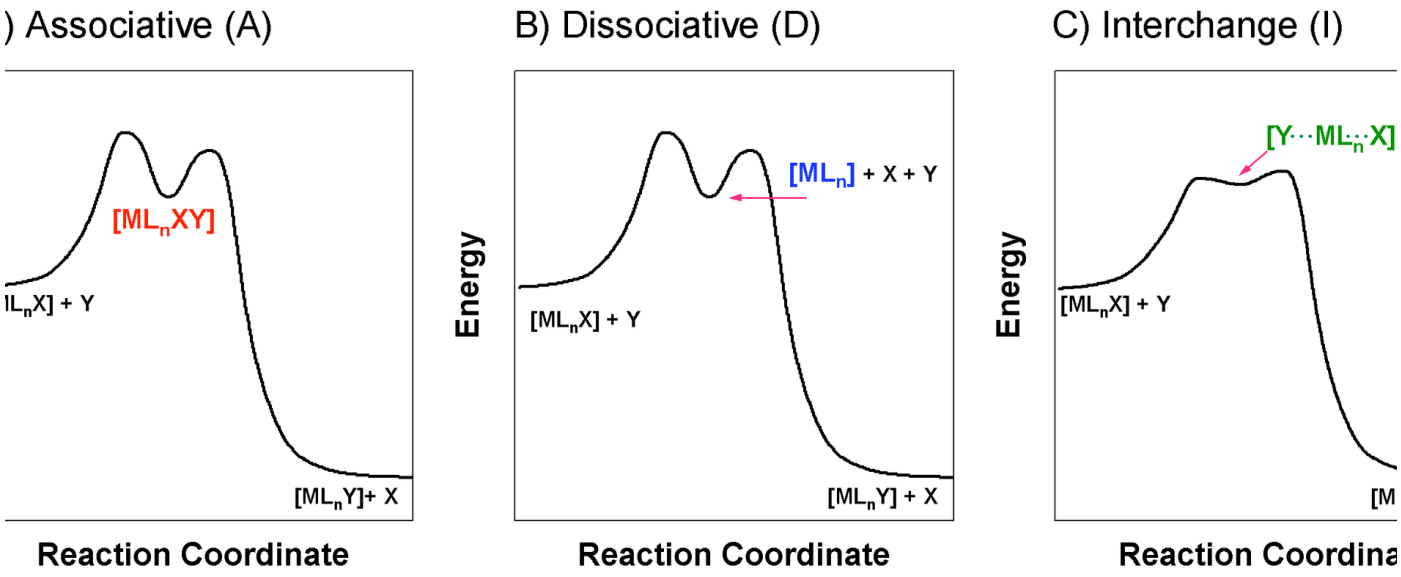


Figure 12.2.3.1: Example reaction coordinate diagrams for generic reactions that proceed through associative, dissociative, or interchange mechanisms. (Panel A) A reaction proceeds through an Associative pathway if it forms an intermediate with higher coordination number than its reactant complex. Here, an exergonic reaction is shown, where intermediate Extra close brace or missing open brace has a higher coordination number than reactant Extra close brace or missing open brace. (Panel B) A reaction proceeds through a Dissociative pathway if it forms an intermediate of lower coordination number than its reactant. Here, an exergonic reaction is shown where intermediate, Extra close brace or missing open brace, has lower coordination number than the reactant complex, Extra close brace or missing open brace. (Panel C) A reaction proceeds through an Interchange pathway if there is no true intermediate and the reaction proceeds in one step where bonds are broken and formed simultaneously. Shown here is an exergonic reaction where there is a high-energy species that is too unstable to be isolated; thus it is not a true intermediate and is considered equivalent to a transition state. (CC-BY-SA; Kathryn Haas).

Intimate Mechanisms

The intimate mechanism is defined by characteristics of the rate-limiting step. The reaction is classified as associatively-activated (using a subscript, a) if the rate changes by more than 10-fold as the entering group is varied. The reaction is classified as dissociatively-activated (using a subscript, d) if the rate changes by less than 10-fold as the entering group is varied.

Associatively-Activated Mechanisms

The rate-limiting step of an associatively activated pathway is formation of a bond between the entering group and the central metal ion. These reactions also require formation of an encounter complex in a pre-equilibrium step prior to bond forming or bond breaking steps discussed here (see Eigen-Wilkins Mechanism).

Associatively-activated A and I (A_a and I_a)

In the case of an associatively-activated associative pathway ($\mathrm{A_a}$) or an associatively-activated interchange pathway ($\mathrm{I_a}$), the rate-limiting step is the association of the entering group (Y) with the reactant, $\mathrm{ML}_n\mathrm{X}$. In the case of the A_a pathway, it is the first step (bolded) below.

A_a Mechanism

$$\textbf{Step 1 (Association):}\quad \mathrm{ML_nX + Y} \underset{\blacksquare}{\overset{\mathrm{k_1}}{\rightleftharpoons}} \mathrm{ML_nXY} \quad \Longleftarrow \textbf{RATE LIMITING ASSOCIATION}$$

$$\text{Step 2 (Dissociation):}\quad \mathrm{ML}_n\mathrm{XY} \underset{\blacksquare}{\overset{\mathrm{k_2}}{\rightleftharpoons}} \mathrm{ML}_n\mathrm{Y + X}$$

In the case of A_a, the first step shown above is slower than the second step ($k_1 < k_2$). In this case, an intermediate may not be detected because its steady state concentration is close to zero (ie it reacts as soon as it forms). Thus, distinguishing between A_a and I_a mechanisms is often impossible.

Associatively-activated D (D_a)

In the case of an associatively-activated dissociative reaction ($\mathrm{D_a}$), the rate limiting step is the association of the entering group (Y) with the intermediate ML_n; the second step (bolded) in the mechanism shown below:

D_a Mechanism

$$\text{Step 1 (Dissociation):}\quad \mathrm{ML}_n\mathrm{X} \underset{\blacksquare}{\overset{\mathrm{k_1}}{\rightleftharpoons}} \mathrm{ML}_n + \mathrm{X}$$

$$\textbf{Step 2 (Association):}\quad \mathrm{ML_nX + Y} \underset{\blacksquare}{\overset{\mathrm{k_2}}{\rightleftharpoons}} \mathrm{ML_nY} \quad \Longleftarrow \textbf{RATE LIMITING ASSOCIATION}$$

In this case, the intermediate concentration should be measurable since the second step is slower than the first ($k_1 > k_2$).

Exercise 12.2.3.1

Draw the reaction coordinate diagrams (aka reaction profiles) of reactions that proceed through A_a, I_a, and D_a pathways. Use these diagrams to explain why it is impossible to distinguish between A_a and I_a.

Hint available at the end of this section.

Answer available at the end of this section.

Dissociatively-Activated Mechanisms

When the rate-determining step is the breaking of a bond between the central metal ion and the leaving group, it is considered a dissociatively-activated (subscript d) mechanism. The rates of these reactions are largely independent of the identity of the incoming ligand.

Dissociatively-activated A (A_d)

In the case of a dissociatively-activated associative pathway ($\mathrm{A_d}$), the rate-limiting step is the dissociation of the leaving group (X) from the intermediate, $\mathrm{ML}_n\mathrm{XY}$; the second step (bolded) below.

A_d Mechanism

$$\text{Step 1 (Association):} \quad \mathrm{ML}_n\mathrm{X} + \mathrm{Y} \underset{[redacted]}{\overset{k_1}{\rightleftharpoons}} \mathrm{ML}_n\mathrm{XY}$$

$$\textbf{Step 2 (Dissociation):} \quad \mathrm{ML_nXY} \underset{[redacted]}{\overset{k_2}{\rightleftharpoons}} \mathrm{ML_nY} + \mathrm{X} \quad \Longleftarrow \textbf{RATE LIMITING DISSOCIATION}$$

In this case, the intermediate concentration should be measurable since the second step is slower than the first ($k_1 > k_2$.

Dissociatively-activated D and I (D_a and I_a)

In the case of a dissociatively-activated dissociative reaction ($\mathrm{D_d}$), or a dissociatively-activated interchange pathway ($\mathrm{I_d}$), the rate limiting step is the dissociation of the leaving group (X) from the reactant, $\mathrm{ML}_n\mathrm{X}$. For D_d the rate limiting step is the first step (bolded) in the mechanism shown below:

D_d Mechanism

$$\textbf{Step 1 (Dissociation):} \quad \mathrm{ML_nX} \underset{[redacted]}{\overset{k_1}{\rightleftharpoons}} \mathrm{ML_n} + \mathrm{X} \quad \Longleftarrow \textbf{RATE LIMITING DISSOCIATION}$$

$$\text{Step 2 (Association):} \quad \mathrm{ML}_n\mathrm{X} + \mathrm{Y} \underset{[redacted]}{\overset{k_2}{\rightleftharpoons}} \mathrm{ML}_n\mathrm{Y}$$

In the case of D_d, the first step shown above is slower than the second step ($k_1 < k_2$ and an intermediate may not be detected because its steady state concentration is close to zero (ie it reacts as soon as it forms). Thus, distinguishing between D_d and I_d mechanisms is often impossible.

Exercise 12.2.3.2

You should complete Excercise 12.2.3.1 before attempting this excercise.
Draw the reaction coordinate diagrams (aka reaction profiles) of reactions that proceed through A_d, I_d, and D_d pathways.

Answer available at the end of this section.

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Answers

Exercise 12.2.3.1

Notice that the reaction coordinate diagrams for A and D pathways, shown in Figure 12.2.3.1, are similar. The only necessary difference between them is the identity of the intermediate. These diagrams can be modified to represent associatively-activated pathways by altering the relative energy of the transition state for the associative step; the energy barrier for the associative step must be greater than that of the dissociative step. In other words, the difference between A_a, D_a is in the relative energies of the first and second transition states. In the case of I_a, the diagram could be similar to the I profile shown in Figure 12.2.3.1, with the exception that the energy barrier for making the M-Y bond is greater than the energy barrier for breaking the M-X bond.

Exercise 12.2.3.1

The three reaction coordinate diagrams shown in the figure below represent A_a, I_a, and D_a mechanisms respectively. If your diagram does not match this perfectly, that may be OK. The important features are:

- A_a: This reaction profile should show an intermediate with higher coordination number than the reactant. The intermediate should be relatively stable. The energy barrier for formation of this intermediate is the associative step, and therefore it should also be the rate-limiting step for an A_a mechanism; in other words, the first step should have the highest energy barrier.
- I_a: This reaction profile should lack a stable intermediate. The energy barrier for creating of the M-Y bond must be rater-limiting. The diagram shown below is an acceptable solution, but a diagram like shown in Panel C of Figure 12.2.3.1 is also correct. It is not clear from the diagram alone whether bond breaking or bond making are rate-limiting; this nuance would lie primarily in the identity of the transition state, and whether the M-Y bond is stronger or weaker than the M-X bond in the transition state.
- D_a: This reaction profile should show an intermediate with lower coordination number than the reactant. The intermediate should be relatively stable. The energy barrier for association of the entering group with the intermediate (the second step) must be rate-limiting in a D_a mechanism. In other words, the second step should have the highest energy barrier.

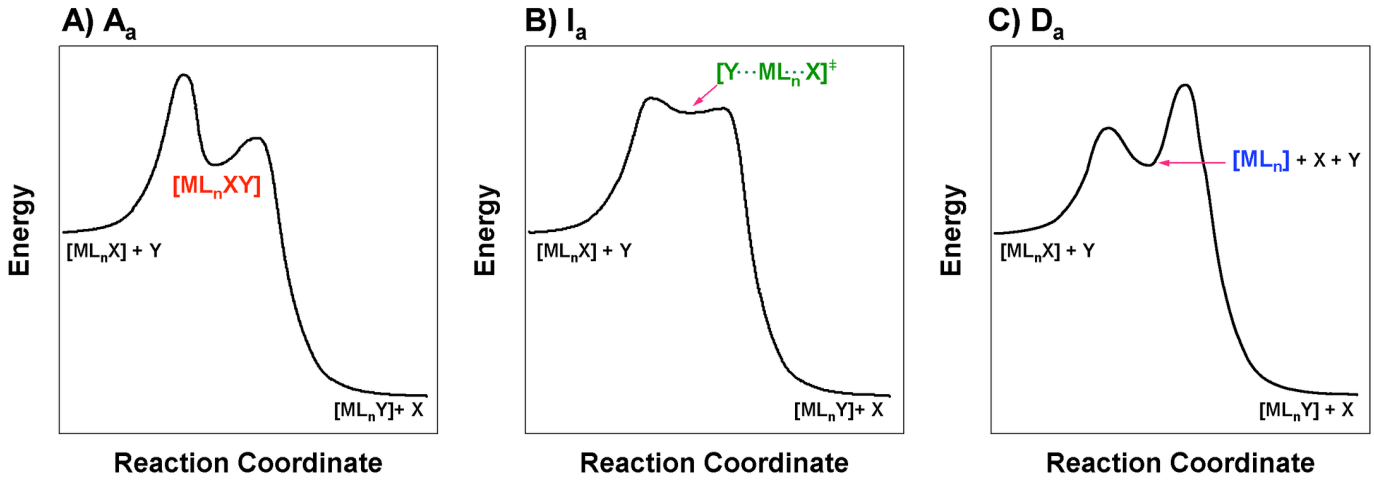


Figure for Excercise 12.2.3.1: Reaction coordinate diagrams for associatively-activated mechanisms. (A) Associatively-activated associative, A_a. (B) Associatively-activated interchange, I_a. (C) Associatively-activated dissociative, D_a. (CC-BY-SA; Kathryn Haas)

The A_a and I_a mechanisms have different reaction profiles while still the rate-limiting step is the initial association of the incoming ligand to the metal center. These two types of mechanisms are difficult to distinguish because in the case of A_a, there is a relatively small energy barrier for reaction of the intermediate to form product; thus this intermediate is not long-lived and would be difficult to detect. Experimental distinction between A_a and I_a lies in the detection and characterization of this intermediate, and since it may be elusive in A_a, it is difficult to unambiguously determine whether an associatively-activated mechanism is A_a or I_a.

Exercise 12.2.3.2

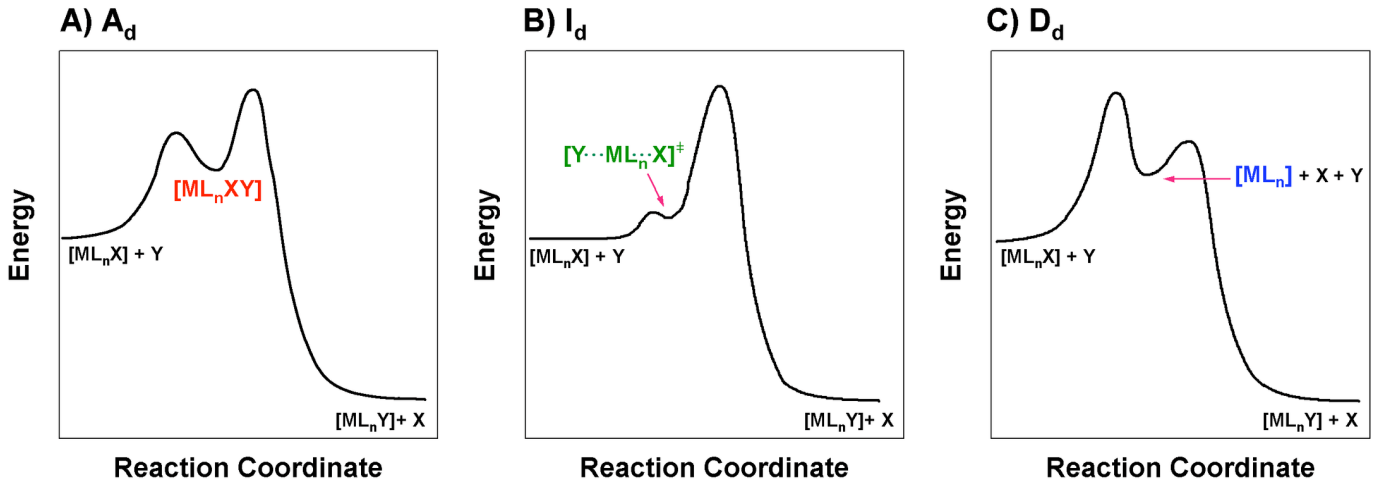


Figure for Excercise 12.2.3.2: Reaction coordinate diagrams for dissociatively-activated mechanisms. (A) Dissociatively-activated associative, A_d. (B) Dissociatively-activated interchange, I_d. (C) Dissociatively-activated dissociative, D_d. (CC-BY-SA; Kathryn Haas)

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12.3: KINETICS HINT AT THE REACTION MECHANISM

Since the different mechanisms have different rate-limiting steps, there are kinetic consequences for each type of mechanism. We can used kinetic data, therefore, to help distinguish the mechanism of a reaction. However, the information gleaned from rate laws alone can be ambiguous. For example, what does it mean if a reaction depends on on the concentration of incoming ligand? How can we distinguish between an associative mechanism (A), and an associatively-activated dissociative mechanism (D_a?

12.3.1: Rate Law for Dissociative Mechanisms

12.3.2: Rate Laws for Interchange Mechanisms

12.3.3: Rate Law for Associative Mechanisms

12.3.4: Preassociation Complexes

12.3.5: Activation Parameters

12.3.6: Some Reasons for Differing Mechanisms

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12.3.1: Rate Law for Dissociative Mechanisms

Derrivation of the Rate Law

A Dissociative (D) mechanism is two steps in which the first step is the dissociation of a ligand. The intermediate, ML_n, has a lower coordination number than that of the reactant, $\mathrm{ML}_n\mathrm{X}$.

$$\text{Step 1 (Dissociation):} \quad \mathrm{ML}_n\mathrm{X} \underset{\blacksquare}{\overset{k_1}{\rightleftharpoons}} \mathrm{ML}_n + \mathrm{X}$$

$$\text{Step 2 (Association):} \quad \mathrm{ML}_n + \mathrm{Y} \underset{\blacksquare}{\overset{k_2}{\rightleftharpoons}} \mathrm{ML}_n\mathrm{Y}$$

$$\text{Overall Reaction:} \quad \mathrm{ML}_n\mathrm{X} + \mathrm{Y} \rightleftharpoons \mathrm{ML}_n\mathrm{Y} + \mathrm{X}$$

If we assume that \(k_{-2}<

$$\frac{d\left[\mathrm{ML}_n\right]}{dt} = k_2[\mathrm{ML}_n][\mathrm{Y}]$$

We can assume that the concentration of the intermediate is small enough that it would be difficult or impossible to measure its concentration. Here, we can evoke the steady-state approximation and assume that the concentration, $[\mathrm{ML}_n]$, is approximately unchanging over the course of reaction. The $[\mathrm{ML}_n]$ depends on k_1, k_{-1} and k_2. These assumption are expressed mathematically as follows.

$$\frac{d\left[\mathrm{ML}_n\right]}{dt} = k_1\left[\mathrm{ML}_n\mathrm{X}\right] - k_{-1}\left[\mathrm{ML}_n\right]\left[\mathrm{X}\right] - k_2\left[\mathrm{ML}_n\right]\left[\mathrm{Y}\right] = 0$$

We can then use the equation above to solve for $[\mathrm{ML}_n]$.

$$\mathrm{ML}_n = \frac{k_1\left[\mathrm{ML}_n\mathrm{X}\right]}{k_{-1}[\mathrm{X}] + k_2[\mathrm{Y}]}$$

Then substitution this into the rate law given above for the second step of the mechanism. This would yield a rate law that depends only on species with measurable concentrations.

$$\frac{d\left[\mathrm{ML}_n\mathrm{Y}\right]}{dt} = \frac{k_2k_1\left[\mathrm{ML}_n\mathrm{X}\right]\left[\mathrm{Y}\right]}{k_{-1}[\mathrm{X}] + k_2[\mathrm{Y}]}$$

The rate law above suggests that the rate of product formation has an inverse relationship to the concentration of the outgoing ligand, X. This is one piece of evidence that can be used to distinguish a Dissociative mechanism; that is if the rate of reaction decreases as [X] in solution is increased it is evidence of a D mechanism. This rate law also suggests that ther is a complicated dependence of the reaction rate on the concentration of incoming ligand, Y. The importance of [Y] compared to [X] depends mathmatically on the weight of the two values in the demoninator of the rate law. If [X] >> [Y], then a valid approximation is to assume that the $k_2[\mathrm{Y}]$ term is relatively small and simplify the rate law by dropping it out completely.

$$\text{If } \mathrm{X} >> \mathrm{Y}\text{, then simplify: } \frac{d\left[\mathrm{ML}_n\mathrm{Y}\right]}{dt} = \frac{k_2k_1\left[\mathrm{ML}_n\mathrm{X}\right]\left[\mathrm{Y}\right]}{k_{-1}[\mathrm{X}]}$$

The resulting rate law (above) has a simpler dependence on [Y]; that is when [X] is large, the reaction rate is directly related to [Y].

The opposite extreme is under conditions of high [Y]. This yields a rate law that is first order in its dependence on the reactant metal complex. When [Y] is large, and the $k_{-1}[\mathrm{X}]$ term is relatively insignificant, the rate law can be simplified to the pseudo-first order rate law as follows.

$$\text{If } \mathrm{Y} >> \mathrm{X}\text{, then simplify: } \frac{d\left[\mathrm{ML}_n\mathrm{Y}\right]}{dt} = k_1[\mathrm{ML}_n\mathrm{X}]$$

The best type of experimental evidence to determine a dissociative mechanism would be a systematic study of the dependence

of rate on both [X] and [Y]. However, the dissociative reaction is unique in that it displays this type of saturation kinetics at high concnetration of the incoming ligand, and so the study of how a reaction rate behaves under high [Y] is common.

First-order reactions

Under conditions of high [Y], the a reaction following a D mechanism is said to follow "first order" kinetics. This type of reaction is sometimes called a first order reaction. That means the rate law depends on only one concentration term.

Why does the dissociative mechanism depend on concentrations in this specific way?

The rate depends on one molecule losing a ligand. Once it does so, a second ligand can replace the one that left. However, losing a ligand may be harder to do than gaining a new one. To lose a ligand, a bond must be broken, which costs energy. To gain a new ligand, a bond is made, releasing energy. That first step is harder to do, so it takes longer. It is a bottleneck that slows the reaction down. It is called the rate-determining step.

- The rate-determining step is the slow step of the reaction.
- The rate-determining step controls the rate of the overall reaction; everything else has to wait for that step to happen.
- Once the rate-determining step has occurred, everything else follows very quickly.

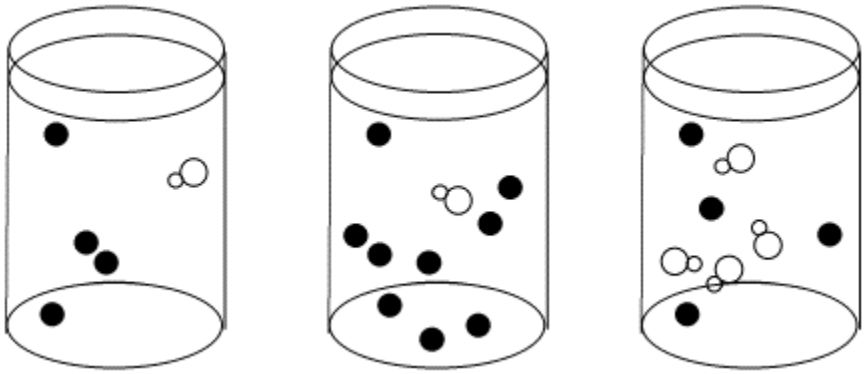


Figure 12.3.1.1: A bottleneck in a reaction. If the reaction must wait for the white molecule to dissociate, it doesn't matter how many black molecules there are; the reaction still goes just as slow. However, the more white molecules there are, the more frequently they will be able to react with the black molecules as dissociation occurs.

No collision is necessary for the metal complex to lose a ligand. Instead, a bond in the metal complex has to break. That just takes time and energy. As a result, concentration of the incoming ligand matters very little.

We should think a little more about energy requirements, available energy and reaction rate. It takes a certain amount of energy to break a bond. Over any given period of time, a specific amount of energy is available in the surroundings to use. That energy is not available uniformly. Some molecules will get more energy from their surroundings and others will get less. There will be a statistical distribution, like a bell curve, of energy available in different molecules. That means bond-breaking events are governed by statistics.

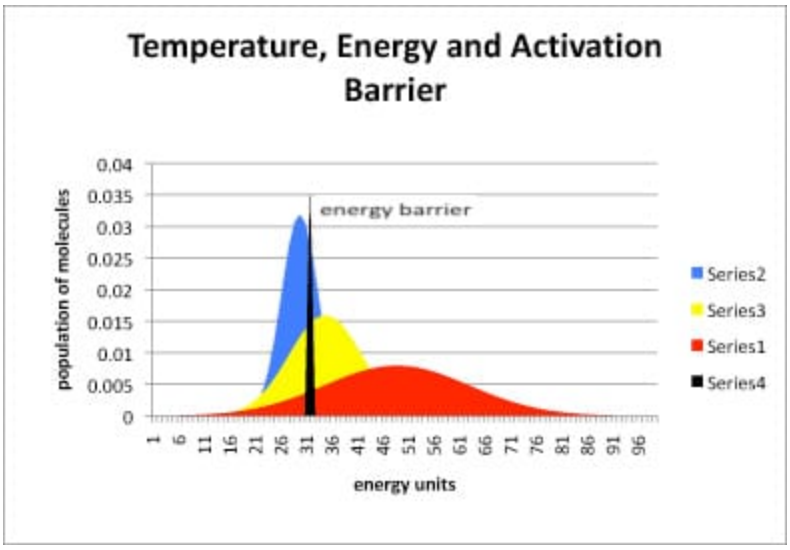


Figure 12.3.1.2: The relationship between temperature, energy available, and energy barrier. The black line represents energy needed to start the reaction, also called the energy barrier or the activation barrier. The blue curve is the distribution of available energy in a group of molecules at a cooler temperature. The yellow curve is for a group of molecules that is a little warmer, and the red curve even warmer.

In figure 12.3.1.2, most of the molecules at the low temperature (blue) do not have enough energy to begin the reaction. A small portion do, and so the reaction will proceed, but very slowly. In the yellow curve, there is more energy available, and so a large fraction of molecules have the energy necessary to begin the reaction. In the red curve, the vast majority have sufficient energy to react. Thus, one of the factors governing how quickly a reaction will happen is the energy needed, or activation barrier. A second factor is the energy available, as indicated by the temperature.

Of course, even if there is enough energy for the reaction, the reaction might not occur yet. Energy is necessary but not sufficient to start a reaction. There are also statistical factors in terms of whether a molecule has its energy allotted into the right places, or in some cases, whether two molecules that need to react together are oriented properly.

Suppose at a given temperature it takes a specific amount of time for half the molecules to gain enough energy so that they can undergo the reaction. That amount of time is called the half life of the reaction. After one half life, half the molecules have reacted and half remain. After a second half life, half the remaining molecules (another quarter, for three quarters of the original material in all) have also reacted, and a quarter still remain. After a third half life, half the remaining ones (another eighth, making it seven eighths reacted in total) will have reacted, leaving an eighth of the original material behind.

- Exponential decay is based on a statistical distribution of energy availability.
- The concept of half life is related to exponential decay.
- It takes a fixed period of time for a half of the metal complex obtain enough energy to dissociate.

Thus, the time it takes for the reaction to happen does not really depend on the concentration of anything.

However, the change in *concentration* over time -- the quantity that we can usually measure most easily -- depends on the original concentration, and for that reason the concentration of the metal complex appears in the rate law.

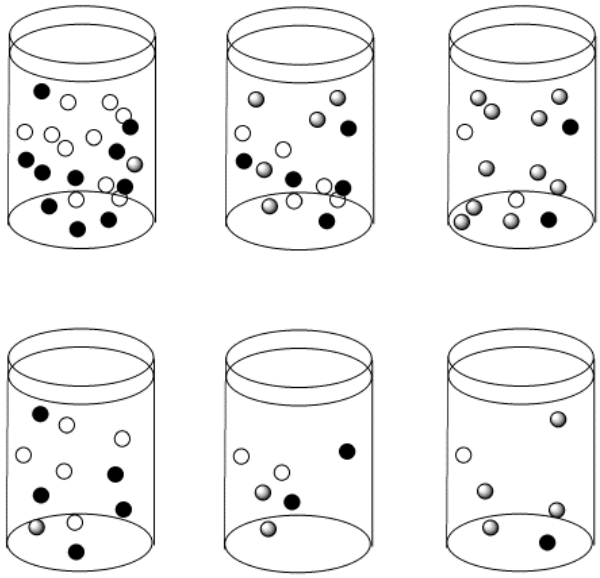


Figure 12.3.1.3: The reactions in the top row and bottom row are proceeding with the same half-life as we move from left to right. However, the top row starts out more concentrated than the bottom row. As a result, the *concentrations* in the top row are changing more quickly than in the bottom row.

Suppose the half life for a particular case of ligand substitution is one second. After a half life, a 1 M solution becomes 0.5 M, so the rate of change in concentration per time is 0.5M/s. But after the same half life, a 0.5 M solution becomes 0.25 M, so the change in concentration is 0.25 M/s.

Exercise 12.3.1.1

If a first order reaction has a half-life of 120 seconds, how much of the original material is left after

a) four minutes? b) six minutes? c) eight minutes? d) ten minutes?

Answer a available at the end of this section.

Exercise 12.3.1.2

Given the first-order dissociative rate law above, what would happen to the reaction rate for substitution in each of the following cases?

a. the concentration of ligand is doubled, and the concentration of metal complex is doubled
b. the concentration of ligand is tripled, and the concentration of metal complex is halved
c. the concentration of ligand is doubled, and the concentration of metal complex is tripled
d. the concentration of ligand is halved, and the concentration of metal complex is halved

Answer a available at the end of this section.

Exercise 12.3.1.3

Plot graphs of initial rate vs concentration to show what you would see in dissociative substitution.

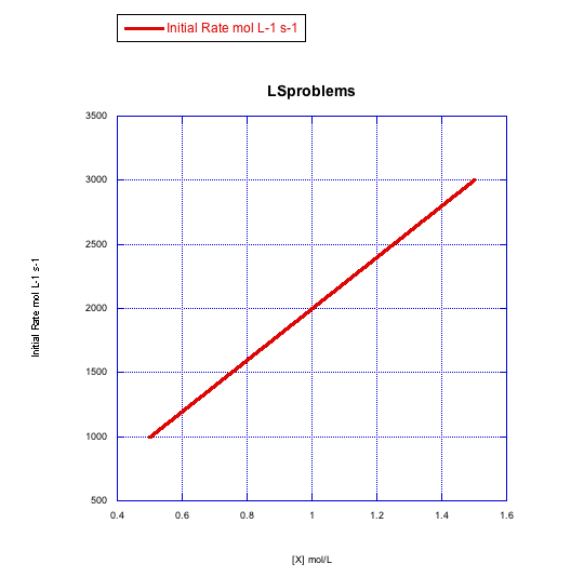
a) The concentration of metal complex, $[ML_n]$, is held constant at 0.1 mol/L and the concentration of ligand is changed from 0.5 mol/L to 1 mol/L and then to 1.5 mol/L.

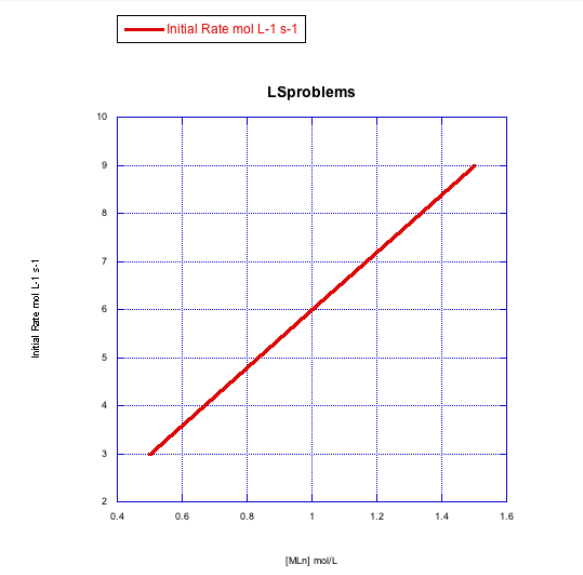
b) The concentration of new ligand, [X], is held constant at 0.1 mol/L and the concentration of metal complex is changed from 0.5 mol/L to 1 mol/L and then to 1.5 mol/L

Exercise 12.3.1.4

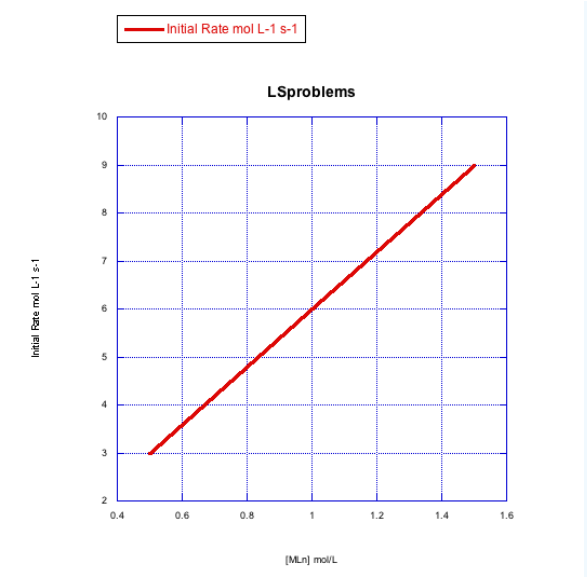
Given the following sets of initial rate data, determine whether each case represents a dissociative substitution. [MLn] = concentration of the coordination complex; [X] = concentration of incoming ligand.

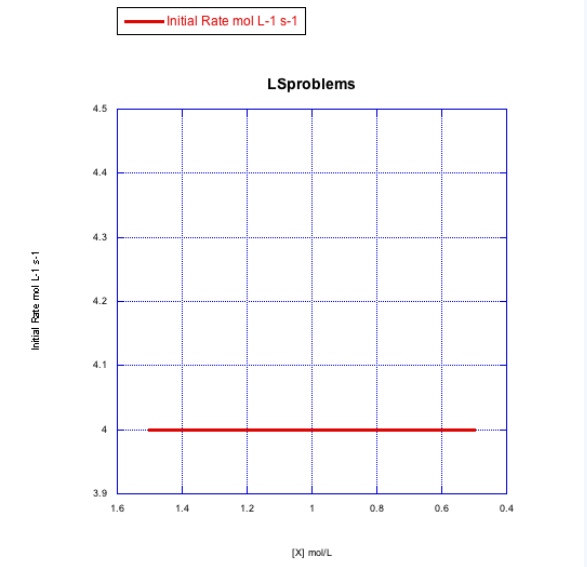
a)





b)

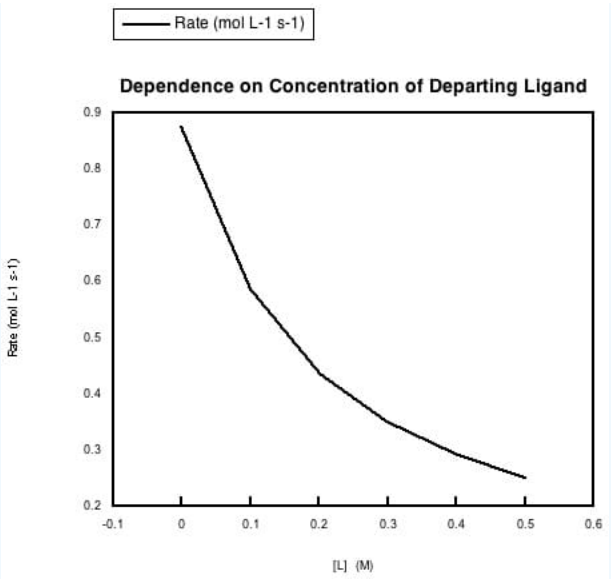




Answer a available at the end of this section.

Exercise 12.3.1.5

In the following data, the concentration of the metal complex and the incoming ligand were held constant, but more of the departing ligand was added to the solution.



a) Explain what the data says about rate dependence on this concentration.

b) Explain this rate dependence in terms of the reaction.

Answer a available at the end of this section.

Exercise 12.3.1.6

In certain solvents, such as THF, acetonitrile and pyridine, the rate law for substitution often appears to be Rate = $k_1[ML_n]$ + $k_2[ML_n][X]$, in which X is the incoming ligand and ML_n is the metal complex.

a) What do these solvents have in common?

b) What is a possible explanation for this rate law?

c) This rate law has been shown to be consistent with an entirely associative mechanism. How is that possible?

Answer a available at the end of this section.

Answers

Exercise 12.3.1.1

4 minutes = 240 seconds = 2 x 120 second = 2 half lives.
Material left = 50% x 50% = 0.5 x 0.5 = 0.25 = 25% left
6 minutes = 360 seconds = 3 x 120 second = 3 half lives.
Material left = 0.5 x 0.5 x 0.5 = 0.125 = 12.5% left
8 minutes = 480 seconds = 4 x 120 second = 4 half lives.
Material left = 0.5 x 0.5 x 0.5 x 0.5 = 0.0625 = 6.25% left
10 minutes = 600 seconds = 5 x 120 second = 5 half lives.
Material left = 0.5 x 0.5 x 0.5 x 0.5 x 0.5 = 0.03125 = 3.125% left

Exercise 12.3.1.2

Dissociative Rate Law: Rate = $[ML_n]$, if ML_n is the complex. There is no dependence on [X], if X is the new ligand.

Rate will double: Rate = 2 x $[ML_n]_0$, if $[ML_n]_0$ is the original concentration.
Rate will be halved: Rate = 0.5 x $[ML_n]_0$.
Rate will triple: Rate = 3 x $[ML_n]_0$.

Rate will be halved: Rate = 0.5 x $[ML_n]_0$.

Exercise 12.3.1.4

The rate increases with both concentration of metal complex and incoming ligand. This looks like an associative mechanism.

The rate depends on concentration of the metal complex, but not the incoming ligand. This looks like a dissociative mechanism.

The rate depends on the concentration of incoming ligand, but not the metal complex. Whatever is going on here, it isn't a simple dissociative mechanism.

Exercise 12.3.1.5

The rate of the reaction is depressed when the concentration of the departing ligand is increased.

This dependence could indicate an equilibrium in the dissociative step. The more departing ligand is added, the more the equilibrium is pushed back towards the original metal complex. With less dissociated metal complex around, the entering ligand cannot form the new complex as quickly.

Exercise 12.3.1.6

These solvents all have lone pairs. They could be Lewis bases or nucleophiles.

It looks like two competing mechanisms. On term suggests a dissociative mechanism, whereas the other term suggests a dissociative mechanism. They could be happening in competition with each other.

On the other hand, it could be that there is one mechanism with two different nucleophiles. If the incoming ligand is the nucleophile, the term on the right shows up in the rate law. If the solvent is the nucleophile, forming a third complex, the term on the left shows up in the rate law. That's because we would typically change the amount of metal complex and the amount of ligand that we add to the solution in order to determine the rate law, but we wouldn't normally be able to change the concentration of the solvent, so it would be a constant. (How could you confirm this explanation in an experiment?)

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12.3.2: Rate Laws for Interchange Mechanisms

Interchange (I) Mechanisms take place in one concerted step where there is no intermediate, or the intermediate is elusive. The reactio nessentially occurs in once step in which bond forming and bond breaking is concerted, as shown below. The species, $[\mathrm{Y}\cdots\mathrm{ML}_n\cdots\mathrm{X}]^{\ddagger}$, can be defined as either a transition state or a very short-lived intermediate.

$$\text{Step 1 (Concerted):}\quad \mathrm{ML}_n\mathrm{X}+\mathrm{Y} \rightleftharpoons [\mathrm{Y}\cdots\mathrm{ML}_n\cdots\mathrm{X}]^{\ddagger} + \overset{k_1}{\rightleftharpoons} \mathrm{ML}_n\mathrm{Y}+\mathrm{X}$$

The rate law of this one-step reaction depends on whether the relative rates of the forward and reverse reactions. When the reaction is practically irreversible, then the rate depends only on the formation of product, and not its reaction to re-form product. In this case, the rate law is a simple second-order rate law.

$$\frac{d[\mathrm{ML}_n\mathrm{Y}]}{dt} = k_1[\mathrm{ML}_n\mathrm{X}][\mathrm{Y}]$$

On the other hand, if the rate of re-formation of reactant is significant, then the rates of forward and reverse reactions must be considered in the rate law.

$$\frac{d[\mathrm{ML}_n\mathrm{Y}]}{dt} = k_1[\mathrm{ML}_n\mathrm{X}][\mathrm{Y}] - k_{-1}[\mathrm{ML}_n\mathrm{X}][\mathrm{X}]$$

In the latter case where there is a dependence of rate on both [X] and [Y], an effective strategy is to employ the condition where solution concentration of both [X] and [Y] are simultaneously high so that the reaction is effectively a competition of two pseudo-first order reactions that depend primarily on the metal complex concentrations. In such a case as this, another helpful piece of information is the equilibrium constant for the reaction ($K = \frac{k_1}{k_{-1}}$). The rate law is written below.

$$\text{When [X] and [Y] are very high: } \frac{d[\mathrm{ML}_n\mathrm{Y}]}{dt} = k_1[\mathrm{ML}_n\mathrm{Y}] - k_{-1}[\mathrm{ML}_n\mathrm{X}] = -\frac{d[\mathrm{ML}_n\mathrm{X}]}{dt}$$

One distinguishing feature of an I mechanism compared to a D mechanism can be determined from such an experiment under high concentration of X and Y. In the case of a D mechanism and sufficiently high concentration of incoming ligand, [Y], the reaction demonstrations saturation kinetics to give a pseudo-first order rate law depending only on the concentration of reactant metal complex. In the case of I, the reaction rate is not a simple first order rate law because even under high [Y] and [X], there is a dependence of rate on concentration of the product complex.

Reactions that are I_a or I_d are distinguished by the relative strength of the M-X and M-Y bond in the transition state. These reactions can be distinguished by varying the Identities of X and Y to determine how the reaction rate depends on identity of X and Y. If there is a large dependence on the incoming ligand, and less so on the outgoing ligand, it could be classified as an I_a mechanisms. The opposite is also true.

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12.3.3: Rate Law for Associative Mechanisms

Associative (A) mechanisms involve a first step where the incoming ligand bonds to the metal ion, creating an intermediate, $\mathrm{ML}_n\mathrm{XY}$, with a higher coordination number than that of the reactant, $\mathrm{ML}_n\mathrm{X}$.

$$\text{Step 1 (Association):} \quad \mathrm{ML}_n\mathrm{X} + \mathrm{Y} \underset{[redacted]}{\overset{k_1}{\rightleftharpoons}} \mathrm{ML}_n\mathrm{XY}$$

$$\text{Step 2 (Dissociation):} \quad \mathrm{ML}_n\mathrm{XY} \underset{[redacted]}{\overset{k_2}{\rightleftharpoons}} \mathrm{ML}_n\mathrm{Y} + \mathrm{X}$$

$$\text{Overall Reaction:} \quad \mathrm{ML}_n\mathrm{X} + \mathrm{Y} \rightleftharpoons \mathrm{ML}_n\mathrm{Y} + \mathrm{X}$$

To determine the rate law, we can use a similar process as we followed for D mechanisms, which are also two steps. Assuming that $k_2 >> k_{-2}$, the rate of formation of product from the second step is:

$$\frac{d[\mathrm{ML}_n\mathrm{Y}]}{dt} = k_2[\mathrm{ML}_n\mathrm{XY}]$$

The steady state approximation allows us to assume that the intermediate is in low concentration (too low to be reliably measured) and that it is unchanging. We can use the rate law for the first step to find $[\mathrm{ML}_n\mathrm{XY}]$ in terms of species that can be reliably measured.

$$\frac{d[\mathrm{ML}_n\mathrm{XY}]}{dt} = k_1[\mathrm{ML}_n\mathrm{X}][\mathrm{Y}] - k_{-1}[\mathrm{ML}_n\mathrm{XY}] - k_2[\mathrm{ML}_n\mathrm{XY}] = 0$$

...solving this first-step rate law for $[\mathrm{ML}_n\mathrm{XY}]$ gives $[\mathrm{ML}_n\mathrm{XY}] = \dfrac{k_1[\mathrm{ML}_n\mathrm{X}][\mathrm{Y}]}{k_{-1} + k_2}$

And then substitution $[\mathrm{ML}_n\mathrm{XY}]$ into the rate law for the second step, and let $k = \frac{k_1 k_2}{k_{-1}+k_2}$ to gives the overall rate law below.

$$\frac{d[\mathrm{ML}_n\mathrm{Y}]}{dt} = \frac{k_1 k_2[\mathrm{ML}_n\mathrm{X}][\mathrm{Y}]}{k_{-1} + k_2} = k[\mathrm{ML}_n\mathrm{X}][\mathrm{Y}]$$

This overall rate law is second order, and first order with respect to each of the reactants. This means that there is a direct (linear) relationship between concentration of either reactant and the rate of reaction.

Why does the associative mechanism depend on concentrations in this specific way?

This is a case of two molecules coming together. If both compounds are dissolved in solution, they must “swim around” or travel through the solution until they bump into each other and react. The more concentrated the solution is, or the more crowded it is with molecules, the more likely are the reactants to bump into each other. If we double the amount of new ligand in solution, an encounter between ligand and complex becomes twice as likely. If we double the amount of metal complex in solution, an encounter also becomes twice as likely.

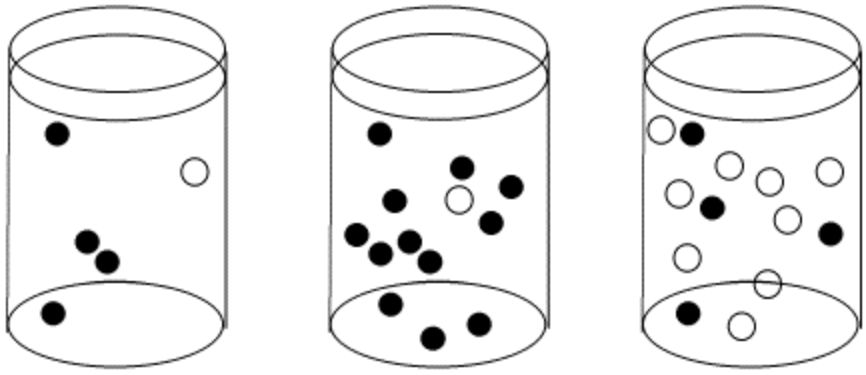


Figure 12.3.3.1: The effect of concentration on collision probability. In the first beaker, there is a chance that a black molecule and white molecule will meet and react together. The chance of a meeting is much higher in both the second beaker, where there are lots more black molecules, and in the third beaker, where there are many more white molecules.

Exercise 12.3.3.1

Given the associative rate law above, what would happen to the reaction rate for an associative substitution in the following cases?

a. the concentration of ligand is doubled, and the concentration of metal complex is doubled
b. the concentration of ligand is tripled, and the concentration of metal complex is doubled
c. the concentration of ligand is tripled, and the concentration of metal complex is tripled
d. the concentration of ligand is halved, and the concentration of metal complex is doubled

Answer a available at the end of this section.

Exercise 12.3.3.2

Plot graphs of initial rate vs. concentration to show what you would see in associative substitution.

a) The concentration of new ligand, [X], is held constant at 0.1 mol/L and the concentration of metal complex is changed from 0.5 mol/L to 1 mol/L and then to 1.5 mol/L.

b) The concentration of metal complex, [ML_n], is held constant at 0.1 mol/L and the concentration of ligand is changed from 0.5 mol/L to 1 mol/L and then to 1.5 mol/L.

Answer available at the end of this section.

Exercise 12.3.3.3

In the previous problem, the experiment was run in a particular way for particular reasons.

a) Why was one concentration held constant while the other one was changed? Why not change both?

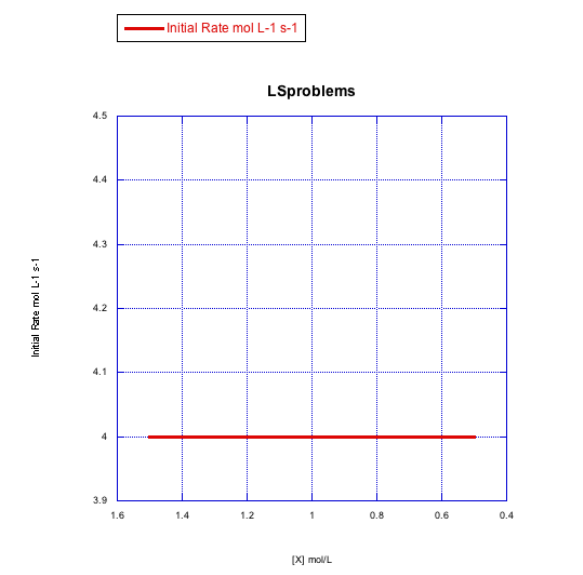
b) Why does the graph report "initial rate" -- just the rate at the very beginning of the reaction?

Answer a available at the end of this section.

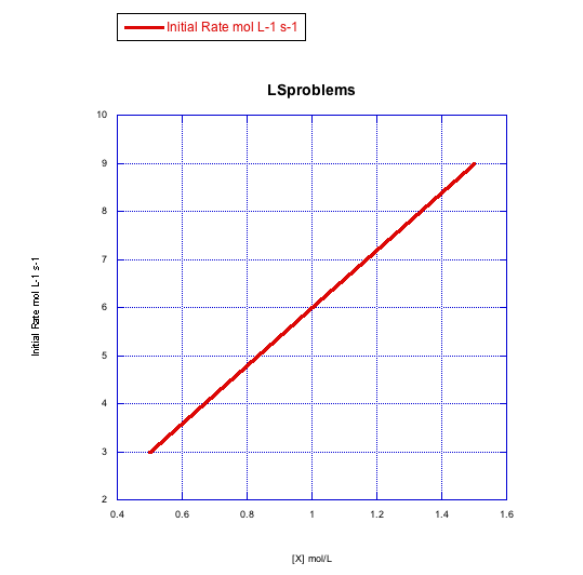
Exercise 12.3.3.4

Given the following sets of initial rate data (rates measured at the beginning of a reaction), determine whether each case represents an associative substitution.

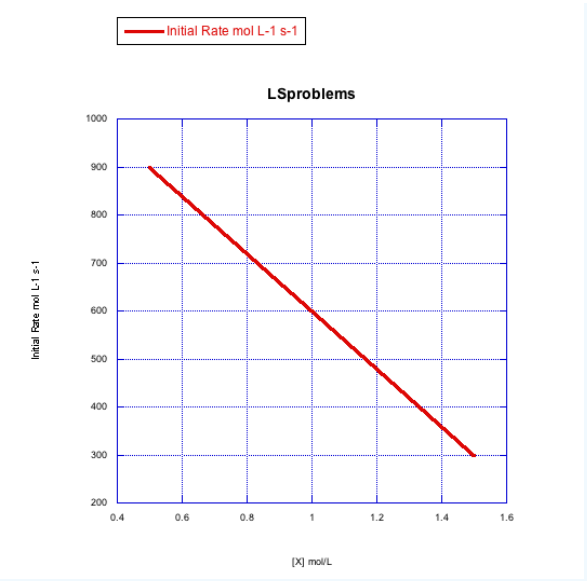
a)



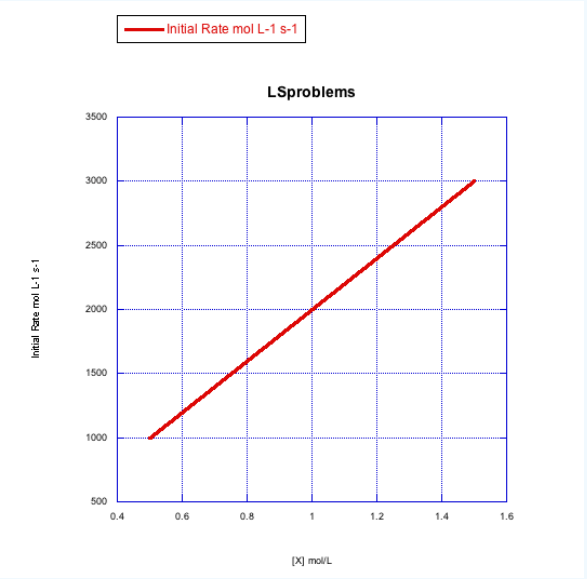
b)



c)



d)



Answer a available at the end of this section.

Exercise 12.3.3.5

What information can be gained from the slopes of lines in Exercise 12.3.3.4 ?

Answer available at the end of this section.

Note that the rate law for an A mechanism, and a reversible I mechanism are of the same form: they are each first order with respect to each reactant. Thus, an unambiguous determination between the two is difficult because it would require detection of the intermediate, which exists only at a very low concentration.

Answers

Exercise 12.3.3.1

Associative Rate Law: $Rate = [ML_n][X]$, if ML_n is the complex and X is the new ligand.

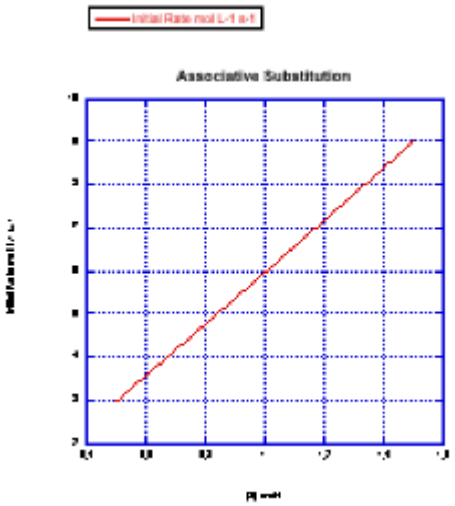
Rate will quadruple: $Rate = (2 \times [ML_n]_0) \times (2 \times [X]_0) = 4 \times [ML_n]_0[X]_0$, if $[X]_0$ and $[ML_n]_0$ are the original concentrations.

Rate will sextuple: $Rate = (3 \times [ML_n]_0) \times (2 \times [X]_0) = 6 \times [ML_n]_0[X]_0$.

Rate will nonuple: $Rate = (3 \times [ML_n]_0) \times (3 \times [X]_0) = 9 \times [ML_n]_0[X]_0$.

Rate will stay the same: $Rate = (0.5 \times [ML_n]_0) \times (2 \times [X]_0) = 1 \times [ML_n]_0[X]_0$.

Exercise 12.3.3.2



Exercise 12.3.3.3

Changing both concentrations at once would leave some doubt about whether one concentration had affected the rate, or the other concentration, or both. In practice, one concentration is usually held constant while the other is kept in excess and varied.

Rate changes over time because the concentrations of reactants change as they are consumed. By reporting only the initial rate (usually meaning less than 5% or 10% complete, but possibly even less than that if a lot of data can be gathered very quickly), the concentrations are still about what you started with. That means you can report a rate that corresponds to a given concentration with confidence.

Exercise 12.3.3.4

The rate would change with the ligand concentration if associative. This rate is constant over a range of ligand concentrations, so the reaction is not associative.

The rate increases linearly with ligand concentration. This reaction proceeds via an associative mechanism.

The rate changes over the concentration range, but it decreases. This is the opposite of what should happen. This reaction does not follow a simple associative pathway.

The rate increases linearly with ligand concentration. This reaction proceeds via an associative mechanism.

Exercise 12.3.3.5

Because $Rate = k[ML_n][L]$ is held constant while [L] is varied, then the slope of the line is k $[ML_n]$. Since you would know the value of $[ML_n]$, you could obtain the rate constant from the quantity (slope/ $[ML_n]$).

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12.3.4: Preassociation Complexes

Most octahedral complexes react through either an associative or dissociative interchange mechanism (I_a or I_d). Although the rate laws should be different for these two cases, it is difficult to distinguish between them. The difficulty lies in the seemingly conflicting observations from experiments performed under limiting conditions of the incoming ligand. For example, in the case of the reaction of hexaaquochromium(III) ($[Cr(H_2O)_6]$) with ammonia (NH_3), the rate laws determined at high and low concentrations of the incoming ligand give different apparent rate laws. Under most conditions, the rate law appears to indicate a dissociative mechanism (ie rate is independent of the $[NH_3]$). But, at very high $[NH_3]$, the rate law appears to indicate an associative mechanism (ie the rate depends on $[NH_3]$).

This information might seem contradictory. However, it can be explained by the formation of a transient ion pair, usually called an encounter complex, in a step prerequisite to the rate-determining step(s). The Eigen-Wilkins Mechanism is based on this idea.

The Eigen-Wilkins mechanism

The Eigen-Wilkins *mechanism* is also a rate law, and it governs the reactions of octahedral metal complexes. This mechanism does not define the rate-limiting step; rather, it defines the existence of a pre-equilibrium step (ie an initial step that is *not rate-determining*) that results in formation of an encounter complex. The encounter complex is a short-lived ion pair of the metal complex and the incoming ligand; it is an intermediate formed through Coulomb interactions. For the conversion of a generic metal complex, where X is the leaving group and Y is the entering group, the overall reaction, pre-equilibrium step, and formation of products from the encounter complex are shown below:

	CHEMICAL EQUATION	EQUILIBRIUM EXPRESSION
Formation of Encounter Complex	$ML_5X + Y \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (ML_5X \cdot Y)$	$K_E = \frac{[(ML_5X \cdot Y)]}{[ML_5X][Y]}$
Formation of Products:	$(ML_5X \cdot Y) \xrightarrow{k_2} ML_5Y + X$	$K_2 = \frac{[ML_5Y][X]}{[(ML_5X \cdot Y)]}$
Overall Reaction:	$ML_5X + Y \rightleftharpoons ML_5Y + X$	$K = \frac{[ML_5Y][X]}{[ML_5X][Y]}$

Fast pre-association

One possibility (that is most common) is that k_1 and $k{-}1$ are much larger than k_2. In this case, the encounter complex forms quickly, and once it forms, it also can quickly fall apart to re-form the reactant complex. When k_2 is relatively small then reaction of the encounter complex to form the product is the rate-determining step, and sometimes the concentration of encounter complex can be experimentally determined. However, it is rare that this is the case. A second, more common scenario iis that k_2 is also relatively large. Assuming that the formation of the encounter complex is still a fast step, then the rate still depends on the reaction of that encounter complex to form product. In either case, one path for deriving the rate laws is given below. The rate of formation of the product is defined by the second step:

$$\text{Rate} = \frac{d[ML_5Y]}{dt} = k_2[(ML_5X \cdot Y)]$$

Although the encounter complex may exist in high enough concentration to be detected, that is rare and technically difficult. Rather, the concentration of the encounter complex can be determined by manipulation of the equilibrium constant expression and some helpful assumptions. The equilibrium constant for formation of the encounter complex is:

$$K_E = \frac{[(ML_5X \cdot Y)]}{[ML_5X][Y]}$$

This can be rearranged to solve for concentration of the encounter complex.

$$[(ML_5X \cdot Y)] = K_E[ML_5X][Y] \tag{12.3.4.1}$$

...and we can re-write the rate experssion to remove the encounter complex from the expression. But by doing so, we remove the problem of the unmeasurable encounter complex being in the expression, but add the problem of the reactant metal complex

being part of the expression:

$$\text{Rate} = k_2 K_E [\text{ML}_5\text{X}][\text{Y}]$$

The problem is that we don't precisely know what the value of $[\text{ML}_5\text{X}]$. We only know the total amount we initially added. But, we assume that k_1 is large, and so the initial concentration of the metal complex may change immediately to produce some of the encounter complex. As long as k_2 is relatively small, we can assume that the initial total concentration of metal complex at the start of reaction consists primarily of the reactant complex plus the encounter complex:

$$[\text{M}]_{\text{total}} = [\text{ML}_5\text{X}] + [(\text{ML}_5\text{X} \cdot \text{Y})]$$

We can substitute XXX into XXX to remove the encounter complex from the expression, then rearrange to solve for the reactant metal ion concentration, $[\text{ML}_5\text{X}]$:

$$\begin{aligned} [\text{M}]_{\text{total}} &= [\text{ML}_5\text{X}] + K_E[\text{ML}_5\text{X}][\text{Y}] \\ &= [\text{ML}_5\text{X}](1 + K_E[\text{Y}]) \\ [\text{ML}_5\text{X}] &= \tfrac{[\text{M}]_{\text{total}}}{1+K_E[\text{Y}]} \end{aligned}$$

Now this allows us to do one more substitution into the rate expression to get the rate into terms of constants and solution concentrations that are known:

$$\text{Rate} = k_2 K_E \frac{[\text{M}]_{\text{total}}[\text{Y}]}{1 + K_E[\text{Y}]}$$

This rate expression is complex, but can be simplified under extremely high or low concentrations of the incoming ligand, [Y].

High [Y]: If the recation proceeds at high concentration of Y, then the denominator, $1 + K_E[\text{Y}]$ becomes approximately $K_E[\text{Y}]$. The expression is simplified to a first-order rate law under high [Y]:

$$\text{Rate} = k_2 K_E \frac{[\text{M}]_{\text{total}}[\text{Y}]}{K_E[\text{Y}]} = k_2[\text{M}]_{\text{total}}$$

This would allow determination of k_2 because the rate could be directly observed by varying the concentration of $[\text{M}]_{\text{total}}$ at high [Y].

Low [Y]: If the reaction is run at very low [Y], then the denominator, $1 + K_E[\text{Y}]$ becomes approximately 1. We can let the observed rate constant, $k_{obs} = k_2 K_E$ to get a simplified second-order rate law under very low [Y]:

$$\text{Rate} = k_2 K_E \frac{[\text{M}]_{\text{total}}[\text{Y}]}{K_E[\text{Y}]} = \frac{d[\text{ML}_5\text{Y}]}{dt} = k_{obs}[\text{M}]_{\text{total}}[Y]$$

The observed rate constant can be measured experimentally, and K_E can be determined theoretically ($k_{obs} = k_2 K_E$)

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12.3.5: Activation Parameters

The rate law shows how the rate of a reaction depends on concentrations of different species in solution. The proportionality constant, k, is called the rate constant. It contains other information about the energetic requirements of the reaction.

All reactions must overcome activation barriers in order to occur. The activation barrier is the sum of the energy that must be expended to get the reaction going. An activation barrier is often thought of, cartoonishly, as a hill the molecule has to climb over during the reaction. Once, there, it can just slide down the other side of the hill to become products. At the top of the hill, the molecule exists in what is called the "transition state". At the transition state, the structure is somewhere between its original form and the structure of the products.

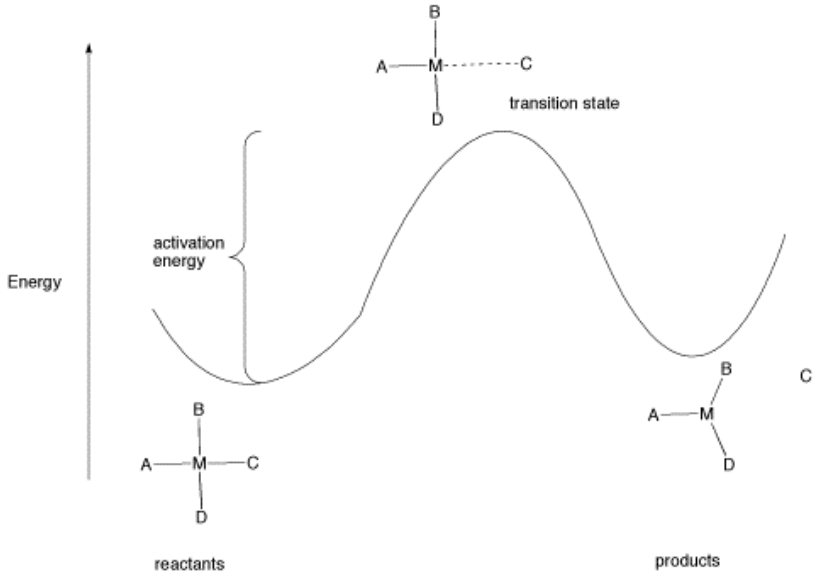


Figure 12.3.5.1: The activation barrier for a ligand dissociation step.

The type of diagram shown in figure LS6.1 is sometimes called a "reaction progress diagram". It shows energy changes in the system as a reaction proceeds. One or more activation barriers may occur along the reaction pathways, as various elementary steps occur in the reaction. In the above case, it is easy to imagine the source of the energy barrier, because some energy must be expended to break the bond to ligand C.

However, after that barrier is passed, energy is lowered again. This can happen for several reasons. Once C has separated from the metal complex, it is free to vibrate, tumble, roll and zip around all on its own. That means it can put its energy into any of those modes, independently of the metal complex. As a result, the entropy of the system increases. That lowers the overall "free energy" of the system. In addition, there may be some relief of crowding as the molecule changes from a four-coordinate complex to a three-coordinate complex, so strain energy is also lowered.

Exercise 12.3.5.1

Make drawings depicting the relationship between reaction progress and energy for the following cases:

a) a new ligand binds to a four-coordinate complex, forming a five coordinate complex.

b) a two-step process in which a new ligand binds to a four-coordinate complex, forming a five coordinate complex, and then an old ligand dissociates to form a new, four-coordinate complex.

The rate constant gives direct insight into what is happening at the transition state, because it gives us the energy difference between the reactants and the transition state. Based on that information, we get some ideas of what is happening on the way to the transition state.

The rate constant can be broken down into pieces. Mathematically, it is often expressed as

$$k = (\frac{RT}{Nh})e^{-\frac{\Delta G^{\ddagger}}{RT}}$$

In which R = the ideal gas constant, T = temperature, N = Avogadro's number, h = Planck's constant and $\Delta G^{\ddagger}$ = the free energy of activation.

The ideal gas constant, Planck's constant and Avogadro's number are all typical constants used in modeling the behaviour of molecules or large groups of molecules. The free energy of activation is essentially the energy requirement to get a molecule (or a mole of them) to undergo the reaction.

Note that k depends on just two variables:

- $\Delta G^{\ddagger}$ or the energy required for the reaction
- T or the temperature of the surroundings, which is an index of the available energy

The ratio of activation free energy to temperature compares the energy needs to the energy available. The more energy available compared to the energy needed, the lower this ratio becomes. As a result, the exponential part of the function becomes larger (since the power has a minus sign). That makes the rate constant bigger, and the reaction becomes faster.

The activation free energy is constant for a given reaction. It can be broken down in turn to:

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

in which $\Delta H^{\ddagger}$ = activation enthalpy and $\Delta S^{\ddagger}$ = activation entropy.

The activation enthalpy is the energy required for the reaction. The activation entropy deals with how the energy within the molecule must be redistributed for the reaction to occur. These two parameters can be useful in understanding events leading to the transition state.

For example, in ligand substitution, an associative pathway is marked by low enthalpy of activation but a negative entropy of activation. The low enthalpy of activation results because bonds don't need to be broken before the transition state, so it doesn't cost much to get there. That's favorable and makes the reaction easier. However, a decrease in entropy means that energy must be partitioned into fewer states. That's not favorable and makes the reaction harder. The reason the energy must be redistributed this way is that two molecules (the metal complex and the new ligand) are coming together to make one bigger molecule. They can no longer move independently of each other, and all of their combined energy must be reapportioned together, with a more limited range of vibrational, rotational and translational states to use for that purpose.

- Associative pathway: more bond making than bond breaking; lower enthalpy needs
- Associative pathway: two molecules must be aligned and come together; fewer degrees of freedom for energy distribution; decrease in entropy

On the other hand, the dissociative pathway is marked by a higher enthalpy of activation but a positive entropy of activation. The higher enthalpy of activation results because a bond must be broken in the rate determining step. That's not favorable. However, the molecule breaks into two molecules in the rate determining step. these two molecules have more degrees of freedom in which to partition their energy than they did as one molecule. That's favorable.

- Dissociative pathway: more bond breaking in rate determining step, higher enthalpy needs
- Dissociative pathway: one molecule converts to two molecules in rate determining step, greater degrees of freedom in two independently moving molecules, entropy increases

Thus, looking at the activation parameters can reveal a lot about what is going on in the transition state.

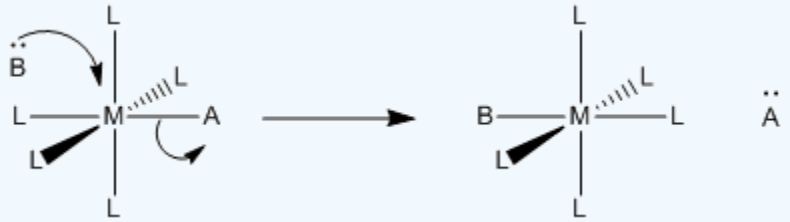
Exercise 12.3.5.2

What factor(s) other than entropy might raise the free energy of the transition state going into an associative step between a metal complex and an incoming ligand? (What factor might make the first, associative step slower than the second, dissociative step?)

Answer available at the end of this section.

Exercise 12.3.5.3

Other mechanisms for ligand substitution are also possible. The following case is referred to as an associative interchange (I_A).



a) Describe in words what happens in an associative interchange.

b) Predict the rate law for the reaction.

c) Qualitatively predict the activation entropy and enthalpy, compared with

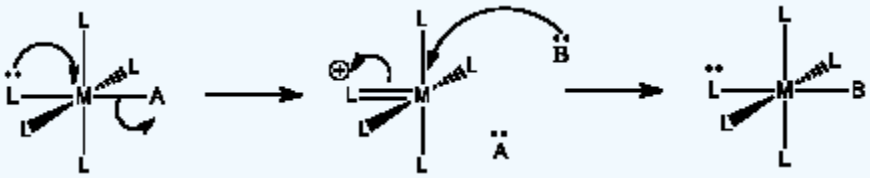
i) an associative mechanism and

ii) a dissociative mechanism.

Answer a available at the end of this section.

Exercise 12.3.5.4

For the following mechanism:



a) Describe in words what is happening.

b) Predict the rate determining step.

c) Predict the rate law for the reaction.

d) Qualitatively predict the activation entropy and enthalpy, compared with

i) both an associative mechanism and

ii) a dissociative mechanism.

e) Suggest some ligands that may be able to make this mechanism occur.

Answer a available at the end of this section.

Answers

Exercise 12.3.5.2

The metal centre is becoming more crowded as the new ligand arrives, so an increase in energy owing to steric hindrance may also play a role in the transition state energetics.

Exercise 12.3.5.3

The new ligand, B, is arriving at the same time as the old ligand, A, is departing. We might also describe it as new ligand B pushing old ligand A out of the complex.

$Rate = k[ML_5A][B]$, which looks like an associative rate law.

This is a thought-provoking question without a definite answer. Associative mechanisms typically have lower activation enthalpy than dissociative mechanisms, because there has also been some bond-making prior to the bond-breaking in the rate determining step. The associative interchange would be a little more like the associative mechanism than dissociative. The mix of bond-making and bond-breaking at the transition state would make the enthalpy of activation relatively low.

Associative mechanisms have negative activation entropies, whereas dissociative mechanisms have positive activation entropies. The associative interchange could be in between the two, given that the elementary step would be close to entropically neutral overall. What happens at the transition state is a little harder to imagine, but it might reflect the small changes in entropy through the course of the reaction, producing a small entropy of activation. On the other hand, if the incoming ligand is forced to adopt some specific approach as it comes into the molecule (to stay out of the way of the departing ligand, for example) then that restriction could show up as a small negative activation entropy.

Exercise 12.3.5.4

The lone pair donation from one ligand appears to push another ligand out.

The first step is probably rate determining, because of the bond breaking involved.

If the first step is rate determining, $Rate = k[ML_5A]$.

Another question without a very clear answer. Compared with an associative mechanism, the activation entropy is probably much more positive, because additional degrees of freedom are being gained as the molecule heads over the activation barrier and one of the ligands separates to be on its own. However, the activation entropy may be less positive than in a regular dissociation, because in this case the breaking of one bond has to be coordinated with the formation of another.

The enthalpy of activation has both a bond-making and bond-breaking component, a little like in an associative mechanism. However, the amount of bond making here is probably less important, because pi bonds are typically not as strong as sigma bonds. The activation enthalpy is probably higher than an associative pathway but not as high as a dissociative one.

The donor ligand must have a lone pair. Oxygen donors would be good candidates, because even if one lone pair is already donating in a sigma bond, an additional lone pair may be available for pi donation. The same thing is true for halogen donors. It would also be true for anionic nitrogen donors but not for neutral nitrogen donors, because a neutral nitrogen has only one lone pair.

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12.3.6: Some Reasons for Differing Mechanisms

We usually look for physical reasons why a given compound might undergo a reaction via one mechanism and not another. That ability adds to our understanding of chemistry. If we can take information and give it predictive value, then we may be able to make educated decisions about what is probably happening with new reactions.

Why might a reaction undergo a dissociative reaction rather than an associative one? What factors might prevent an associative pathway?

One reason may be that there is not enough room. In an associative step, an additional ligand comes in and binds to the metal. If it is already crowded, that may be difficult.

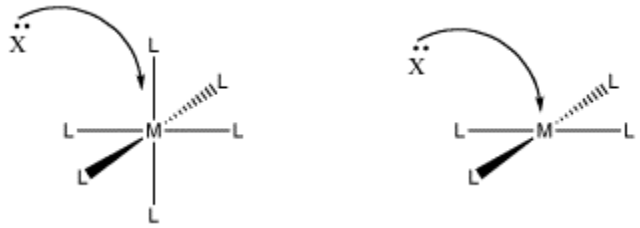


Figure 12.3.6.1: The role of steric crowding in ligand substitution. In one of these cases, the associative mechanism is less favored because of crowding that will occur in the transition state.

- Steric crowding may lead to a dissociative, rather than associative, mechanism.

Another reason has to do with electronics. Maybe the compound cannot easily accept an additional bonding pair. That may be the case if the compound already has eighteen electrons.

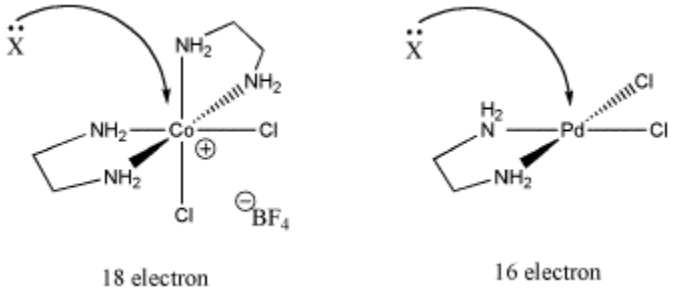


Figure 12.3.6.2: The role of electron count in ligand substitution. In one of these cases, the associative mechanism is less favored because the metal is already electronically saturated.

- Electronic saturation may lead to a dissociative, rather than associative, mechanism.

However, if there is less crowding, and more electrons can be accommodated, an associative pathway may result.

Exercise 12.3.6.1

i) Draw structures for the following reactions. Pay attention to geometry.

ii) Predict whether each of the substitutions would occur through associative or dissociative mechanisms.

a) $AuCl_3py + Na\ N_3 \rightarrow Na^+\ [AuCl_3N_3]^-$ + py

b) $Rh(C_2H_4)_2(acac) + C_2D_4 \rightarrow Rh(C_2D_4)_2(acac) + C_2H_4$

c) $[Co(NH_3)_5Cl]^{2+} + H_2O \rightarrow [Co(NH_3)_5(OH_2)]^{2+} + Cl^-$

d) *trans*-$(Et_3P)_2PtCl_2 + {}^-SCN \rightarrow$ *trans*-$(Et_3P)_2PtCl(SCN) + Cl^-$

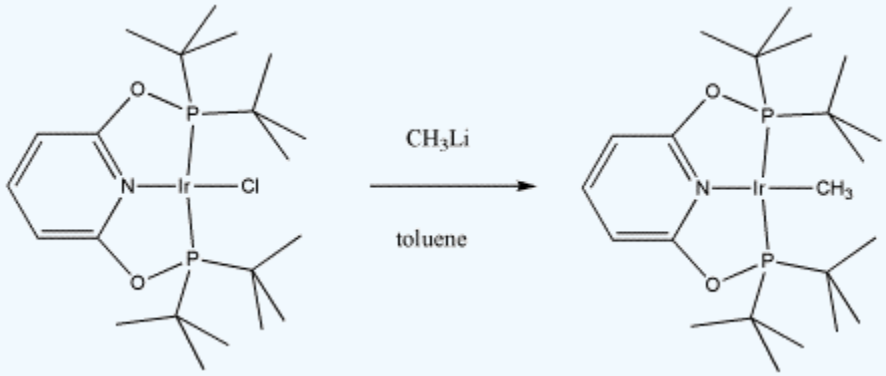
e) $Rh(NH_3)_4Cl_2^+ + {}^-CN \rightarrow Rh(NH_3)_4Cl(CN)^+ + Cl^-$

f) *trans*-$[Cr(en)_2Br_2]^+ + {}^-SCN \rightarrow$ *cis*- and *trans*-$[Cr(en)_2Br(SCN)]^+ + Br^-$

Answer available at the end of this section.

Exercise 12.3.6.2

Maurice Brookhart of UNC, Chapel Hill, makes organometallic compounds in order to study fundamental questions about reactivity. In this case, he has reported making a new compound capable of "C-H activation", a reaction in which unreactive C-H bonds can be forced to break. This process holds the future promise of converting coal and natural gas into important commodities currently obtained from petroleum.



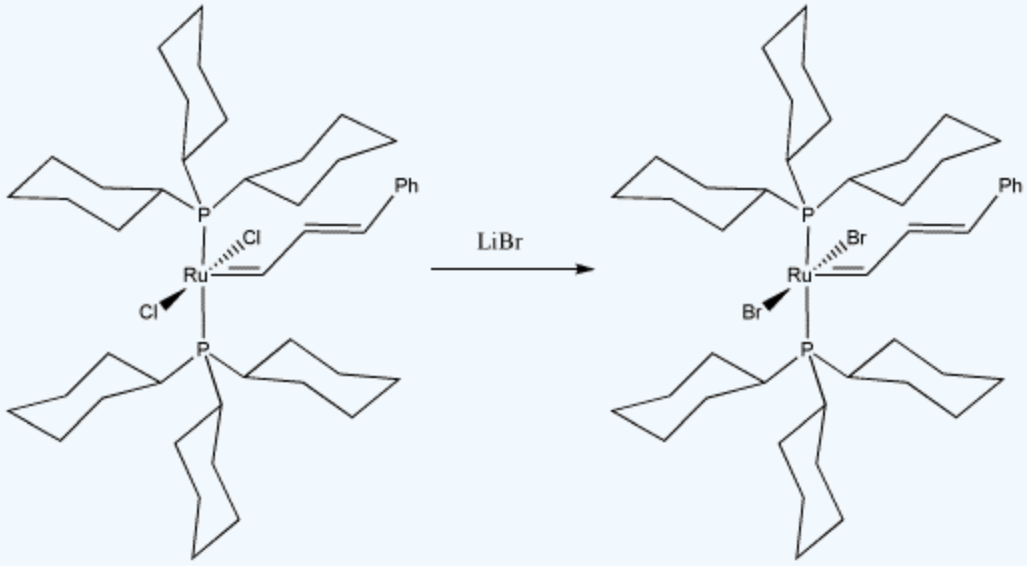
a) Draw, with curved arrows, a mechanism for the ligand substitution in the synthesis of this C-H activating complex.

b) Explain your reasons for your choice of reaction mechanism.

Answer available at the end of this section.

Exercise 12.3.6.3

Bob Grubbs of Cal Tech was awarded the Nobel Prize in chemistry for his development of catalysts for olefin metathesis. Olefin metathesis is important both in the reforming of petroleum and in the synthesis of important commodities such as pharmaceuticals. In the following study, he replaced chlorides on a "Grubbs Generation I catalyst" to study the effect on the olefin metathesis reaction.



a) Draw, with curved arrows, a mechanism for the ligand substitution in this complex.

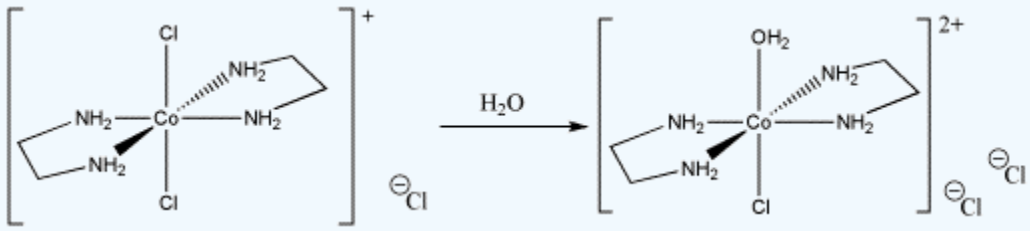
b) Explain your reasons for your choice of reaction mechanism.

c) What factor(s) do you think Grubbs hoped to study by making this substitution in the catalyst?

Answer available at the end of this section.

Exercise 12.3.6.4

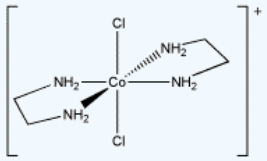
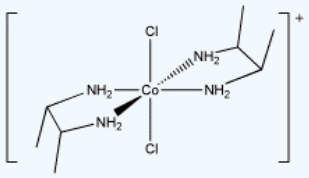
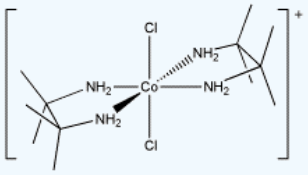
Sometimes, kinetic studies can give insight into a reaction if controlled changes in the reaction produce measurable results.



a) Draw, with curved arrows, a mechanism for the ligand substitution in this reaction.

b) Explain your reasons for your choice of reaction mechanism.

c) Explain the following kinetic data.

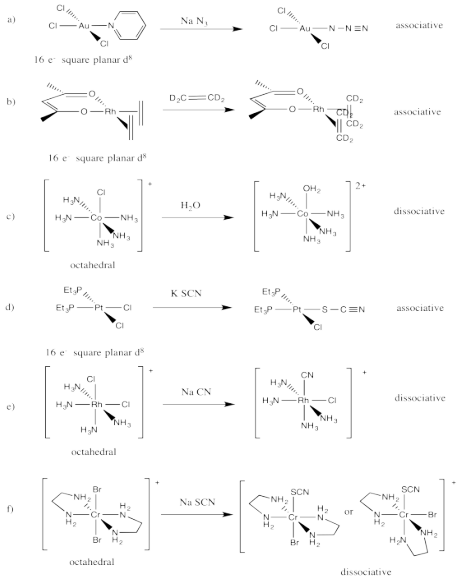
complex	substitution rate constant
	$3.2 \times 10^{-5}\ s^{-1}$
	$4.1 \times 10^{-3}\ s^{-1}$
	too fast to measure easily

Exercise 12.3.6.5

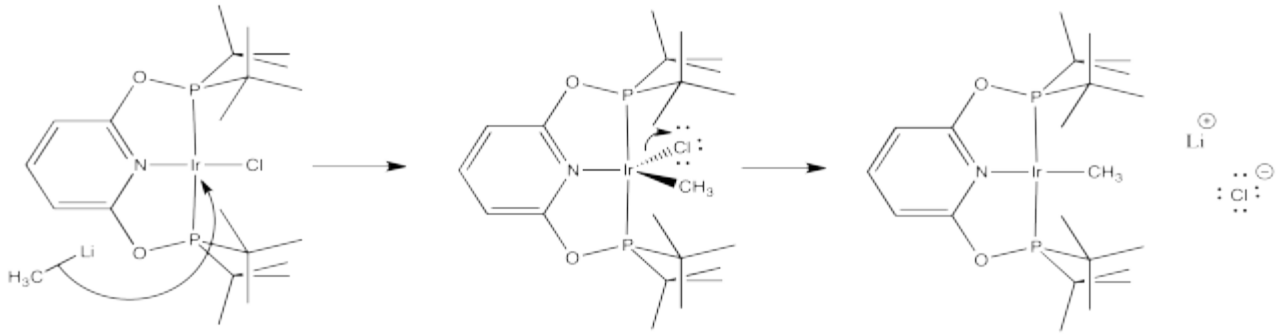
Several different structures were proposed for Ni(cysteine)$_2^{2-}$. Kinetic studies of substitution in this complex showed the rate was dependent in the concentration of both the metal complex and the incoming ligand. Which structure do you think is correct? Why?

Answers

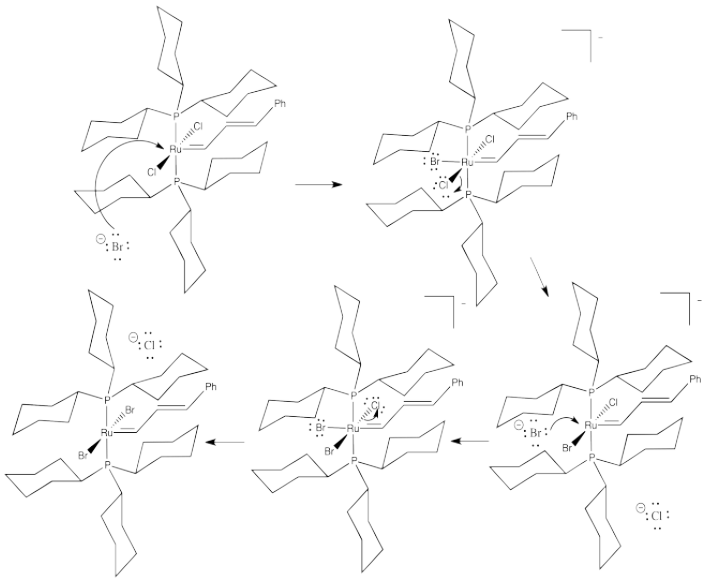
Exercise 12.3.6.1



Exercise 12.3.6.2



Exercise 12.3.6.3



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12.4: Experimental Evidence in Octahedral Substitutions

This section will review some of the common experiments that can provide evidence supporting different mechanisms, with a focus on the reactions of octahedral complexes.

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12.4.1: Dissociation

Consider what must happen for the simplest case of a purely dissociative (D) reaction mechanism for an octahedral metal complex. The first step, and the rate-limiting step must be dissociation of one ligand to form an intermediate with a lower coordination number. Such a situation, where an octahedral complex looses a ligand, X, to become a square pyramidal intermediate is shown below in Figure 12.4.1.1.

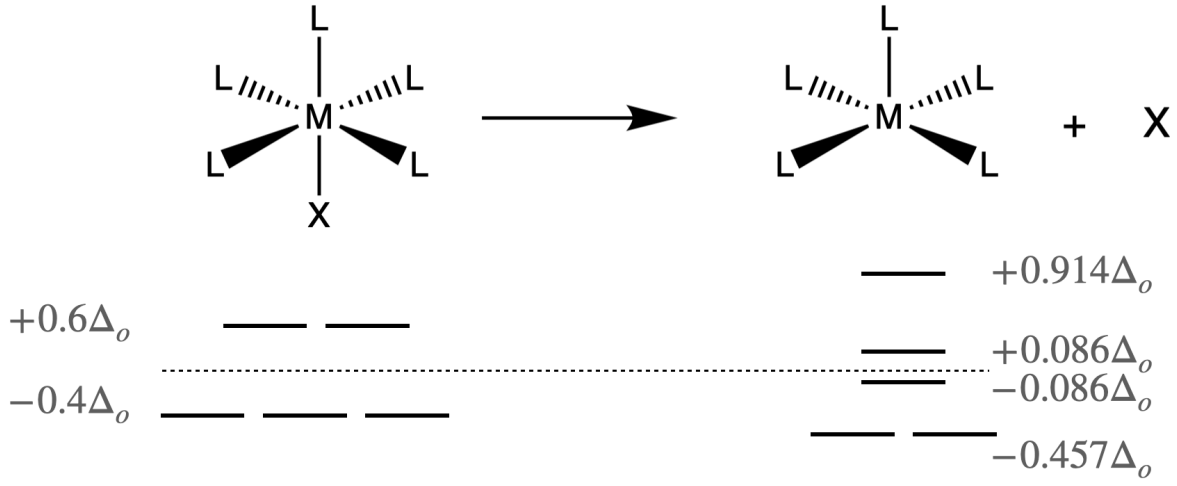


Figure 12.4.1.1: Dissociation of a ligand to form a square pyramidal intermediate. This would be the first step of a dissociative (D) reaction mechanism. The Ligand Field Activation Energy (LFAE) can be calculated from the splitting energies of the octahedron compared to the square planar intermediate. (CC-BY-SA; Kathryn Haas)

If the dissociation of a ligand is rate-determining, factors that lower the energy of the transition state or intermediate structures will speed the reaction rate. Here we could consider the differences in ligand-field stabilization energy (LFSE). The difference between the LFSE of the octahedral reactant and that of the intermediate is defined as the ligand field activation energy (LFAE). The LFAE can be calculated for a given d-electron count for an octahedral reactant and a square pyramidal intermediate using the information provided in Figure 12.4.1.1. Metal ions with particularly low (more negative) LFAE values tend to be more labile, while those with particularly high (less negative) values tend to be more inert. However, most octahedral complexes are expected to react through dissociative mechanisms due to the unfavorable steric crowding that must occur during an associative pathway.

The ease by which the M-X bond is broken will also influence rate of a dissociative reaction, and this can be probed experimentally. The following experiments can give evidence that support the argument that a reaction occurs by a dissociative pathway, or that it is dissociatively activated.

Experimental evidence that supports dissociative mechanism

1. Identity of the entering ligand has little effect on reaction rate.

If dissociation is the rate-determining step, the identity of the entering ligand, Y, should have little effect on the reaction rate. Therefore, an experiment that varies Y while holding X constant can indicate whether or not Y is involved in the rate-determining step. If the identity of Y has little effect on rate, then it must not be involved in the rate-determining step. Such experimental evidence can be taken as evidence of a dissociative mechanism. For example, the rate constants for reaction of Extra close brace or missing open brace with different incoming ligands, shown below, has rate constants of similar magnitude (they are approximately within one order of magnitude), indicating a dissociatively activated mechanism. In this case, other lines of evidence suggest this is a reaction with a I_d mechanism.

$$[\mathrm{Cr(NH_3)_5H_2O}]^{3+} + \mathrm{Y^-} \rightleftharpoons [\mathrm{Cr(NH_3)_5Y}]^{2+} + \mathrm{H_2O}$$

Table 12.4.1.1: Rate Constants for Exchange of Aquo Ligand of pentaammineaquo chromium(III) ion by incoming ligand, Y (chemical equation shown above). There is little effect of the identity of the incoming ligand on the rate constant. This data was sourced from Miessler, Fischer and Tarr's Inorganic Chemistry, 5th edition, pg 449.

Entering Ligand, Y^-	Rate Constant, k_1 $(10^{-4}M^{-1}s^{-1})$
NCS^-	4.2
Cl^-	0.7
Br^-	3.7
$CF_3CO_2^-$	1.4

2. Steric Crowding of the Metal Complex

Steric crowding of the metal complex would inhibit a dissociative pathway through steric crowding of the entering ligand. However, steric crowding can increase the stability of the intermediate after dissociation of the ligand from the crowded octahedral complex. If the reaction rate increases with steric crowding of the reactant complex, this is taken as evidence to support a dissociative mechanism.

3. Volume of Activation

One molecule generally takes up less space than two sperate molecules. This usually holds true in solution. Measurement of a rate constant's dependence on pressure can be used to determine the volume of activation (ΔV_{act}) and give insight into the mechanism of that reaction. In a dissociation mechanism, the dissociation causes one metal complex to become two separate molecules. Thus, the intermediate should, in principle, take up more space than the reactant complex. In a situation like this, we expect that the rate of reaction should decrease with increasing pressure, giving a positive value for ΔV_{act}. However, solvation of ions can influence volume, and this should be considered in interpretation of pressure-dependence data.

4. Increased coulombic attraction with the leaving group decreases reaction rate.

Couloubic (electrostatic) attraction between the dissociating ligand, X, and the metal complex should slow ligand dissociation. Coulombic attraction increases with increased magnitude of charges and with decreased distance. If the reaction rate slows with increased charge of the metal ion or the ligand itself, this is taken as evidence of a dissociative mechanism. Likewise, if rate decreases as the radius of the central metal ion is decreased, this is evidence to support a dissociative mechanism.

5. Increased strength of the M-X bond decreases reaction rate.

Free energy relationships between the formation constant of M-X and the kinetic rate constant of the reaction can provide evidence to support a dissociative mechanism (Discussed in the next section).

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12.4.2: Linear Free Energy Relationships

The Linear Free Energy Relation (LFER) is a tool that can indicate the importance of bond breakage or bond formation in the rate-determining step. In the case of a dissociative mechanism, for example, bond breaking is critical for reaction progress. Therefore, the strength of the M-X bond influences not only the extent to which the reaction will happen, but also the rate. Although thermodynamic stability of a complex does not necessarily indicate the kinetic rate at which it will react, there is a relationship between bond stability and the rate of reaction *if the breaking or formation of that bond is involved in the rate-determining step*. The relationship can be stated as follows:

$$ln\ k = ln\ K + c$$

And this relationship can be justified using the Arrhenius equation and equation for the temperature-dependence of the equilibrium constant.

$$\ln k = \ln A - \frac{E_A}{RT} \quad \text{and} \quad \ln K = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

In an experiment designed to test the Linear Free Energy Relationship, several reactions would be conducted under nearly identical conditions, where only the identity of the leaving group, X, is varied. In these experiment, the temperature would be constant and the same in each case. If we assume that the pre-exponential factor, A is the same for each reaction condition (and it should be at identical temperatures for analogous reactions), then the $\ln K$ term of the Arrhenius equation becomes proportional to the activation energy, E_a (and proportional to Gibb's energy of activation, $\Delta G^\ddagger$, and Gibb's energy ΔG). And since the Gibb's energy is related to the equilibrium constant, K, by $\Delta G = RT \ln K$, the value of K and k should be correlated. Likewise, if T is constant over the reaction conditions and ΔS° is similar across the analogous reactions (which it should be), then $\ln K$ becomes proportional to enthalpy, ΔH°, which is proportional to Gibb's free energy of reaction ΔG°.

If a Linear Free Energy Relation plot of $\ln K$ vs $\ln k$ is linear, but with a slope less than one, it indicates a dissociative mechanism with some degree of associative character (for example, an I_d mechanism or a mechanism involving the formation of preassociation complex). If the plot of $\log K$ vs $\log k$ for the reactions is linear, this is evidence that the reaction is dissociative. An example for a linear free energy plot is shown in Figure $12.4.2.1$ for the hydrolysis of $[\mathrm{Co(NH_3)_5X}]^+_2$ (this is the substitution of $\mathrm{X^-}$ with $\mathrm{H_2O}$).

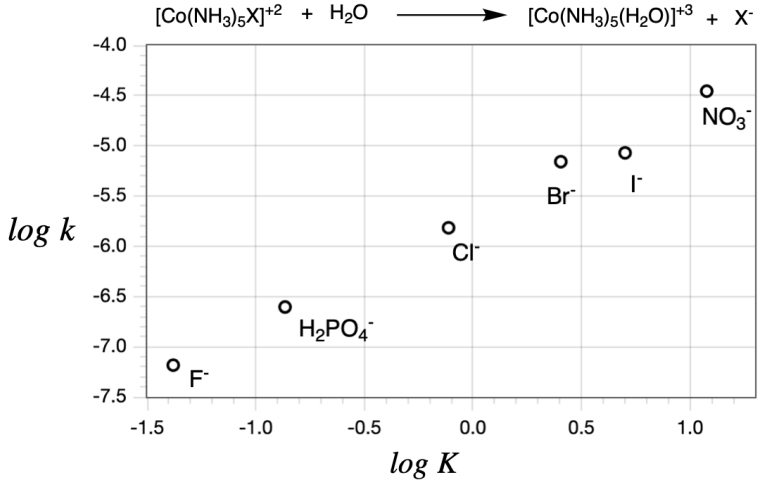


Figure $12.4.2.1$: Linear Free Energy relationship lot for $[\mathrm{Co(NH_3)_5X}]^+_2$ where $\mathrm{X^-} = \mathrm{F^-}$, $\mathrm{H_2PO_4^-}$, $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{I^-}$, $\mathrm{NO_3^-}$. This is summarized in Cooper H. Langford, *Inorganic Chemistry* **1965** *4* (2), 265-266, DOI: 10.1021/ic50024a041. (CC-BY-SA; Kathryn Haas)

When the slope is approximately 1, as it is in the case of $[\mathrm{Co(NH_3)_5X}]^+_2$ in Figure $12.4.2.1$, it indicates that the variation of the $\mathrm{X^-}$ leaving group has a similar effect on the magnitude of both ΔG (thermodynamic, related to K) and $\Delta G^\ddagger$ (kintetic, related to k). In other words, a slope close to 1 indicates a purely dissociative pathway (D). This data shown in Figure $12.4.2.1$, for example, is

evidence of a dissociative mechanism for $[Co(NH_3)_5X]^{+}_{2}$.

The argument that a reaction is dissociative can also be supported by evidence showing little effect of the incoming ligand on reaction rate. For example, data supporting the argument that $[Co(NH_3)_5H_2O]^{+}_{3}$ reacts by a dissociative pathway is shown below. The data show that variation of the identity of the incoming ligand, Y^{-}, has little effect on the rate constant (they are approximately within one order of magnitude).

$$\text{For the reaction: } [Co(NH_3)_5H_2O]^{3+} + Y^{m-} \rightleftharpoons [Co(NH_3)_5Y]^{(3-m)+} + H_2O$$

Table 12.4.2.1*: Rate Constants for Exchange of Aquo Ligand of pentaammineaquo cobalt(III) ion by incoming ligand, Y (chemical equation shown above). There is little effect of the identity of the incoming ligand on the rate constant. This data was sourced from Miessler, Fischer and Tarr's Inorganic Chemistry, 5th edition, pg 448.*

Entering Ligand, Y^{-}	**Rate Constant,** k_1 $(10^{-6}s^{-1})$ **(pseudo-first order with excess** $[Y^{-}]$**)**
H_2O	100
$N_3{}^{-}$	100
$SO_4{}^{2-}$	24
Cl^{-}	21
NCS^{-}	16

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12.4.3: Associative Mechanisms

Associative mechanisms tend to be less common for octahedral complexes as a result of steric hindrance of the metal ion by six ligands. However, reactions of octahedral complexes with associative character are more likely if the ligands have low steric bulk and/or the central metal ion is larger with longer bonds (as in the case of $4d$ and $5d$ metal ions). Reactions of octahedrons have also been observed in cases of low d-electron count or low electron density around the central ion, presumably making nucleophilic reaction more favorable. If an octahdral complex is determined to have associative character, in most cases it is associatively-active interchange (I_a).

The evidence that supports arguments for associative mechanisms is somewhat the opposite as that which would support dissociative character. One typical piece of evidence that supports an associative pathway is **a large effect of the incoming ligand on the reaction rate constant**. For example, in the reaction of hexaaquo chromium (III) ion (Extra close brace or missing open brace) with various incoming ligands (shown below), rate constants vary by several orders of magnitude. This data is evidence of an associative mechanism (I_a). In contrast, the reaction of pentaamineaquo chromium (III) ion (Extra close brace or missing open brace) occurs by an associative mechanism (data shown in Section 12.4.1). The difference in reaction mechanisms for different chromium (III) complexes can be justified by the different electron densities around their metal ion center. The ammine ligand is a stronger sigma donor and thus the metal center is more electron rich in the case of Extra close brace or missing open brace . Nucleophilic reaction by an incoming ligand is thus more likely in the case of Extra close brace or missing open brace , which has a more electrophilic center.

$$[\mathrm{Cr(H_2O)_6}]^{3+} + \mathrm{Y^-} \rightleftharpoons [\mathrm{Cr(H_2O)_5Y}]^{2+} + \mathrm{H_2O}$$

Table 12.4.3.1*: Rate Constants for Exchange of Aquo Ligand of hexaaquo chromium(III) ion by incoming ligand, Y (chemical equation shown above). There is little effect of the identity of the incoming ligand on the rate constant. This data was sourced from Miessler, Fischer and Tarr's Inorganic Chemistry, 5th edition, pg 449.*

Entering Ligand, $\mathrm{Y^-}$	**Rate Constant,** k_1 $(10^{-4}M^{-1}s^{-1})$
$\mathrm{NCS^-}$	180
$\mathrm{NO_3{}^-}$	73
$\mathrm{Cl^-}$	2.9
$\mathrm{Br^-}$	0.9
$\mathrm{I^-}$	0.08

Another piece of evidence that can support associative mechanisms is the temperature-dependence of the rate law, which in turn can yield the entropy of activation (represented as $\Delta S^{\ddagger}$ or ΔS_{act}). When an incoming ligand associates with a metal complex and two molecules beome one, there would be a negative change in the entropi (entropy decreases). A negative value for the entropy of activation indicates an associative pathway. An example of this is in the substitution of the aquo ligand in $[\mathrm{Ru(EDTA)(H_2O)}]^-$, which has a negative value of $\Delta S^{\ddagger}$, indicating an I_a mechanism.

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12.4.4: The conjugate base mechanism

The substitution reaction of acidic octahedral complexes (with ligands that can donate a proton) can be catalyzed in the presence of hydroxide ion ($\mathrm{OH^-}$. Through an initial acid-base reaction, the metal complex can be deprotonated to its conjugate base. The deprotonation increases electron density on the metal center, facilitating the loss of the leaving group ligand, especially when the leaving ligand is trans to the deprotonation site. This mechanism is referred to as the **conjugate-base mechanism** or the $\mathrm{S_N1CB}$ (**S**ubstitution, **N**ucleophilic, first-order in the **C**onjugate **B**ase mechanism) mechanism. Although it involves a dissociative rate-limiting step, the rate law is consistent with the second-order kinetics because the rate also depends on the initial reaction of the base with the metal complex. In this mechanism, the first step is formation of the conjugate base of the metal complex by deprotonation of one of its ligands. This is a case where numerous lines of evidence are necessary to establish the mechanism.

Cobalt pentammine complexes, $\mathrm{Co(NH_3)_5X^{n+}}$, have been studied extensively and are found to react through the conjugate-base mechanism. The way in which the actual mechanism was determined, and how other possible mechanism were ruled out are described below.

Evidence under acidic aqueous conditions

In acidic aqueous solutions, the reaction

$$\mathrm{[Co(NH_3)_5X]^{2+} + Y^- \longrightarrow [Co(NH_3)_5Y]^{2+} + X^-}$$

was found to proceed through an aquo complex intermediate, $\mathrm{[Co(NH_3)_5OH_2]^{3+}}$, which is also the dominant product despite the identity of the incoming ligand. In other words, to form the product of the reaction above, there are two substitution steps necessary (shown below).

$$\mathrm{[Co(NH_3)_5X]^{2+} + H_2O \rightleftharpoons [Co(NH_3)_5(OH_2)]^{3+} + X^-} \qquad \text{(step 1, form aquo intermediate)}$$

$$\mathrm{[Co(NH_3)_5(OH_2)]^{3+} + Y^- \rightleftharpoons [Co(NH_3)_5Y]^{2+} + H_2O} \qquad \text{(step 2, form final product)}$$

The first step in the reaction is the breaking of a $\mathrm{Co-X}$ bond and the formation of a $\mathrm{Co-OH_2}$ bond (step 1). Subsequently, $\mathrm{Y^-}$ can replace the aquo group (step 2).

In aqueous solution, water is always present at a much higher concentration than the various possible entering groups $\mathrm{Y^-}$, so it is reasonable that the aquo complex should be favored in the competition to form the new bond to $\mathrm{Co(III)}$. Nevertheless, the strength of the $\mathrm{Co-Y}$ bond should depend on the nucleophilicity of $\mathrm{Y^-}$ in these substitution reactions. Thus, the amount of $\mathrm{[Co(NH_3)_5Y]^{2+}}$ product should increase with increasing nucleophilicity of $\mathrm{Y^-}$. The fact that the aquo complex is the predominant reaction product despite the identity of $\mathrm{Y^-}$ strongly suggests that the the $\mathrm{Co-X}$ bond breaking is more important in the reaction outcome than formation of the new bond to the incoming $\mathrm{Y^-}$.

This evidence indicates dissociative character in the reaction. But the nature of the substitution mechanism is still unclear. For example, is the original $\mathrm{Co-X}$ bond completely broken before the new $\mathrm{Co-OH_2}$ bond has begun to form so that $\mathrm{Co(NH_3)_5}^{3+}$ is a true intermediate? Does the mechanism involve a transitory intermediate where bonds are breaking and forming in a concerted fashion?

Evidence under basic aqueous conditions

The evidence of reaction mechanism under basic conditions is seemingly contradictory to what is described above. When the entering group, Y^-, is the hydroxide ion, the reaction is

$$\mathrm{Co(NH_3)_5X^{n+} + OH^- \rightarrow Co(NH_3)_5OH^{2+} + X^{q-}}$$

Substitution by hydroxide ion is kinetically faster than by the aquo ligand in acidic solutions, and the rate is law found to be second-order:

$$\frac{d\left[\mathrm{Co(NH_3)_5OH^{2+}}\right]}{dt} = k\ \left[\mathrm{Co(NH_3)_5X^{n+}}\right]\left[\mathrm{OH^-}\right]$$

This rate law is consistent with an associative reaction involving nucleophilic attack by the hydroxide ion at the cobalt center. In an associative interchange mechanism, the $\mathrm{Co-OH}$ bond formation occurs simultaneously with breaking of the $\mathrm{Co-X}$ bond. However, just as in the case above, the hydroxo complex dominates even in the presence of $\mathrm{Y^-}$. Thus, the hydroxide ion seems to be a uniquely effective nucleophile toward cobalt(III). However, nucleophilic displacements have been investigated on many other electrophile, and in general, hydroxide is not a particularly effective nucleophile toward other electrophilic centers. So, assignment of an associative mechanism to this reaction is reasonable only if we can explain why hydroxide is uniquely reactive in this case and not in others.

The conjugate-base mechanism

An alternative mechanism, referred to as the **conjugate-base mechanism** or the $\mathrm{S_N1CB}$ (**S**ubstitution, **N**ucleophilic, first-order in the **C**onjugate **B**ase mechanism) mechanism, is also consistent with the second-order rate law. In this mechanism, the first step is formation of the conjugate base of the metal complex by deprotonation of one of its ligands. An important requirement of this mechanism is the presence of a metal-bound ligand with acidic protons (including amine, ammine, or aquo ligands). Under basic conditions the mecahnism is catalyzed by hydroxide ion.

In the case of $\mathrm{[Co(NH_3)_5OH_2]^{3+}}$ reacting under basic conditions, the hydroxide removes a proton from one of the ammine ligands to give a six-coordinate conjugate base intermediate (step 1 below). This conjugate base intermediate contains an amido ($\mathrm{NH_2^-}$) ligand which is a π-donor ligand, allowing facilitated dissociation of one of the other ligands (particulary the ligand in the trans position). This intermediate loses the leaving group X^- in the rate determining step to form a five-coordinate intermediate, $\mathrm{Co(NH_3)_4NH^{2+}}$ (step 2 below). This five-coordinate intermediate quickly picks up a water molecule from the bulk solution to give the aquo complex (step 3 below). In a series of proton transfers to (step 4) and from (step 5) the aqueous solvent, the aquo complex rearranges to the final product. The mechanism is shown below for $\mathrm{[Co(NH_3)_5OH_2]^{3+}}$ reacting with $\mathrm{Cl^-}$:

$$\mathrm{[Co(NH_3)_5Cl^{2+}OH]^- \rightleftharpoons [Co(NH_3)_4(NH_2)Cl]^+ + H_2O} \quad \text{(step 1, conjugate base)}$$

$$\mathrm{[Co(NH_3)_4(NH_2)Cl]^+ \rightleftharpoons [Co(NH_3)_4(NH2)]^{2+} + Cl^-} \quad \text{(step 2, dissociation)}$$

$$\mathrm{Co(NH_3)_4(NH2)^{2+} + H_2O \rightleftharpoons Co(NH_3)_4(NH2)(OH2)^{2+}} \quad \text{(step 3, association)}$$

$$\mathrm{Co(NH_3)_4(NH2)(OH2)^{2+} + OH^- \rightleftharpoons Co(NH_3)_4(NH2)OH^+ + H_2O} \quad \text{(step 4, proton transfer)}$$

$$\mathrm{Co(NH_3)_4(NH2)OH^+ + H_2O \rightleftharpoons Co(NH_3)_5OH^{2+} + OH^-} \quad \text{(step 5, proton transfer)}$$

The evidence in favor of the $\mathrm{S_N1CB}$ mechanism is persuasive. It requires that the ammine protons be acidic, so that they can undergo the acid–base reaction in the first step. That this reaction occurs is demonstrated by proton-exchange experiments. In basic $\mathrm{D_2O}$, the ammine protons undergo $\mathrm{H-D}$ exchange according to

$$\mathrm{[Co(NH_3)_5Cl]^{2+} + D_2O \rightleftharpoons [Co(ND_3)_5Cl]^{2+} + HDO}$$

The ammine protons are also necessary; the reaction does not occur for similar compounds, like $\mathrm{Co(2,2'-bipyridine)_2(O_2CCH_3)_2^+}$, which lack acidic protons on the nitrogen atoms that are bound to cobalt (*i.e.*, there are no $\mathrm{H-N-Co}$ moieties).

The evidence that $\mathrm{Co(NH_3)_4(NH2)^{2+}}$ is an intermediate is also persuasive. When the base hydrolysis reaction is carried out in the presence of other possible entering groups, Y^{p-}, the *rate* at which $\mathrm{[Co(NH_3)_5X]^{n+}}$ is consumed is unchanged, but the product is a mixture of $\mathrm{[Co(NH_3)_5OH]^{2+}}$ and $\mathrm{[Co(NH_3)_5Y]^{n+}}$. If this experiment is done with a variety of leaving groups, X^{q-}, the proportions of $\mathrm{[Co(NH_3)_5OH^{2+}]}$ and $\mathrm{[Co(NH_3)_5Y]^{n+}}$ are constant despite which leaving group exists in the reactant complex. These observations are consistent with the hypothesis that all reactants, $\mathrm{[Co(NH_3)_5X]^{n+}}$, give the same intermediate, $\mathrm{[Co(NH_3)_4(NH2)]^{2+}}$. The product distribution is always the same, because it is always the same species undergoing the product-forming reaction.

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- 5.16: The Mechanism of the Base Hydrolysis of $\mathrm{Co(NH_3)_5X^{n}}$ by Paul Ellgen is licensed CC BY-SA 4.0. Original source: https://www.amazon.com/Thermodynamics-Chemical-Equilibrium-Paul-Ellgen/dp/1492114278.

12.4.5: The Kinetic Chelate Effect

We discussed the increased thermodynamic stability of chelating ligands in a previous section on the chelate effect (Section 10.1.1). This thermodynamic benefit is related to a change in the rate of binding and dissociation events called the kinetic chelate effect. This effect was also mentioned earlier in this chapter (Section 12.2.2).

Recall that there is a relationship between the equilibrium constant and rate constants of any chemical reaction. The relationship is demonstrated below for a general reaction.

$$aA + bB \rightleftharpoons cC + dD$$

$$\text{forward rate} = k_f[A]^a[B]^b$$

$$\text{reverse rate} = k_r[C]^c[D]^d$$

At equilibrium, the rate of the forward reactions is equal to the rate of the reverse reaction. Therefore:

$$\text{forward rate} = \text{reverse rate}$$

$$k_f[A]^a[B]^b = k_r[C]^c[D]^d$$

Rearrangement of the equation above gives:

$$\frac{k_f}{k_r} = \frac{[C]^c[D]^d}{[A]^a[B]^b} = K_{eq}$$

Because chelating ligands have larger values of K_{eq} than analogous monodentate ligands, there must also be a change in the relative rates of the forward (binding) and reverse (dissociation) reactions. In fact, there is a kinetic benefit that makes a metal bound to a polydentate ligand more inert than the analogous complex with monodentate ligands: this is called the ***kinetic chelate effect***.

The kinetic chelate effect is a result of a slower first dissociation step and faster re-association step relative to that of a monodentate ligand. The complete dissociation of a bidentate ligand, for example, would require two dissociation steps (see first reaction in figure below). It is the first dissociation step that is slower in a bidentate ligand ($k_1 < k_1'$ in the figure below). This first dissociation step is slower in part because the chelate would have to rotate to move the free ligand away from the open coordinate site on the metal ion. For the same reason, the reverse of this step (association) is faster than the association of a monodentate ligand ($k_{-1} > k'_{-1}$).

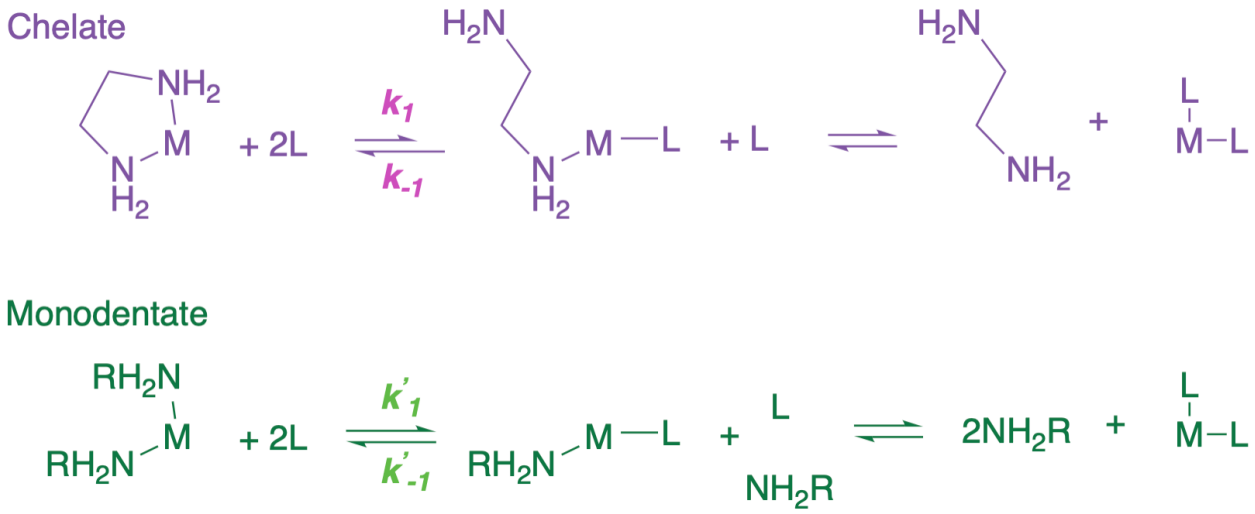


Figure 12.4.5.1: Step-wise dissociation of a bidentate ligand and analogous monodentate ligands. (CC-BY-SA; Kathryn Haas)

(1) Carter, M. J.; Beattie, J. K. Kinetic Chelate Effect. Chelation of Ethylenediamine on Platinum(II). Inorg. Chem.1970, 9 (5), 1233–1238. https://doi.org/10.1021/ic50087a044.

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12.5: Stereochemistry of Octahedral Reactions

The stereochemical outcomes of a reaction can depend on numerous factors. For simplicity, the discussion in this section will be limited to octahedral complexes that react through dissociative mechanisms, with emphasis on those that occur through the limiting case of a dissociative (D) mechanism. In light of this focus, the reactions of Co(III) complexes, particularly those with ethylenediamine ligands, provide appropriate examples of well-characterized systems.

In the purely dissociative case, the octahedral metal complex completely loses one ligand to become a five-coordinate intermediate. Therefore, the structure of the product depends primarily on the structure of the intermediate and its interaction with the entering ligand. The outcome of a D reaction should not be influenced by the identity of the leaving group. However, the identity of the entering group and the reaction conditions are appropriate considerations. For example, under basic aqueous conditions, the conjugate base mechanism can alter the stereochemical outcome compared to the same reaction under more acidic conditions.

Structure of the intermediate

When an octahedral metal complex reacts through a D mechanism, a six-coordinate metal complex forms a five-coordinate intermediate, which goes on to react with the entering group. The structure of that 5-coordinate intermediate has a major influence on the stereochemistry of the product. Recall from a previous section (Section 9.4) that 5-coordinate metal complexes can adopt either a **square pyramidal** or **trigonal bipyramidal geometry**. * In general, if the intermediate adopts a square pyramidal structure, the incoming ligand will enter at the same site where the leaving group was lost, and stereochemistry is retained from reactant to product. On the other hand, if the intermediate structure is a trigonal pyramid, at least some of the product will not retain the original configuration.

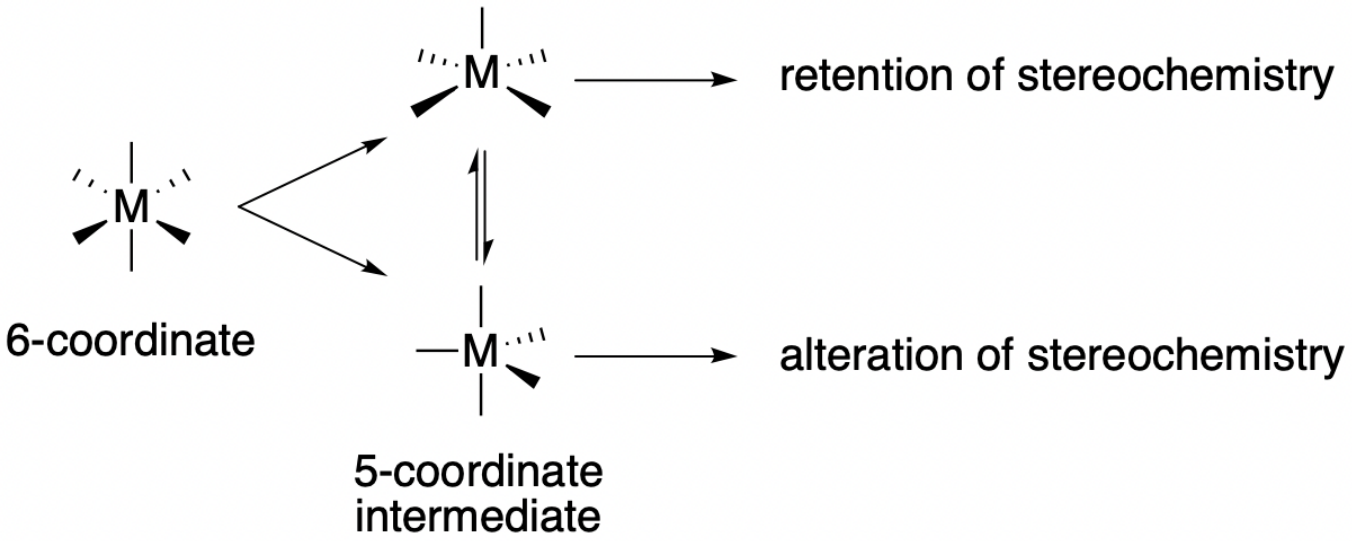


Figure 12.5.1: In the context of a substitution reaction, the loss of a ligand from an octahedral complex results in a five-coordinate intermediate. When the intermediate structure is a square pyramid, the new ligand enters so that the original sterochemistry is retained. The adoption of a trigonal bipyramid leads to changes in the stereochemistry of at least some of the product compared to the reactant. (CC-BY-SA; Kathryn Haas)

* Note: Recall from a previous section (Section 9.4) that square pyramid and trigonal bipyramid geometries typically have similar energies and readily interconvert through pseudorotation. However, during a D reaction, the intermediate exists for such a short moment in time, that interconversion is assumed not to occur unless there is an unusually long-lived intermediate.

Cis vs trans reactants

This section will present generalizations for the stereochemical consequences of substitution in *trans*-bisethylenediamine

(*trans*-en) and *cis*-bisethylenediamine (*cis*-en) octahedral Co(III) complexes. Cis-en complexes tend to retain a square pyramidal intermediate structure and retain the cis stereochemistry of the product, except when the conjugate base mechanism promotes isomerization. On the other hand, trans-en complexes are more likely to undergo stereochemical rearrangments through a trigonal pyramidal intermediate. However, especially in the case of trans-en complexes, the product ratios are a result of mixtures of intermediates.

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12.5.1: Substitution in trans-en octahedral complexes

The reaction of metal complexes of the form $[\mathrm{M(en)_2LX}]^{n+}$ have multiple possible pathways in terms of the structure of the intermediate.

When the X ligand departs from a trans complex, the most likely case is that the L ligand will remain in the axial position. In that case, there is one primary structure for the square pyramidal intermediate. Reaction of that intermediate with the incoming ligand, Y, will result in retention of trans stereochemistry.

An alternative possibility is that the intermediate adopts a trigonal bipyramidal structure. In that case, the outcome of the reaction depends on which of the possible trigonal bipyramidal structures exist and their relative amounts. There are two chemically distinguishable positions on the trigonal bipyramid; the axial and equatorial positions. The remaining L ligand can occupy either the axial position, which has a slightly longer bond, or the equatorial positions, which are slightly closer to the metal and more sterically hindered in space. To adopt either of the trigonal bipyramidal structures, rearrangement of the complex is necessary. It is more likely that the rearrangement will result in the trans ligand being in the equatorial position, since that requires less distortion of the original positions of each ligand (this is not obvious from the structures in Figure $12.5.1.1$). A trigonal structure with axial L requores one of the en ligand nitrogens to move by 90 degrees, while a structure with equitoral L requires only 30 degree movement from any ligand. As a result, the trigonal bipyramid with equitorial L (bottom of Figure $12.5.1.1$) is the dominant trigonal bipyramidal structure. That structure can produce three optical isomers from the three different angles of ligand Y entering along the equitorial plane. When Y enters trans to L, it produces the trans product. When Y enters cis to L, it produces either of the two cis optical isomers. The cis-$\backslash\mathrm{Lamda}$ and $cis-\Delta$ isomers are equally likely, and are produced as a racemic miture from an optically inactive starting trans reactant. The expected ratios of cis to trans are 2:1.

Regarding the trigonal bipyramidal intermediates, the identity of L influences its preference for the axial or equatorial positions. For example, π-donor ligands prefer equatorial positions due to the shorter bond lengths involved in π-donor interactions. Thus, when L is a strong π-donor, reaction products are more likely to come from the trigonal intermediate with an equatorial L. This last point is relevant to reactions where the conjugate base mechanisms is at play. The deprotonated ligand that results from the conjugate base mechanism is a stronger π-donor, and has preference for occupation of the equatorial positions of a trigonal bipyramidal intermediate. Even in cases where the square pyramid is typically preferred, the conjugate base mechanism can result in preference for a trigonal intermediate.

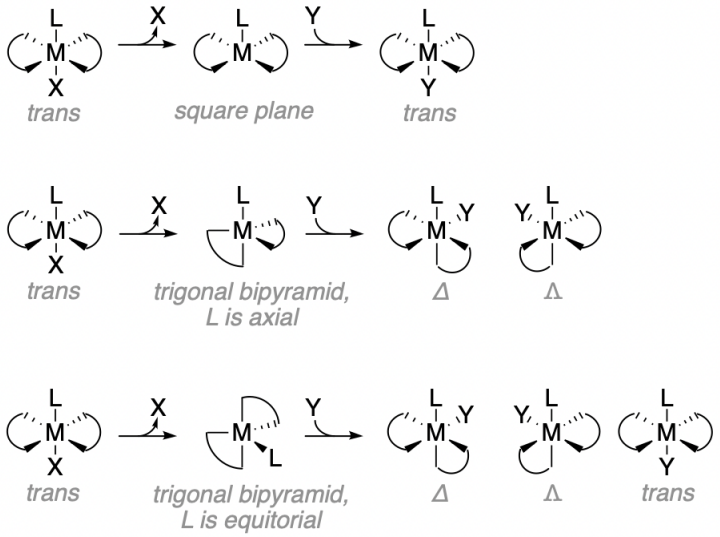


Figure $12.5.1.1$: Three different possibilities for the five-coordinate intermediate yield different possibilities for the stereochemistry of the product complex. The possibility of a square pyramid with basal ligand is not shown and is considered less likely than the three pathways shown because it would require a long-lived intermediate to allow time for the rearrangement of the square planar intermediate shown. (CC-BY-SA; Kathryn Haas)

The actual proportion of reaction products of a given stereochemistry depends on the extent to which each of the possible

intermediates leads to the products. However, the expected percentages of cis-trans from any single intermediate is rarely found in experimental data (See Table 12.5.1.1).

Table 12.5.1.1 gives the % of trans stereochemistry retained in the displacement of Cl^- by either H_2O or OH^-in a series of $trans-[Co(en)_2LCl]^+$ complexes where the identity of the *trans* ligand, L^-, is varied.

The reactions run under acidic conditions is shown below, and its data is shown in the middle column in Table 12.5.1.1 :

$$trans-[Co(en)_2LCl]^+ + H_2O <==> [Co(en)_2L(H_2O)]^{2+} + Cl^-$$

The reactions run under basic conditions is shown below, and its data is shown in the right column in Table 12.5.1.1 :

$$trans-[Co(en)_2LCl]^+ + OH^- <==> [Co(en)_2L(OH)]^+ + Cl^-$$

Table 12.5.1.1: % trans product under different conditions

L^-	% trans product under acidic conditions (stereochemistry of reactant is retained)	% trans product under basic conditions (stereochemistry of reactant is retained)
OH^-	25	6
NCS^-	30-50	24
Br^-	50	100
Cl^-	65	95
$NH_3{}^-$	100	24
$NO_2{}^-$	100	94
Data from Miessler, G. L.; Fischer, P. J.; Tarr, D. A. *Inorganic Chemistry, 5th Ed.* Pearson: Boston, 2014, p. 459.		

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12.5.2: Substitution in cis-en octahedral complexes

The D substitution reactions of cis complexes occur through the same intermediate structures described above for trans complexes. For example, the reaction,

$$\text{cis-}[\text{M(en)}_2\text{LX}]^+ + \text{Y}^- \longrightarrow [\text{Co(en)}_2\text{LY}]^{2+} + \text{X}^-$$

can proceed through square planar or trigonal bipyramidal intermediates. Complete the exercise below.

Exercise 12.5.2.1

Follow the example of Figure 12.5.1.1 to sketch the possible reaction intermediates and products for $\text{cis-}[\text{M(en)}_2\text{LX}]^+ + \text{Y}^-$. Which intermediates are most likely? In the case of each trigonal bipyramid, what would be the ratios of products if ligand attack from the three angles along the trigonal plane are equally likely?

Answer available at the end of this section.

Table 12.5.2.1 gives the % of cis stereochemistry in the displacement of Cl^- by either H_2O or OH^- in a series of $\text{cis}-[\text{Co(en)}_2\text{LCl}]^+$ complexes where the identity of the *trans* ligand, L^-, is varied.

The reactions run under acidic conditions is shown below, and its data is shown in the middle column in Table 12.5.2.1 :

$$\pm\text{cis}-[\text{Co(en)}_2\text{LCl}]^+ + \text{H}_2\text{O} <==> [\text{Co(en)}_2\text{L(H}_2\text{O)}]^{2+} + \text{Cl}^-$$

The reactions run under basic conditions is shown below, and its data is shown in the right column in Table 12.5.2.1. Note that in all but one case, the reactions run under basic conditions were done so using optically pure starting material, and gave an optically active product.

$$\Delta-\text{cis}-[\text{Co(en)}_2\text{LCl}]^+ + \text{OH}^- <==> [\text{Co(en)}_2\text{L(OH)}]^+ + \text{Cl}^-$$

Table 12.5.2.1: % cis product under different conditions

L^-	% cis product under acidic conditions from racemic cis reactant (stereochemistry of reactant is retained)	% cis and trans product under basic conditions from $\Delta - cis$ starting material (stereochemistry of reactant is retained)
OH^-	100	61% $\Delta - cis$ | 36% $\Lambda - cis$ | 3% trans
NCS^-	100	56% $\Delta - cis$ | 24% $\Lambda - cis$ | 20% trans
Br^-	100	-
Cl^-	100	21% $\Delta - cis$ | 16% $\Lambda - cis$ | 63% trans
$\text{NH}_3{}^-$	-	60% $\Delta - cis$ | 24% $\Lambda - cis$ | 16% trans
$\text{NO}_2{}^-$	100	46% $\Delta - cis$ | 20% $\Lambda - cis$ | 34% trans
Data from Miessler, G. L.; Fischer, P. J.; Tarr, D. A. *Inorganic Chemistry, 5th Ed.* Pearson: Boston, 2014, p. 459.		

Under acidic conditions, and when the conjugate base mechanism is unlikely, the product specifically retains the stereochemistry of the starting material. This data (middle column above) indicates that the D reaction of the cis isomer, in contrast to trans, reacts exclusively through the square pyramidal intermediate under acidic conditions. This is because in every case, the ligand trans to the X leaving group is an amine from the en ligand, which is not a π donor. The ligand cis to the leaving group (L) has no influence on the reaction outcome under acidic conditions.

Under basic conditions, where the conjugate base mechanism is possible, cis stereochemistry is not entirely retained, and the cis products are produced in approximately a 2:1 ration of $Delta : \Lambda$ from a $Delta$ reactant.

Exercise 12.5.2.1

Consider the data in the right colum of Table 12.5.2.1. What does the presence of trans product and a 2:1 ratio of the two cis isomers indicate about the intermediates of reaction under basic conditions?

Answer available at the end of this section.

Answers

Exercise 12.5.2.1

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Exercise 12.5.2.1

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12.5.3: Isomerization of Chelate Rings

Recall that the stereoisomers of octahedral complexes with two and three bidentate ligands were discussed previously (Section 9.3). This page will discuss the interconversion of stereoisomers, which can occur through two primary mechanisms involving either (1) bond breaking and bond making steps, and (2) twisting.

Isomerization through dissociative substitution

One way to convert one steroisomer to another is through bond breaking and bond re-making steps. This type of structural rearrangement is essentially a substitution reaction, as described previously in this chapter, except that the leaving group and entering group are the same ligand. Evidence for this type of mechanism comes from the study of isotopically labeled amibidentate ligands (those that have different modes of coordination). For example, an acetyl group with a labeled $\mathrm{CD_3}$ can be added as an "outside" group (adjacent to the coordinating groups) in a tris(acac)cobalt(III) complex. The labeled group moves to the "inside" (directly coordinated to the metal ion) during isomerization from an optically pure solution to a racemic mixture. This change can only occur through bond breaking and re-forming steps.

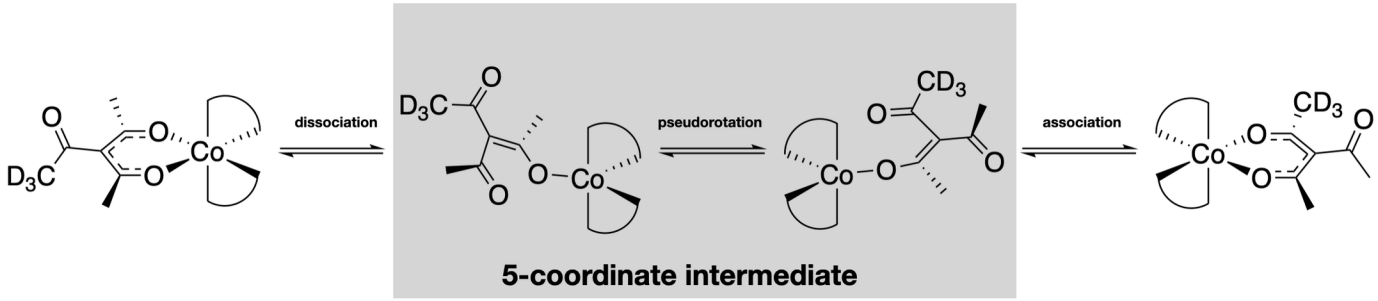


Figure 12.5.3.1: The rearrangement of a $\mathrm{CD_3}$ group from an "outer acetyl" to one directly coordinating to the metal complex of an $\mathrm{CD_3}$-labeled acetyl group on acetylacetone (acac) provides evidence of isomerization through a mechanism related to dissociative substitution. (CC-BY-SA; Kathryn Haas)

Isomerism through twisting

The second pathway of isomerism is through twisting; it does not involve bond breaking or bond forming. Twisting that causes interconversion of octahedral isomers was also discussed in Chapter 9. A figure from that chapter is re-posted here for convenience.

An octahedroal coordination sphere is just a trigonal antiprism in which all edge lengths are identical. Rotation of one triangular face relative to its opposite until the two are eclipsed gives a triganal prismatic geometry. In fact, since continuation of this rotation gives another octahedral complex the trigonal prismatic geometry is an intermediate in isomerization reactions involving octahedral complexes. In tris- and bis-chelates such isomerizations are said to occur by a **Bailar twist** or a **Ray-Dutt twist**, which differ only in the relationship between the chelate rings and the faces twisted.

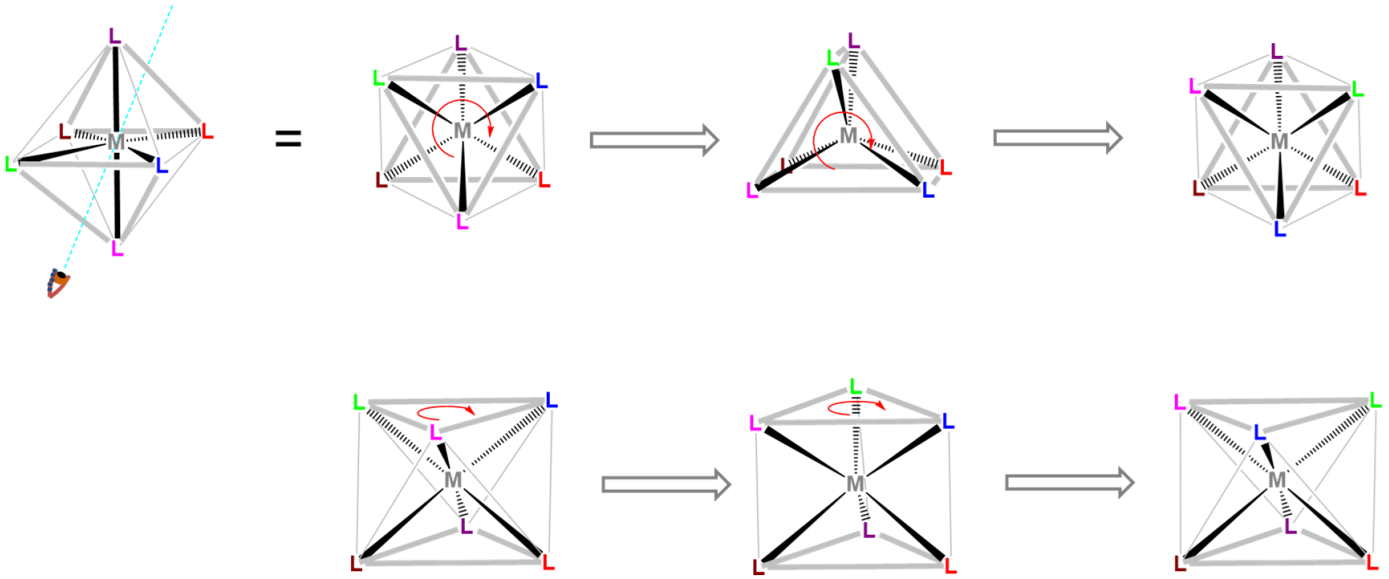


Figure 12.5.3.2. Since an octahedron is a trigonal antiprism a trigonal prism may be produced by rotating or "twisting" one face of the octahedron relative to its opposite. Since continuation of the rotation gives an isomer of the original octahedron, when the energy landscape for twists like these is thermally or photochemically accessible twists like these provide one pathway for isomerisation reactions involving octahedral complexes. In tris- and bis-chelates such isomerizations are said to occur by Bailar and Ray-Dutt twists, which differ only in the relationship between the chelate rings and the faces twisted. Top: View down looking down an axis bisecting a pair of opposing faces. Bottom: View perpendicular to that shown at top. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

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12.6: Substitutions in Square Planar Complexes

Substitutions in square planar complexes tend to occur through mechanisms with associative character, although the degree of associative character may vary (eg $A,\ I_a,\ I_d$. The outcome of square planar substitutions depend on the identities of the leaving group, the ligand trans to the leaving group, and the entering group. The reactions of Pt(II) are well studied and will serve as the primary examples in this section. Pt(II) complexes are of particular interest because of their role as effective chemotherapeutics in the treatment of several types of solid tumor cancers.

The generic chemical equation for substitution in a square planar complex is shown below, where X is the leaving group, Y is the entering group, and $[\mathrm{ML_3X}]$ is the reactant complex:

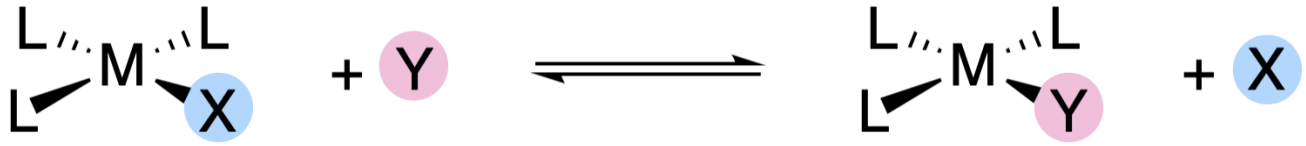


Figure 12.6.1: Generic form of square planar metal complex undergoing a substitution reaction. (CC-BY-SA; Kathryn Haas)

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12.6.1: Kinetics and Stereochemistry of Square Planar Reactions

Kinetics

In general, the reaction kinetics of square-planar associative substitution takes the form of the following rate law, which has two terms:

$$\frac{d[\mathrm{ML_3Y}]}{dT} = k_1[\mathrm{ML_3X}] + k_2[\mathrm{ML_3X}][\mathrm{Y}]$$

Each of the terms corresponds to one of the two possible reaction pathways. The term, $k_2[\mathrm{ML_3X}][\mathrm{Y}]$, is second-order, and corresponds to a simple associative pathway. The $k_1[\mathrm{ML_3X}]$ term is first-order, although it also corresponds to an associative pathway. The reason it appears to be first order is because square planar complexes can react through a solvent-assisted pathway where bulk solvent replaces the leaving group, and then is replaced by the entering group (Figure $12.6.1.2$). Because solvent concentration does not appreciably change as the reaction proceeds, it is not part of the rate law term even though it is involved in the rate-determining association. The step in which solvent is substituted by the entering group must happen faster than the solvent-assisted replacement of X.

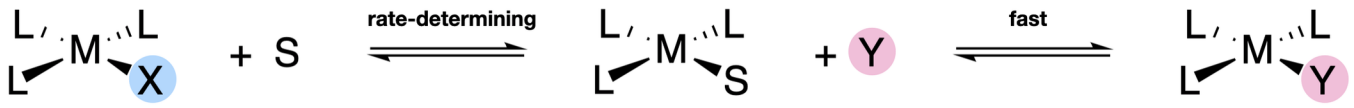


Figure $12.6.1.2$: Solvent-assisted substitution pathway where X is the leaving group, Y is the entering group, and S is solvent. (CC-BY-SA; Kathryn Haas)

The kinetic rate constats in square planar substitution can depend on the identities of the leaving group, the ligand trans to the leaving group, and the entering group. The ligands that are in the cis positions with respect to the leaving group do not have a significant affect on the rate, and these are referred to as spectator ligands.

Stereochemistry

Square planar complexes react to give products in which the stereochemistry of the reactant is retained. In other words, a *trans*-reactant will give a *trans*-product, and a *cis*-reactant will give a *cis*-product (Figure $12.6.1.3$). The identity of the trans ligand has particular importance in the outcome of square planar substitutions (discussed further in the next sections). We will designate the trans ligand generally with the symbol T to indicate its position (Figure $12.6.1.3$), the leaving group as X, and the entering group as Y. The spectator ligands (ligands that are cis to X) will be desginated L and L'. For the discussion that follows, the plane of the metal complex will be designated as the xy plane, while the z axis is perpendicular to the plane (Figure $12.6.1.3$). The x and y axes will run colinear to the bond axes, with the x axis running colinear to the T-M-X bonds (Figure $12.6.1.3$).

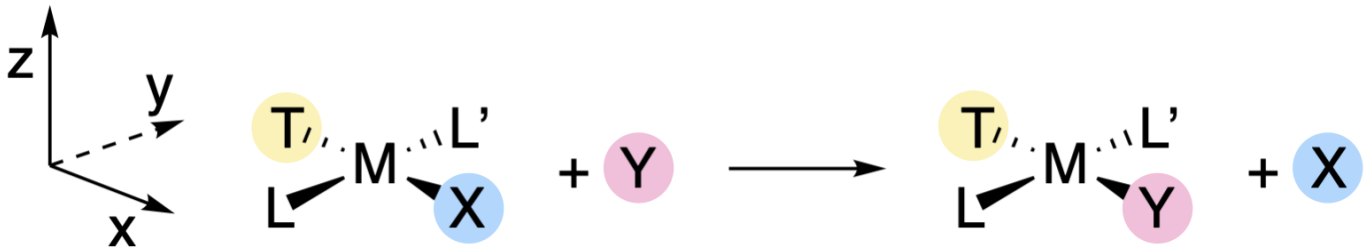


Figure $12.6.1.3$: Stereochemistry is strictly retained in the reactions of square planar complexes. By convention, the plane of the metal complex is the xy plane, with the x axis colinear with the T-M-X bonds. M = metal ion | X = leaving group ligand | Y = entering group ligand | T = ligand trans to the leaving/entering group. (CC-BY-SA; Kathryn Haas)

The retention of stereochemistry, and the fact that X, Y, and T can influence the rate of reaction provide hints at the nature of intermediates and/or transition states involved in these reactions. The existence of five-coordinate square pyramidal structures, like those of $[\mathrm{Ni(CN)_5}]^{3-}$ and $[\mathrm{Pt(SnCl_3)_5}]^{3-}$, suggests that five-coordinate intermediates are possible. However the substitutions of square planar complexes are generally classified as associative interchange mechanisms (I_a) because isolation of a true intermediate is rarely accomplished. In any case, the retention of stereochemistry is explained by a five-coordinate trigonal bipyramidal transition state in which X, Y, and T are each in the trigonal plane (along with the metal center). As the M-X bond is breaking, the M-Y bond is forming and Y replaces X in the position trans to T. Because T, Y and X are in the trigonal plane in the transition state, all three ligands are able to interact with the same d orbitals of the central metal ion. Thus the identities of X, Y, and T should influence the ability of the M-X bond to break and the M-Y bond to form. On the other hand, L and L' are in a perpendicular plane, and would interact with different orbitals than X and Y. This explains why spectator ligands L and L' have little effect on the reaction rate, as they are interacting with different orbitals than those involved in bond breaking and bond making.

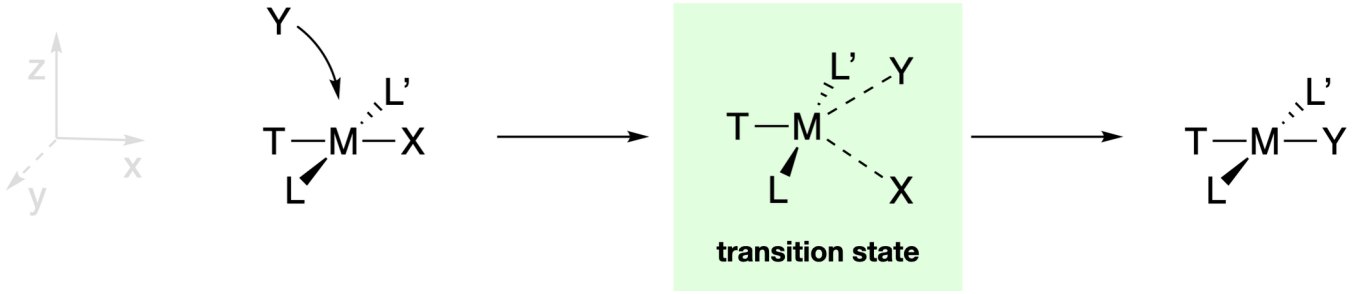


Figure 12.6.1.4: Mechanism for simple I_a substitution. The structure of the transition state is trigonal bipyramidal, with T, X, and Y in the trigonal plane with M. The spectator ligands, L and L', are in a perpendicular plane and are coplanar with T and M. (CC-BY-SA; Kathryn Haas)

The solvent-assisted pathway can occur through similar transition states and mechanistic steps, except that there are additional steps involving solvent association and displacement.

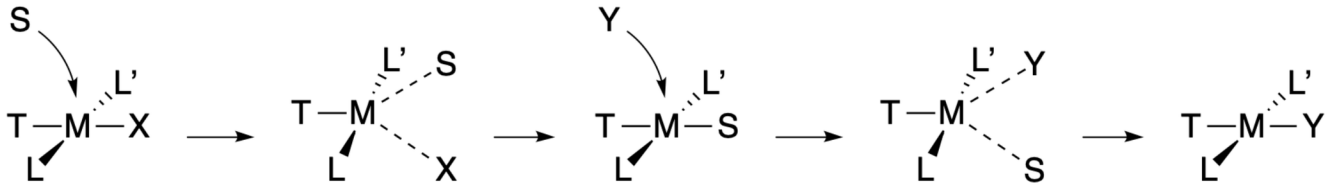


Figure 12.6.1.5: Solvent-assisted I_a substitution. Compare to Figure 12.6.1.4. S is solvent. (CC-BY-SA; Kathryn Haas)

Although there is general consensus that square planar complexes react through associative pathways, the characterization of intermediates and/or transition states has remained elusive, and there is still debate as to the intricate details of the reaction mechanisms involving square planar complexes. For example, there are arguments that a six-coordinate transition state may exist in the solvent-assistant pathway.

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12.6.2: Evidence for Associative Reactions

The reactions of Pt(II) complexes have been thoroughly investigated, and there are several lines of experimental evidence that have lead to the general conclusion that square planar complexes react through associative mechanisms. The experimental evidence is presented here.

The entering group

In the reaction of $\mathrm{trans{-}[PtL_2Cl_2]}$, the rate of reaction depends on the identity of the incoming ligand Y.

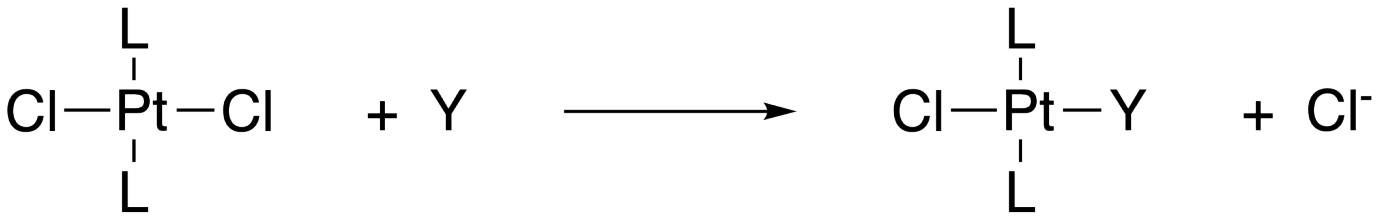


Figure 12.6.2.1: Substitution reaction of $\mathrm{trans{-}[PtL_2Cl_2]}$. (CC-BY-SA; KAthryn Haas)

For example, the rate of the reaction shown above depends heavily on the ligand, Y, as follows:

$$\text{most kinetically labile } \mathrm{PR_3} > \mathrm{CN^-} > \mathrm{SCN^-} > \mathrm{I^-} > \mathrm{Br^-} > \mathrm{N_3^-} > \mathrm{NO_2^-} > \mathrm{py} > \mathrm{NH_3} \quad \mathrm{Cl^-} > \mathrm{CH_3OH} \text{ most kinetically inert}$$

In general, ligands that would form the strongest bonds with Pt(II) due to their soft character or π-binding ability react fastest. The rate constants in the above series range by nearly ten orders of magnitude. This huge range of rate constants as a factor of Y demonstrates suggests that M-Y bond formation is part of the rate limiting step. This is evidence for rate-determining association A or I_a.

The leaving group

Since the leaving group occupies a similar position in the transition state as the entering group, we should expect the leaving group to have a similar effect on the rate constants as was found for Y. In fact, this is true. For the reaction of $\mathrm{[Pt(diene)X]^+}$ with pyridine, the follow trend was observed by varying the leaving group, X:

$$\text{most kinetically labile } \mathrm{NO_3^-} > \mathrm{Cl^-} > \mathrm{Br^-} > \mathrm{I^-} > \mathrm{N_3^-} > \mathrm{SCN^-} > \mathrm{NO_2^-} > \mathrm{CN^-} \text{ most kinetically inert}$$

The rate of reaction follows an order that is nearly opposite as that observed for Y: The softer the ligand, the slower the dissociation. The rate constants in this series span a range of approximately five orders of magnitude, illustrating that breaking of the M-X bond is part of the rate-determining step. This is evidence for a mechanism involving associative interchange character (I_a or I_d. The importance of the leaving group somewhat depends on the identity of the entering group, and vice-versus.

The trans ligand

The trans ligand also occupies a similar position to X and Y in the transition state. So, as you might expect, it too has influence on the rate of reaction. In general, the rate of substitution of X in Pt(II) complexes general follows the order given below when T is varied as:

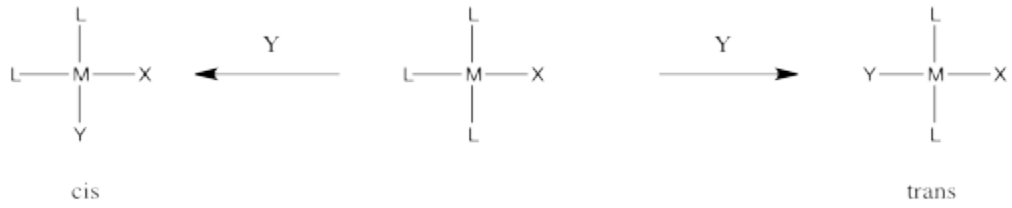
$$\text{M-X most kinetically labile } \mathrm{CN^-} \quad \mathrm{CO} \quad \mathrm{C_2H_4} > \mathrm{PH_3} \quad \mathrm{SH_2} > \mathrm{NO_2^-} > \mathrm{I^-} > \mathrm{Br^-} > \mathrm{py} \quad \mathrm{NH_3} > \mathrm{OH^-} > \mathrm{H_2O} \text{ M-X most kinetically i}$$

The effect of the trans ligand deserves a more through discussion, and will be addressed in the next section. It is mentioned here because it is evidence for the trigonal bipyramidal intermediate that was described earlier for associative substitution in square planar metal complexes.

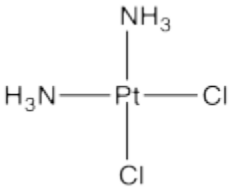
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12.7: The Trans Effect

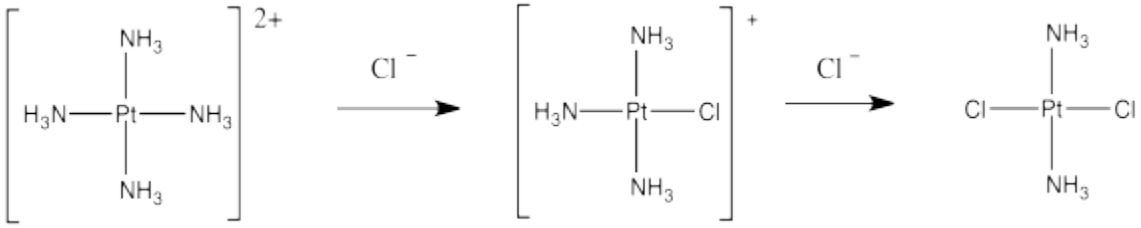
Occasionally in ligand substitution there is a situation in which there are two identical ligands that could be replaced, but two different products would result depending on which ligand left. This situation often happens in square planar complexes, for example. Replacement of one ligand would lead to a *cis* product. Replacement of the other one would lead to a *trans* product.



An important example of this issue is in the synthesis of cis-platin, an antitumour medication frequently used to treat ovarian and testicular cancer.

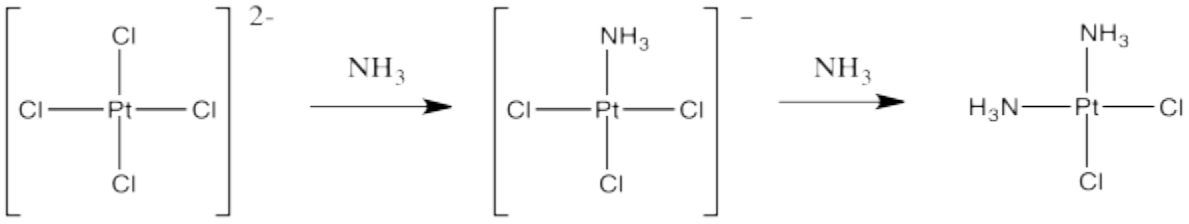


Cis-platin could be made from treatment of tetraammineplatinum(II) with chloride salts. The chloride ion could replace two of the ammonia ligands.



But that doesn't work. That synthesis results in the formation of *trans*-platin, a compound that has all of the nasty side effects of the *cis* isomer but with none of the therapeautic benefit.

If instead you were to start with tetrachloroplatinate salts and treat them with ammonia, you could replace two of the chloride ligands. That works really well, and it provides *cis*-platin, not *trans*-platin.



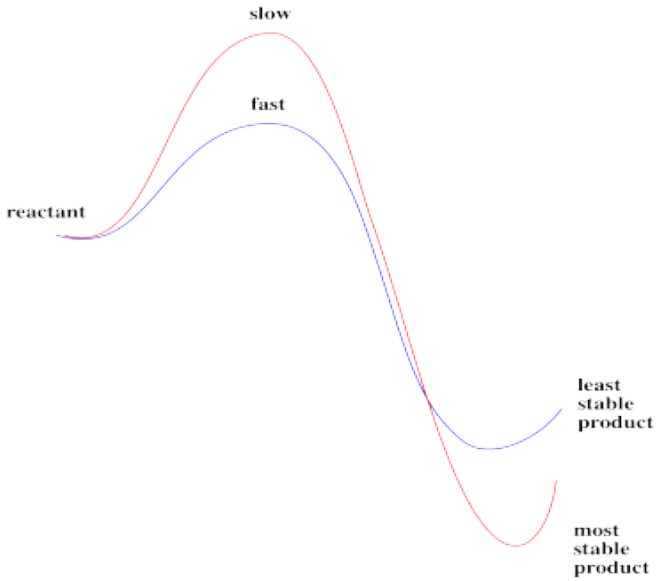
Exercise 12.7.1

What do you think is the mechanism of substitution of the two reactions above? Why?

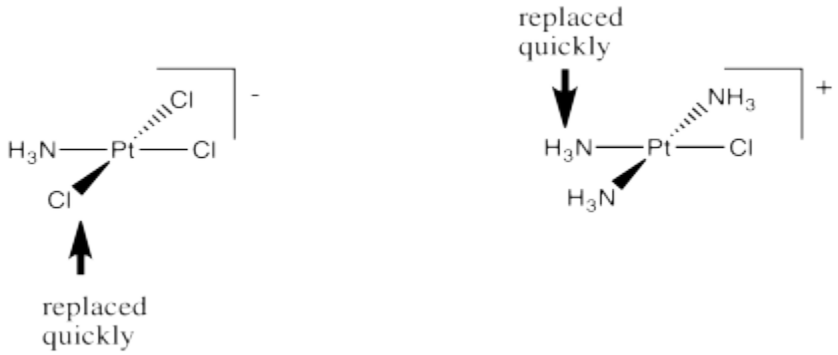
Answer available at the end of this section.

This reaction, if run under these conditions, is clearly not always under thermodynamic control. Two different products result, depending on how the reaction is done. One of those isomers is probably more stable than the other; if thermodynamics were in charge, it would form the same thing both times.

Instead, there may be an element of kinetic control for at least one of the pathways. A given product might be made, not because it is more stable, but simply because it forms more quickly than the other one.



Take another look at those two reactions. One of the things that they have in common is that the ligand that gets replaced is *trans* to a chloride. It is not *trans* to an ammonia. Maybe the other ligands in the complex can influence how quickly one ligand can leave.



Specifically, the "*trans* effect" is the role of *trans*-ligands in influencing substitution rates in square planar complexes.

The following kinetic data were obtained for substitutions on square planar platinum complexes, in the reaction:

$$trans-(PEt_3)_2PtLCl + py \rightarrow trans-(PEt_3)_2PtLpy^+ + Cl^-$$

L	k_{obs} (s^{-1})	T, °C
PMe_3	0.20	0
H^-	0.047	0
PEt_3	0.041	0
CH_3^-	6.0×10^{-4}	25

$C_6H_5^-$	1.2×10^{-4}	25
Cl^-	3.5×10^{-6}	25

Ref: Cooper Langford & Harry Gray, *Ligand Substitution Processes*, W.A. Benjamin, NY, 1965, p. 25.

Exercise 12.7.2

Draw structures for each of the complexes listed in the table.

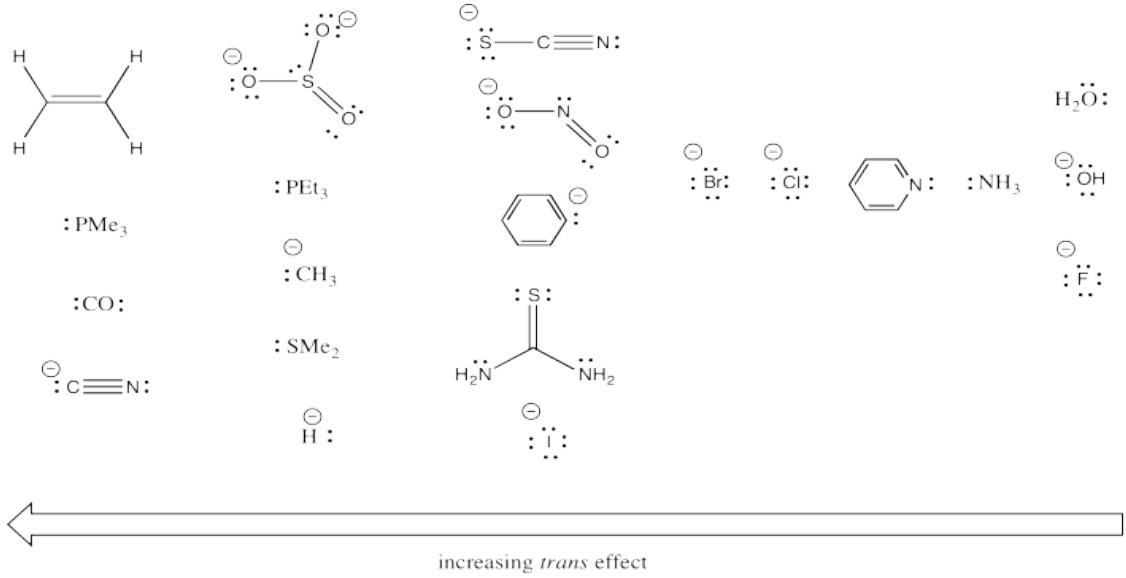
Answer available at the end of this section.

Exercise 12.7.3

Provide a mechanism with arrows for the reaction studied in the table.

Answer available at the end of this section.

Clearly that *trans* ligand has a dramatic effect on how quickly the chloride can be substituted in the above study. Additional studies like this one have led to some general trends. Below, the ligands on the left have strong *trans*-effects. Ligands *trans* to them are substituted very quickly. The ligands on the right have very modest *trans* effects. Ligands *trans* to them are substituted only slowly.



Exercise 12.7.4

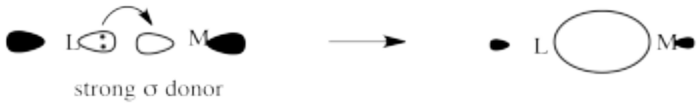
Look for empirical trends in the series of ligands above. Without trying to explain exactly why, find chemically relevant factors that may be responsible for these reactivity trends.

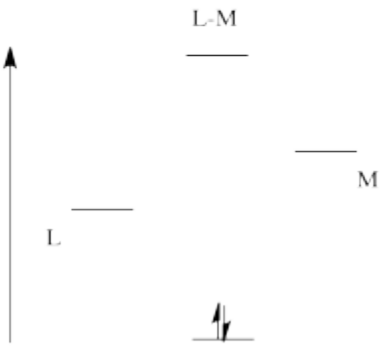
Answer available at the end of this section.

In general, explanations of the trans effect have focused on two separate types of ligands. These are strong sigma donors and strong pi acceptors.

Strong sigma donors donate electrons very effectively to the metal via a sigma bond. Because the ligand trans to this donor would

be bonding via donation to the same metal p orbital, there is a competition. The metal p orbital bonds more favorably with the strong sigma donor, and the ligand trans to it is left with a weaker bond.

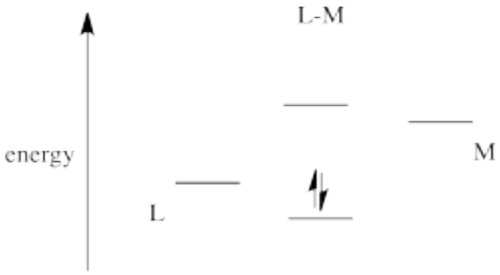




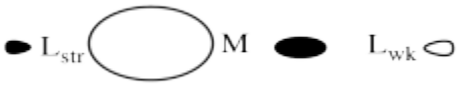
The strong sigma donor gets good overlap with the metal orbital and the resulting interaction goes down low in energy.

The weak sigma donor gets poorer overlap with the metal orbital and only weak stabilization of the donor electrons.





Place these two choices together, and the metal orbital will engage in a strong bonding interaction with the strong σ-donor. Doing so lowers the electronic energy significantly. It won't interact very much with the weak σ-donor, because doing that won't result in as much lowering of electronic energy. The result is a strong bond on one side of the metal and a weak bond on the other. That weak bond will break easily and that ligand will be replaced easily.

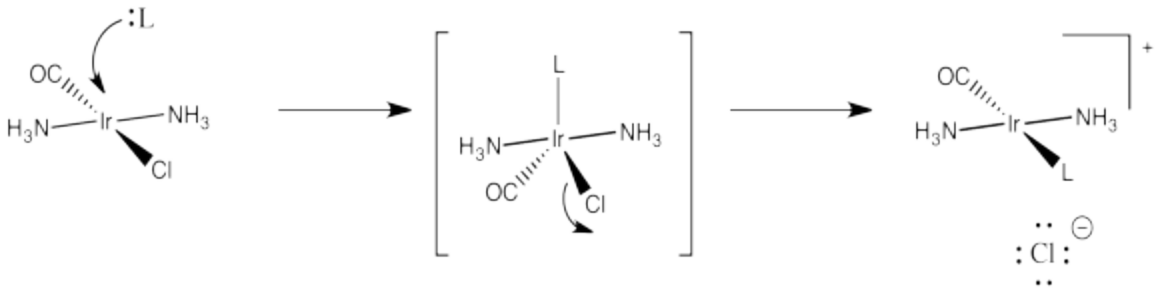


Exercise 12.7.5

Which of the ligands in the *trans* effect series are probably strong σ-donors? Why?

Answer available at the end of this section.

Strong pi acceptors exert their trans effect in a different way. They are thought to stabilize a particular geometry of the five-coordinate intermediate in substitution of square planar complexes. We haven't worried too much about the geometry of that intermediate, but it is probably trigonal bipyramidal. It would have three ligands in an equatorial plane and two more directly opposite each other, in the axial positions.



Essentially, the incoming ligand pushes two of the ligands down from the square plane to form this trigonal bipyramid. When it comes time for a ligand to leave, it is probably going to be one of these ligands that is already on the move. They are already on a trajectory out of the square plane, anyway.

A strong pi acceptor like CO exerts its *trans* effect by making sure it, along with the ligand opposite it, gets into that equatorial plane. It does that by a stabilizing delocalization that happens when the π-acceptor is in the electron-rich equatorial plane. In that position, it can draw electron density via π-donation from two different donors. If it were in an axial position, it could still delocalize electrons this way, but it would draw most effectively from just one donor rather than two.



favoured

So which of those two ligands is going to keep moving and leave the complex? It certainly won't be the one that is exerting a stabilizing, delocalizing effect on the complex via its strong bonding interactions. It will be the unlucky *trans* ligand that got dragged along with it.

Exercise 12.7.6

Which of the ligands in the *trans*-effect series are probably strong π-acceptors? Show why.

Exercise 12.7.7

Draw an orbital picture showing the -delocalization described in the trigonal bipyramidal intermediate. Label the orbitals, assuming the z axis is along the axis of the trigonal bipyramid (i.e. the equatorial plane is the xy plane).

Answer available at the end of this section.

Exercise 12.7.8

Substitution of trans ligands in μ-oxo-bis(μ-acetato)diruthenium complexes: Synthesis and kinetic studies. Hussain, Bhatt, Kumar, Thorat, Padhiyar and Shukla, *Inorganica Chemica Acta*, **2009**, *362*, 1101-1108.

Given the structure $[Ru_2O(L)_6(acetate)_2](PF_6)_2$, in which L is a neutral donor,

a) Draw the structure of the counterion, PF_6^-.

b) Provide an account of the valence electron count in the ruthenium coordination complex.

Valence electrons on metal	
Total charge on ligands	
Charge on the metal	
Revised count on metal	
Electrons donated by ligands	
Total electrons on metal in complex	

Data shows that the ligands L are *trans* to the bridging oxo ligand are labile.

c) Use orbital cartoons and words to provide an explanation for this effect.

When water is added to an acetone solution of $[Ru_2O(pyridine)_4(L)_2(acetate)_2](PF_6)_2$, then $[Ru_2O(pyridine)_4(H_2O)_2(acetate)_2](PF_6)_2$ is formed.

d) Draw the product of this reaction.

When pyridine is added to $[Ru_2O(pyridine)_4(H_2O)_2(acetate)_2](PF_6)_2$, then $[Ru_2O(pyridine)_6(acetate)_2](PF_6)_2$ is formed. The following rate constants were observed for this reaction.

[pyridine] mol L^{-1}	k_{obs} s^{-1} (x 10^{-3})
0.005	1.75
0.012	2.53
0.025	9.7
0.049	16.7
0.100	35.2

e) Use the data from this table to determine the order in pyridine. Provide an explanation for your conclusion.

f) Draw a mechanism for the reaction, consistent with the data.

g) Write a rate law for the reaction.

h) The authors studies the same reaction with different ligands instead of pyridine. They observed an increase in rate constants with increasing basicity of the incoming ligands. Provide an explanation for this observation.

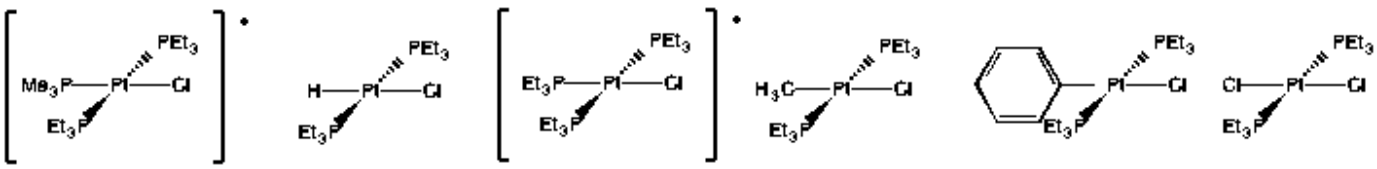
Answer a available at the end of this section.

Answers

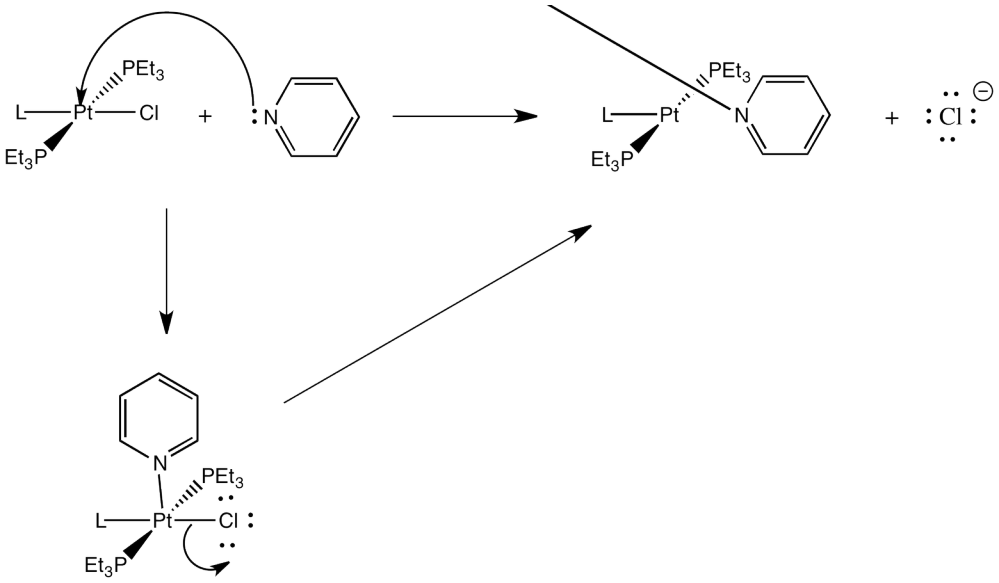
Exercise 12.7.1

This is probably an associative mechanism because of the square planar geometry.

Exercise 12.7.2



Exercise 12.7.3



Exercise 12.7.4

There is an electronegativity trend: the less electronegative, the greater the *trans* effect (see the halogens, as well as the series O,N,C and also the orders within several pairings: S,P; O,S and N,P).

Alternatively, some of the above could be described by a polarizability trend: more polarizable atom, greater *trans* effect (for example, the halogens).

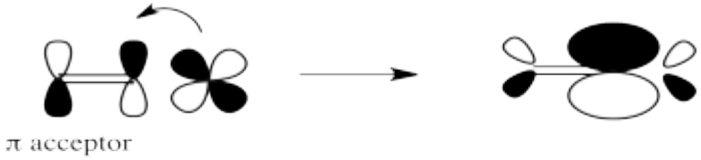
Most of the ligands containing π-bonds have strong *trans* influence (but not all).

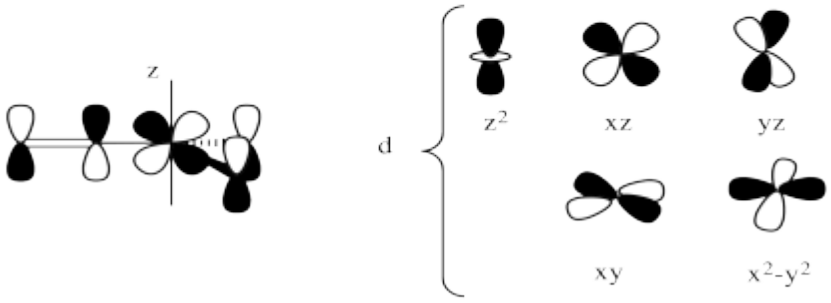
Most of the π-donors have a weaker *trans* influence. However, these ligand cover a very broad range in this series.

Exercise 12.7.5

The strongest σ-donors are typically those with more polarizable donor atoms (such as S, P, I) as well as those with less electronegative donor ions such as C^- and H^-.

Exercise 12.7.7





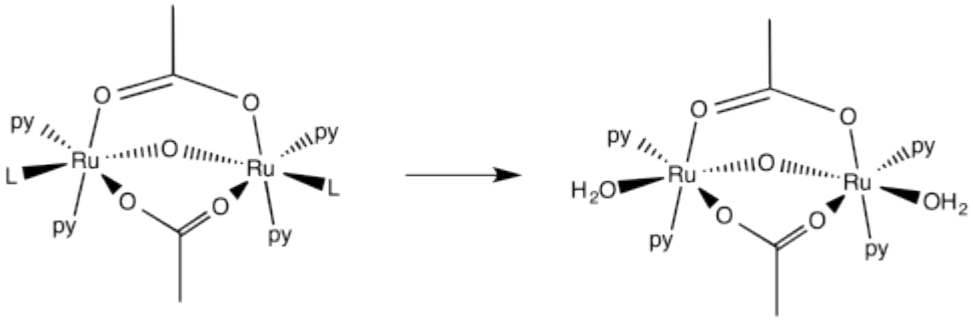
Exercise 12.7.8



5 valence electrons - 6 bonds - 0 nonbonding = -1

Valence electrons on metal	8
Total charge on ligands	-4 (-2 per Ru)
Charge on the metal	+2
Revised count on metal	6
Electrons donated by ligands	12
Total electrons on metal in complex	18

The oxo is a strong sigma donor and hogs the orbital with the metal thus leaving very little room for orbital bonding trans to the sigma donor.



First order. Although there is some amount of error in the data, doubling the pyridine concentration generally results in a doubling of the rate.
The mechanism you draw would have to involve a first associative step; because the complex is already 18 electrons, associative interchange is likely.

$$Rate = k[ML_n][py]$$

Basic ligands have stronger attraction to the metal thus accelerating the reaction.

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12.8: Redox Mechanisms

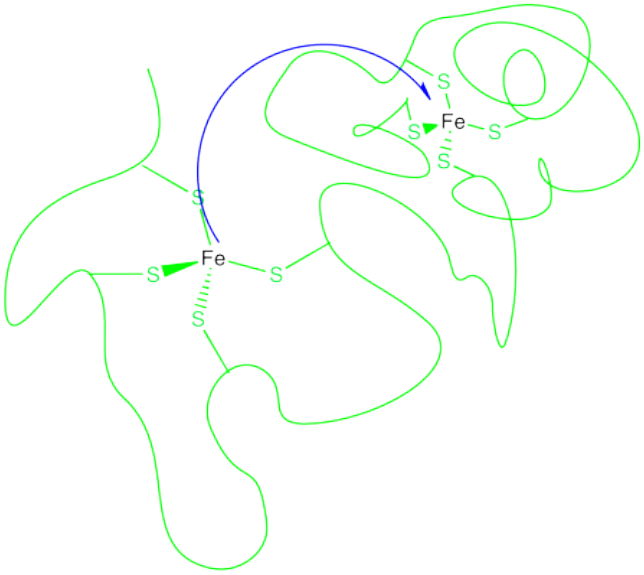
The oxidation state of a metal ion can be changed by **red**uction/**ox**idation (redox) reactions in which electrons are transferred between a metal center and another species. The other species could be another metal ion or some other redox partner. In the case of metal complexes, the electron transfer often occurs at the metal center, changing the oxidation state of the metal ion(s) involved. This section will focus on the redox reactions involving change in metal ion oxidation state.

There are two general mechanisms by which electrons can be transferred to or from a metal center. The definition of these two mechanisms depends on whether the redox partner is bound within the metal ion's inner sphere (bound directly to the metal ion), or whether it is just nearby the metal complex (in the metal ion's outer sphere). If the redox partner is bound to the metal ion itself, it is called an **inner-sphere electron transfer**. Electrons can also be transferred between two species that are close in proximity, but not bound to one another. When electrons are transferred to or from a metal through close proximity, but not through direct bonds to the metal center, it is an **outer-sphere electron transfer**.

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12.8.1: Outer Sphere Electron Transfer

How does an electron get from one metal to another? This might be a more difficult task than it seems. In biochemistry, an electron may need to be transfered a considerable distance. Often, when the transfer occurs between two metals, the metal ions may be constrained in particular binding sites within a protein, or even in two different proteins.



That means the electron must travel through space to reach its destination. Its ability to do so is generally limited to just a few Angstroms (remember, an Angstrom is roughly the distance of a bond). Still, it can react with something a few bond lengths away. Most things need to actually bump into a partner before they can react with it.

This long distance hop is called an outer sphere electron transfer. The two metals react without ever contacting each other, without getting into each others' coordination spheres. Of course, there are limitations to the distance involved, and the further away the metals, the less likely the reaction. But an outer sphere electron transfer seems a little magical.

Barrier to Reaction: A Qualitative Picture of Marcus Theory

So, what holds the electron back? What is the barrier to the reaction? Rudy Marcus at Caltech has developed a mathematical approach to understanding the kinetics of electron transfer, in work he did beginning in the late 1950's. We will take a very qualitative look at some of the ideas in what is referred to as "Marcus Theory". An electron is small and very fast. All those big, heavy atoms involved in the picture are lumbering and slow. The barrier to the reaction has little to do with the electron's ability to whiz around, although even that is limited by distance. Instead, it has everything to do with all of those things that are barely moving compared to the electron.

Imagine an iron(II) ion is passing an electron to an iron(III) ion. After the electron transfer, they have switched identities; the first has become an iron(III) and the second has become an iron(II) ion.

Nothing could be simpler. The trouble is, there are big differences between an iron(II) ion and an iron(III) ion. For example, in a coordination complex, they have very different bond distances. Why is that a problem? Because when the electron hops, the two iron atoms find themselves in sub-optimal coordination environments.

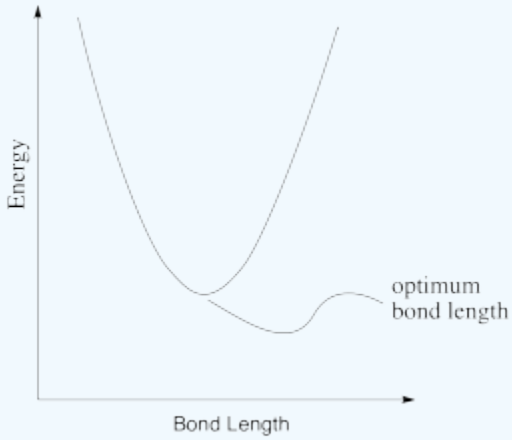
Exercise 12.8.1.1

Suppose an electron is transferred from an Fe(II) to a Cu(II) ion. Describe how the bond lengths might change in each case, and why. Don't worry about what the specific ligands are.

Answer available at the end of this section.

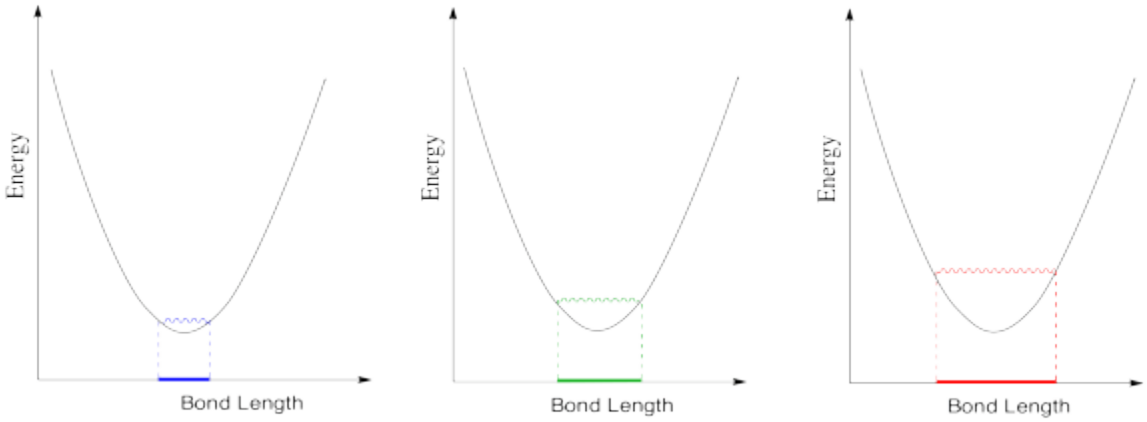
Exercise 12.8.1.2

In reality, a bond length is not static. If there is a little energy around, the bond can lengthen and shorten a little bit, or vibrate. A typical graph of molecular energy vs. bond length is shown below.



a. Why do you think energy increases when the bond gets shorter than optimal?
b. Why do you think energy increases when the bond gets longer than optimal?
c. In the following drawings, energy is being added as we go from left to right. Describe what is happening to the bond length as available energy increases.

Answer a available at the end of this section.



Exercise 12.8.1.3

The optimum C-O bond length in a carbon dioxide molecule is 1.116 Å. Draw a graph of what happens to internal energy when this bond length varies between 1.10 Å and 1.20 Å. Don't worry about quantitative labels on the energy axis.

Answer available at the end of this section.

Exercise 12.8.1.4

The optimum O-C-O bond angle in a carbon dioxide molecule is 180 °. Draw a graph of what happens to internal energy when this bond angle varies between 170 ° and 190 °. Don't worry about quantitative labels on the energy axis.

Answer available at the end of this section.

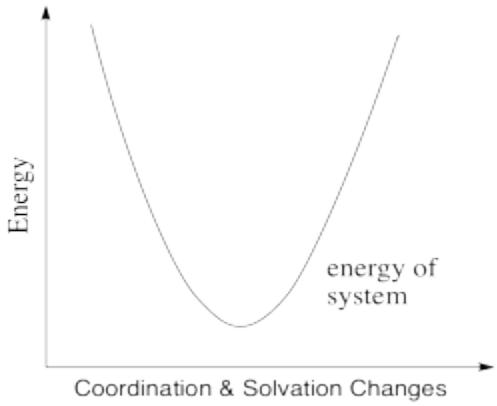
The barrier to electron transfer has to do with reorganizations of all those big atoms before the electron makes the jump. In terms of the coordination sphere, those reorganizations involve bond vibrations, and bond vibrations cost energy. Outside the coordination sphere, solvent molecules have to reorganize, too. Remember, ion stability is highly influenced by the surrounding medium.

Exercise 12.8.1.5

Draw a Fe(II) ion and a Cu(II) ion with three water molecules located somewhere in between them. Don't worry about the ligands on the iron or copper. Show how the water molecules might change position or orientation if an electron is transferred from iron to copper.

Answer available at the end of this section.

Thus, the energetic changes needed before electron transfer can occur involve a variety of changes, including bond lengths of several ligands, bond angles, solvent molecules, and so on. The whole system, involving both metals, has some optimum set of positions of minimum energy. Any deviations from those positions requires added energy. In the following energy diagram, the x axis no longer defines one particular parameter. Now it lumps all changes in the system onto one axis. This picture is a little more abstract than when we are just looking at one bond length or one bond angle, but the concept is similar: there is an optimum set of positions for the atoms in this system, and it would require an input of energy in order to move any of them move away from their optimum position.

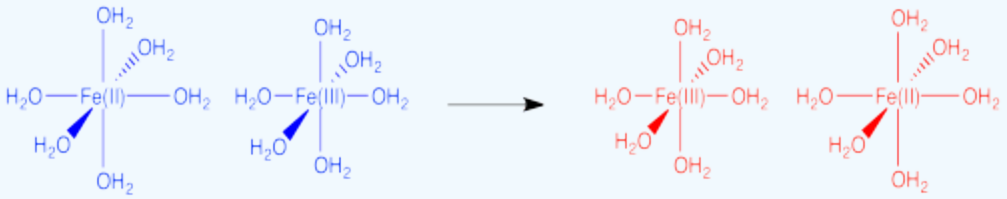


It is thought that these kinds of reorganizations -- involving solvent molecules, bond lengths, coordination geometry and so on -- actually occur prior to electron transfer. They happen via random motions of the molecules involved. However, once they have happened, there is nothing to hold the electron back. Its motion is so rapid that it can immediately find itself on the other atom before anything has a chance to move again.

Consequently, the barrier to electron transfer is just the amount of energy needed for all of those heavy atoms to get to some set of coordinates that would be accessible in the first state, before the electron is transferred, but that would also be accessible in the second state, after the electron is transfered.

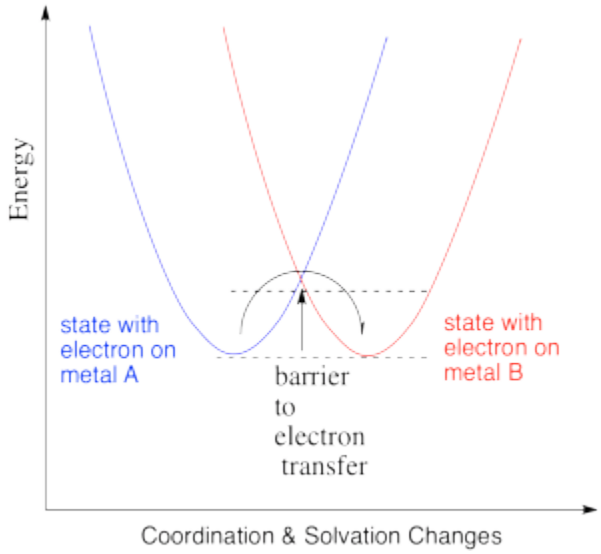
Exercise 12.8.1.6

Describe some of the changes that contribute to the barrier to electron transfer in the following case.

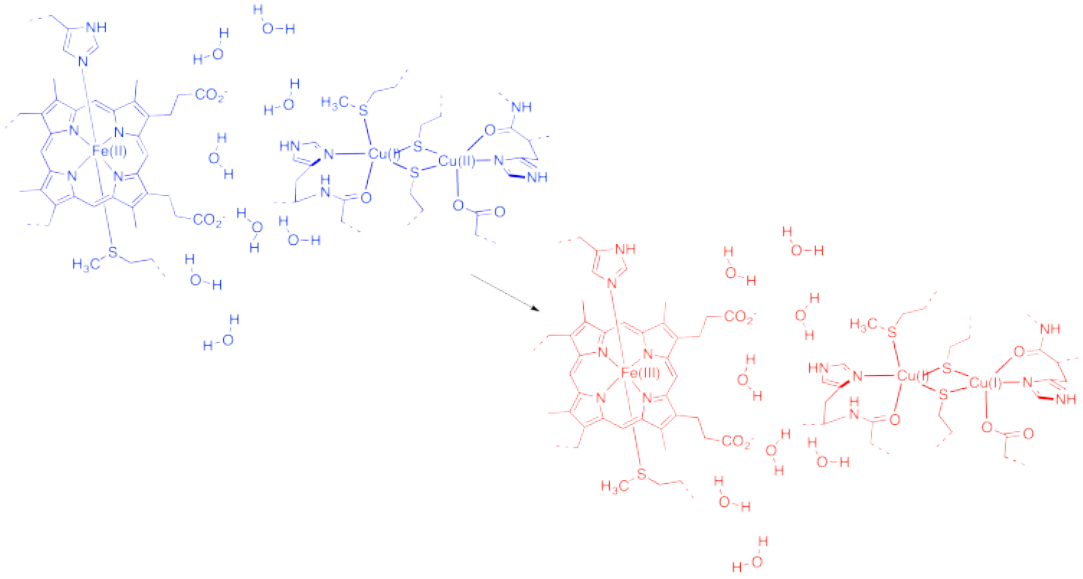


Answer available at the end of this section.

In the drawing below, an electron is transferred from one metal to another metal of the same kind, so the two are just switching oxidation states. For example, it could be an iron(II) and an iron(III), as pictured in the problem above. In the blue state, one iron has the extra electron, and in the red state it is the other iron that has the extra electron. The energy of the two states are the same, and the reduction potential involved in this transfer is zero. However, there would be some atomic reorganizations needed to get the coordination and solvation environments adjusted to the electron transfer. The ligand atoms and solvent molecules have shifted in the change from one state to another, and so our energy surfaces have shifted along the x axis to reflect that reorganization.



That example isn't very interesting, because we don't form anything new on the product side. Instead, let's picture an electron transfer from one metal to a very different one. For example, maybe the electron is transferred from cytochrome c to the "copper A" center in cytochrome c oxidase, an important protein involved in respiratory electron transfer.



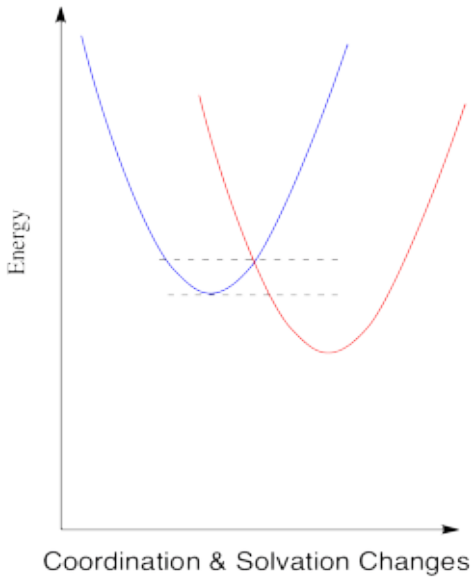
Exercise 12.8.1.7

In the drawing above, some water molecules are included between the two metal centres.

a. Explain what happens to the water molecules in order to allow electron transfer to occur, and why.
b. Suppose there were a different solvent, other than water, between the complexes. How might that affect the barrier to the reaction?

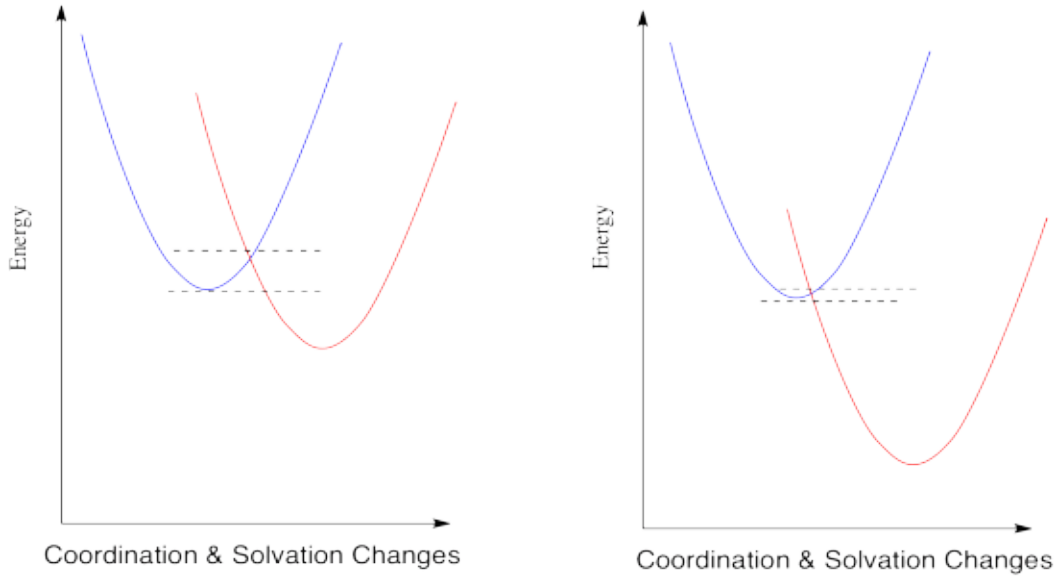
Answer a available at the end of this section.

The energy diagram for the case involving two different metals is very similar, except that now there is a difference in energy between the two states. The reduction potential is no longer zero. We'll assume the reduction potential is positive, and so the free energy change is negative. Energy goes down upon electron transfer.



Compare this picture to the one for the degenerate case, when the electron is just transferred to a new metal of the same type. A positive reduction potential (or a negative free energy change) has the effect of sliding the energy surface for the red state downwards. As a result, the intersection point between the two surfaces also slides downwards. Since that is the point at which the electron can slide from one state to the other, the barrier to the reaction decreases.

What would happen if the reduction potential were even more positive? Let's see in the picture below.



The trend continues. According to this interpretation of the kinetics of electron transfer, the more exothermic the reaction, the lower its barrier will be. It isn't always the case that kinetics tracks along with thermodynamics, but this might be one of them.

But is all of this really true? We should take a look at some experimental data and see whether it truly works this way.

Oxidant	E°	k ($M^{-1}s^{-1}$) (margin of error shown in parentheses)
$Co(diene)(NH_3)_2^{3+}$	0.12	3.0(4)
$Co(diene)H_2O)NCS^{2+}$	0.38	11(1)
$Co(diene)(H_2O)_2^{3+}$	0.53	800(100)
Co(EDTA)	0.60	6000(1000)

As the reduction potential becomes more positive, free energy gets more negative, and the rate of the reaction dramatically increases. So far, Marcus theory seems to get things right.

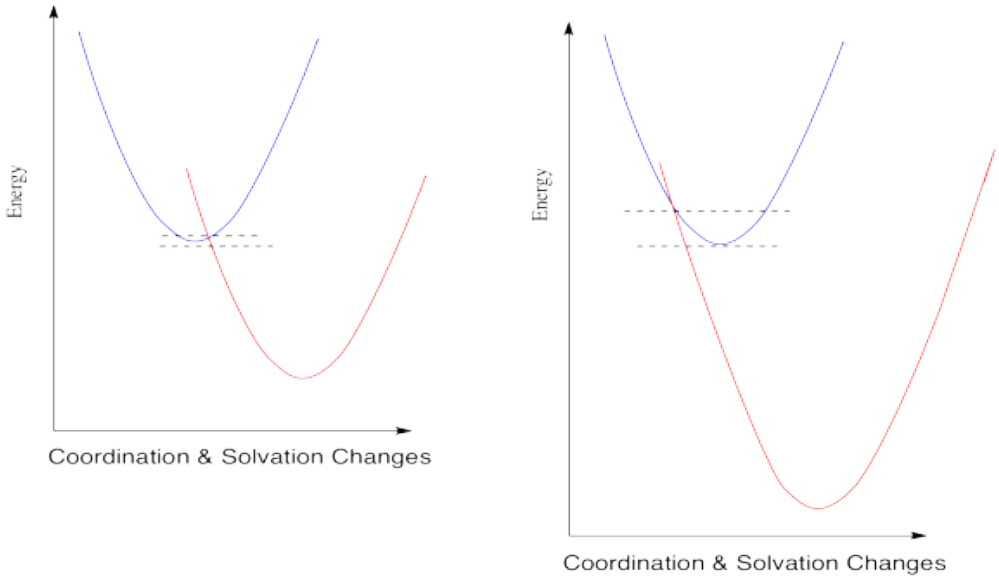
Exercise 12.8.1.8

a. Plot the data in the above table.
b. How would you describe the relationship? Is it linear? Is it exponential? Is it direct? Is it inverse?
c. Plot rate constant versus free energy change. How does this graph compare to the first one?

Answer a available at the end of this section.

Marcus Inverted Region

When you look a little closer at Marcus theory, though, things get a little strange. Suppose we make one more change and see what happens when the reduction potential becomes *even more* positive.

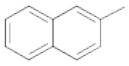
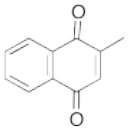
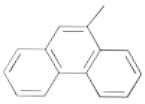
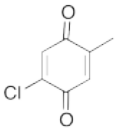
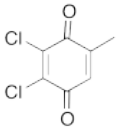


So, if Marcus is correct, at some point as the reduction potential continues to get more positive, reactions start to slow down again. They don't just reach a maximum rate and hold steady at that plateau; the barrier gets higher and higher and the reactions get slower and slower. If you feel a little skeptical about that, you're in good company.

Marcus always maintained that this phenomenon was a valid aspect of the theory, and not just some aberration that should be ignored. The fact that nobody had ever actually observed such a trend didn't bother him. The reason we didn't see this kind of thing, he said, was that we just hadn't developed technology that was good enough to measure these kind of rates accurately.

But technology did catch up. Just take a look at the following data (from Miller, *J. Am.Chem. Soc.* **1984**, *3047*).



Acceptor	ΔG	k	Acceptor	ΔG	k
	-0.05	2×10^6		-1.9	6×10^8
	-0.2	2×10^7		-2.2	1×10^8
	-0.5	1×10^9		-2.4	6×10^7

Don't worry that there are no metals involved anymore. An electron transfer is an electron transfer. Here, an electron is sent from the aromatic substructure on the right to the substructure on the left. By varying the part on the left, we can adjust the reduction potential (or the free energy change, as reported here.

Exercise 12.8.1.9

a. Plot the data in the above table.

b. How would you describe the relationship?

Answer a available at the end of this section.

As the reaction becomes more exergonic, the rate increases, but then it hits a maximum and decreases again. Data like this means that the "Marcus Inverted Region" is a real phenomenon. Are you convinced? So were other people. In 1992, Marcus was awarded the Nobel Prize in Chemistry for this work.

Exercise 12.8.1.10

Take a look at the donor/acceptor molecule used in Williams' study, above. a) Why do you suppose the free energy change is pretty small for the first three compounds in the table? b) Why does the free energy change continue to get bigger over the last three compounds in the table?

Answer available at the end of this section.

Exercise 12.8.1.11

The rates of electron transfer between cobalt complexes of the bidentate bipyridyl ligand, $Co(bipy)_3^{n+}$, are strongly dependent upon oxidation state in the redox pair. Electron transfer between Co(I)/Co(II) occurs with a rate constant of about 10^9 $M^{-1}s^{-1}$, whereas the reaction between Co(II)/Co(III) species proceeds with k = 18 $M^{-1}s^{-1}$.

a. What geometry is adopted by these complexes?
b. Are these species high spin or low spin?
c. Draw d orbital splitting diagrams for each complex.
d. Explain why electron transfer is so much more facile for the Co(I)/Co(II) pair than for the Co(II)/Co(III) pair.

Answer a available at the end of this section.

Answers

Exercise 12.8.1.1

The bonds to iron would contract because the increased charge on the iron would attract the ligand donor electrons more strongly. The bonds to copper would lengthen because of the lower charge on the copper.

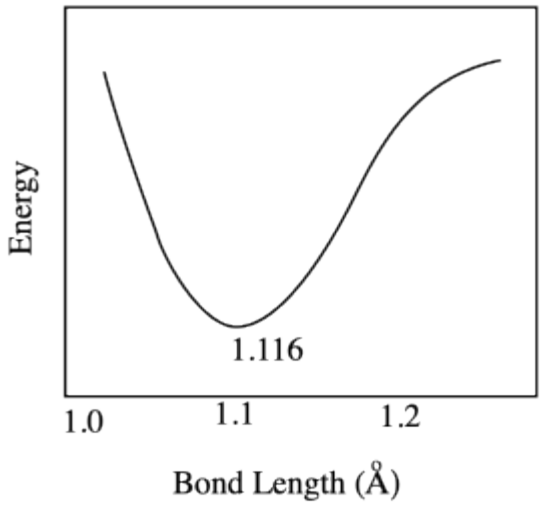
Exercise 12.8.1.2

a) Most likely there are repulsive forces between ligands if the bonds get too short.

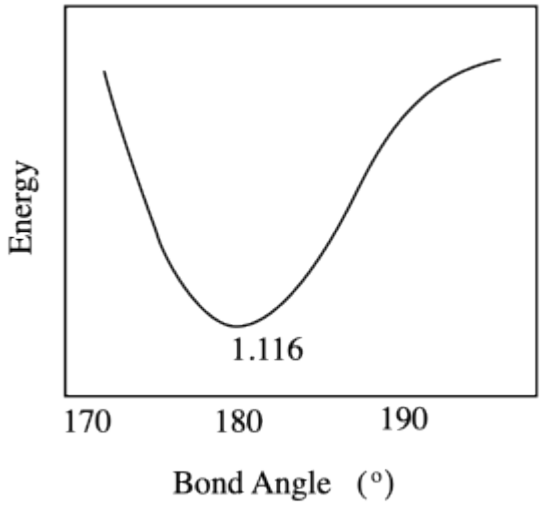
b) Insufficient overlap between metal and ligand orbitals would weaken the bond and raise the energy.

c) The range of possible bond lengths gets broader as energy is increased. The bond has more latitude, with both longer and shorter bonds allowed at higher energy.

Exercise 12.8.1.3

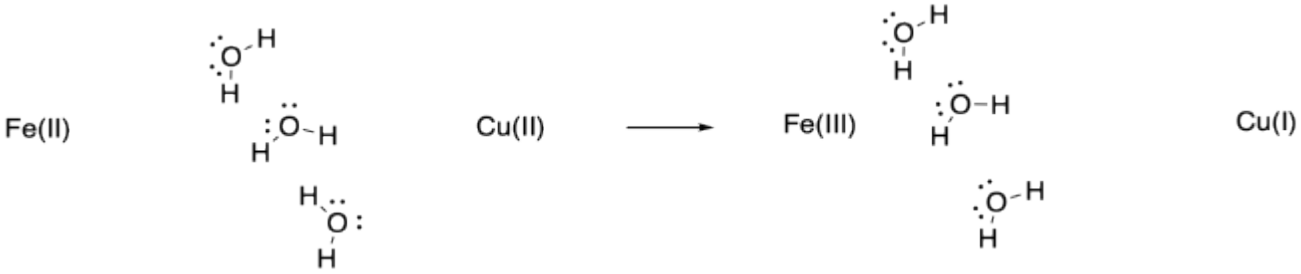


Exercise 12.8.1.4



Exercise 12.8.1.5

The water molecules may pivot toward the more highly charged Fe(III), or they may shift closer to it because of the attraction between the ion and the dipole of the water molecule.



Keep in mind that such adjustments would happen in non-polar solvents, too, although they would involve weaker IMFs such as ion - induced dipole interactions.

Exercise 12.8.1.6

The reactants and products are very similar in this case. However, the Fe(III) complex has shorter bonds than the Fe(II) complex because of greater electrostatic interaction between the metal ion and the ligands. These changes in bond length needed in order to get ready to change from Fe(III) to Fe(II) (or the reverse) pose a major barrier to the reaction.

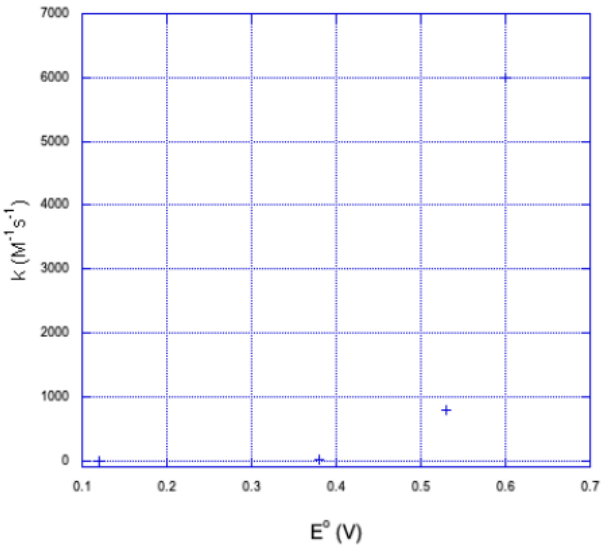
Exercise 12.8.1.7

a) The drawing is an oversimplification, but in general the water molecules are shown reorienting after the electron transfer because of ion-dipole interactions. In this case, the waters are shown orienting to present their negative ends to the more positive iron atom after the electron transfer. In reality, in a protein there are lots of other charges (including charges on the ligand) that may take part in additional ion-dipole interactions.

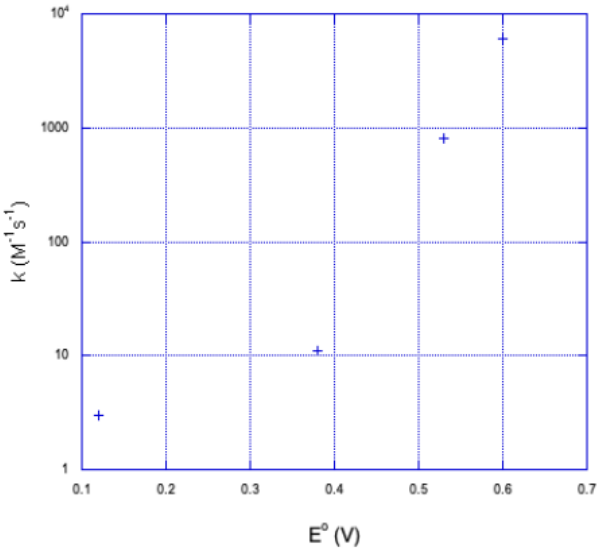
b) Because electron transfer is so fast, atomic and molecular reorganisations are actually thought to happen before the electron transfer. The water molecules would happen to shift into a position that would provide the greatest possible stabilisation for the ions and then the electron would be transferred. A less polar solvent than water would be less able to stabilize ions and the electron would be slower to transfer as a result. In addition, a less polar solvent than water would be a poor medium to transmit an electron, which is charged and therefore stabilized by interactions with polar solvents.

Exercise 12.8.1.8

a) Here is a plot of the data.

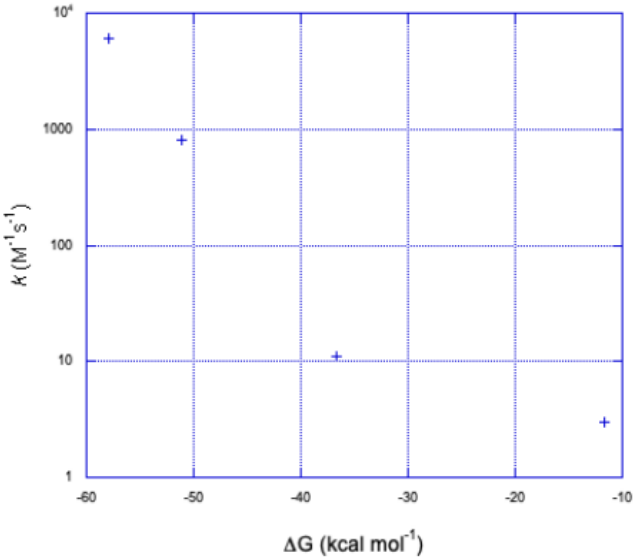


b) It doesn't look linear. If we plot the y axis on a log scale, things become a little more linear.



It looks closer to a logarithmic relationship than a linear one.

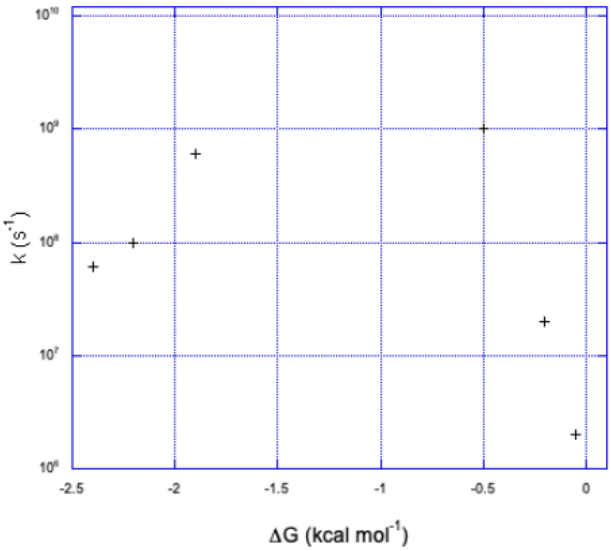
c) Assuming one electron transfer:



The graph takes the same form but in the opposite direction along the x axis.

Exercise 12.8.1.9

a)



b) We can see two sides of an inverted curve. The reaction gets much faster as the free energy becomes more negative, but at some point the rate begins to decrease again.

Exercise 12.8.1.10

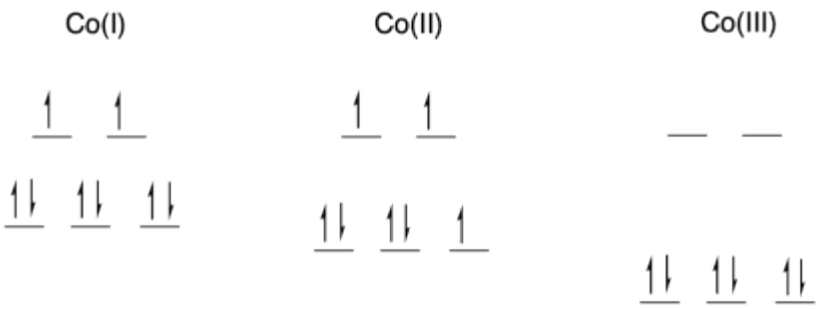
The acceptor compound becomes an anion when it accepts an electron. The first three compounds do not appear to be strongly electrophilic; they can accept electrons simply because of resonance stability of the resulting anion. The last three have electron withdrawing groups (chlorines and oxygens) that would stabilize the anion even further.

Exercise 12.8.1.11

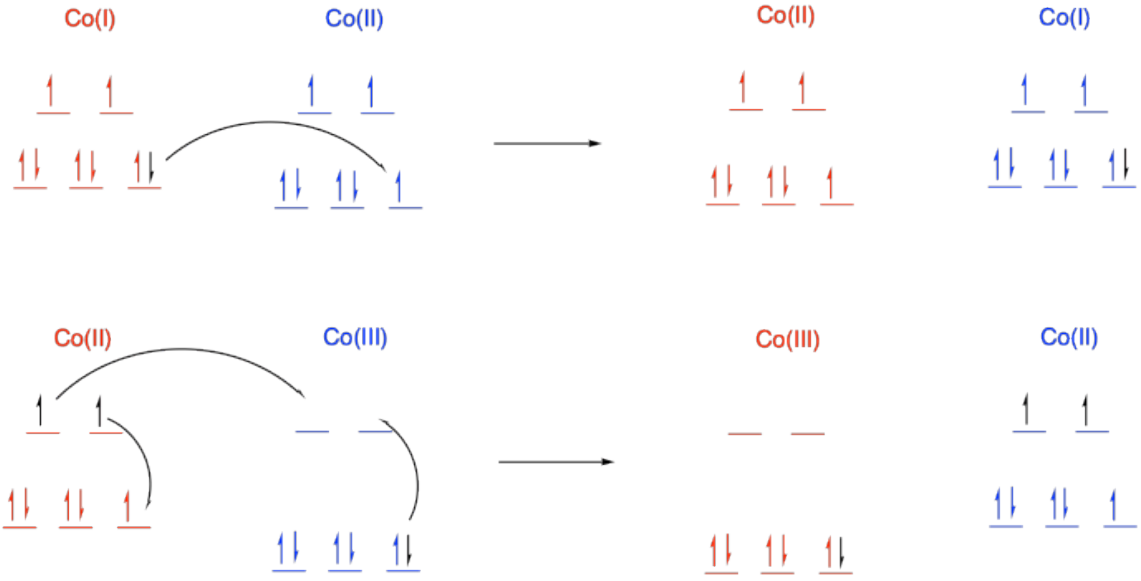
a) octahedral; bpy is a bidentate ligand.

b) Co is first row; Co(I) and Co(II) have relatively low charge. Usually we would expect them to be high spin. Co(III) is at a cut-off point in the first row; it is just electronegative enough that it is usually low spin.

c)



d) In a transfer from Co(II) to Co(III), there is additional reorganization needed because the metal changes between high and low spin. Not only does one electron have to move from one metal to another metal, but additional electrons have to shuffle from one orbital to another on the same metal to accommodate the change. These reorganizations have a barrier, slowing the reaction.



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12.8.2: Inner Sphere Electron Transfer

In some cases, electron transfers occur much more quickly in the presence of certain ligands. For example, compare the rate constants for the following two electron transfer reactions, involving almost exactly the same complexes:

$$Co(NH_3)_6{}^{3+} + Cr^{2+} \longrightarrow Co^{2+} + Cr^{3+} + 6\,NH_3 \;\; k = 10^{-4} M^{-1} s^{-1}$$

$$Co(NH_3)_5Cl^{2+} + Cr^{2+} \longrightarrow Co^{2+} + CrCl^{2+} + 6\,NH_3 \;\; k = 6 \times 10^{5} M^{-1} s^{-1}$$

(Note: aqua ligands are omitted for simplicity. Ions, unless noted otherwise, are aqua complexes.)

Notice two things: first, when there is a chloride ligand involved, the reaction is much faster. Second, after the reaction, the chloride ligand has been transferred to the chromium ion. Possibly, those two events are part of the same phenomenon.

Similar rate enhancements have been reported for reactions in which other halide ligands are involved in the coordination sphere of one of the metals.

In the 1960's, Henry Taube of Stanford University proposed that halides (and other ligands) may promote electron transfer via bridging effects. What he meant was that the chloride ion could use one of its additional lone pairs to bind to the chromium ion. It would then be bound to both metals at the same time, forming a bridge between them. Perhaps the chloride could act as a conduit for electron transfer. The chloride might then remain attached to the chromium, to which it had already formed a bond, leaving the cobalt behind.

Electron transfers that occur via ligands shared by the two metals undergoing oxidation and reduction are termed "inner sphere" electron transfers. Taube was awarded the Nobel Prize in chemistry in 1983; the award was based on his work on the mechanism of electron transfer reactions.

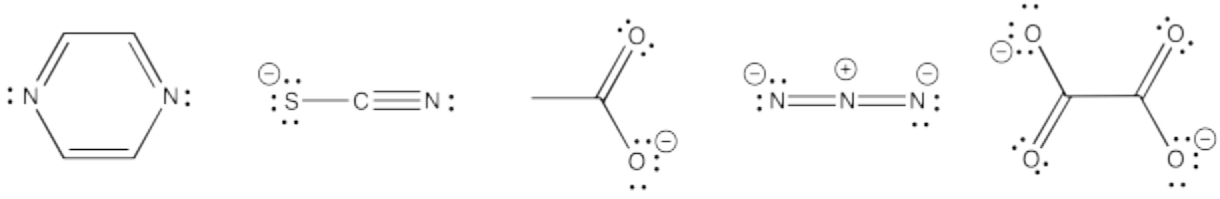
Exercise 12.8.2.1

Take another look at the two electron transfer reactions involving the cobalt and chromium ion, above.

a. What geometry is adopted by these complexes?
b. Are these species high spin or low spin?
c. Draw d orbital splitting diagrams for each complex.
d. Explain why electron transfer is accompanied by loss of the ammonia ligands from the cobalt complex.
e. The chloride is lost from the cobalt complex after electron transfer. Why does it remain on the chromium?

Answer a available at the end of this section.

Other ligands can be involved in inner sphere electron transfers. These ligands include carboxylates, oxalate, azide, thiocyanate, and pyrazine ligands. All of these ligands have additional lone pairs with which to bind a second metal ion.



pyrazine thiocyanate acetate azide oxalate

Exercise 12.8.2.2

Draw an example of each of the ligands listed above bridging between a cobalt(III) and chromium(II) aqua complex.

Answer available at the end of this section.

Exercise 12.8.2.3

Explain, with structures and d orbital splitting diagrams, how the products are formed in the following reaction, in aqueous solution.

$$\mathrm{Fe(OH_2)_6}^{2+} + \mathrm{(SCN)Co(NH_3)_5}^{2+} \longrightarrow \mathrm{(NCS)Fe(OH_2)_5}^{2+} + \mathrm{Co(OH_2)_6}^{2+} + 5\,\mathrm{NH_3}$$

Answer available at the end of this section.

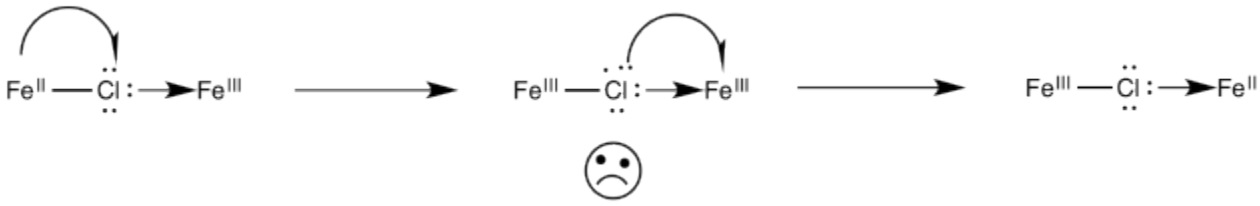
How does the electron travel over the bridge?

Once the bridge is in place, the electron transfer may take place via either of two mechanisms. Suppose the bridging ligand is a chloride. The first step might actually involve an electron transfer from chlorine to the metal; that is, the chloride could donate one electron from one of its idle lone pairs. This electron could subsequently be replaced by an electron transfer from metal to chlorine.



Sometimes, we talk about the place where an electron *used to be*, describing it as a "hole". In this mechanism, the electron donated from the bridging chloride ligand leaves behind a hole. The hole is then filled with an electron donated from the other metal.

Alternatively, an electron might first be transferred from metal to chlorine, which subsequently passes an electron along to the other metal. In the case of chlorine, this idea may be unsatisfactory, because chlorine already has a full octet. Nevertheless, some of the other bridging ligands may have low-lying unoccupied molecular orbitals that could be populated by this extra electron, temporarily.



Exercise 12.8.2.4

For the iron / cobalt electron transfer in problem Exercise 12.8.2.3 (RO9.3.), show

a. an electron transfer mechanism via a hole migration along the bridge
b. an electron transfer mechanism via an electron migration along the bridge

Answer a available at the end of this section.

Exercise 12.8.2.5

One of the many contributions to the barrier for electron transfer between metal ions is internal electronic reorganization.

a) Draw d orbital splitting diagrams for each of the following metal ions in an octahedral environment.

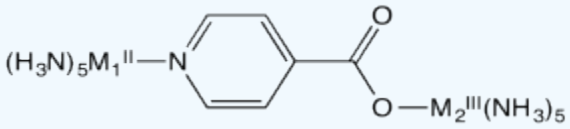
Ru(II) or Os(II)

Ru(III) or Os(III)

Co(II)

Co(III)

Flash photolysis is a method in which an electron can be moved instantly "uphill" from one metal to another (e.g. from M_2^{II} to M_1^{III}, below); the electron transfer rate can then be measured as the electron "drops" back from M_1^{II} to M_2^{III}.



b) Explain the relative rates of electron transfer reaction in this system, as measured by flash photolysis in the table below.

M_1^{II}	M_2^{III}	k_{obs} s^{-1}
Os	Ru	$> 5 \times 10^9$
Os	Co	1.9×10^5

c) Does the reaction above probably occur via an inner sphere or by an outer sphere pathway? Why?

Answer a available at the end of this section.

Exercise 12.8.2.6

Outer sphere electron transfer rates depend on the free energy change of the reaction (ΔG°) and the distance between oxidant and reductant (d) according to the relation

Rate constant = $k = Ae^{(-\Delta G)}e^{-d}$

a) What happens to the rate of the reaction as distance increases between reactants?

One potential problem in measuring rates of intramolecular electron transfer (i.e. *within* a molecule) is competition from intermolecular electron transfer (*between* molecules).

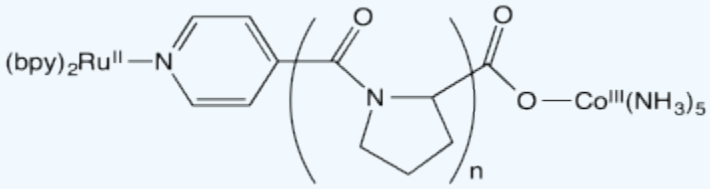
b) What would you do in the flash photolysis experiment above to discourage intermolecular electron transfer?

c) How could you confirm whether you were successful in discouraging intermolecular reaction?

Answer a available at the end of this section.

Exercise 12.8.2.7

Stephan Isied and coworkers at Rutgers measured the following electron transfer rates between metal centers separated by a peptide. (*Chem Rev* **1992**, *92*, 381-394)



a. The proline repeating unit is crucial in ensuring a steady increase in distance between metal centers with increased repeat units, n. Why?
b. An inner sphere pathway in this case is expected to be somewhat slow because of the lack of conjugation in the polyproline bridge. Explain why.
c. Plot the data below, with log*k* on the y axis (range from 4-9) and d on the x axis (12-24 Angstroms).

n	d (Å)	k_{obs} (s^{-1})
1	12.2	5×10^{8}
2	14.8	1.6×10^{7}
3	18.1	2.3×10^{5}
4	21.3	5.1×10^{4}
5	24.1	1.8×10^{4}

d) A linear relationship is in agreement with Marcus theory; log*k* = - c x d. Is your plot linear?

Isied offers a number of possible explanations for the data, all of which involve two competing reaction pathways.

e) Suggest one explanation for the data.

Answer a

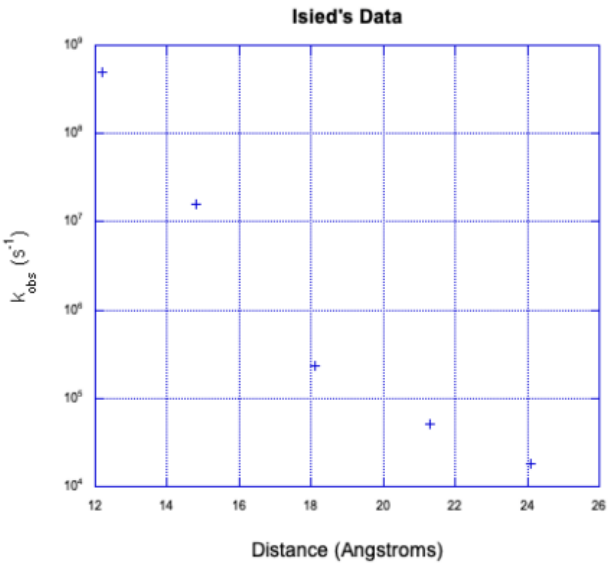
a) Rings are frequently used to introduce conformational rigidity (or decrease conformational flexibility), limiting the range of potential shapes a molecule could adopt. If the molecule can't wiggle around as much, then the distance between the ends of the molecule should be more constant.

Answer b

b) Although the ligand is bridging, it would be difficult to picture either an electron or hole mechanism of inner sphere electron transfer. There are few pi bonds or lone pairs to use as places to put electrons or temporarily remove electrons from, shuttling the electrons from place to place along the ligand. A conjugated system would be much more likely to carry out inner sphere electron transfer.

Answer c

c)



Answer d

d) The data is not linear.

Answer e

e) The data appear to show two lines that cross. That's a classic symptom of two competing mechanisms. The faster mechanism, to the left, is probably an intramolecular electron transfer. The slower mechanism, to the right, may be an intermolecular electron transfer.

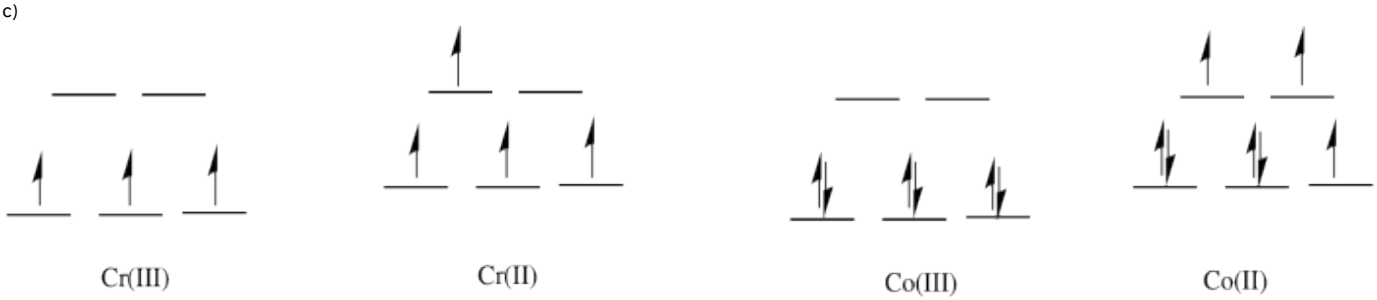
Answers

Exercise 12.8.2.1

a) octahedral

b) In the first row, 2^+ complexes are almost always high spin. However, 3^+ complexes are sometimes low spin.

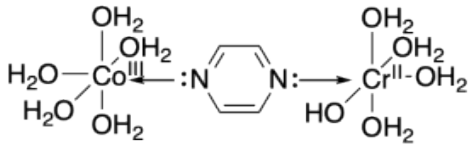
c)

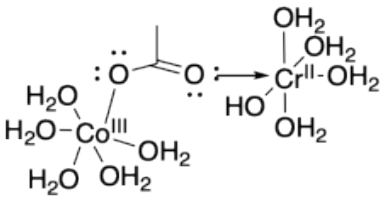


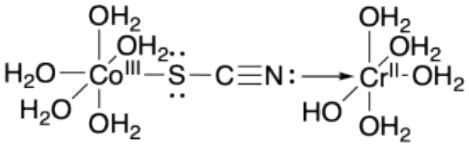
d) The Co(II) complex is high spin and labile. The ligands are easily replaced by water.

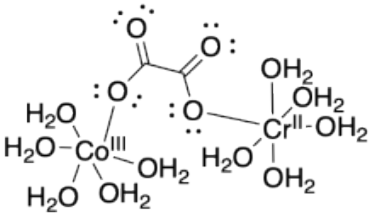
e) The Cr(III) complex is only d^3; it is inert.

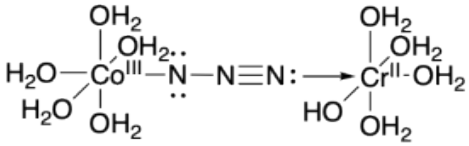
Exercise 12.8.2.2



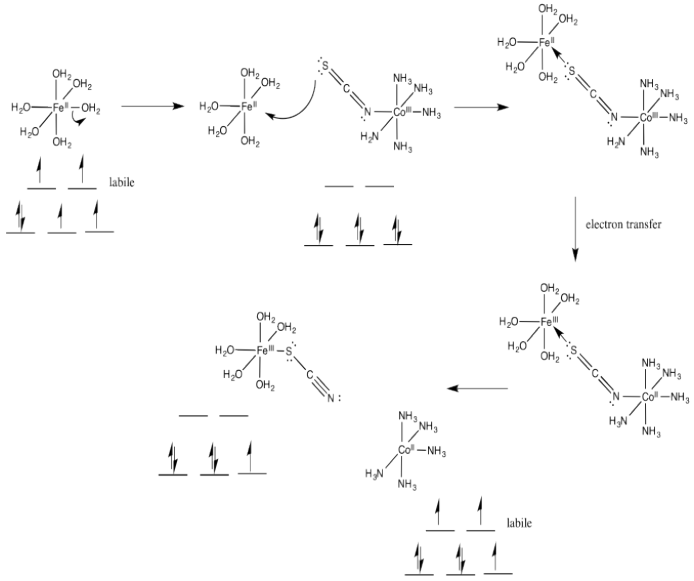




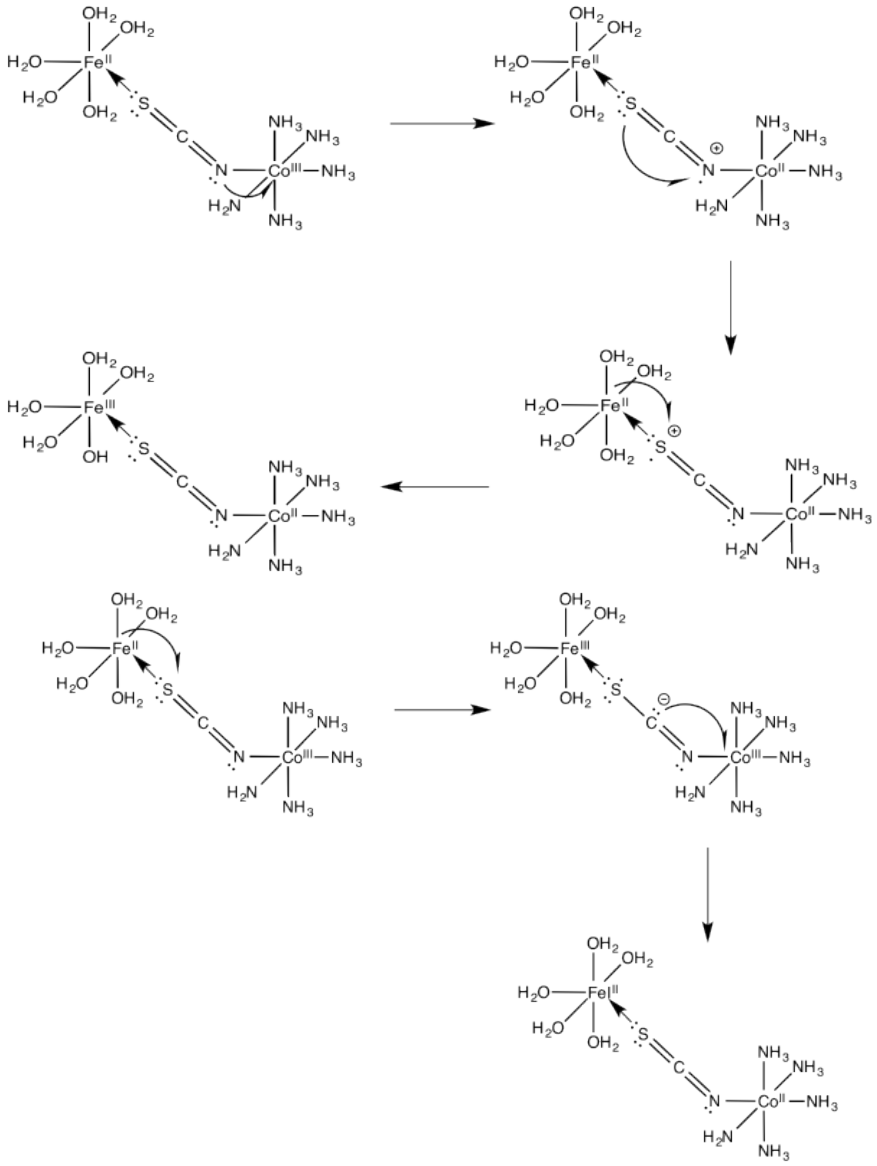




Exercise 12.8.2.3

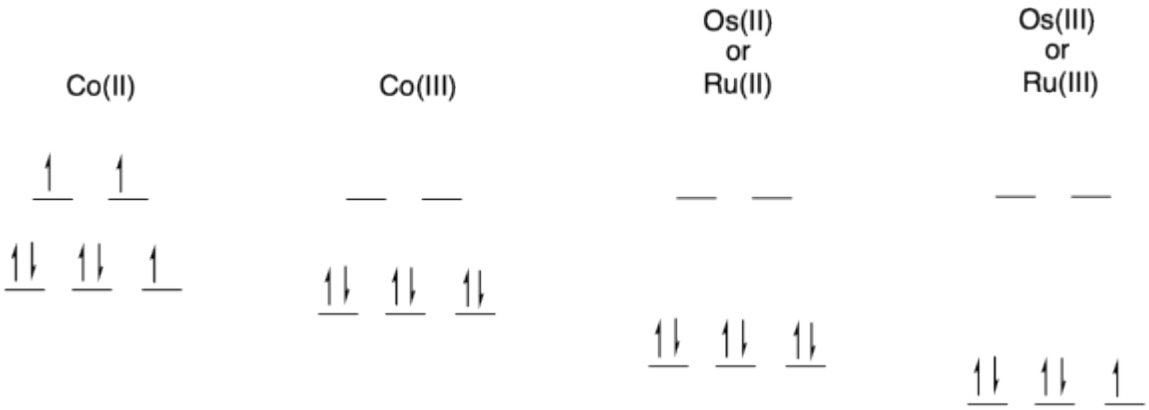


Exercise 12.8.2.4



Exercise 12.8.2.5

a)



b) The electron transfer between Os(II) and Ru(III) will not involve any electron reorganization because both are low spin to begin with. However, the electron transfer between Os(II) and Co(III) will result in cobalt changing from low spin to high spin. The need to move electrons between different d orbitals on the cobalt will add to the barrier, slowing down the reaction.

c) The pathway is probably inner sphere because of the bridging ligand. Furthermore, the conjugation in the bridging ligand would help in conducting an electron from one end of the ligand to the other, either through an electron mechanism or a hole mechanism.

Exercise 12.8.2.6

a) The rate decreases exponentially as distance increases.

b) You might keep the concentration low in order to increase the distance between molecules, reducing the likely hood of an outer-sphere electron transfer.

c) If you ran the experiment at a series of dilutions, intramolecular electron transfer would be unaffected but outer sphere electron transfer would not. If the rates were the same across a number of different concentrations, the reaction would probably be intramolecular.

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12.9: Reactions of Coordinated Ligands

So far, our coverage of the reactions of metal complexes has focused only on the reactions that occur at the metal center. However, there are also reactions that can occur to the ligands bound at the metal center. When a ligand binds to an electropositive metal center, bonds within the ligand can be polarized in new ways, leading to new or enhanced reactivity. Some of these reactions are covered in the chapters on organometallic chemistry, and there are many examples of how biology employs metal ions at enzyme active sites to catalyze biological transformations. This section will briefly describe some of the most common types of reactions that can be catalyzed by metal ion binding.

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12.9.1: Metal-catalyzed Hydrolysis

Transition metal ions (but not alkali metal ions) act as Lewis acids in metal-ligand interactions. As a consequence of the metal ion interacting with the ligand, the electronic structure of the ligand is altered. In some cases, the metal-ligand interaction causes changes in the strength and reactivity of other bonds within the ligand itself. For example, when a ligand has an acidic proton, interactions with a metal ion will make that acidic proton more acidic. In other words, interaction with the metal ion can cause a decrease in the ligand's pK_a. The metal-ligand complex itself can act as a stronger Bronsted acid (giving off a proton) compared to the "free" ligand. We can see this type of alteration in the pK_a of water when it is "free" compared to when it is bound to a metal ion.

Example: Water meets a transition metal ion[1]

In biology, the solvent is water. Water is also a ligand that binds to metal ions, according to the equation shown below.

$$n\,\mathrm{H_2O} + \mathrm{M}^{x+} \rightleftharpoons [\mathrm{M(H_2O)}_n]^{x+}$$

There is a LOT of water around in biological systems. Consequently, the reaction shown above is shifted far to the right (toward the aquo metal complex, $[\mathrm{M(H_2O)}_n]^{x+}$) in aqueous solution. Consequently, when metals are dissolved in aqueous solution, the "free" ion does not exist, and rather the metal is in complex with water. This is generally true unless there are other ligands present that have stronger affinity for the metal ion.

Consider the two equilibrium reactions shown below. The autoionization of water is shown on the left. This reaction has a very small equilibrium constant ($K_W = 10^{-14}$) and thus the pK_a for dissociation of a proton from water is $pK_a = 14$. On the left is the dissociation of a proton from a water molecule bound to Zn^{2+} ion (other water ligands are not drawn for simplicity). The bond between $\mathrm{H_2O}$ and Zn is considered to be covalent.

$$\mathrm{H_2O} \rightleftharpoons \mathrm{H}^+ + \mathrm{OH}^- \qquad \text{vs.} \qquad [\mathrm{Zn(H_2O)}]^{2+} \rightleftharpoons \mathrm{H}^+ + [\mathrm{Zn(OH)}]^+$$

Exercise 12.9.1.1

Predict which reaction above is more favorable. In other words, in which case is water a better acid; when water is "free", or when it is bound to a transition metal ion like Zn^{2+}? Defend your prediction.[1]

Hint available at the end of this section.

Answer available at the end of this section.

Exercise 12.9.1.2

Water has a pK_a of 14. When water is bound to a Zn^{2+} ion in aqueous solution, its pK_a is lowered to 10. Calculate the pH of pure water and the pH of a solution of 0.1 M $ZnSO_4$.

Hint available at the end of this section.

Answer available at the end of this section.

Exercise 12.9.1.3

Transition metals dramatically decrease solution pH compared to pure water. On the other hand, alkali metals do not significantly affect pH.

a) Based on this information, what can you conclude about the relative covalent nature of water's interactions with transition metals compared to alkali metals?

b) Rationalize this based on the element's position on the periodic table and their consequent electron configurations.

Answer available at the end of this section.

Exercise 12.9.1.4

When a transition metal binds to a Cys side chain, it usually binds to the thiolate anion form of this side chain. Explain why the Cys loses its proton when a metal ion binds. Use drawings to describe what happens to the pK_a of the thiol hydrogen.

Hint available at the end of this section.

Answer available at the end of this section.

Biological hydrolysis[2]

Above you learned how metals can act as Lewis Acids to increase the acidity of a bound water molecule (or other ligand). This modulation of water's pK_a can be really useful to catalyze reactions in which hydroxide ion is a reactant. The enzyme **carbonic anhydrase (CA)** is a prime example of how biology uses this property to catalyze an important biological acid/base reaction. CA is the enzyme that converts CO_2 into bicarbonate (HCO_3^-) very quickly. This is important in the blood to get to CO_2 to the lungs to be exhaled. Conversion of CO_2 to bicarbonate is also important in production of the aqueous fluid of eye and other secretions; and CA is an important drug target for treatment of glaucoma.

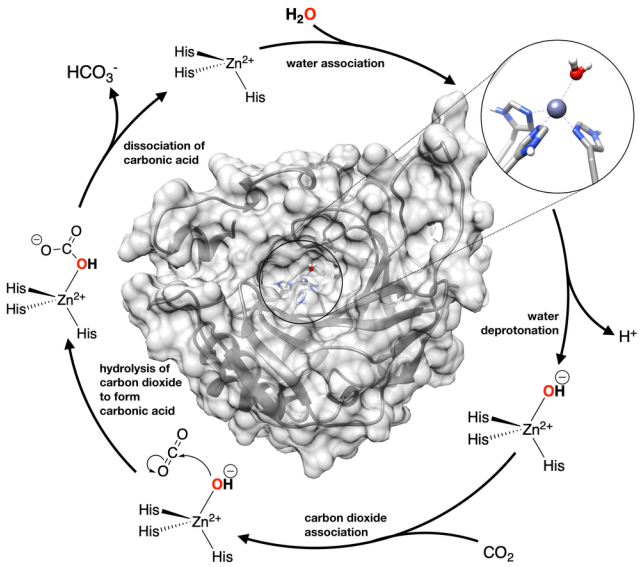


Figure 12.9.1.4: Formation of carbonic acid from carbon dioxide catalyzed by human carbonic anhydraze IV. The structure of protein and acitve site were created from PDB 1znc. (CC-BY-SA; Kathryn Haas)

The figure shows the structure of human carbonic anhydrase IV (from PDB 1znc), with a blow up of the Zn active site where Zn is bound to 3 histidine side chains (His). The mechanism for this enzyme is shown in the chemical equations circling the structure in Figure 12.9.1.4. As we discused above, binding water to a metal ion can change its pK_a, and make its protons more acidic by

stabilizing the hydroxide ion. When hydroxide is needed to carry out hydrolysis reactions, acidic metal ions, like Zn^{2+} are often used to stabilize the hydroxide nucleophile in order to catalyze the reaction (lower the activation energy). The pK_a of "free" water is 14. For water in $[Zn(H_2O)_6]^{2+}$ in aqueous solution, the pK_a is 10. But, in the active site of carbonic anhydrase, the pK_a of water is lowered even more, to 7, by the protein environment around the Zn active site. The active site of this protein has the "power" to lower the pKa of water even more than in the case of aqueous Zn as a virtue of the hydrophobic pocket of the active site that makes charge separation more unstable compared to bulk water where charges can be better solubilize by bulk water.

Look carefully at the catalytic cycle shown in Figure $12.9.1.4$ and identify the step in which water looses a proton (the step labeled "water deprotonation". This step would be nearly impossible under biological conditions at pH 7.4. In other words, it would happen too infrequently to be useful in biological systems. But, when the pKa is lowered to 7, which is below the pH, that step becomes so favorable, that it would happen spontaneously in solution.

Carbonic anhydrase is just one example of how metal ions can be useful for catalyzing hydrolysis reactions. There are several more examples of catalytic enzymes and small molecule metal complexes that use metals (Cu, Co, Ni, Mn, Ca, and Mg) to catalyze hydrolysis of esters (eg hydrolysis of fats), amides (eg hydrolysis of peptide bonds with water), phosphate esters (eg hydrolysis of DNA and RNA) using mechanisms simlar to that shown above for hydrolysis of carbon dioxide.

Sources

1. Inspired by or taken directly from *Metals in Acid Base Chemistry*, an in-class activity created by Sheila Smith, University of Michigan- Dearborn (sheilars@umd.umich.edu) and posted on VIPEr (www.ionicviper.org) on October 17, 2009. Copyright Sheila Smith 2009. This work is licensed under the Creative Commons Attribution Non-commercial Share Alike License. To view a copy of this license visit http://creativecommons.org/about/license/.

2. From *Metals in Biological Systems - Who? How? and Why?*, a 5 slides about learning object created by Adam R. Johnson, Harvey Mudd College (adam_johnson@hmc.edu), Hilary Eppley, DePauw Univeristy (), and Sheila Smith, University of Michigan-Dearborn (sheilars@umd.umich.edu) and posted on VIPEr (www.ionicviper.org) on January 20, 2010. Copyright Sheila Smith 2009. This work is licensed under the Creative Commons Attribution Non-commercial Share Alike License. To view a copy of this license visit http://creativecommons.org/about/license/.

Answers

Exercise $12.9.1.1$

Consider these two things:

(1) In which case is the hydroxide ion more stable: when it is a free ion or when it is bound to Zn? How will this effect one case relative to the other?

(2) Consider separation of charge in each equilibrium. Is the localization of positive and negative charge more energetically favorable in the reactands or in the products in each case? How will this effect one case relative to the other?

Exercise $12.9.1.1$

Water is a better acid when it has a covalent bond to a metal ion. The metal-ligand interaction weakens the H-O bond and stabilizes the conjugate base that forms after deprotonation.

Exercise $12.9.1.2$

You will need the chemical equations above and you will need to recall the definitions of K_a and pK_a, as well as pH to complete this task. Recall that $pK_a = -\log K_a$ and $pH = -\log[H^+]$. The K_a is the equilibrium constant for the chemical equation. Use an I.C.E. table to calculate the amount of hydrogen ion at equilibrium.

Exercise $12.9.1.2$

The pH of pure water is 7. The pH of 0.1 M $ZnSO_4$ depends only on the concentration of the Zn aquo complex that forms after dissociation of $ZnSO_4$ to Zn^{2+} and $SO_4{}^{2-}$. We can use the I.C.E method to determine that the concentration of hydrogen ion at equilibrium is approximately 3.2×10^{-6} after 0.1M Zn^{2+} is initially added to water. This gives approximately $pH = 5.5$.

Exercise $12.9.1.3$

a) transition metals form more covalent bonds with water, while alkali metal's interactions are more electrostatic in character.

b) transition metals have partially-filled d subshells, while alkali metals have the electron configurations of the nobel gases. Perhaps the nobel gas electron configuration makes covalent bonding unfavorable, while partially filled d-orbitals enables productive bonding interactions with ligands.

Exercise $12.9.1.4$

A cystein side chain has a thiol (R-SH) group. Recall that thiols behave similarly to alcohols, but thiols are more acidic than alcohols.

Exercise $12.9.1.4$

Bonding of a cystein S to a metal ion would weaken the S-H bond and increase the acidity of that proton (it's pKa would decrease). In bilogical conditions, near neutral pH, this bonding could decrease the pKa of the thiol group so much that the H is lost to give the conjugate base thiolate bound to the metal.

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12.9.2: Template Reactions

A template reaction is one in which a metal ion acts as a template to bring reactive sites in close proximity. In the absence of the metal ion, the same reaction would proceed to form a different product. An example of the template effect is the dialykation of nickel dithiolate (Figure 12.9.2.1). The same dialkylation in the absence of the Ni template creates a polymer.

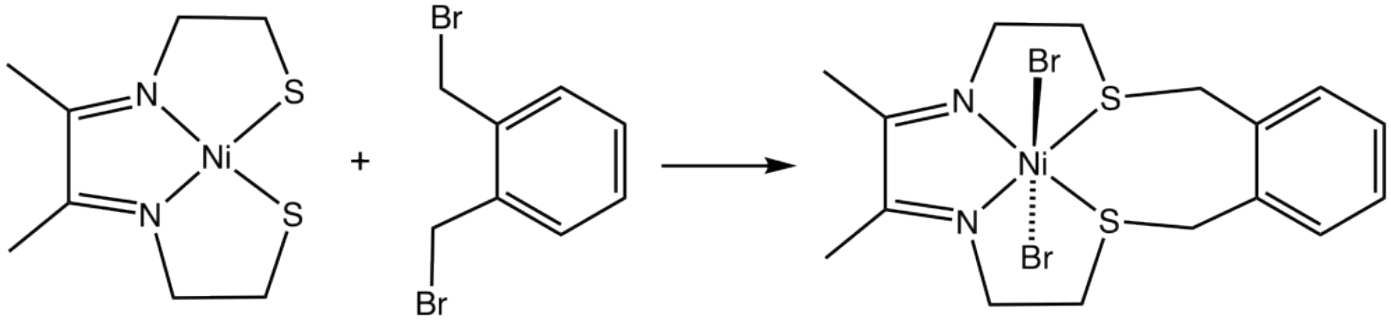


Figure 12.9.2.1: The Dialkylation of nickle dithiolate. (Public Domain; Smokefoot)

Another example of a template reaction is in the synthesis of crown ethers from dialkylations that are templated by metal ions. Again, the same reaction carried out without the template metal would form a polymer.

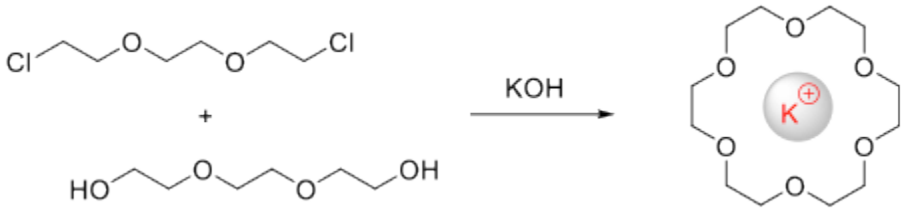


Figure 12.9.2.1: 18-Corwn-6 can be synthesized by the Williamson ether synthesis using potassium ion as the template cation. (Carolineneil, 18-crown-6 was synthesized using potassium ion as the template cation, CC BY-SA 4.0)

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12.9.3: Electrophilic Substitutions

We have seen how metal ion binding can alter the pKa of a bound ligand by polarizing bonds. In a similar fashion, binding of a ligand to a metal ion can alter the location of electron density so that positions on the ligand take on new reactivity. This can be seen in the case of acetylacetone (acac) complexes (most recently discussed in section 12.5.3). The metal coordination to the acac ligand induces enol tautomerization, placing electron density at the central alpha carbon and causing it to become a potent nucleophile. Reactions occur at that nucleophilic carbon in similar manner to the electrophilic aromatic substitution reactions that you may have learned about in an Organic Chemistry course.

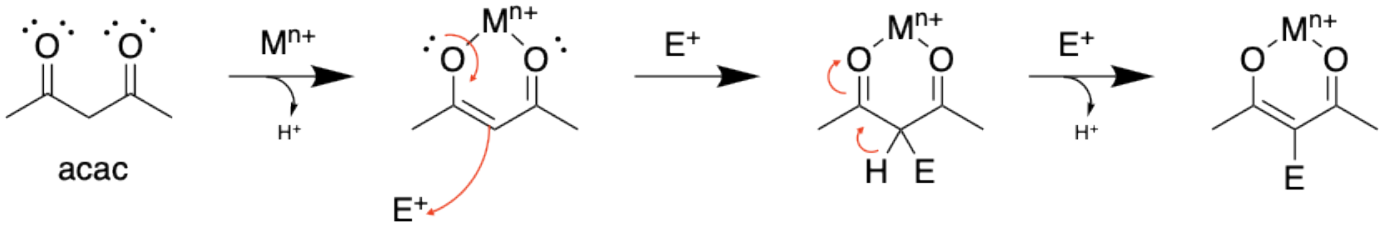


Figure 12.9.3.1: Electrophilic substitution of the acac ligand. E^+ = electrophile. (CC-BY-SA; Kathryn Haas)

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13: ORGANOMETALLIC CHEMISTRY

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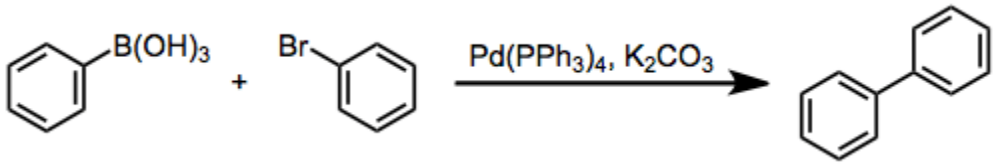
13.1: Introduction to Organometallic Chemistry

What is Organometallic Chemistry?

This chapter will introduce a subfield of inorganic coordination chemistry; organometallic chemistry. Let's begin with a few simple questions: what is organometallic chemistry? What, after studying organometallic chemistry, will we know about the world that we didn't know before? Why is the subject worth studying? And what kinds of problems is the subject meant to address? The purpose of this introduction is twofold: (1) to help motivate us as we move forward (that is, to remind us that there is a point to all this!); and (2) to illustrate the kinds of problems we'll be able to address using concepts from the field. You might be surprised by the spine-chilling power you feel after learning about the behavior of organometallic compounds and reactions!

Put most bluntly, **organometallic chemistry is the study of compounds containing, and reactions involving, metal-carbon bonds**. The metal-carbon bond may be transient or temporary, but if one exists during a reaction or in a compound of interest, we're squarely in the domain of organometallic chemistry. Despite the denotational importance of the M-C bond, bonds between metals and the other common elements of organic chemistry also appear in organometallic chemistry: metal-nitrogen, metal-oxygen, metal-halogen, and even metal-hydrogen bonds all play a role. Metals cover a vast swath of the periodic table and include the alkali metals (group 1), alkali earth metals (group 2), transition metals (groups 3-12), the main group metals (groups 13-15, "under the stairs"), and the lanthanides and actinides. We will focus most prominently on the behavior of the transition metals, so called because they cover the transition between the electropositive group 2 elements and the more electron-rich main group elements.

Why is organometallic chemistry worth studying? Well, for me, it mostly comes down to synthetic flexibility. There's a reason the "organo" comes first in "organometallic chemistry"—our goal is usually the creation of new bonds in *organic* compounds. The metals tend to just be along for the ride (although their influence, obviously, is essential). And the fact is that you can do things with organometallic chemistry that you cannot do using straight-up organic chemistry. Case in point:



The venerable Suzuki reaction...unthinkable without palladium!

The establishment of the bond between the phenyl rings through a means other than dumb luck seems unthinkable to the organic chemist, but it's natural for the palladium-equipped metal-organicker. Bromobenzene looks like a potential electrophile at the bromine-bearing carbon, and if you're familiar with hydroboration you might see phenylboronic acid as a potential nucleophile at the boron-bearing carbon. Catalytic palladium makes it all happen! Organometallic chemistry is full of these mind-bending transformations, and can expand the synthetic toolbox of the organic chemist considerably.

To throw another motive into the mix for the non-specialist (or the synthesis-spurning chemist), organometallic chemistry is full of intriguing stories of scientific inquiry and discovery. Exploring how researchers take a new organometallic reaction from "ooh pretty" to strong predictive power is instructive for anyone interested in "how science works," in a practical sense. We'll examine a number of classical experiments in organometallic chemistry, both for their value to the field and their contributions to the general nature of scientific inquiry.

What kinds of problems should we be able to address as we move forward? Here's a bulleted list of the most commonly encountered types of problems in an organometallic chemistry course:

- Describe the structure of an organometallic complex...
- Predict the product of the given reaction conditions...
- Draw a reasonable mechanism based on evidence...
- Devise a synthetic route to synthesize a target organometallic compound...
- Explain the observation(s)...

- Predict the results of a series of experiments...

The first four are pretty standard organic-esque problems, but it's the last two, more general classes that really make organometallic chemistry compelling. Just imagine putting yourself in the shoes of the pioneers and making the same predictions they did!

There you have it, a short introduction to organometallic chemistry and why it's worth studying. The rest of this chapter will describe what organometallic chemistry really is...it will be helpful to keep these motives in mind as you study. Keep a thirst for predictive power, and it's hard to go wrong with organometallic chemistry!

Resources for learning organometallic chemistry

For the penny-pinching student or layman, there are several good resources for organometallic chemistry on the Web. Nothing as exhaustive as Reusch's Virtual Textbook of Organic Chemistry exists for organometallic chemistry, but the base of resources available on the Web is growing. Rob Toreki's Organometallic HyperTextBook could use a CSS refresh, but contains some nice introductions to different organometallic concepts and reactions. Try the electron-counting quiz!

VIPER is a collection of electronic resources for teaching and learning inorganic chemistry, and includes a nice section on organometallic chemistry featuring laboratory assignments, lecture notes, and classroom activities. Awesome public lecture notes are available from Budzelaar at the University of Manitoba and Shaughnessy at Alabama (Roll Tide?). For practice problems, check out Fu's OpenCourseWare material from MIT and Shaughnessy's problem sets.

Historical Background and Introduction to Metallocenes

Definition: Organometallic Complex

Organometallic Complex: A complex with bonding interactions between a metal atom and one or more carbon atoms of an organic group or molecule.

An **organometallic complex** is defined as a complex with bonding interactions between one or more carbon atoms of an organic group or molecule and at least one metal atom. It is important to understand that *just the presence of an organic ligand is not sufficient to define an organometallic compound*. If there are organic ligands present, but no metal-carbon bonds, the complex is said to be "**metal-organic**". There must be interactions between a carbon and a metal for the complex to be considered organometallic.

Example 13.1.1

Which of the molecules below is an organometallic complex?

$$[\mathrm{Sn(Me)_4}] \qquad \mathrm{Sn(OMe)_4} \qquad \mathrm{cis{-}[PtCl_2(NH_3)_2]} \tag{13.1.1}$$

Solution

The tetramethyl tin ($\mathrm{Sn(Me)_4}$) has metal-carbon bonds, and thus it is an organometallic complex.

Tetramethoxy tin ($\mathrm{Sn(OMe)_4}$) has metal-oxygen bonds. It lacks metal-carbon bonds, but it does contain organic ligands; thus it is a "metal-organic" complex rather than organometallic.

Cisplatinum ($\mathrm{cis{-}[PtCl_2(NH_3)_2]}$) contains no carbon and thus it is neither organometallic or metal-organic; it is just a coordination compound.

Industrial Importance of Organometallic Compounds

Organometallic compounds are a very important class of compounds in industry. For example, tens of thousand of tons of

aluminum and tin alkyl compounds are produced each year for industrial purposes. The use of organometallic compounds as catalysts to produce other compounds is even more important. Organometallic catalysts are used for a range of industrial syntheses from manufacture of commodity polymers like polypropylene and polyethylene to production of simple organic molecules like acetaldehyde and acetic acid. These compounds are produced at a scale in the order of millions of tons per year.

History of Organometallic Chemistry

Let us take a historical approach to organometallic chemistry and see how the field has evolved. Arguably, the first organometallic compound was kakodyl oxide, an organo-arsenic compound (Figure 13.1.2). It was accidentally produced by the French chemist Louis Cadet in 1760 when he was working on inks. He heated arsenic oxide and potassium acetate and obtained a red-brown oily liquid, known as Cadet's fuming liquid. It consists mostly of cacodyl and cacodyl oxide (Figure 13.1.2). In cacodyl, there is an As-As bond and two methyl groups attached to each As atom. In the other product, cacodyl oxide, there is an O atom bridging the two As atoms, and each As is bound to two methyl groups. The names of these two compounds come from the greek word "kakodes", meaning "bad smell". Indeed, they have a very intense, garlic-like smell. The reaction can be used to identify arsenic in samples. For instance, if you suspected your food was poisoned with arsenic, you could heat a sample together with potassium acetate. If a bad, garlic-like smell evolved, this would indicate that there is arsenic in your sample.

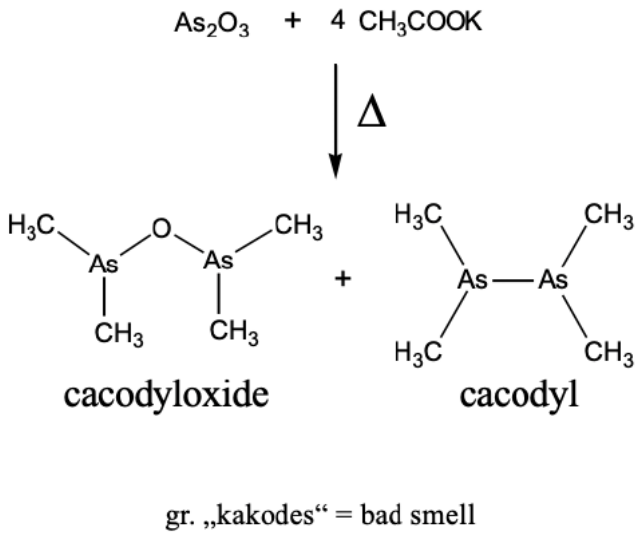
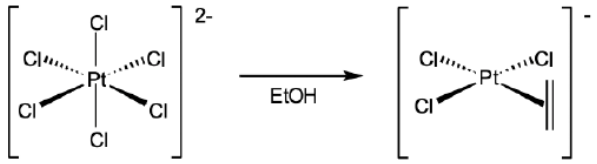


Figure 13.1.2: Cacodyl and cacodyl oxide

Another important milestone in coordination chemistry was the discovery of Zeise's salt by the Danish chemist William Zeise in 1827 (Figure 13.1.3). Zeise's salt was the first olefin complex in which an olefin was bound side-on to a metal using its π-electrons for σ-bonding. Zeise observed that when sodium hexachloroplatinate (2-) was heated in ethanol, a compound with the composition $Na[PtCl_3(C_2H_4)]$ could be isolated. The chemical composition of the compound suggested that there was a C_2H_4 organic fragment bonded to the platinum, but it was not clear how.

This question was only answered more than 100 years later in 1969 with the crystal structure analysis of Zeise's salt. The crystal structure revealed that an ethylene molecule was bound side-on to the platinum (Figure 13.1.3). The two carbon atoms had about the same distance to the Pt arguing that they were equally strongly involved in the bonding with Pt. The first C had a distance of 216 pm while the second carbon had a distance of 215 pm. The ethylene molecule was oriented perpendicular to the plane made of the three chloro ligands and the platinum atom. The Cl-Pt-Cl bond angles were near 90°. Overall, the structure could be described as a structure derived from a square planar structure with the ethylene as the fourth ligand that would stand perpendicular to the plane in order to minimize steric repulsion with the chloro ligands.



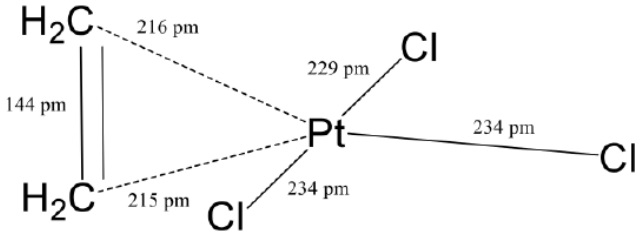


Figure 13.1.3: Zeise's salt: Synthesis and crystal structure.

An important question was how to describe the bonding in the compound. It was noteworthy that the C-C bond length in Zeise's salt was significantly longer (144 pm) than that in a free ethylene molecule (134 pm). Based on the bond-strength bond-length concept this argued that the bond was weaker than a regular C=C double bond, and that the bond order was smaller than 2. What could explain this lower bond order and the side-on coordination of the ethylene in Zeise's salt?

The answer is that the ethylene molecule uses its π-electrons for σ-bonding with a metal d-orbital (Figure 13.1.4). You can see above that the lobe of a $d_{x^2-y^2}$ orbital has the correct orientation to overlap with the bonding π-orbitals of the ethylene ligand in a σ-fashion. Through this interaction electron density gets donated from the bonding ligand π-orbital into the metal-d-orbital. This results in a lower electron density for π-bonding within the ligand, and thus the bond order is decreased. In addition, there is another effect that lowers the bond order. A metal d-orbital can interact with the π*-orbitals in π-fashion. In this process, electron density can be donated from the metal d-orbital into the empty π-orbitals of the ligand. The increased electron density in the π-orbitals further decreases the bond order.

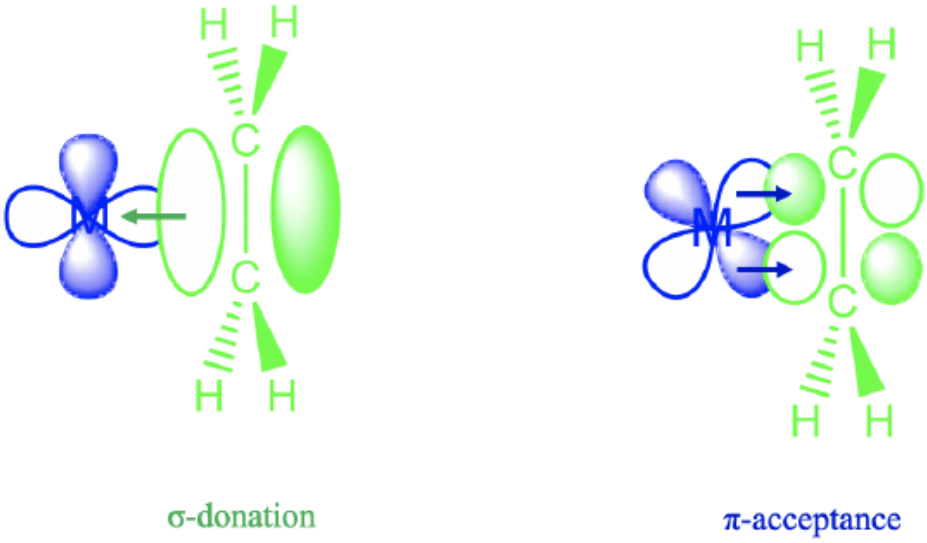


Figure 13.1.4: An orbital view of bonding in Zeise's salt

In 1890, a further milestone in organometallic chemistry was reached with the synthesis of the first carbonyl complex, the nickel tetracarbonyl. Nickel tetracarbonyl is a colorless liquid that boils at 43°C. The compound was prepared by the German chemist Ludwig Mond. Nickel tetracarbonyl forms spontaneously from nickel metal and carbon monoxide at room temperature. The reaction is the basis of the Mond-process that is used up to date in order to purify nickel (Figure 13.1.5). Carbon monoxide

gas can be streamed over impure Ni metal at temperatures of 50-60°C to form $Ni(CO)_4$ in gaseous form. Impurities are left behind in solid form. Then, the nickel tetracarbonyl is thermally decomposed at ca. 220° to form nickel and carbon monoxide. The process can be varied to produce nickel in powder form, as spheres (Figure 13.1.5), and as coatings. The Mond process is still used despite the very high toxicity of nickel tetracarbonyl.

$$\mathrm{Ni_{(s,\ impure)} + 4\,CO_{(g)} \longrightarrow Ni(CO)_{4\,(g)}} \qquad 50 - 60^{\circ}\mathrm{C\ (also\ spontaneous\ at\ room\ temp)}$$

$$\mathrm{Ni(CO)_{4\,(g)} \longrightarrow Ni_{(s,\ purified)} + 4\,CO} \qquad 220 - 250^{\circ}\mathrm{C\ (Ni\ is\ purified)}$$



Figure 13.1.5: Purified Ni spheres prepared through the Mond process (René Rausch, Nickel kugeln, CC BY-SA 3.0 DE)

In 1900 the first Grignard reagents were discovered. Victor Grignard (Figure 13.1.9) was an enthusiastic young French chemist who discovered how to make organomagnesium halides (RMgX) while working for his Ph.D.. His supervisor, Sabatier, had been trying this chemistry for some time, but Victor was the genius who solved the problem. Organomagnesium halides form from magnesium and organic halides in ethers. This discovery in 1900 changed the course of organic chemistry and won Grignard and Sabatier the Nobel Prize in 1912.

Extra close brace or missing open brace

In 1917, the first lithium alkyls were prepared by Wilhelm Schlenk. Like Grignard reagents, lithium alkyls are very valuable reactants in synthetic organic chemistry. Lithium alkyls are very air-sensitive compounds, and some even self-ignite in air (for example tert-butyl lithium is explosive when exposed to air). Therefore, they need to be handled carefully under inert gas. So that the reactions could be carried out under air0free conditions, Wilhelm Schlenk made an important invention: The Schlenk-lines (Figure 13.1.6). The Schlenk lines allows a chemist to remove all gas (air) from a reaction flasks and back-fill the flask with an inert gas. A Schlenk line has a dual manifold with several ports. One manifold is connected to a source of purified inert gas, while the other is connected to a vacuum pump. The inert-gas line is vented through an oil bubbler, while solvent vapors and gaseous reaction products are prevented from contaminating the vacuum pump by a liquid nitrogen or dry ice/acetone cold trap. Special stopcocks or Teflon taps allow vacuum or inert gas to be selected without the need for placing the sample on a separate line.



Figure 13.1.6: A Schlenk-line (Polimerek, Double vac line front view, CC BY-SA 3.0)

Discovery of Metallocenes

The discoveries discussed above were important milestones in the development of organometallic chemistry. But the field expanded more rapidly with the discovery of the first metallocene: ferrocene. Like often in science, ferrocene was discovered through an accident. In 1951 Peter Pauson and Thomas Kealy attempted to synthesize the organic compound fulvalene through oxidative coupling of cyclopentadienyl magnesium chloride with iron (III) chloride. However, instead of obtaining fulvalene they observed the formation hydrofulvalene together with an orange powder with “remarkable stability”. Analysis of the powder showed that the chemical compound contained two cyclopentadienyl rings and one iron atom. According to the knowledge on bonding in organometallic compounds that was known at the time Kealy and Pauson suggested a structure for the molecule in which two cyclopentadienyl group were bound to a single Fe atom via two Fe-C bonds (Figure 13.1.7).

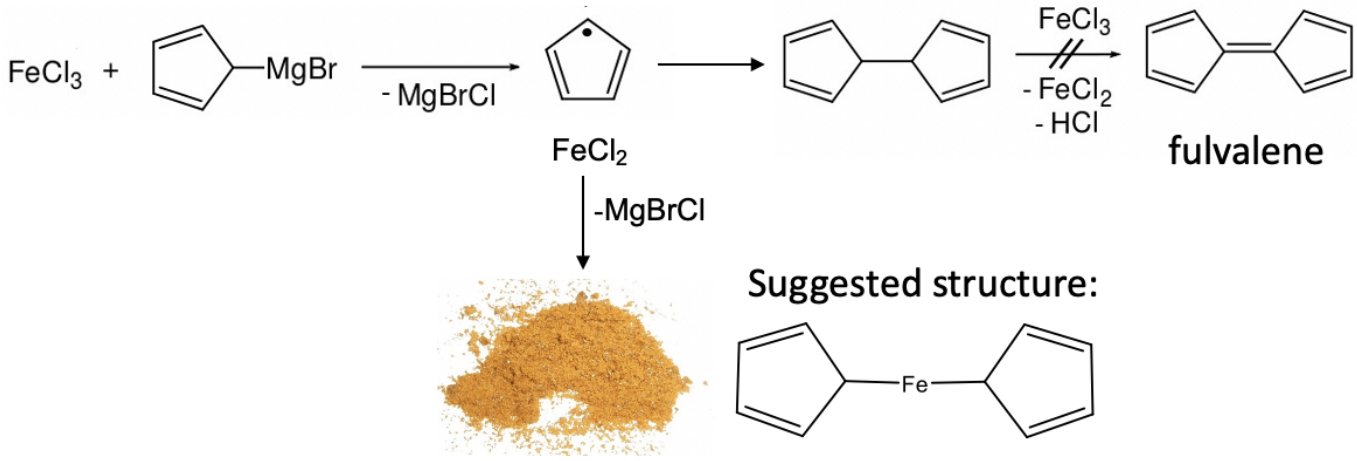
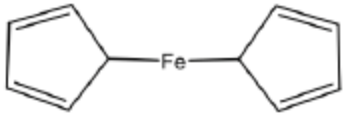


Figure 13.1.7: Synthesis of ferrocene (Attribution: T.J. Kealy, P.L. Pauson, Nature 1951, 168, 1039.)

However, the remarkable stability of the compound was in contradiction to the proposed structure. The structure would be a 10 electron complex which would be highly coordinatively unsaturated. This would be inconsistent with the observed stability. We can briefly practice our electron counting skills again in order to prove that there are only 10 electrons (Figure 13.1.8). (Electron counting will be discussed in more depth later in this chapter)

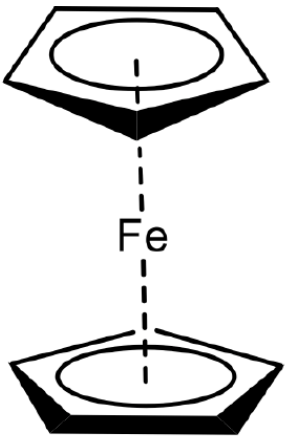


Structure is coordinatively unsaturated and has 10 valence electrons.

Fe:	8e
Ox-State (+2):	-2e
Ligands:	2x2e = 4e
Sum:	10e

Figure 13.1.8: Electron counting in the wrong structure for $Fe(Cp)_2$

The compound was stable in air, and could be sublimed without decomposition. Further, the double-bonds in the cyclopentadienyl rings resisted hydrogenation. In addition, the structure was inconsistent with spectroscopic observations. Only one C-H stretch vibration was observed in the IR and only one signal was observed in the ^1H NMR. Kealy and Pauson's structure would have been consistent with three C-H stretch vibrations and three NMR resonances. For these reasons, Kealy's and Pausons structure was soon questioned. Ernst Otto Fischer at University of Munich and Sir Geoffrey Wilkinson at Harvard University (Figure 13.1.9) suggested an alternative structure that was very different from all known organometallic structures. The bonding in this structure was completely different from all bonding concepts considered thus far for organometallics. What structure did they propose? They proposed a sandwich structure in which the two aromatic cyclopentadienyl anions would sandwich an Fe^{2+} ion. What would be the bonding in this structure? The cylopentadienyl anion would donate its six π-electrons into the valence orbitals of the metal. Thus, all five carbon atoms would be equally involved in the bonding, the ligand would act as a η^5-ligand. Because of the donation of π-electrons in the cycopentadiene unit, the structure was called "ferrocene". The ferrocene structure would explain the stability and low reactivity of the compound.



Ferrocene

Figure 13.1.9: The sandwich structure of ferrocene

Electron-counting gives an 18 electron complex (Figure 13.1.10). Let us verify this using the oxidation state method. Fe would contribute eight electrons in the neutral state. The ligands would be considered as cyclopendienyl anions with a 1- charge. This would give an oxidation state of +2 for Fe reducing the number of electrons from eight to six. The two ligands would contribute six electrons each giving twelve electrons. 12+6=18. Hence, the structure fulfills the 18 electron rule. The structure is also consistent with the spectroscopic observation of one NMR resonance and one C-H stretch vibration. All these were excellent arguments to support the ferrocene sandwich structure, however they were not an absolute proof. The proof finally came with the X-ray crystal structure determination which unambiguously confirmed the sandwich structure.

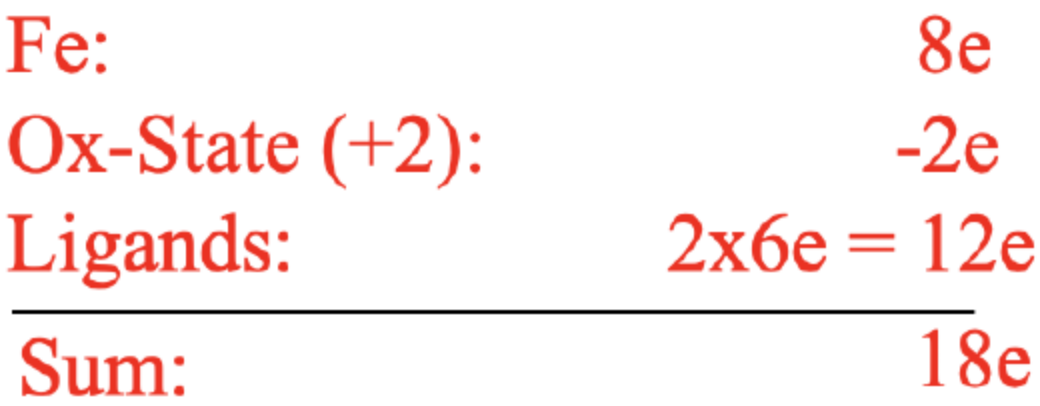


Figure 13.1.10: Electron counting in ferrocene using the oxidation state method

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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13.2: Nomenclature, Ligands, and Classification

The nomenclature of coordination compounds was described in an earlier section (Section 9.2). Organometallic compounds are named using this same system, so it may be helpful to review before proceeding. Here, we will point out some of the symbols and terminology that are used heavily in naming organometallic complexes.

Hapticity

The eta (η) symbol is used to indicate the variable **hapticity** of ligands with conjugated π systems. For example, the cyclopentadiene anion (Cp, C_5H_5) ligand has the capability to coordinate a metal ion in several ways due to its cyclic conjugated π system. The hapticity (the number of atoms involved in the metal bonding interaction) must be indicated in the formula with the η^n notation, and in the name with the appropriate prefix. Figure $13.2.1$ illustrates three different hapticities, and the relevant formula symbols and names.

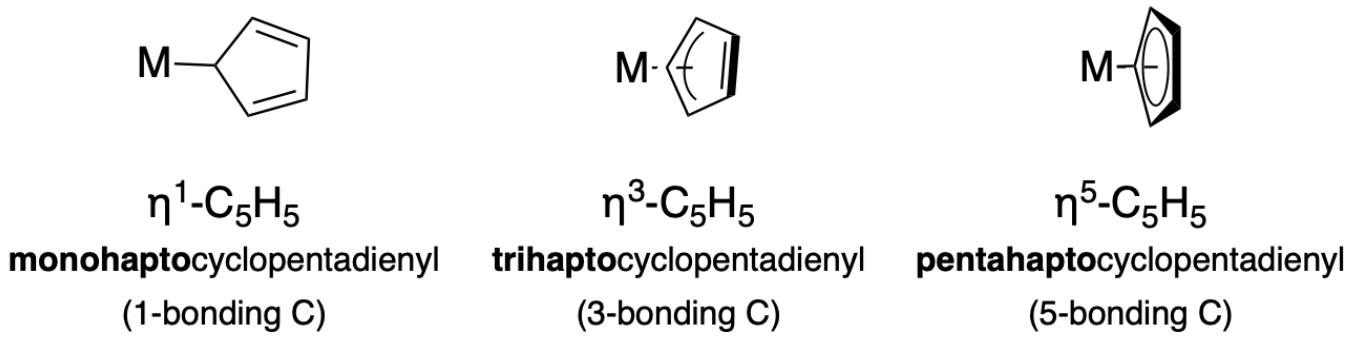


Figure $13.2.1$: The cyclopentadiene anion is shown coordinating to a metal ion (M) using three different coordination modes: On the left, Cp as a monohapto ligand. In the center, Cp is shown bonding to a metal in a trihapto fashion where the metal interacts with three carbons. On the right, Cp is shown bonding in a pentahapto fashion, where the five ligand carbons interact equally through the π system . (CC-BY-SA 4.0; Kathryn Haas)

Another common ligand is the π-allyl anion (C_3H_3), which can coordinate in either an η^1 or η^3 fashion, as illustrated below (Figure $13.2.2$).

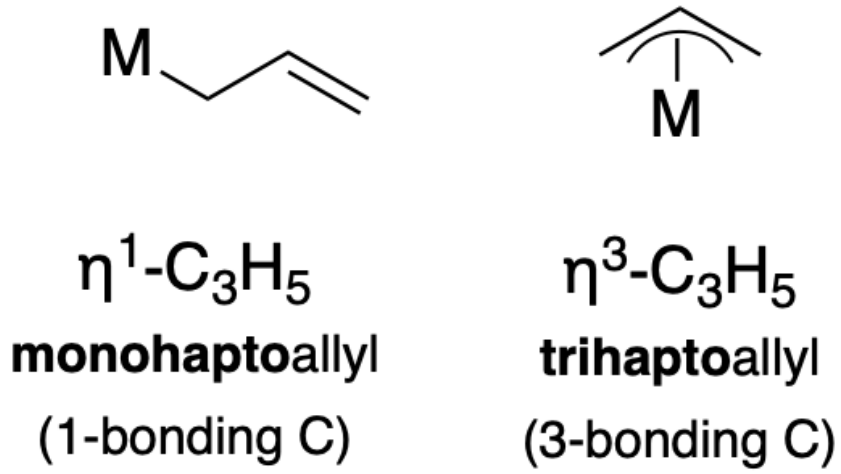


Figure $13.2.2$: The allyl anion is shown coordinating in a η^1 and eta^3 modes. (CC-BY-SA 4.0; Kathryn Haas)

Bridging ligands

Ligands that bridge two or more metal ions are indicated using the symbol, mu (μ). For a ligand that bridges n metal ions, the symbol is written as μ_n. However the subscript is often ommitted when $n = 2$. Some examples of the carbonyl ligand are given below. More specific rules for naming are found in Section 9.2.

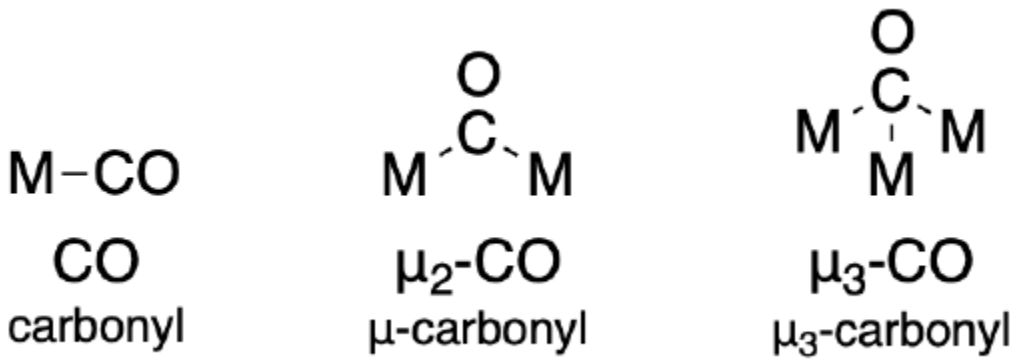
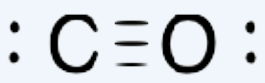
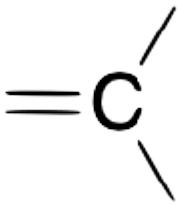
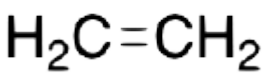
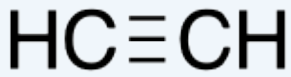
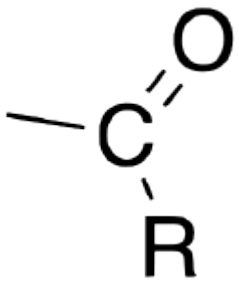
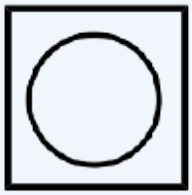
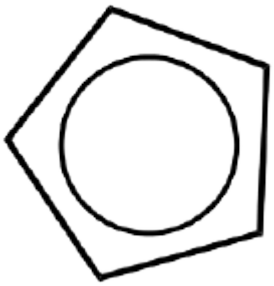


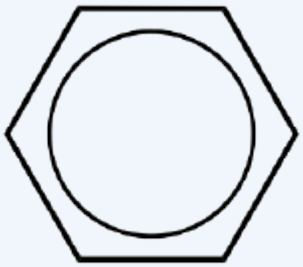
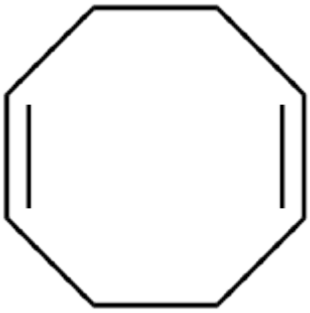
Figure 13.2.3: The carbonyl ligand is shown as a terminal ligand (with no μ necessary), bridging two metals (μ_2), and bridging three metals μ_3). (CC-BY-SA 4.0; Kathryn Haas)

Common Ligands and Classifications

Some common organic ligands found in organometallic compounds are listed below with their names and structures.

Name	Structure	CBC description
Alkyl		X
Carbonyl		L
Carbene (alkylid**e**ne)		X_2
Carbyne (alkylid**y**ne)		X_3

Name	Structure	CBC description
Ethylene		L
Acteylene		L
Acyl		X
π-allyl ($C_3H_5^-$)		X for η^1 LX for η^3
Cyclopropenyl (cyclo-C_3H_3)		X for η^1 LX for η^3
Cyclobutadiene (cyclo-C_4H_4)		L_2 for η^4
Cyclopentadienyl (cyclo-C_5H_5, Cp)		X for η^1 LX for η^3 L_2X for η^5

Name	Structure	CBC description
Benzene		L_3 for η^6
1,5-cyclooctadiene (1,5-COD)		L_2 for η^4

Covalent Bond Classification Method (CBC)

Later in this chapter, you will learn to count electrons. The way in which you count depends on what counting scheme you choose to use. But in any case, the way in which we "count" the electrons from ligands depends on the ligand type. The covalent bond classification method (CBC) has been in use since the late 1990's to classify ligands in organometallic complexes. This method classifies ligands into three main types as follows. (see Application of the Covalent Bond Classification Method for the Teaching of Inorganic Chemistry. Malcolm L. H. Green and Gerard Parkin, Journal of Chemical Education 2014 91 (6), 807-816, DOI: 10.1021/ed400504f.)

CBC Ligand Class/ Type	Examples	Use in neutral Ligand Method of Electron Counting	Use in Donor Pair Method of Electron Counting
X-type	H^-, Cl^-, H_3C^-	Considered neutral Donates 1 electron to the metal	Considered anionic Donates 2 electrons to the metal
L-type	CO, NH_3, H_2O	Considered neutral Donates 2 electrons to the metal	Considered neutral Donates 2 electrons to the metal
Z-type (rarely used)	BR_3, Lewis acids	Considered neutral Accepts 2 electrons	Considered cationic Donates 0 electrons

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13.3: Electron Counting in Organometallic Complexes

In this section we will learn how to **count valence electrons in coordination compounds**. Electron counting is important because the number of electrons in a complex can be used to predict the compound's stability and reactivity. There are two different methods that are commonly used, and each is described below. Each of the two methods will lead to the same result if done correctly. Which method you prefer is “personal taste”, but each method is about equally common in the literature, so it is good to be familiar with both of them.

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13.3.1: The 18 Electron Rule

Method A for counting electrons: The Donor Pair Method

The donor pair method consider ligands to donate pairs of electrons to the metal. Each ligand-metal bond is considered a pair of electrons donated to the metal by the ligand. The method consists of the steps described in the box below.

How to count with the DONOR PAIR METHOD

1. **Determine the oxidation state of the metal center.** This step can be done by first deconstructing the complex so that each ligand "keeps" its bonded electrons (See Figure 13.3.1.2). by considering the overall charge of the complex and the charge of each ligand, the oxidation state of the metal center can be determined. An alternative to deconstruction is to consider each ligand's class according to the Covalent Bond Classification (CBC) method discussed earlier.
2. **Determine the number of metal ion valence electrons**. The number of valence electrons can be determined from the metal's group on the periodic table and its oxidation state. If the oxidation state is positive we subtract electrons from the group number, if it is negative, which is rare, then we add electrons.
3. **Determine the number of bonded electrons derived from ligands**. Each ligand single bond provides two electrons, double bonds provide four electrons, etc.
4. **Add** the number of electrons from the metal ion valence (step 2) to the number of bonded electrons from the ligands to get the total valence electron count for the complex.

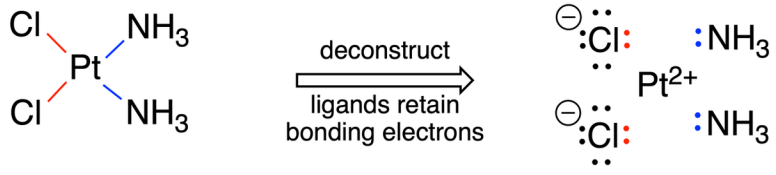
Below is an example of using the donor pair method to count electrons in the chemotherapy drug $\mathrm{cis{-}[PtCl_2(NH_3)_2]}$, also called *cis*-platinum (Figure 13.3.1.1). This compound is neutral in charge.

Step 1: Deconstruction of the complex using the donor pair method would convert each metal-ligand bond to a pair of electrons on the ligand. Without consulting the Covalent Bond Classification (CBC) method, we can determine the charge on each ligand using the simple Lewis dot diagrams that result. The ligands consist of two neutral ammines and two negatively charged chlorides. The ligands account for a total negative charge of -2. Since the metal complex is neutral, there must be a +2 change on the metal. Thus, the metal oxidation state is +2.

Step 2: With the knowledge that the Pt has an oxidation state of +2, and is in group 10 of the periodic table, we can determine the number of valence electrons on Pt(II). Subtract the oxidation state from the group number to get 8 valence electrons on the Pt(II) ion.

Step 3: Each of the ligands had one bond to Pt, thus each is a 2-electron donor. The ligands combined contribute a total of 8 electrons.

Step 4: Adding the 8 electrons from Pt(II) and the 8 electrons from the ligands gives a total electron count of 16.



Fragment	Electron Count
Pt(II)	8
2x Cl^-	4
2x NH_3	4
Total	**16**

Figure 13.3.1.1: Example of the oxidation state method

Method B for counting electrons: The Neutral Atom Method (aka Neutral Ligand Method)

The “neutral atom method”, is sometimes called "the neutral ligand method". In this method, each ligand is considered to donate

the number of electrons that it would *if the ligand were neutral*. The neutral atom method is carried out according to the steps described below.

How to count using the NEUTRAL LIGAND/ATOM METHOD

1. Determine the number of valence electrons on the metal center, as if it were a neutral atom. Add those electrons to the total count.
   Hint: The number valence electrons is the same as the group number of the transition metal in the periodic table (groups 3-12 for the transition metals).
2. Account for the ionic charge on the entire coordination complex. If the charge is neutral, you can ignore this step. If the complex has a positive charge, you subtract that many electrons from the total count. If the complex is an anion, you add the anionic charge to the total electron count.
3. Determine how many electrons are contributed by each ligand. (This is the most complicated step)
   - Deconstruct the metal ion (break its M-L bonds) so that each resulting ligand fragment and the central metal are neutral.
   - Then count the number of electrons from each ligand that contributed to the bond. Add the sum of those electrons from all the ligands to the total count.
     (Remeber you've already accounted for the electrons from the neutral atom in step #1)
4. Add the metal ion valence electrons (step 1), the total ligand electrons (step 3), and accounting for the charge of the complex (step 2). The total sum is the total valence electron count for the metal complex.

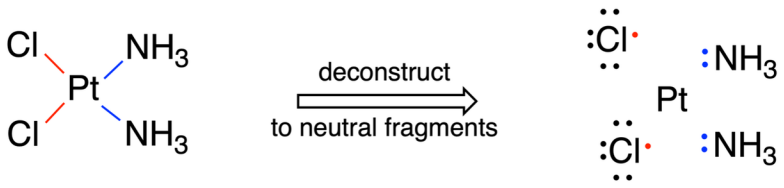
Below is an example of applying the neutral atom method to count electrons in the *cis*-platinum complex ($[\mathrm{Pt(Cl)_2(NH_3)_2}]$ (Figure \({13{.}3{.}1{.}\eatSpaces{2} \endSpaces}\)).

Step 1: The metal is platinum which is located in group 10 of the periodic table. Therefore, a neutral platinum atom has ten valence electrons.

Step 2: The complex is neutral, this we can ignore this step.

Step 3: Each Cl is considered to donate 1 electron and each ammine ligand is considered to donate two electrons. The Cl's donate a total of two electrons, and the ammines donate a total of four electrons to give a total of 6 from all ligands.

Step 4: Ten electrons from Pt and six electrons from the ligands combine to give a total electron count of 16.



Neutral fragment	Electron Count
Pt	10
2x Cl	2
2x NH_3	4
Total	**16**

Figure 13.3.1.2: Example of applying the neutral fragment method to count the total valence electrons in $[\mathrm{Pt(Cl)_2(NH_3)_2}]$.

There are pros and cons to each of the methods presented above. The neutral atom method has the advantage that we do not have to calculate charges of ligands or the metal oxidation states to reach the final answer. However, the disadvantage is that we must think about how to cleave bonds to create neutral fragments. We may need to cleave bonds in an way that is contrary to the real donor-acceptor nature of a coordination compound. The donor-pair method does account for the donor-acceptor nature of a coordination compound because the bonds are considered dative bonds, and the electrons are assigned to the ligands and metals accordingly. And advantage to the donor-pari method is that we do not need to think how to cleave bonds in artificial ways because we cleave the bonds always heteroleptically. However, the disadvantage is that it requires us to calcuate charges at the ligands to determine metal oxidation states, which is an additional, non-trivial step.

The 18 Electron Rule

Electron counting is a critical step in the context of an important rule in coordination chemistry: The 18 electron rule. **The 18 electron rule states that transition metal complexes are *normally* most stable when they have a total count of 18**

electrons in the valence shell. In other words, for d-block metal complexes, a valence configuration that fills all valence orbitals ($ns^2\ \ (n-1)d^{10}\ \ np^6$) is most stable; it is equivalent to a nobel-gas configuration for the metal atom, and is analogous to the "octet rule" for the main-group elements. Complexes that have 18 electrons in their count are considered to be **coordinatively saturated**. In general, coordinatively saturated compounds are considered to be relatively stable, and when they react they usually undergo dissociation or oxidation reactions that decrease the electron count. If the there are less than 18 electrons, the species is **coordinatively unsaturated**, and considered less stable than a species with 18 electrons. In general, coordinatively unsaturated complexes tend to react in ways that can increase the electron count. They tend to undergo reactions involving associations to add more electrons to the system and/or tend to gain electrons through redox reactions (the metal becomes reduced). If a species has more than 18 electrons it is **coordinatively oversaturated** and tends to lose ligands. It is usually easily oxidized. Both loss of ligands and oxidation reduces to the number of electrons to or at least closer to 18.

Definitions:

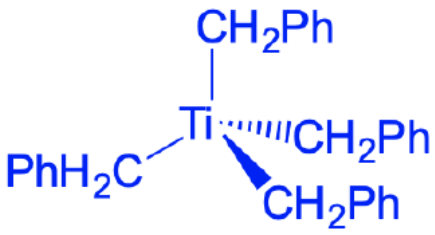
Coordinatively saturated: when the complex has an electron count =18 electrons. These complexes are considered most stable.

Coordinatively unsaturated: when the complex has an electron count <18 electrons. These complexes tend to add more ligands, and to become reduced.

Coordinatively oversaturated: when the complex has an electron count >18 electrons. These complexes tend to lose ligands and become oxidized.

Exceptions to the 18-electron rule:

The 18 electron rule has many exceptions, and therefore needs to be applied with caution. In particular, group 3, 4, and 10 complexes deviate often from the 18 electron rule.



Contribution metal:	4e
Oxidation state: +4	-4e
Electrons contributed by ligands:	4x2e=8e
Sum:	**8e**

Figure 13.3.1.3: Example of counting electrons in the tetrahedral tetrabenzyltitanium(0) complex using the oxidation state method

For illustration purposes, let us count the number of electrons of the tetrahedral tetrabenzyltitanium(0) complex by the oxidation state method. We could also use the neutral atom method, which would give the same results. This complex is a group 4 complex because titanium is in group 4. How many electrons will the titanium contribute? Because the number of electrons is always the same as the group number, it will contribute four electrons. Next, what is oxidation state of Ti? To determine it we must determine the charge at the ligands. To do that we cleave the bonds heteroleptically. This will give benzylate anions with -1 charge. There are four of these ions, and therefore there will be four negative charges overall. The complex is charge-neutral, and thus the oxidation state is +4 because -4+4=0. Therefore, we need to subtract four electrons. Because we cleaved the bond heteroleptically, each ligand contributes two electrons, giving overall eight electrons coming from the four ligands. This means that we have overall eight electrons, or an 8-electron complex. This is far, far away from 18 electrons. Nonetheless, the complex is stable. How can we explain

this? The answer is that in order to achieve 18 electrons it would need to add five additional ligands if each ligand is considered a 2-electron donor. This would increase the coordination number to 9 which is too high to produce a stable complex. In order to reduce the complex to an 18 electron complex, 10 electrons would need to be added. This would produce a complex with a -10 charge which is way to high to be stable. The arguments are generalizable for group 3 and group 4 complexes. Because these elements only have a few d electrons, the ligands would need to contribute a lot of electrons to produce an 18 electron complex. This would require just too many ligands to add. The coordination numbers would get too high. If electrons are added instead of ligands, the negative charge at the complex would be to high to be stable based on electron-electron repulsion arguments.



Contribution metal:	10e
Charge:	0e
Electrons contributed by Cl ligands:	2x1e=2e
Electrons contributed by NH_3 ligands:	2x2e=4e
Sum:	**16e**

Figure 13.3.1.4: Counting electrons in the diamminedichloro palladium complex using the neutral atom method.

These arguments cannot be applied for group 10 elements, because these elements have many d electrons. The explanation in this case is that these elements like to make square planar complexes when in the oxidation number is +2. Square planar complexes prefer 16 instead of 18 electrons. We will learn later, when we discuss bonding in coordination compounds, why this is. You can see that the square planar diamminedichloro palladium complex shown is square planar and has sixteen electrons. There are 10 electrons coming from Pd. If we use the neutral atom method, no electrons need to be added or subtracted due to the charge at the complex. The complex is charge-neutral. To assess how many electrons come from the ligands we need to cleave the bonds so that neutral ligands are produced. The Pd-Cl bonds need to be cleave homoleptically, the Pd-N bonds need to be cleave heteroleptically. Therefore, the two chloro ligands are 1e donors, and the two ammine ligands are 2e donors. This gives 10+4+2=16 electrons.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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13.3.2: Simplifying the Organometallic Complex by Deconstruction

Organometallic complexes, which consist of centrally located metals and peripheral organic compounds called ligands, are the workhorses of organometallic chemistry. Just like organic intermediates, understanding something about the structure of these molecules tells us a great deal about their expected reactivity. Some we would expect to be stable, and others definitely not! A big part of our early explorations will involve describing, systematically, the principles that govern the stability of organometallic complexes. From the outset, I will say that these principles are not set in stone and are best applied to well controlled comparisons. Nonetheless the principles are definitely worth talking about, because they form the foundation of everything else we'll discuss. Let's begin by exploring the general characteristics of organometallic complexes and identifying three key classes of organic ligands.

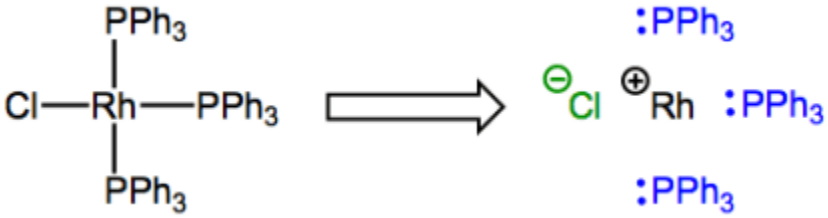
When we think of metals we usually think of electropositive atoms or even positively charged ions, and many of the metals of OM chemistry fit this mold. In general, it is useful to imagine organic ligands as electron donors and metals as electron acceptors. When looking at a pair of electrons shared between a transition metal and main-group atom (or hydrogen), I imagine the cationic metal center and anionic main-group atom racing toward one another from oblivion like star-crossed lovers. In the opposite direction (with an important caveat that we'll address soon), we can imagine ripping apart metal–R covalent bonds and giving both electrons of the bond to the organic atom. This heterolytic bond cleavage method reproduces the starting charges on the metal and ligand. Unsurprisingly, the metal is positive and the ligand negative.

FYI, you might see the blue bipyridine referred to as an L2 ligand elsewhere; this just means that a single bipyridine molecule possesses two L-type binding points. Ligands with multiple binding points are also known as chelating or polydentate ligands. Chelating ligands may feature mixed binding modes; for instance, the allyl ligand is of the LX-type. Chelating ligands can also bind to two different metal centers; when they act in this way, they're called bridging ligands. But don't let all this jargon throw you! Deconstruct complexes one binding point at a time, and you cannot go wrong.

Next, we'll take a closer look at the metal center and expand on the purpose of the deconstruction process described here.

"Bookkeeping" through deconstruction of organometallic complexes

Now it's time to turn our attention to the metal center, and focus on what the deconstruction process can tell us about the nature of the metal in organometallic complexes. Let's turn our attention now to a new complex. I've gone ahead and deconstructed it for us.



Say hello to rhodium (Rh)! Don't fret; it's just a group 9 element.

The complex possesses one X-type and three L-type ligands, so the rhodium atom ends up with a formal charge of +1. The formal charge on the metal center after deconstruction has a very special name that you will definitely want to commit to memory: it's called the oxidation state. It's usually indicated with a roman numeral next to the atomic symbol of the metal (the "+" is implied). In the complex shown above, rhodium is in the Rh(I) or +1 oxidation state. Oxidation state is most useful because changes in oxidation state indicate changes in electron density at the metal center, and this can be a favorable or unfavorable occurrence depending on the other ligands around. We will see this principle in action many, many times! Get used to changes in oxidation state as everyday events in organometallic reaction mechanisms. Unlike carbon (with the exception of carbene...what's its oxidation state?!) and other second-row elements, the transition metals commonly exhibit multiple different oxidation states. More on that later, though. For now, training yourself to rapidly identify the oxidation state of a complexed metal is most important.

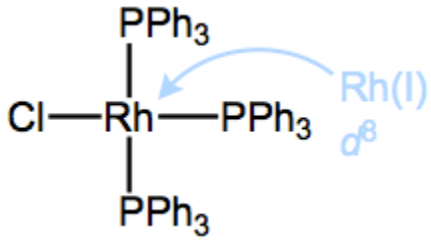
Please note that when a complex possesses an overall charge, the oxidation state is affected by this charge!

$$\text{oxidation state} = \text{number of X-type ligands bound to metal} + \text{overall charge of complex}$$

What of this number of d electrons concept? A very useful way to think about "number of d electrons" is as the "number of non-bonding electrons on the metal center," and you're probably familiar with identifying non-bonding electrons from organic chemistry. The numbers of valence electrons of each organic element are set in stone: carbon has four, nitrogen has five, et cetera. Furthermore, using this knowledge, it's straightforward to determine the number of lone pair electrons associated with an atom by subtracting its number of covalent bonds from its total number of valence electrons. E.g., for a neutral nitrogen atom in an amine NR_3, 5 – 3 = 2 lone pair electrons, typically. The extension to organometallic chemistry is natural! We can analyze complexed metal centers in the same way, but they tend to have a lot more non-bonding electrons than organic atoms, and the number depends on the metal's oxidation state. For instance, the deconstructed rhodium atom in the figure above has 8 d electrons: 9 valence electrons minus 1 used for bonding to Cl. Dative bonds don't affect d electron count since both electrons in the bond come from the ligand.

$$\text{number of non-bonding electrons} = \text{number of d electrons} = \text{metal's group number} - \text{oxidation state}$$

Drawing all the non-bonding d electrons out as lone pairs would clutter things up, so they are never drawn...but we must remember that they're around! Why? Because the number of d electrons profoundly affects a complex's geometry. We will return to this soon, but the key idea is that the ligands muck up the energies of the d orbitals as they approach the metal (recall the "star-crossed lovers" idea), and the most favorable way to do so depends on the number of non-bonding electrons on the metal center.



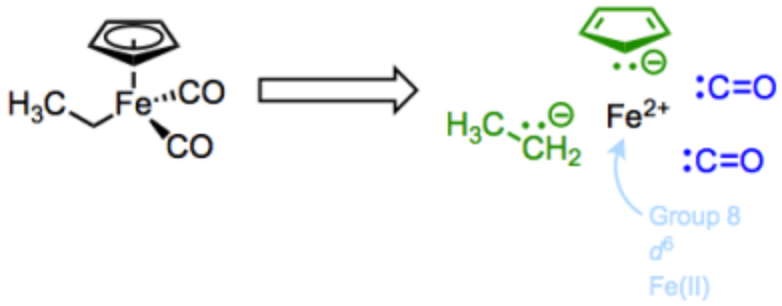
Oxidation state and d electron count: two tools the OM chemist can't live without!

This post introduced us to two important bookkeeping tools, oxidation state and number of d electrons. In the final installment of the "Simplifying the Organometallic Complex" series, we'll bring everything together and discuss total electron count. We'll see that total electron count may be used to draw a variety of insightful conclusions about organometallic complexes.

Apply deconstruction to gain insight

So far, we've seen how deconstruction can reveal useful "bookkeeping" properties of organometallic complexes: number of electrons donated by ligands, coordination number, oxidation state, and d electron count (to name a few). Now, let's bring everything together and discuss total electron count, the sum of non-bonding and bonding electrons associated with the metal center. Like oxidation state, total electron count can reveal the likely reactivity of OM complexes—in fact, it is often more powerful than oxidation state for making predictions. We'll see that there is a definite norm for total electron count, and when a complex deviates from that norm, reactions are likely to happen.

Let's begin with yet another new complex. This molecule features the common and important cyclopentadienyl and carbon monoxide ligands, along with an X-type ethyl ligand.



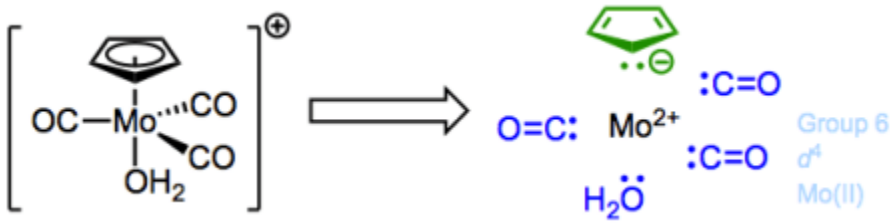
What is the total electron count of this Fe(II) complex?

The Cp or cyclopentadienyl ligand is a polydentate, six-electron L2X ligand. The two pi bonds of the free anion are dative, L-type ligands, which we'll see again in a future post on ligands bound through pi bonds. Think of the electrons of the pi bond as the source of a dative bond to the metal. Since both electrons come from the ligand, the pi bonds are L-type binders. The anionic carbon in Cp is a fairly standard, anionic X-type binder. The carbon monoxide ligands are interesting examples of two-electron L-type ligands—notice that the free ligands are neutral, so these are considered L-type! Carbon monoxide is an intriguing ligand that can teach us a great deal about metal-ligand bonding in OM complexes...but more on that later.

After deconstruction, we see that the Fe(II) center possesses 6 non-bonding d electrons. The total electron count is just the d electron count plus the number of electrons donated by the ligands. Since the d electron count already takes overall charge into account, we need not worry about it as long as we've followed the deconstruction procedure correctly.

total electron count = number of d electrons + electrons donated by ligands

For the Fe(II) complex above, the total electron count is thus 6 + (6 + 2 + 2 + 2) = 18. Let's work through another example: the complex below features an overall charge of +1. Water is a dative ligand—that "2" is very important!

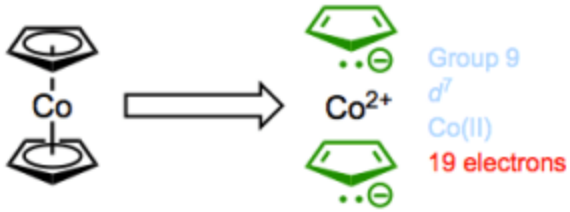


Note that the overall charge is lumped into the oxidation state and d electron count of Mo.

The oxidation state of molybdenum is +2 here...remember that the overall charge factors in to that. When everything is said and done, the total electron count is 4 + (6 + 2 + 2 + 2 + 2) = 18.

What's up with 18?! As it turns out, 18 electrons is a very common number for stable organometallic complexes. So common that the number got its own rule—the 18-electron rule—which states that stable transition-metal complexes possess 18 or fewer electrons. The rule is analogous to organic chemistry's octet rule. The typical explanation for the 18-electron rule points out that there are 9 valence orbitals (1 s, 3 p, 5 d) available to metals, and using all of these for bonding seems to produce the most stable complexes. Of course, as soon as the rule left the lips of some order-craving chemist, researchers set out to find counterexamples to it, and a number of counterexamples are known. Hartwig describes the rule as an "empirical guideline" with little theoretical support. In fact, theoretical studies have shown that the participation of p orbitals in complex MOs is unlikely. I know that's not what you want to hear—but hang with me! The 18-electron rule is still a very useful guideline. It's most interesting, in fact, when it is not satisfied.

One last example...how would you expect the complex below to react?



Cobaltocene: jonesing for chemical change.

If we assume that the 18-electron rule is true, then cobaltocene has a real problem. It possesses 7 + (6 + 6) = 19 total valence electrons! Yet, we can also reason that this complex will probably react to relieve the strain of not having 18 electrons by giving up an electron. Guess what? In practice, cobaltocene is a great one-electron reducing agent, and can be used to prepare anionic complexes through electron transfer.

$$CoCp_2 + ML_n \rightarrow [CoCp_2] + [ML_n]^- \tag{13.3.2.1}$$

This post described how to calculate total electron count and introduced the power of the 18-electron rule for predicting whether a complex will donate or accept electrons. We will definitely see these ideas again! But what happens when the electron counts of two complexes we're interested in comparing are the same? We'll need more information. In the next post, we'll explore the periodic trends of the transition series. Our goal will be to make meaningful comparisons between complexes of different metals.

Contributors and Attributions

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13.4: Survey of Organometallic Ligands

Organometallic chemistry may be taught in many ways. Some textbooks spend a significant chunk of time discussing ligands, while others forego ligand surveys to dive right in to reactions and mechanisms. I like the ligand survey approach because it allows you to get a grip on expected behaviour for each type of ligand before you see them pop up as intermediates in reaction cycles. With the general principles in hand, it becomes easier to generate explanations for observed each ligan's effect on a reactions. Instead of generalizing from complex, specific examples in the context of reaction mechanisms, we'll look at general trends first and apply these to reaction intermediates and mechanisms later. This section will kick off with carbon monoxide, a simple but fascinating ligand.

This section begins a survey of some of the most common or most interesting ligands in organometallic complexes. We will begin with a survey of ligands that participate in "dative" bonding to metal ions in this section (), followed by ligands that interact with metal ions through their π electrons, and those that have multiple metal-carbon bonds in the following sections.

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13.4.1: Carbon Monoxide (Carbonyl Complexes)

Introduction into Carbonyl Complexes

In this chapter we will look closer at carbonyl complexes, often just called carbonyls. Why? They are interesting for a number of reasons. Firstly, they are a quite extensive class of compounds with a diverse coordination chemistry. We will learn that the CO ligand can bind to a metal in various, sometimes non-obvious ways. Further, carbonyls are frequently used as starting materials for other coordination compounds. This is because the carbonyl ligand has no charge and carbon monoxide is a gas. Because of that a ligand substitution reaction can be easily driven to the right side by purging CO out of the reaction vessel. CO is a C_1 unit, and this is frequently used in catalysis with carbonyls. Carbonyls are often intermediates in reactions that add a single carbon atom to a hydrocarbon chain. A fascinating fundamental property of carbonyls is that its π-accepting properties stabilize metals in low, sometimes even negative oxidation numbers.

Bonding in CO

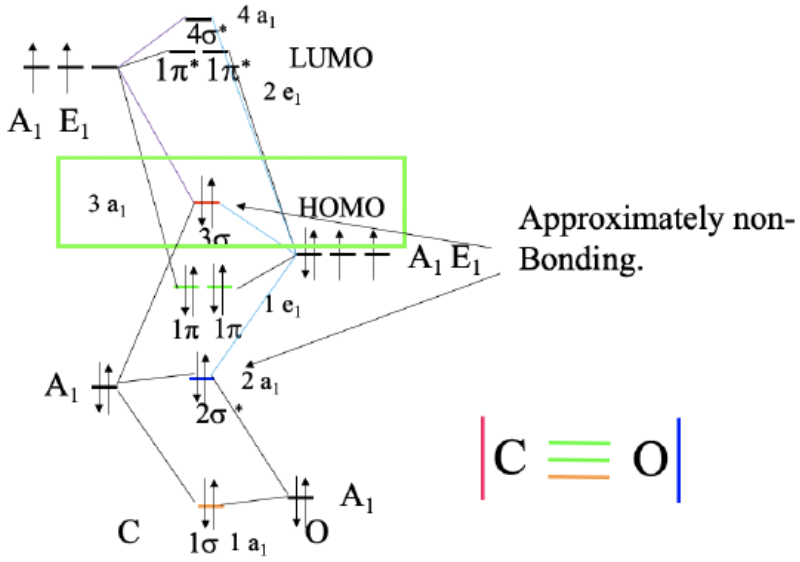


Figure 13.4.1.1: Bonding in the CO molecule. MO diagram (left), and corresponding valence bond structure (right). For more explaination click here.

The carbon in the CO molecule is the more reactive end, and thus CO prefers to bind with the carbon to a metal, and not with oxygen. This is not obvious because the carbon is less electronegative than oxygen. The reason is that the HOMO of the CO molecule is an approximately non-bonding orbital which is primarily localized at the carbon (Figure 13.4.1.1). In the valence bond picture it is resembled by the electron-lone pair at the carbon atom. The electron lone pair at the oxygen is resembled by the $2a_1$ molecular orbital which has a significantly lower energy, therefore it is rarely used in bonding. Both the π and π*-orbitals are relatively close in energy to the HOMO, and thus these orbitals can also be used for bonding in carbonyls. This explains the diverse coordination chemistry of carbonyls.

σ-binding Modes of The Carbonyl Ligand

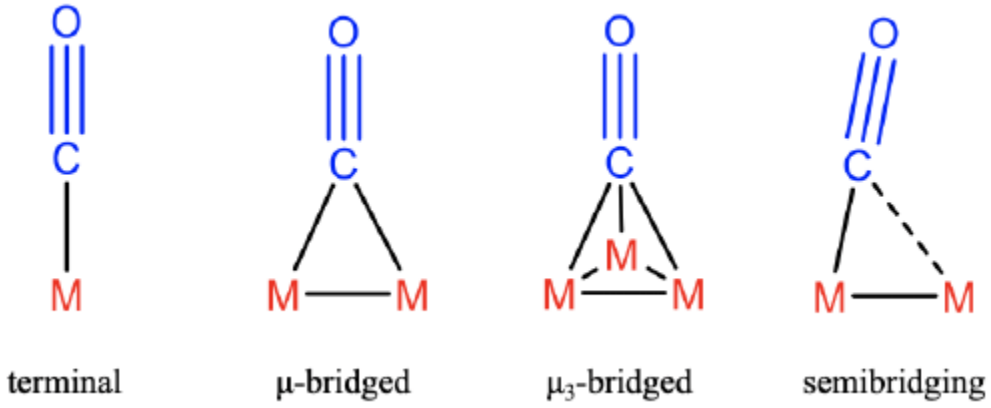


Figure 13.4.1.2: σ-binding modes of the carbonyl ligand. Attribution: W. Petz

In the most simple case the CO uses its electron lone pair at the carbon to bind to single metal atom M (Figure 13.4.1.2). In this case we call CO a terminal carbonyl ligand. In addition, it is possible that the electron lone pair is shared between two or even three metals that are interconnected via metal-metal bonds. In these cases, we say that the CO acts as a μ-bridged, and μ_3 -brigded ligand, respectively. If two metals held together by a metal-metal bond are different, then the interaction of CO with one metal may be stronger than with the other. In this case the CO ligand acts as a semibridging ligand. In all these cases CO acts as a 2-electron donor because it donates its two electrons in the electron lone pair in the carbon atom.

In addition to the electron lone pair at the carbon the CO ligand can also use its binding π-orbitals for electron-donation into metal orbitals (Figure 13.4.1.3). However, these electrons can only be used in conjunction with the electron lone pair at C because the electron pair has a higher energy than the π-electrons, and electrons of higher energy are always used first. For steric reasons the electron lone pair and the π-electrons are always donated to different metals that are held together by metal-metal bonds.

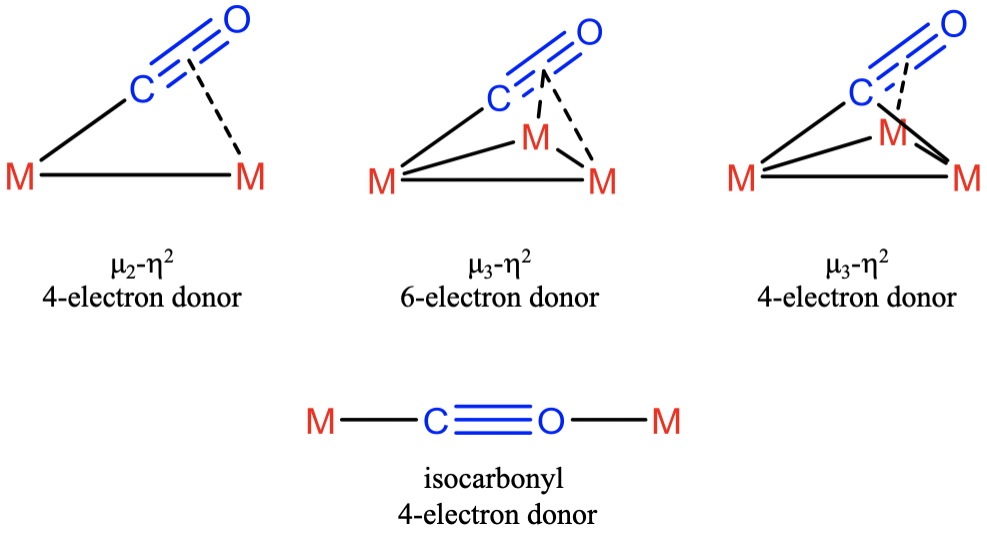


Figure 13.4.1.3: Binding in π-orbitals for electron-donation into metal orbitals. Attribution: W. Petz

In the most simple case the CO ligand binds in μ_2-η_2-mode which implies that the electron lone pair binds to one metal and two π-electrons bind to another. In this this case the CO ligand acts as a 4-electron donor. In addition, it is possible that all four π -electrons are involved involved in the bonding in addition to the electron lone pair. In this case three metal atoms are involved. The first one interacts with the electron-lone pair, the second one with the two π-electrons, and the third one with the other two π-electrons. Because three metals are bridged and both atoms of the ligand are involved in the bonding with the metal we can say that CO binds in μ_3-η_2-fashion and acts as a 6-electron donor. It is also possible that the electron-lone pair is being shared between two metals, and two π-electrons are donated to the third metal. Also in this case the ligand binds in μ_3-η_2-fashion, but acts as a 4-electron donor. Another way the CO ligand can act as 4-electron donor is when it acts as an isocarbonyl ligand. In this

case it uses its electron pairs at both the C and the O-atoms. This is only possible when steric circumstances favor the utilization of the O-electron lone pair over the energetically higher π-electrons. This is rare.

π-binding Modes of The Carbonyl Ligand

The carbonyl ligand can use its π*-orbitals for bonding with metal d-orbitals in π-fashion. The ligand acts as a π-acceptor. There are two possibilities for the binding (Figure 13.4.1.4).

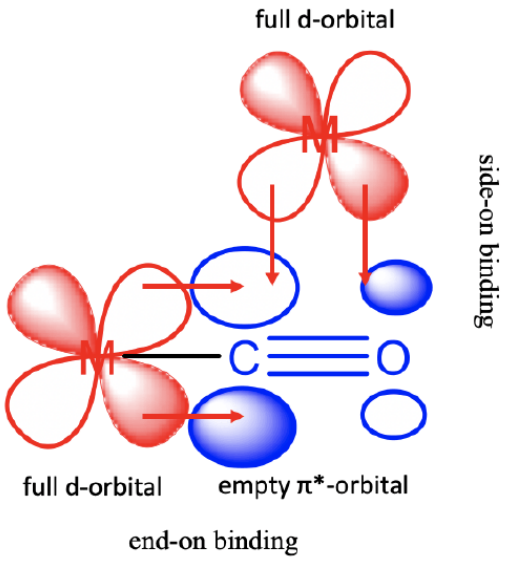


Figure 13.4.1.4: π-binding modes of the carbonyl ligand

The first one occurs when the CO-ligand acts as a terminal ligand binding end-on. In this case the two lobes of the π*-orbitals at the carbon interact with the the lobes of a metal d-orbital. Also the bonding π-orbitals have the right symmetry to overlap with the metal d-orbital in this mode, but their energies are much further away from those of the d-orbitals, so that these interactions can be neglected. The second possibility is that the CO binds side-on to the a metal-d-orbital. In this case one lobe at C and one lobe at O interacts with the metal d-orbital. These interactions are less strong compared to the end-on interactions because the orbital overlap is less efficient due to the unequal size of the lobes of the π*-orbital. The π*-orbital is mostly localized at the carbon-atom because the carbon atom is the more electropositive atom. Note that the bonding π-orbitals do not have the right symmetry to overlap with a metal-d orbital in π-fashion, they can only overlap in σ-fashion when the binding is side-on.

The Dewar-Chatt-Duncanson model

The σ-donor and the π-acceptor interactions in carbonyl complexes synergistically reinforce each other. This synergistic effect is called the Dewar-Chatt-Duncanson model for carbonyls. How can we understand the synergistic interactions. Let us consider a carbonyl ligand that binds end-on to a metal.



Figure 13.4.1.5: σ-donor and the π-acceptor interactions in carbonyl complexes.

Let us first look at the σ-donor interactions. The electron lone pair at the carbon donates electron density into empty metal d-orbitals and a dative bond is formed between the metal and the carbon. The donated electron density enhances the energy of the metal d-electrons due to increased electron-electron repulsion. Because of their increased energy the d-electrons get more easily accepted by the carbonyl ligand through the π-acceptor interactions. The π-acceptor interactions increase the bond order between the metal and the carbon bond. At the same time the bond order between carbon and oxygen gets decreases because electron density has been transferred from the metal into the π*-orbitals (Figure 13.4.1.5).

The strength of the π-acceptor interactions can differ significantly in carbonyls. One can draw three different structures for weak, intermediate, and strong π-acceptor interactions (Figure 13.4.1.6 to 13.4.1.8).



Figure 13.4.1.6: Weak π-acceptor interactions

When only weak interactions are present we can represent the M-C bond as a single bond, and the C-O bond as a triple bond.



Figure 13.4.1.7: Intermediate π-acceptor interactions

When the interactions have intermediate strength we can represent both the M-C bond and the C-O bond as a double-bonds.



Figure 13.4.1.8: Strong π-acceptor interactions

When the π-acceptor interactions are strong then the M-C bond becomes a triple bond and the C-O bond becomes a single bond.

On what does the strength of the π-acceptor interactions depend? It depends mostly on the charge on the carbonyl. Carbonyl cations with a charge of +2 or higher tend to have weak π-acceptor interactions. Neutral carbonyls or carbonyls with a +1 or -1 charge have intermediate π-acceptor interactions. and those with a negative charge of 2- or higher have strong π-acceptor interactions. One can see from this that the smaller the positive charge and the higher the negative charge, the higher the metal-carbon bond-order, and the stronger the metal-carbon bond. As a consequence negative charges tend to stabilize carbonyls, while positive charges destabilize them. Therefore, carbonylate anions tend to be more stable compared to carbonyl cations. The stability of neutral carbonyls is intermediate.

Homoleptic Carbonyls of The Transition Metals

After having understood the principles of the bonding in carbonyls let us next think about what structures transition metal carbonyls make. The structures follow mostly the 18 electron rule. For the most simple homoleptic carbonyls, in which the carbonyl ligand binds end-on to the transition metal acting as a two-electron donor, we would just assemble as many ligands as needed until we have 18 electrons. This would give us the coordination number in the carbonyl from which we could deduct the structure. This works well for transition metals with an even number of valence electrons.

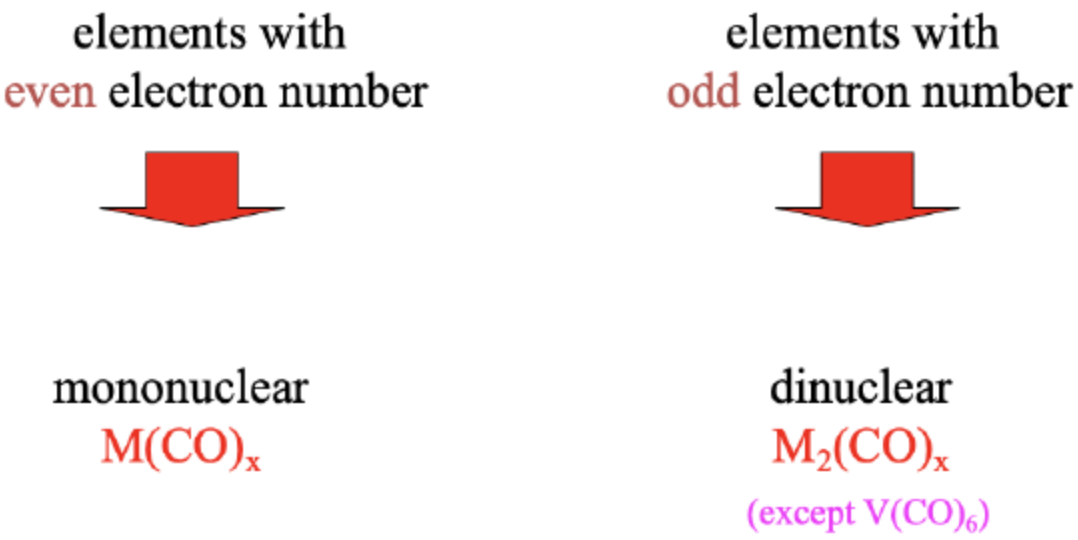


Figure 13.4.1.9: Mononuclear carbonyls vs dinuclear carbonyls. Attribution: W. Petz

In this case the number of ligands x is just 18 minus the number of metal electrons divided by 2. We would therefore expect a mononuclear carbonyl of the type $M(CO)_x$ (Figure 13.4.1.9). For metals with an odd number of electrons, the situation is more complicated because an odd number times two multiplied with an integer number never gives 18. In this case, as many ligands x as needed to make a 17 valence electron complex are added to the metal, and then the 17 valence electron complex dimerizes to form a dinuclear carbonyl of the composition $M_2(CO)_x$. An exception is the vanadium. It makes a 17 valence electron vanadium hexacarbonyl that does not dimerize because a coordination number of 7 is not favorable.

Homoleptic carbonyls of the 6th group (M = Cr, Mo, W)

Now let us look closer at the carbonyls with metals with an even number of electrons. We can start out with group 6 which contains the elements chromium, molybdenum, and tungsten. Our task is to determine the composition and structure of the carbonyls.

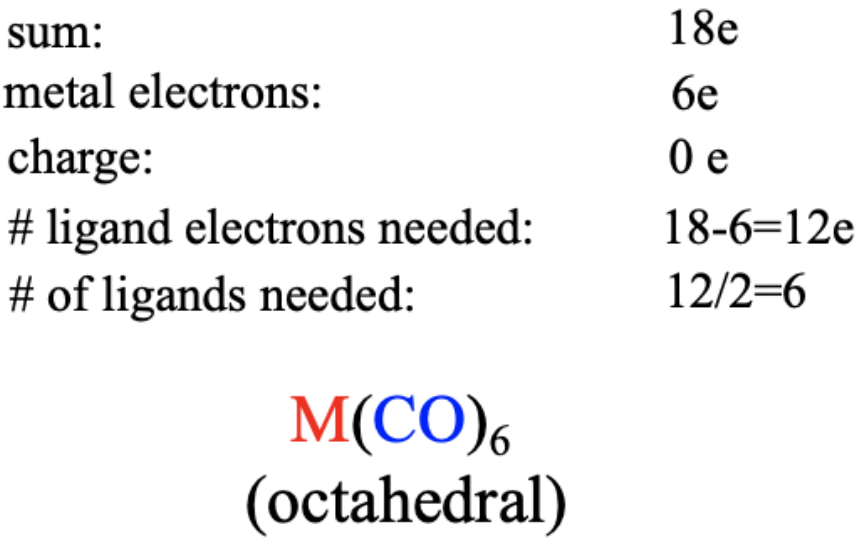


Figure 13.4.1.10: Determining the composition and structure of carbonyls via electron counting

According to the 18 electron rule we need 18 electrons overall. How many are contributed by the metal? Because the metals are in group 6, they all have six electrons. The carbonyls carry no charge, so there are no electrons to be subtracted or added. How many ligand electrons do we need to get to 18? Well, that is 18-6=12 electrons. How many carbonyl ligands are needed then? Because each ligand is considered a two electron donor, we need 12/2=6 ligands. The composition of the carbonyl will therefore

be $M(CO)_6$. The carbonyl adopts octahedral shape in order to maximize the distance of the ligands from each other. The group 6 carbonyls are colorless, crystalline, and sublimable solids.

Charged Octahedral Carbonyls with 18 Electrons

	ν(CO)/cm^{-1}		ν(CO)/cm^{-1}		ν(CO)/cm^{-1}
$[Co(CO)_6]^{3+}$		$[Rh(CO)_6]^{3+}$		$[Ir(CO)_6]^{3+}$	2254
$[Fe(CO)_6]^{2+}$	2204	$[Ru(CO)_6]^{2+}$	2199	$[Os(CO)_6]^{2+}$	2190
$[Mn(CO)_6]^{+}$	2100	$[Tc(CO)_6]^{+}$	not reported	$[Re(CO)_6]^{+}$	2085
$Cr(CO)_6$	1986	$Mo(CO)_6$	1986	$W(CO)_6$	1977
$[V(CO)_6]^{-}$	1847	$[Nb(CO)_6]^{-}$	1850	$[Ta(CO)_6]^{-}$	1850
$[Ti(CO)_6]^{2-}$	1750	$[Zr(CO)_6]^{2-}$	1757	$[Hf(CO)_6]^{2-}$	1757

Figure 13.4.1.11 Charged octahedral 18 electron carbonyls and the wave number of their C-O stretch vibrations. Green: Known charged carbonyls, Red: Unknown charged carbonyls.

Are there also other 18 e carbonyls of the type $M(CO)_6$ with other metals but group 6 metals? Yes, but the charge at the carbonyl needs to be adjusted so that the complex has 18 electrons. For instance, we can replace Cr by V, but then the we need a 1- charge which results in a carbonylate of the formula $V(CO)_6^-$. Why? The vanadium is in group 5 and has one electron less than chromium. For that reason, we must add an electron which gives the complex a 1- charge. Also the higher homologues $Nb(CO)_6^-$ and $Ta(CO)_6^-$ are known. What if we go further to the left in the periodic table? Titanium is left to the vanadium, and has four valence electrons. Therefore, the 18 valence electron hexacarbonyl of titanium has a 2- charge, and the formula is $Ti(CO)_6^{2-}$. Again, the higher homologues of $Ti(CO)_6^{2-}$, the $Zr(CO)_6^{2-}$ and the $Hf(CO)_6^{2-}$ are also known. Can we also go to the right in the periodic table? Manganese sits to the right of the chromium. The manganese has one electron more than the chromium, therefore the 18 electron hexacarbonyl of manganese must be a carbonyl cation with a 1+ charge, and the formula is $Mn(CO)_6^{2+}$. Of the higher homologues, both the $Tc(CO)_6^+$ and the $Re(CO)_6^+$ are known, too. To the right of the Mn, there is the Fe which has 8 valence electrons. Therefore the 18 electron iron hexacarbonyl must have a 2+ charge, and the formula is $Fe(CO)_6^{2+}$. The higher homologues $Ru(CO)_6^{2+}$ and $Os(CO)_6^{2+}$ are also known. Can we go even further to the left, to the Co? The expected formula for Co carbonyl would be $Co(CO)_6^{3+}$, but it is not known, and neither is the higher homologue, the $Rh(CO)_6^{3+}$. Only the $Ir(CO)_6^{3+}$ has been isolated. This reflects a general trend in carbonyl chemistry. Positive charges destabilize the carbonyl, and carbonyls with high positive charges are frequently not stable. On the other hand, negative charges stabilize a carbonyl and even carbonylates with high negative charges are stable. We can easily explain this by the fact that the bond order between the metal and the carbon decreases with increasing positive charge, and increases with increasing negative charge. Increasing bond order strengthens the stability of the carbonyl. We see from this that the π-acceptor properties are quite important for the stability of carbonyls. We also see that in carbonylates the oxidation numbers of the metals are negative. Negative oxidation numbers are quite unusual for metals. We conclude that the carbonyl ligand has the unusual property to stabilize the metal in negative oxidation states.

Is there a way to easily measure the bond order of an M-C bond? We can do this indirectly by measuring the IR-spectrum of the carbonyl. Because the bond order of the C-O bond decreases with increasing bond order for the M-C bond, the wavenumber for the C-O stretch vibration can be used as a measure for the M-C bond order. The lower the wavenumber, the lower the C-O bond order, and the higher the M-C bond order. When we look at the numbers for the different carbonyls within a period we see that as expected the wavenumbers increase with increasing group number indicating a decreasing bond order. We can also look down the groups. We see that in this case, the numbers hardly change, meaning that the bond order is hardly affected by the period of the metal.

Homoleptic Carbonyls of the 8th Group (Fe, Ru, Os)

What charge-neutral carbonyls would we expect for the group 8 elements Fe, Ru, and Os?

sum:	18e
metal electrons:	8e
charge:	0 e
# ligand electrons needed:	18-8=10e
# of ligands needed:	10/2=5

$M(CO)_5$
(trigonal-bibyramidal)

Figure 13.4.1.12: Carbonyls for the group 8 elements

Overall, these carbonyl need to have 18 electrons. In this case the metals have 8 electrons. The charge is 0. This means that we would have 18-8=10 electrons that would need to come from the ligand. The number of ligands needed would therefore be 10/2=5. Thus, we would expect pentacarbonyls of the composition $M(CO)_5$ (Figure 13.4.1.12). These carbonyls adopt the trigonal-bipyramidal shape. The group 8 carbonyls are all liquids. The iron pentacarbonyl has a light-orange color while the ruthenium and the osmium carbonyls are colorless.

Charged Trigonal-Bipyramidal Carbonyls with 18 electrons

$[Ni(CO)_5]^{2+}$	$[Pd(CO)_5]^{2+}$	$[Pt(CO)_5]^{2+}$
$[Co(CO)_5]^{+}$	$[Rh(CO)_5]^{+}$	$[Ir(CO)_5]^{+}$
$Fe(CO)_5$	$Ru(CO)_5$	$Os(CO)_5$
$[Mn(CO)_5]^{-}$	$[Tc(CO)_5]^{-}$	$[Re(CO)_5]^{-}$
$[Cr(CO)_5]^{2-}$	$[Mo(CO)_5]^{2-}$	$[W(CO)_5]^{2-}$
$[V(CO)_5]^{3-}$	$[Nb(CO)_5]^{3-}$	$[Ta(CO)_5]^{3-}$

Figure 13.4.1.13: 18 Charged trigonal-bipyramidal carbonyls with 18 electrons. Green: Known charged carbonyls, Red: unknown charged carbonyls.

We can again ask if there are charged isosteric pentacarbonyls with 18 e of metals other than group 8 metals. The answer is yes. The manganese is left to the iron in the periodic table and has one electron less. Therefore its pentacarbonyl needs to have a 1- charge and the composition is $Mn(CO)_5^-$. Also the higher homologues, the $Tc(CO)_5^-$ and the $Re(CO)_5^-$ exist. The Cr has one

electron less than than the Mn, therefore its pentacarbonyl has a 2- charge and the formula is $Cr(CO)_5^{2-}$. $Mo(CO)_5^{2-}$ and $W(CO)_5^{2-}$ are also known. The vanadium has another electron less because it is in the 5th group, therefore its pentacarbonyl has a 3- charge, and the formula is $V(CO)_5^{3-}$. Again, the higher homologues, the $Nb(CO)_5^{3-}$ and the $Ta(CO)_5^{3-}$ are also stable. Also for the pentacarbonylates high negative charges are no problem for the stability of the complexes due to the stabilizing effect of the π-acceptor interactions. What about carbonyl cations with trigonal bipyramidal shape? As we go from Fe to Co, we need a 1+ charge at the carbonyl to achieve 18 electrons. The respective $Co(CO)_5^+$ cation is stable, and so are their higher homologues, the $Rh(CO)_5^+$ and the $Ir(CO)_5^+$. However, the group 10 pentacarbonyl cations $Ni(CO)_5^{2+}$, $Pd(CO)_5^{2+}$, and $Pt(CO)_5^{2+}$ are not stable. The 2+ positive charge weakens the metal-carbon bond too much. This behavior is consistent with the weakening of the M-C bond with increasing positive charge due to weaker π-acceptor effects.

Homoleptic carbonyls of group 10 (Ni, Pd, Pt)

What about the group 10 carbonyls?

sum:	18e
metal electrons:	10e
charge:	0 e
# ligand electrons needed:	18-10=8e
# of ligands needed:	8/2=4

$M(CO)_4$
(tetrahedral)

Figure 13.4.1.14: Carbonyls for the group 10 elements

In this case the metals have 10 electrons. There is no charge. The number of ligand electrons needed is 18-10 = 8 electrons. Thus, the number of ligands is 8/2=4. Therefore, the composition is $M(CO)_4$ (Figure 13.4.1.14). The shape is tetrahedral because we have an 18 and not a 16 valence electron complex. Nickel tetracarbonyl is a volatile, colorless liquid. The higher homologues, the $Pd(CO)_4$ and the $Pt(CO)_4$ are not stable. We can explain this when remembering that the π-orbital overlap in tetrahedral complexes is generally weak. Therefore, the M-C carbon bond is less effectively stabilized by the π-acceptor interactions compared to octahedral and trigonal-bipyramidal carbonyls. This effect is even more pronounced for the Pd and Pt carbonyls because they have larger orbitals that can overlap even less effectively with the relatively small π^*-orbitals of the CO ligand. In this case the π -acceptor interactions are so weak so that the entire molecule is no longer stable.

Charged Tetrahedral Carbonyls with 18 electrons

$[Cu(CO)_4]^+$	$[Ag(CO)_4]^+$	$[Au(CO)_4]^+$
$Ni(CO)_4$	$Pd(CO)_4$	$Pt(CO)_4$
$[Co(CO)_4]^-$	$[Rh(CO)_4]^-$	$[Ir(CO)_4]^-$
$[Fe(CO)_4]^{2-}$	$[Ru(CO)_4]^{2-}$	$[Os(CO)_4]^{2-}$
$[Mn(CO)_4]^{3-}$	$[Tc(CO)_4]^{3-}$	$[Re(CO)_4]^{3-}$
$[Cr(CO)_4]^{4-}$	$[Mo(CO)_4]^{4-}$	$[W(CO)_4]^{4-}$

Figure 13.4.1.15: Charged tetrahedral carbonyls with 18 electrons. Green: Known carbonyls. Red: Unknown carbonyls.

What about charged 18 electron tetrahedral carbonyls with other metals? Again, negatively charged carbonylates are stable, even with high negative charges. $Co(CO)_4^-$, $Fe(CO)_4^{2-}$, $Mn(CO)_4^{3-}$, and $Cr(CO)_4^{4-}$ are all stable and so are their higher homologues. The $Cu(CO))_4^+$ which has a 1+ positive charge is also known, but its higher homologues, the $Ag(CO)_4^+$ and the $Au(CO)_4^+$ are not.

Overall Stability Trends

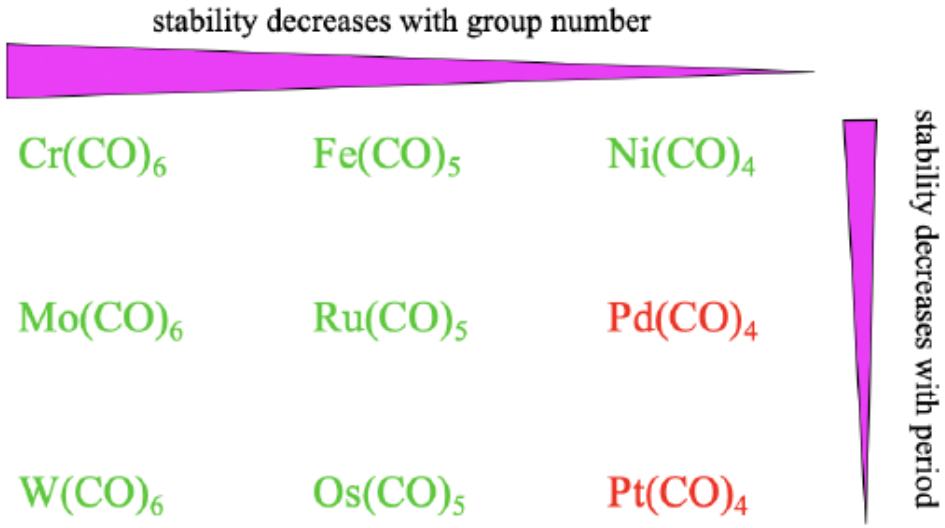


Figure 13.4.1.16: Stability trends. Attribution: W. Petz

Overall the stability of carbonyls tends to decrease from group 6 to group 8 to group 10 (Figure 13.4.1.16). This trend is because the octahedral shape allows for the best orbital overlap for π-acceptor interactions, followed by the trigonal bipyramidal, followed by the tetrahedral shape. The stability also tends to decline from the 4th to the 6th period. This trend can be explained by less efficient orbital overlap due to increasingly different orbital size between the ligand and the metal orbitals. These effects are sufficiently large for $Pd(CO)_4$ and $Pt(CO)_4$ to make them instable.

Group 4 and Group 12 Carbonyls (non-existing)

We have discussed group 6, 8, and 10 carbonyls, but not group 4 and group 12. Why? Because no carbonyls of these groups are stable. What is the reason? For group 4 carbonyls, we would need seven carbonyl ligands. This would lead to a coordination number of seven which is unacceptably high for carbonyls. For group 12 carbonyls, we would only need three carbonyl ligands. This would lead to an unacceptably low coordination number of 3.

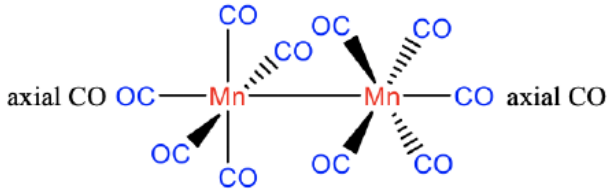
Homoleptic carbonyls of the 7th group (M = Mn, Tc, Re)

Now let us think about what structures the homoleptic carbonyls with metals having an odd number of electrons form. Let us start with the 7th group which consists of the metals Mn, Tc, and Re. Our approach is to see how many ligands we need to produce a 17 valence electron fragment, and then dimerize that fragment.

sum:	17e
metal electrons:	7e
charge:	0 e
# ligand electrons needed:	17-7=10e
# of ligands needed:	10/2=5

$(CO)_5M\text{-}M(CO)_5 = M_2(CO)_{10}$

(derived from octahedral $M(CO)_5L$ (L=$M(CO)_5$))



8 equatorial CO ligands

Figure 13.4.1.17: Homoleptic carbonyls with group 7 metals. Attribution: W. Petz.

The group 7 metals have seven valence electrons. Again, we will assume that there is no charge on the carbonyl. The number of ligand electrons to produce the 17 valence electrons fragment will therefore be 17-7 = 10. The number of ligands needed is therefore 10/2=5 assuming that the carbonyl ligand is a 2-electron donor binding end-on to the metal. This gives an $M(CO)_5$ fragment that dimerizes to form an $M_2(CO)_{10}$ carbonyl with a metal-metal bond. The structure can be thought to be derived from an octahedral structure in which each metal is surrounded octahedrally by five CO ligands and an $M(CO)_5$ fragment acting as the sixth ligand. Each $M(CO)_5$ unit has one axial ligand and four equatorial ligands, whereby the axial ligand is co-directional with the metal-metal bond. The four equatorial ligands of the first metal are in staggered conformation relative to the four equatorial ligands of the second metal due to steric repulsion arguments.

Charged Isoelectronic Carbonyls of the Type $M_2(CO)_{10}$

Can we make charged isoelectronic carbonyls of the type $M_2(CO)_{10}$ with other metals? The answer is yes, but only carbonylate anions with low negative charge, and no carbonyl cations. The formation of carbonyl cations is prohibited because of the weakening of the π-acceptor interactions that result from the positive charge. High negative charges are not possible because too many negative charges on the metal atoms lead to electrostatic repulsion and the destabilization of the metal-metal bonds.

$Mn_2(CO)_{10}$ $Tc_2(CO)_{10}$ $Re_2(CO)_{10}$

$[Cr_2(CO)_{10}]^{2-}$ $[Mo_2(CO)_{10}]^{2-}$ $[W_2(CO)_{10}]^{2-}$

Figure 13.4.1.18: Charged isoelectronic carbonyls of the type $M_2(CO)_{10}$

There are therefore only $Cr_2(CO)_{10}^{2-}$, and the higher homologues $Mo_2(CO)_{10}^{2-}$ and $W_2(CO)_{10}^{2-}$, but no other M_2CO_{10} type carbonyl ions.

Homoleptic carbonyls of the 9th group (M = Co, Rh, Ir)

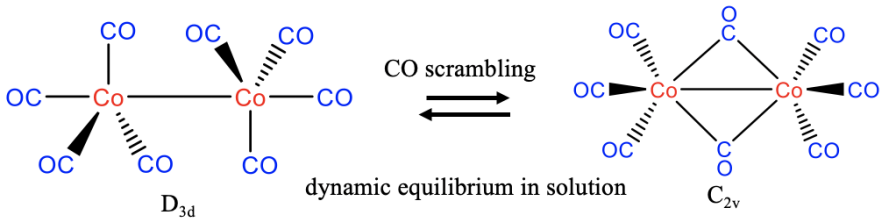
What are the expected structures for the homoleptic carbonyls of group 9?

sum:	17e
metal electrons:	9e
charge:	0 e
# ligand electrons needed:	17-9=8e
# of ligands needed:	8/2=4

$(CO)_4M\text{-}M(CO)_4 = M_2(CO)_8$

(derived from trigonal-bipyramidal $M(CO)_4L$ (L=$M(CO)_4$))

Only $Co_2(CO)_8$ is stable ($Rh_2(CO)_8$ and $Ir_2(CO)_8$ are unstable)



C_{2v} structure is present in solid exclusively.

Figure 13.4.1.19: Homoleptic carbonyls of the group 9 metals. Attribution: W. Petz.

In this case, the metal contributes 9 electrons, and this means that 17-9=8 electrons need to come from the carbonyl ligand. We therefore need 8/2=4 CO molecules to produce an $M(CO)_4$ 17 valence electron fragment. Two of the fragments then dimerize to form a dinuclear carbonyl of the composition M_2CO_8. In nature, however, only the Co-carbonyl is realized, the Rh and the Ir analogs are unstable. The structure of the $Co_2(CO)_8$ carbonyl can be derived from an $M(CO)_4L$ trigonal-pyramid, whereby L is the second $M(CO)_4$ unit (Fig. 10.2.19). According to that, the coordination number is 5. There are two axial and six equatorial ligands whereby the equatorial ligands are oriented in a staggered conformation. In solution this structure is in dynamic equilibrium with a second structure with C_{2v} symmetry in which two CO ligands are bridging. Due to this equilibrium there is constant ligand scrambling, meaning that the CO ligands constantly move from axial to equatorial positions, and migrate from one metal atom to the other. In solid state the C_{2v}-type structure is present exclusively indicating that it is slightly more stable.

Charged Isoelectronic Carbonyls of the Type $M_2(CO)_8$

The charged, isoelectronic carbonyls of the type $M_2(CO)_8$ behave similarly to that of the type $M_2(CO)_{10}$. There are no highly charged binuclear carbonylate anions, and no carbonyl cations.

$Co_2(CO)_8$ $Rh_2(CO)_8$ $Ir_2(CO)_8$

$[Fe_2(CO)_8]^{2-}$ $[Ru_2(CO)_8]^{2-}$ $[Os_2(CO)_8]^{2-}$

Figure 13.4.1.20: Charged isoelectronic carbonyls of the type $M_2(CO)_8$ (green: stable carbonyl. red: unstable carbonyl)

There are only the weakly negatively charged $[Fe_2(CO)_8]^{2-}$, $[Ru_2(CO)_8]^{2-}$, and $[Os_2(CO)_8]^{2-}$. The weakly negative charge stabilizes the metal-carbon bond without destabilizing the metal-metal bond too much. We can further see from this that a weakly negative charge is better for the stability of the species than no charge at all.

Homoleptic Carbonyls of the 11th Group (M = Cu, Ag, Au)

The group 11 metals Cu, Ag, and Au have eleven valence electrons.

sum:	17e
metal electrons:	11e
charge:	0 e
# ligand electrons needed:	17-11=6e
# of ligands needed:	6/2=3

$(CO)_3M\text{-}M(CO)_3 = M_2(CO)_6$

(derived from tetrahedral $M(CO)_3L$ (L=$M(CO)_3$))

$Cu_2(CO)_6$, $Ag_2(CO)_3$, and $Au_2(CO)_3$ are not known. but....

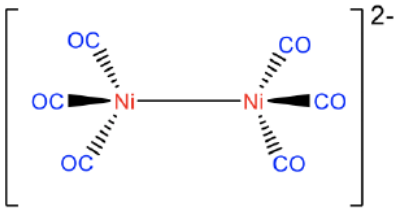


Figure 13.4.1.21: Homoleptic carbonyls of the 11th group metals (Attribution: W. Petz)

Therefore, six ligand electrons are needed to achieve 17 electrons (Figure 13.4.1.21). This means that 6/2=3 CO ligands are required to produce the 17 valence electron fragment. The dimer of it has the composition $M_2(CO)_6$ and its structure can be derived from a tetrahedral $M(CO)_3L$ structure in which L is the second $M(CO)_3$ fragment. Neither the Cu, nor the Ag, nor the Au carbonyl are known due to the weak π-overlap in tetrahedral coordination. However, the weakly negatively $[Ni_2(CO)_6]^{2-}$ ion is known which may be explained by the stabilizing effect of one negative charge on the M-C bond.

Overall Stability Trends

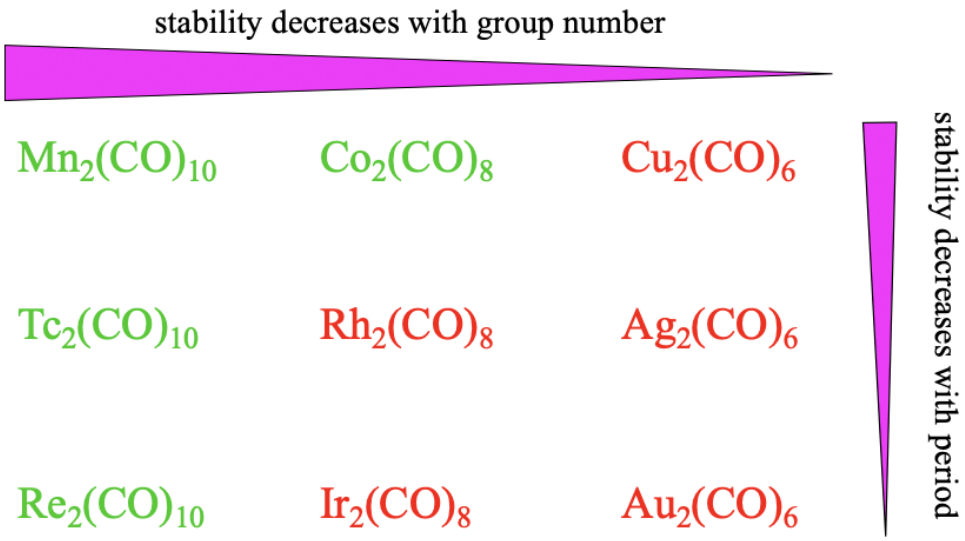


Figure 13.4.1.22: Overall stability trends for dinuclear carbonyls. Green: stable. Red: Unstable.

Overall, we see the same stability trends for the dinuclear carbonyls as compared to the mononuclear ones. The stability decreases with the group number because π-overlap becomes smaller with smaller coordination numbers. Also, we see that the stability decreases with the period because of decreasing match of orbital sizes.

Homoleptic carbonyls of the 5th group (M = V, Nb, Ta)

The 17 valence electron fragment of the carbonyl of vanadium has the composition $V(CO)_6$. It does not dimerize because the coordination number of 6 is much more favorable compared to the coordination number 7. $V(CO)_6$ is a dark violet radical of octahedral shape. The radical electron is sterically inactive. $V(CO)_6$ can be used as an oxidant because it can be reduced easily to the 18 valence electron species $V(CO)_6^-$. The higher homologues $Nb(CO)_6$ and $Ta(CO)_6$ are not known. This may be explained by the weaker orbital overlap between the relatively small π^*-orbitals of the carbonyl ligand and the large metal d-orbitals of Nb and Ta.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

Synthesis

Metal carbonyl complexes containing only CO ligands abound, but most cannot be synthesized by the method we all wish worked, bathing the elemental metal in an atmosphere of carbon monoxide (entropy is a problem, as we already discussed for $W(CO)_6$). This method does work for nickel(0) and iron(0) carbonyls, however.

$M + n\ CO \rightarrow M(CO)_n$ [M = Fe, n = 5; M = Ni, n = 4]

Other metal carbonyl complexes can be prepared by **reductive carbonylation**, the treatment of a high-oxidation-state complex with CO. These methods usually require significant heat and pressure. One example:

$WCl_6 + CO + \text{heat, pressure} \rightarrow W(CO)_6$

Still other methods employ **deinsertion** from organic carbonyl compounds like dimethylformamide. These methods are particularly useful for preparing mixed carbonyl complexes in the presence of reducing ligands like phosphines.

$IrCl_3(H_2O)_3 + 3\ PPh_3 + HCONMe_2 + PhNH_2 \rightarrow IrCl(CO)(PPh_3)_2 + (Me_2NH_2)Cl + OPPh_3 + (PhNH_3)Cl + 2\ H_2O$

The key thing to notice about the reaction above is that the CO ligand is derived from dimethylformamide (DMF).

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13.4.2: Ligands similar to CO

Now let us leave the CO ligand, consider a number of related ligands, and discuss similarities and differences compared to the CO ligand.

The cyano ligand (CN^-)

Let us start with the cyano ligand $\mathrm{CN^-}$. This ligand is isoelectronic to the CO ligand. The N atom has one electron less than O, but the negative charge at the cyanide ligand compensates for that. One question we can ask is: What is the reactive end? The answer is: In analogy to the carbonyl ligand the reactive end is the carbon atom. We can explain this by the fact that the MO diagram is similar to that of CO, only the differences in atomic orbital energies are smaller due to the smaller electronegativity difference between C and N compared to C and O. Therefore, like in CO, the HOMO is represented by the electron lone pair at the C, which makes C the more reactive end. Due to the smaller electronegativity difference, the difference in energy between the lone pair at C and the lone pair at N is smaller, therefore, in contrast to CO, the cyano ligand acts far more often as a bridging ligand between two metals using both of its electron lone pairs.

Would we expect the cyano ligand to be a stronger or weaker σ-donor compared to the CO ligand? Think about it for a moment. The answer is: It is a stronger σ-donor because of its negative charge. The negative charge at the ligand increases electrostatic repulsion between the electrons, and this increases the orbital energies. Therefore, there is a stronger tendency to donate the electrons. Our next question is: Is the $\mathrm{CN^-}$ ligand a stronger or weaker π-acceptor than CO? The energy of the π^*-orbitals is higher compared to CO because of the negative charge at the ligand. Because of that, electrons from the metal cannot be as easily accepted by the ligand. Therefore, the cyano ligand is a weaker π-acceptor than the carbonyl ligand. Our last question is: Are cyano complexes more stable with metals in high or low oxidation states. Because of electrostatic arguments a cyanide anion interacts more strongly with a metal cation rather than a metal in a zero or negative oxidation state. Therefore, unlike CO, $\mathrm{CN^-}$ does not stabilize metals in low oxidation states. It prefers to make complexes with metal in high, positive oxidation numbers.

The Nitrosyl Ligand NO

The nitrosyl ligand NO is another ligand similar to CO. It has one more electron that CO because N has one more electron than C. The additional electron makes NO an “odd” molecule with a radical electron. Like in CO and $\mathrm{CN^-}$, the more electropositive element is the reactive end. In the case of NO it is the N atom. The radical electron is the most reactive electron that can be most easily donated, however the electron lone pair at N may be donated in addition. In the former case, the NO is a 1-electron donor, in the latter it is a 3-electron donor. How can we tell if one or three electrons have been donated? When only one electron is donated, the electron lone pair at the nitrogen is sterically active and leads to a bent structure (Fig. 13.4.2.1).

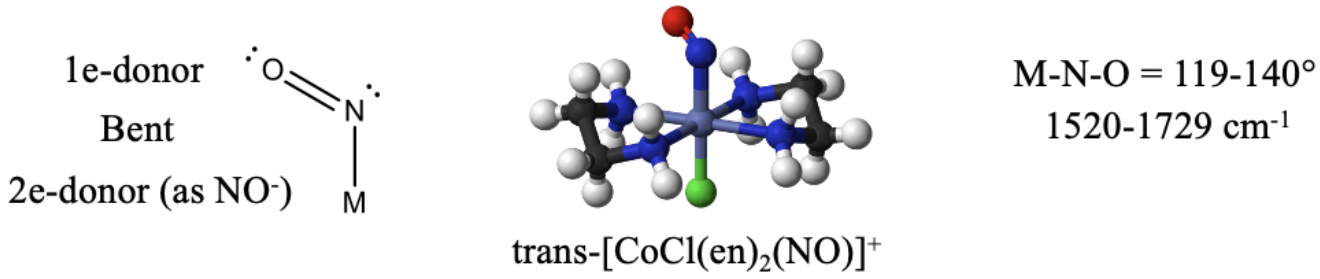


Figure 13.4.2.1: The Trans-bis-(ethylenediamine)chloronitrosyl cobalt (1+) cation as an example of an NO complex with NO as 1e donor.

An example is the trans-bis-(ethylenediamine)chloronitrosyl cobalt (1+) cation. Generally, the $\mathrm{O{-}N{-}M}$ bond angle in nitrosyl complexes with NO as a 1e-donor can vary between 119 and 140°. We can also identify a bent nitrosyl ligand in the IR spectrum. Typical wave numbers are 1520-1729 $\mathrm{cm^{-1}}$.

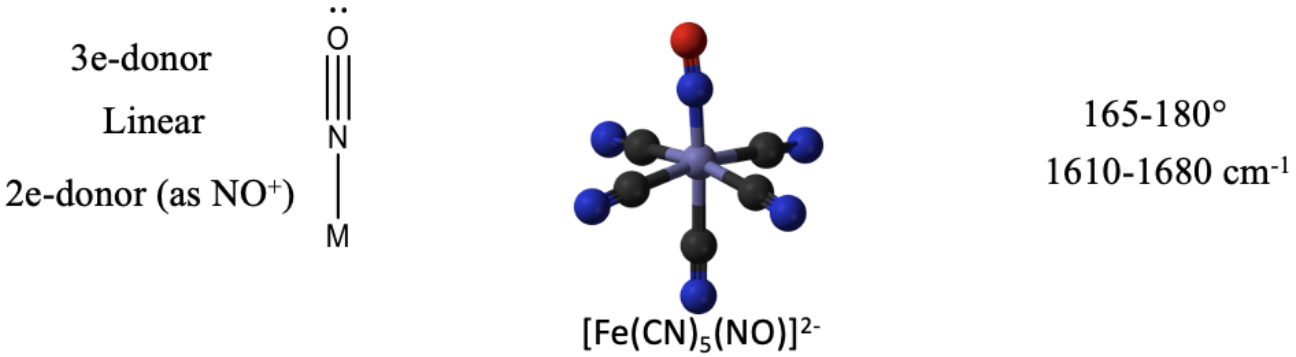


Figure 13.4.2.2: THe Nitroprusside anion as an example of a complex with NO as a 3e donor. (Attribution: Benjah-bmm27 / Public domain https://commons.wikimedia.org/wiki/F...l-3D-balls.png)

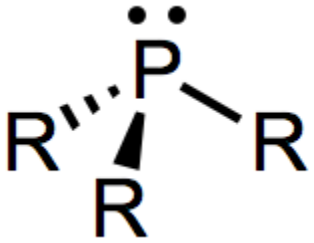
When the nitrosyl ligand donates all three electrons, then it binds to the metal in a linear fashion (Fig. 13.4.2.2). The electron lone pair is no longer sterically active because it is involved in the bonding. An example is the nitroprusside anion $[Fe(CN)_5(NO)]^{2-}$. It is used as a medication for the treatment of high blood pressure. The bond angles in complexes with NO as the 3-electron donor are often not exactly 180°, but vary between 165 and 180°. It can also be identified in the IR because it has a characteristic band between 1610-1680 cm^{-1}.

There is a also a different view on nitrosyl complexes with linear and bent structures. In bent structures we can also consider the ligand as an NO^- anion that donates two electrons. The NO^- anion has two electron lone pairs at N. When it donates two electrons then one sterically active electron lone pair remains at the nitrogen atom. In linear structures we can regard the ligand also as an NO^+ cation that donates two electrons. An NO^+ cation has one electron lone pair at N, and when it donates that lone pair then there is no sterically active electron at the nitrogen left, and thus the ligand binds in a linear fashion.

We could also ask: What can neutral NO not be a 2-electron donor with the radical electron left at N? The answer is: The radical electron is the highest energy electron, and is always used first in interactions with a metal.

Phosphine Ligands

Phosphines are most notable for their remarkable electronic and steric tunability and their “innocence”—they tend to avoid participating directly in organometallic reactions, but have the ability to profoundly modulate the electronic properties of the metal center to which they’re bound. Furthermore, because the energy barrier to umbrella flipping of phosphines is quite high, “chiral-at-phosphorus” ligands can be isolated in enantioenriched form and introduced to metal centers, bringing asymmetry just about as close to the metal as it can get in chiral complexes. Phosphorus NMR is a technique that Just Works (thanks, nature). Soft phosphines match up very well with the soft low-valent transition metals. Electron-poor phosphines are even good π-acids!

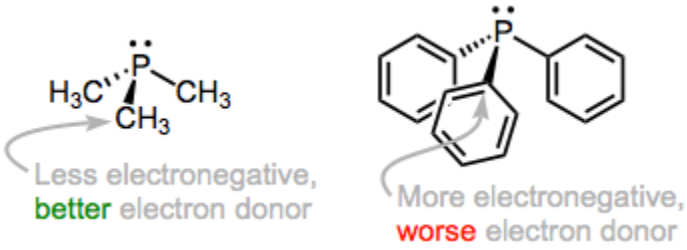


Like CO, phosphines are dative, L-type ligands that formally contribute two electrons to the metal center. Unlike CO, most phosphines are not small enough to form more than four bonds to a single metal center (and for large R, the number is even smaller). Steric hindrance becomes a problem when five or more PR_3 ligands try to make their way into the space around the metal. An interesting consequence of this fact is that many phosphine-containing complexes do not possess 18 valence electrons. Examples include $Pt(PCy_3)_2$, $Pd[P(t\text{-}Bu)_3]_2$, and $[Rh(PPh_3)_3]^+$. Doesn’t that just drive you crazy? It drives the complexes crazy as well—and most of these coordinatively unsaturated compounds are wonderful catalysts.

Bridging by phosphines is extremely rare, but ligands containing multiple phosphine donors that bind in an L_n (n > 1) fashion to a

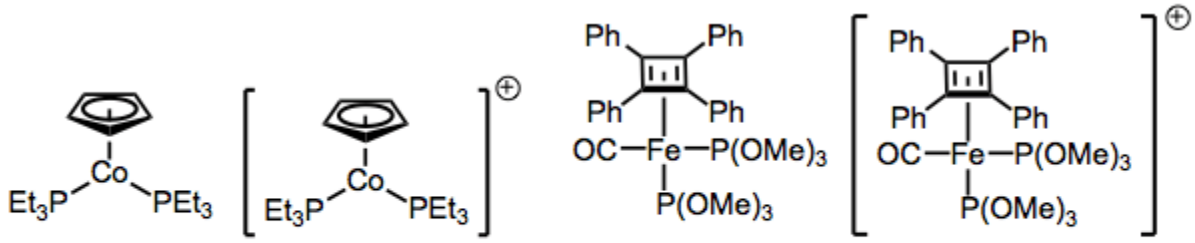
single metal center are all over the place. These ligands are called chelating or polydentate to indicate that they latch on to metal centers through multiple binding sites. For entropic reasons, chelating ligands bind to a single metal center at multiple points if possible, instead of attaching to two different metal centers (the aptly named chelate effect). An important characteristic of chelating phosphines is bite angle, defined as the predominant P–M–P angle in known complexes of the ligand. We'll get into the interesting effects of bite angle later, but for now, we might imagine how "unhappy" a ligand with a preferred bite angle of 120° would be in the square planar geometry. It would much rather prefer to be part of a trigonal bipyramidal complex, for instance.

The predominant orbital interaction contributing to phosphine binding is the one we expect, a lone pair on phosphorus interacting with an empty metallic d orbital. The electronic nature of the R groups influences the electron-donating ability of the phosphorus atom. For instance, alkylphosphines, which possess P–Csp^3 bonds, tend to be better electron donors than arylphosphines, which possess P–Csp^2 bonds. The rationale here is the greater electronegativity of the sp^2 hybrid orbital versus the sp3 hybrid, which causes the phosphorus atom to hold more tightly to its lone pair when bound to an sp^2 carbon. The same idea applies when electron-withdrawing and -donating groups are incorporated into R: the electron density on P is low when R contains electron-withdrawing groups and high when R contains electron-donating groups. Ligands (and associated metals) in the former class are called electron poor, while those in the latter class are electron rich.



As we add electronegative R groups, the phosphorus atom (and the metal to which it's bound) become more electron poor.

Like CO, phosphines participate in backbonding to a certain degree; however, the phenomenon here is of a fundamentally different nature than CO backbonding. For one thing, phosphines lack a π* orbital. In the days of yore, chemists attributed backbonding in phosphine complexes to an interaction between a metallic dπ orbital and an empty 3d orbital on phosphorus. However, this idea has elegantly been proven bogus, and a much more organicker-friendly explanation has taken its place (no d orbitals on P required!). In an illuminating series of experiments, M–P and P–R bond lengths were measured via crystallography for several redox pairs of complexes. I've chosen two illustrative examples, although the linked reference is chock full of other pairs. The question is: how do we explain the changes in bond length upon oxidation?

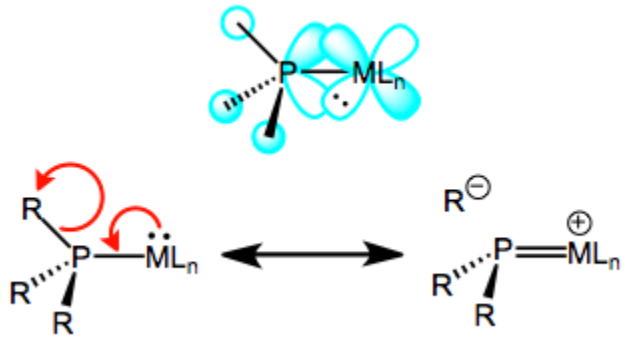


M–P	2.218 Å	2.230 Å	**M–P**	2.146 Å	2.261 Å
P–R	1.846 Å	1.829 Å	**P–R**	1.598 Å	1.578 Å

Upon oxidation, M–P bond lengths increase and and P–R bond lengths decrease. Why?

Oxidation decreases the ability of the metal to backbond, because it removes electron density from the metal. This explains the increases in M–P bond length—just imagine a decrease the M–P bond order due to worse backbonding. And the decrease in P–R bond length? It's important to see that invoking only the phosphorus 3d orbitals would not explain changes in the P–R bond lengths, as the 3d atomic orbitals are most definitely localized on phosphorus. Instead, we must invoke the participation of σ*P–R orbitals in phosphine backbonding to account for the P–R length decreases. When all is said and done, the LUMO of the free phosphine has mostly P–R antibonding character, with some 3d thrown into the mix. The figure below depicts one of the

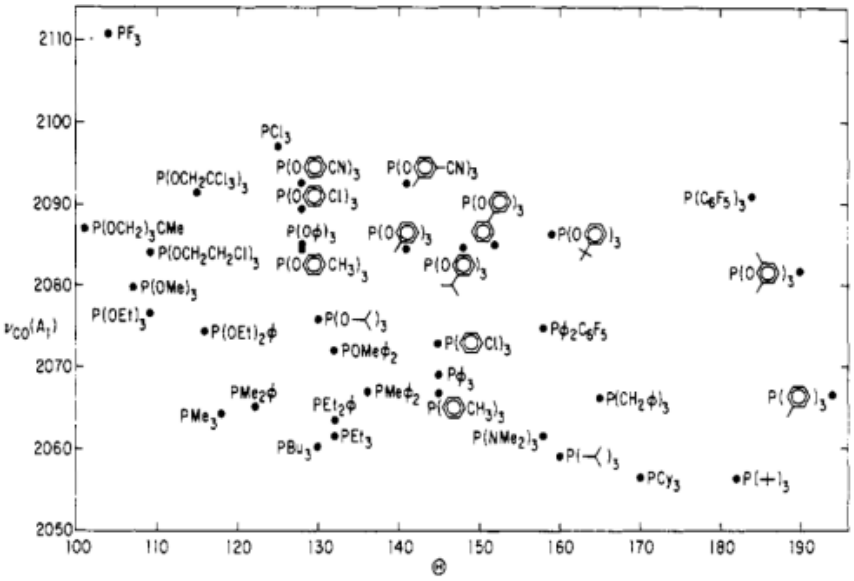
interactions involved in M–P backbonding, a dπ → σ* interaction (an orthogonal dπ → σ* interaction also plays a role). As with CO, a resonance structure depicting an M=P double bond is a useful heuristic! Naturally, R groups that are better able to stabilize negative charge—that is, electron-withdrawing groups—facilitate backbonding in phosphines. Electron-rich metals help too.



Backbonding in phosphines, a sigma-bond-breaking affair.

The steric and electronic properties of phosphines vary enormously. Tolman devised some intriguing parameters that characterize the steric and electronic properties of this class of ligands. To address sterics, he developed the idea of cone angle—the apex angle of a cone formed by a point 2.28 Å from the phosphorus atom (an idealized M–P bond length), and the outermost edges of atoms in the R groups, when the R groups are folded back as much as possible. Wider cone angles, Tolman reasoned, indicate greater steric congestion around the phosphorus atom. To address electronics, Tolman used a not-so-old friend of ours—the CO stretching frequency (νCO) of mixed phosphine-carbonyl complexes. Specifically, he used Ni(CO)3L complexes, where L is a tertiary phosphine, as his standard. Can you anticipate Tolman's logic? How should νCO change as the electron-donating ability of the phosphine ligands increases?

Tolman's logic went as follows: more strongly electron-donating phosphines are associated with more electron-rich metals, which are better at CO backbonding (due fundamentally to higher orbital energies). Better CO backbonding corresponds to a lower νCO due to decreased C–O bond order. Thus, better donor ligands should be associated with lower νCO values (and vice versa for electron-withdrawing ligands). Was he correct? Exhibit A...



Tolman's map of the steric and electronic properties of phosphine ligands.

Notice the poor ligand trifluorophosphine stuck in the "very small, very withdrawing" corner, and its utter opposite, the gargantuan tri(tert-butyl)phosphine in the "extremely bulky, very donating" corner. Intriguing! One can learn a great deal just by studying this chart.

Dr. Michael Evans (Georgia Tech)

Bonding in Phosphine Complexes

Let us have a look at the MO diagram of the PH_3 molecule and compare it with the NH_3 molecule. As one would expect, the MOs are overall similar, but there is one important difference. While the LUMO in NH_3 is the anti-bonding $3a_1$ orbital, the LUMOs in the PH_3 molecule are the anti-bonding 2e orbitals. The relative energies of the $3a_1$ and 2e orbitals in the PH_3 and NH_3 molecules are swapped up. This can be attributed to the fact that the the P atom uses the 3s and the 3p orbitals as valence orbitals, while N uses the 2s and 2p orbitals. The 3s and the 3p orbitals are larger and overlap less effectively with the small 1s orbitals of the hydrogen. They also have a higher energy making the P-H bonds less polar than the N-H bonds. The energy of the PH_3 HOMO is higher than that of the NH_3 HOMO. Both the HOMO and the LUMO of PH_3 are more diffuse and polarizable than the respective orbitals in NH_3.

The higher energy of the HOMO in PH_3 makes it a better donor than NH_3. In addition, the PH_3 has π-acceptor properties because the 2e LUMO are relatively low-lying anti-bonding 2e orbitals and have suitable shape for π-overlap with metal d-orbitals. NH_3 does not have these π-acceptor properties because its LUMO is the $3a_1$ orbital, and not the 2e orbitals. The 2e orbitals in NH_3 are energetically too high in order to allow for significant π-acceptor interactions.

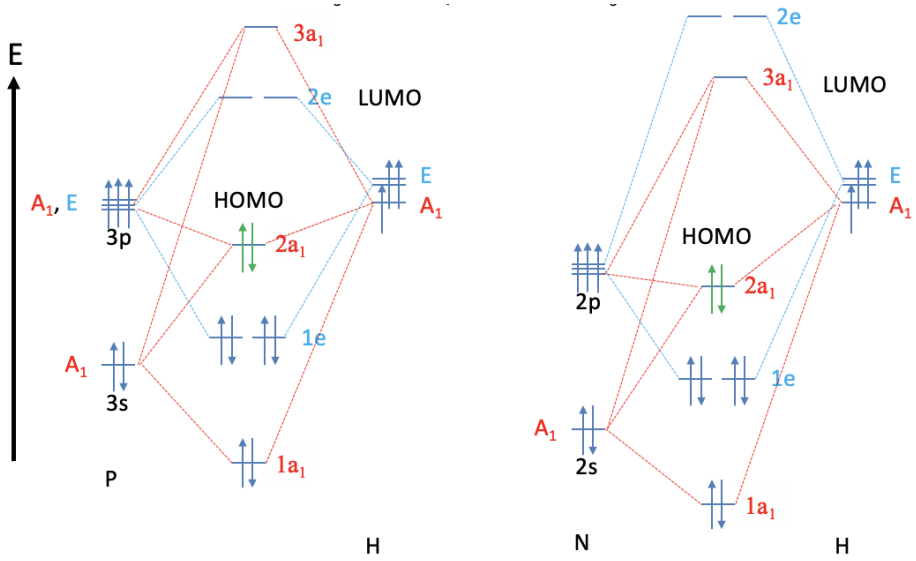


Figure 13.4.2.3: MO diagrams of PH_3 and NH_3

The σ-donor and π-acceptor properties of the phosphine ligand can be modified by substituting H by other groups. Generally, more electron donating groups increase the energy of the HOMO and the LUMO. This strengthens the σ-donor and reduces the π-acceptor properties. Vice versa, more electron withdrawing groups decrease the energy of the HOMO and the LUMO. As a consequence, the ligand becomes a weaker σ-donor and a stronger π-acceptor (Fig. 13.4.2.4).

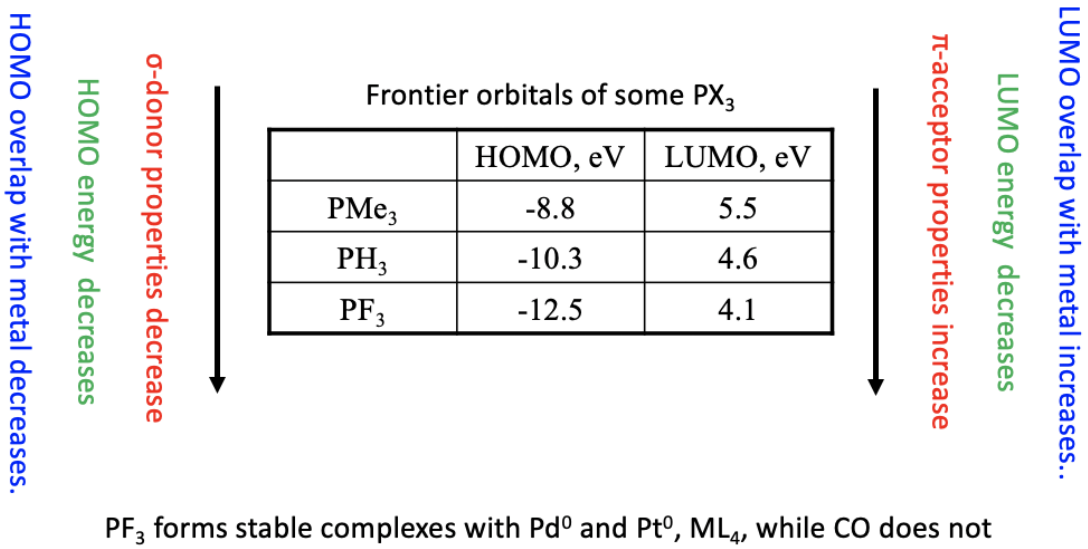


Figure 13.4.2.4: HOMO and LUMO energies of three phosphines

The table above shows the HOMO and LUMO energies of three phosphines. As expected the HOMO and LUMO energies decrease from $\mathrm{PMe_3}$ to $\mathrm{PH_3}$ to $\mathrm{PF_3}$ due to the increasingly electron-withdrawing nature of the substituent. As a consequence, the σ-donor properties weaken and the π-acceptor properties strengthen from to $\mathrm{PMe_3}$ to $\mathrm{PH_3}$ to $\mathrm{PF_3}$.

Not only the energies, but also the orbital overlap is important for the strength of the π-acceptor properties of the phosphine ligands. The more strongly electron-withdrawing the group is the more the anti-bonding e-type LUMO orbitals are located at the P atom. The more these orbitals are localized at P, the better they can overlap with the ligand. Vice versa the localization of the HOMO shifts toward the group as the group becomes more electron-withdrawing, thereby weakening the σ-donor properties.

Phosphine ligands with strongly electron withdrawing groups such as $\mathrm{PF_3}$ have π-acceptor properties strong enough to stabilize metals in low oxidation numbers, similar to CO. For example, the $\mathrm{PF_3}$ ligand forms stable complexes with Pd and Pt atoms in the oxidation number 0, while the respective Pd and Pt carbonyls are not known.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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13.4.3: Hydrides and Dihydrogen Complexes

Ligands can, shockingly enough, bind through the electrons in their own σ bonds in an L-type fashion. This binding mode depends as much on the metal center as it does on the ligand itself—to see why, we need only recognize that σ complexes look like intermediates in concerted oxidative additions. With a slight reorganization of electrons and geometry, an L-type σ ligand can become two X-type ligands. Why, then, are σ complexes stable? How can we control the ratio of σ complex to X_2 complex in a given situation? How does complexation of a σ bond change the ligand's properties? We'll address these questions and more in this post.

General Properties

The first thing to realize about σ complexes is that they are highly sensitive to steric bulk. Any old σ bond won't do; hydrogen at one end of the binding bond or the other (or both) is necessary. The best studied σ complexes involve dihydrogen ($\mathrm{H_2}$), so let's start there.

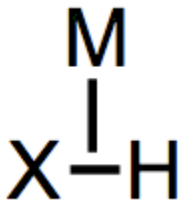


Figure $13.4.3.1$: A bonding interaction between a metal ion and the σ bond of a generic $\mathrm{X{-}H}$ ligand.

Mildly backbonding metals may bind dihydrogen "side on." Like side-on binding in π complexes, there are two important orbital interactions at play here: The first is a sigma bonding interaction ($\sigma \mathrm{H{-}H} \rightarrow \mathrm{d}\sigma$), as pictured on the left in Figure $13.4.3.2$; the second is a π bonding interaction ($\mathrm{d}\ \pi \rightarrow \sigma^{*} \mathrm{H{-}H}$), as pictured on the right in Figure $13.4.3.2$. Dihydrogen complexes can "tautomerize" to hydride $(\mathrm{H})_2$ isomers through cleavage of the $\mathrm{H{-}H}$ bond to the metal (this is an oxidative addition reaction, as discussed in the chapter on organometallic reactions).

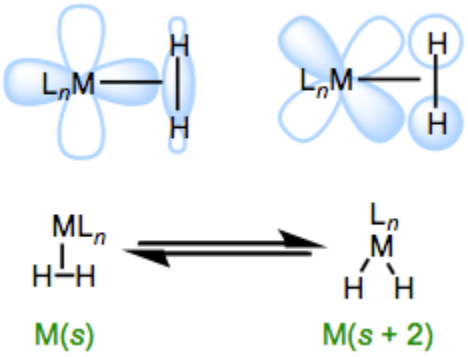


Figure $13.4.3.2$: Orbital interactions and $\mathrm{L{-}X_2}$ equilibrium in σ complexes.

$\mathrm{H_2}$ binding in an L-type fashion massively acidifies the ligand. Changes in of over thirty pKa units have been observed upon metal binding! Analogous acidifications of X–H bonds, rarely exhibit ΔpKa > 5. What's causing the different behavior of X–H and H–H ligands? The key is to consider the conjugate base of the ligand—in particular, how much it's stabilized by a metal center relative to the corresponding free anion. The principle here is analogous to the famous dictum of organic chemistry: consider charged species when making acid/base comparisons. Stabilization of the unhindered anion $\mathrm{H^{-}}$ by a metal is much greater than stabilization of larger, more electronegative anions like $\mathrm{HO^{-}}$ and $\mathrm{NH_2^{-}}$ by a metal. As a result, it's more favorable to remove a proton from metal-complexed $\mathrm{H_2}$ than from larger, more electronegative X–H ligands.

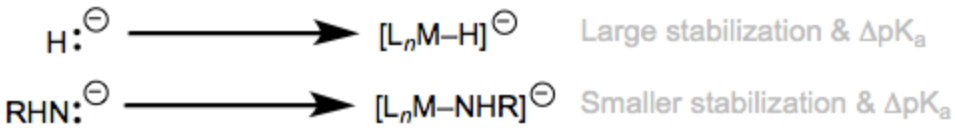


Figure 13.4.3.3: When the conjugate base is stabilized, the pKa of the acid is decreased. The metal ion has a more important stabilizing effect on H^- compared to any other conjugate base (X^-).

Remarkably large stabilization by an acidic metal fragment, without any counterbalancing from steric factors, explains the extreme acidification of dihydrogen upon metal binding.

The electronic nature of the metal center has two important effects on σ complexes. The first concerns the acidity of H_2 upon metal binding. The principle here is consistent with what we've hammered into the ground so far. In the same way cationic organic acids are stronger than their neutral counterparts, σ complexes of electron-poor metals—including (and especially) cations—are stronger acids than related complexes of electron-rich metals. The second concerns the ratio of L-type to X_2-type binding. We should expect more electron-rich metal centers to favor the X2 isomer, since these should donate more strongly into the σ*H–H orbital. This idea was masterfully demonstrated in a study by Morris, in which he showed that H_2 complexes of π-basic metal centers show all the signs of X2 complexes, rather than L complexes. More generally, metal centers in σ complexes need a good balance of π basicity and σ acidity (I like to call this the "Goldilocks effect"). Because of the need for balance, σ complexes are most common for centrally located metals (groups 6-9).

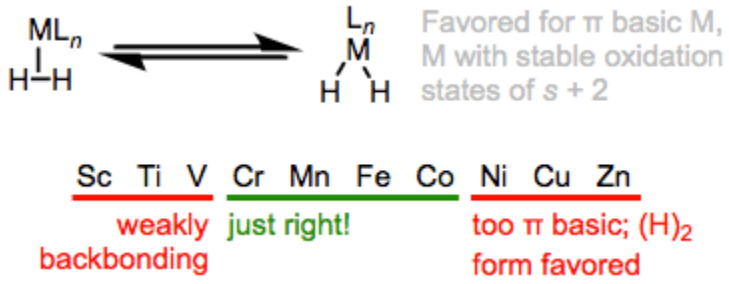


Figure 13.4.3.4: Oxidative addition of H_2 is important for electron-rich, π-basic metal centers. Groups 6-9 hit the "Goldilocks" spot.

The M–H bond in hydride complexes is a good base—anyone who's ever quenched lithium aluminum hydride can attest to this! Intriguingly, because it's a good base, the M–H bond can participate in hydrogen bonding with an acidic X–H bond, where X is a heteroatom. This kind of bonding, called dihydrogen bonding (since two hydrogen atoms are involved), is best described as a sort of σM–H$\rightarrow\sigma$*X–H orbital interaction. Think of it as analogous to a traditional hydrogen bond, but using a σ bond instead of a lone pair. Crazy, right?!

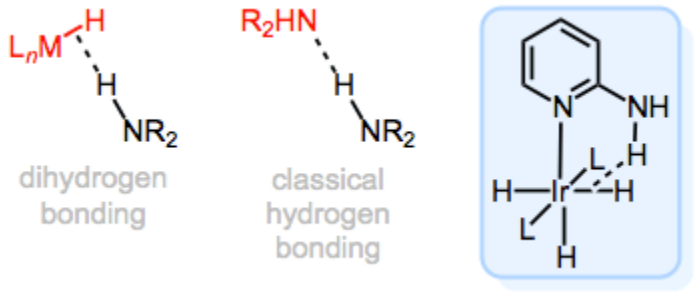


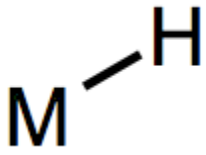
Figure 13.4.3.1:

Dihydrogen bonding in metal hydrides: a sort of "interrupted protonation" of M–H.

Other kinds of σ complexes are known, but these are rarer than H–H complexes. One class that we've seen before involve agostic interactions of C–H bonds in alkyl ligands. σ Complexes of inorganic ligands like silanes and stannanes may involve complex bonding patterns, but we won't concern ourselves with those here.

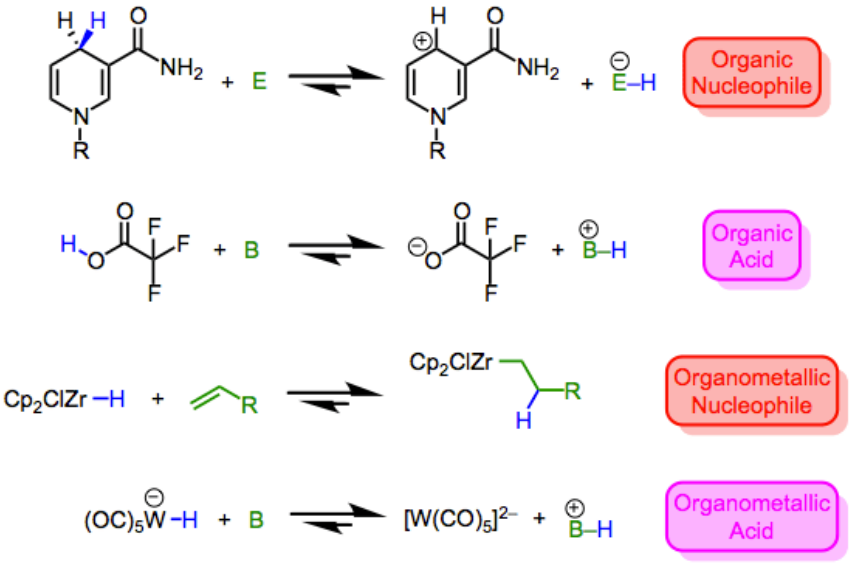
Hydride Complexes

Metal-hydrogen bonds, also known (misleadingly) as **metal hydrides**, are ubiquitous X-type ligands in organometallic chemistry. There is much more than meets the eye to most M-H bonds: although they're simple to draw, they vary enormously in polarization and pKa. They may be acidic or hydridic or both, depending on the nature of the metal center and the reaction conditions. In this post, we'll develop some heuristics for predicting the behavior of M-H bonds so that later, we can discuss their major modes of reactivity (acidity, radical reactions, migratory insertion, etc.).



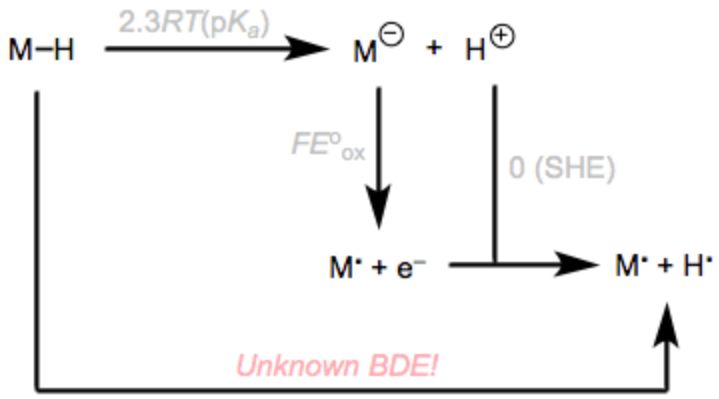
General Properties

Metal hydrides run the gamut from nucleophilic/basic to electrophilic/acidic. Then again, the same can be said of X–H bonds in organic chemistry, which may vary from mildly nucleophilic (consider Hantzsch esters and NADH) to extremely electrophilic (consider triflic acid). As hydrogen is what it is in both cases, it's clear that the nature of the X fragment—more specifically, the stability of the charged fragments X+ and X−—dictate the character of the X–H bond. Compare the four equilibria outlined below—the stabilities of the ions dictate the position of each equilibrium. By now we shouldn't find it surprising that the highly π-acidic W(CO)5 fragment is good at stabilizing negative charge; for a similar reason, the ZrCp2Cl fragment can stabilize positive charge.*



Metal-hydrogen bonds may be either hydridic (nucleophilic) or acidic (electrophilic). The nature of other ligands and the reaction conditions are keys to making predictions.

Let's turn our attention now to *homolytic* M–H bond strength. A convenient thermodynamic cycle allows us to use the acidity of M–H and the oxidation potential of its conjugate base in order to determine bond strength. This clever method, employed by Tilset and inspired by the inimitable Bordwell, uses the cycle in the figure below. BDE values for some complexes are provided as well. From the examples provided, we can see that bond strength increases down a group in the periodic table. This trend, and the idea that bridging hydrides have larger BDEs than terminal M–H bonds, are just about the only observable trends in M–H BDE.

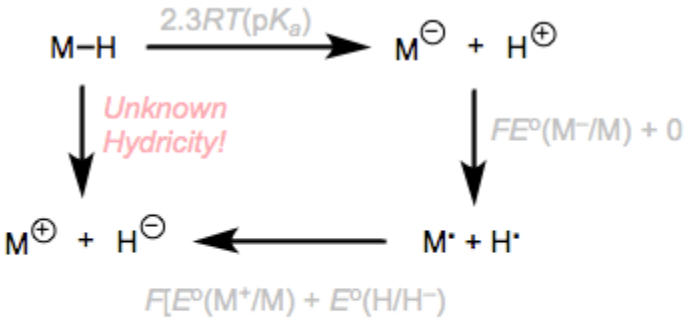


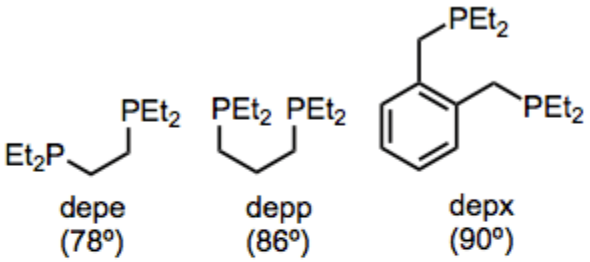
Complex	BDE (kcal/mol)
$CpCr(CO)_3H$	61
$CpMo(CO)_3H$	69
$CpW(CO)_3H$	72
$Mn(CO)_5H$	68
$Re(CO)_5H$	75

A clever cycle for determining BDEs from other known quantities, with select BDE values. I've left out solvation terms from the thermodynamic cycle. For more details, see the Tilset link above.

Why is knowing M-H BDEs useful? For one thing, the relative BDEs of M-C and M-H bonds determine the thermodynamics of β-hydride elimination, which results in the replacement of a covalent M-C bond with an M-H bond. Secondly, complexes containing weak M-H bonds are often good hydrogen transfer agents and may react with organic radicals and double bonds, channeling stannane and silane reductants from organic chemistry.

Hydricity refers to the tendency of a hydride ligand to depart as H–. A similar thermodynamic cycle relates the energetics of losing H– to the oxidation potentials of the conjugate base and the oxidized conjugate base; however, this method is complicated by the fact that hydride loss establishes an open coordination site. I've provided an abridged version of the cycle below. Hydricities are somewhat predictable from the electronic and steric properties of the metal center: inclusion of electron-donating ligands tends to increase hydricity, while electron-withdrawing or acidic ligands tend to decrease it. For five-coordinate hydrides that form 16-electron, square planar complexes upon loss of hydride, the bite angle of chelating phosphines plays an interesting role. As bite angle increases, hydricity does as well.



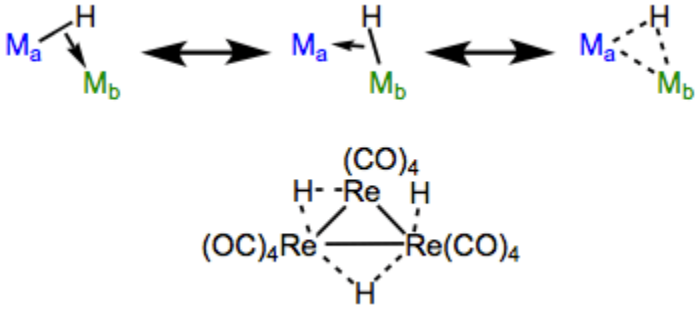


Complex	Hydricity (kcal/mol)
$HPd(depe)_2^+$	43
$HPd(depp)_2^+$	55
$HPd(depx)_2^+$	61

A thermodynamic cycle for hydricity, with some examples. Hydricity and bite angle are well correlated in five-coordinate palladium hydrides.

Bridging hydrides are an intriguing class of ligands. A question to ponder: how can a ligand associated with only two electrons possibly bridge two metal centers? How can two electrons hold three atoms together? Enter the magic of three-center, two-electron bonding. We can envision the M–H sigma bond as an electron donor itself! With this in mind, we can imagine that hydrides are able to bind end-on to one metal (like a standard X-type ligand) and side-on to another (like an L-type π system ligand, but using sigma electrons instead). Slick, no? We'll see more side-on bonding of sigma electrons in a future post on sigma

complexes.



Resonance forms of bridging hydrides, with an example. Sigma complexes like these show up in other contexts, too!

Consistent with the idea that bridging is the result of “end-on + side-on” bonding, bond angles of bridging hydrides are never 180°.

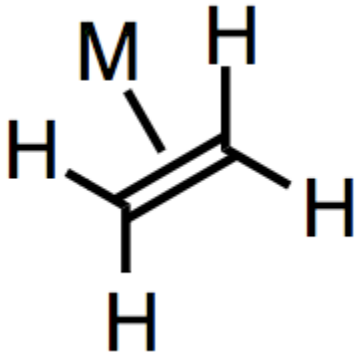
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13.5: Bonding between Metal Atoms and Organic Pi Systems

With this section, we finally reach our first class of dative **actor** ligands, **π systems**. In contrast to the **spectator** L-type ligands we've seen so far, π systems most often play an important role in the reactivity of the OM complexes of which they are a part (since they act in reactions, they're called "actors"). π Systems do useful chemistry, not just with the metal center, but also with other ligands and external reagents. Thus, in addition to thinking about how π systems affect the steric and electronic properties of the metal center, we need to start considering the metal's effect on the ligand and how we might expect the ligand to behave as an active participant in reactions. To the extent that structure determines reactivity—a commonly repeated, and extremely powerful maxim in organic chemistry—we can think about possibilities for chemical change without knowing the elementary steps of organometallic chemistry in detail yet.



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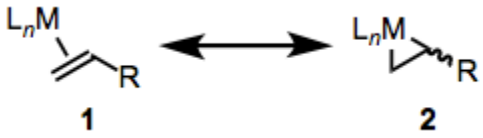
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13.5.1: Linear π Systems

General Properties

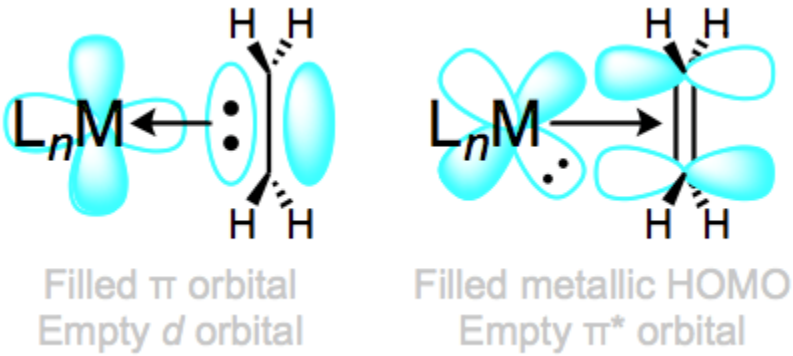
The π bonding orbitals of alkenes, alkynes, carbonyls, and other unsaturated compounds may overlap with dσ orbitals on metal centers. This is the classic ligand HOMO → metal LUMO interaction that we've beaten into the ground over the last few posts. Because of this electron donation from the π system to the metal center, coordinated π systems often act electrophilic, even if the starting alkene was nucleophilic (the **Wacker oxidation** is a classic example; water attacks a palladium-coordinated alkene). The π → dσ orbital interaction is central to the structure and reactivity of π-system complexes.

Then again, a theme of the last three posts has been the importance of orbital interactions with the opposite sense: metal HOMO → ligand LUMO. Like CO, phosphines, and NHCs, π systems are often subject to important backbonding interactions. We'll focus on alkenes here, but these same ideas apply to carbonyls, alkynes, and other unsaturated ligands bound through their π clouds. For alkene ligands, the relative importance of "normal" bonding and backbonding is nicely captured by the relative importance of the two resonance structures in the figure below.



Resonance forms of alkene ligands.

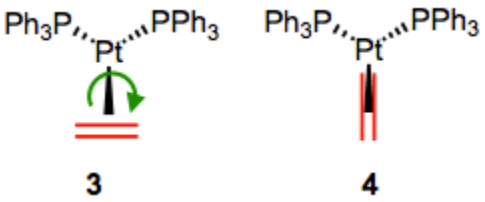
Complexes of weakly backbonding metals, such as the electronegative late metals, are best represented by the traditional dative resonance structure **1**. But complexes of strong backbonders, such as electropositive Ti(II), are often best drawn in the **metallacyclopropane** form **2**. Organic hardliners may have a tough time believing that **1** and **2** are truly resonance forms, but several studies—e.g. of the Kulinkovich cyclopropanation—have shown that independent synthetic routes to metallacyclopropanes and alkene complexes containing the same atoms result in the same compound. Furthermore, bond lengths and angles in the alkene change substantially upon coordination to a strongly backbonding metal. We see an elongation of the C=C bond (consistent with decreased bond order) and some pyramidalization of the alkene carbons (consistent with a change in hybridization from sp2 to sp3). A complete orbital picture of "normal" bonding and backbonding in alkenes is shown in the figure below.



Normal bonding and backbonding in alkene complexes.

Here's an interesting question with stereochemical implications: what is the orientation of the alkene relative to the other ligands? From what we've discussed so far, we can surmise that one face of the alkene must point toward the metal center. Put differently, the bonding axis must be normal to the plane of the alkene. However, this restriction says nothing about rotation about the bonding axis, which spins the alkene ligand like a pinwheel. Is a particular orientation preferred, or can we think about the alkene as a circular smudge over time? The figure below depicts two possible orientations of the alkene ligand in a trigonal planar

complex. Other orientations make less sense because they would involve inefficient orbital overlap with the metal's orthogonal d orbitals. Which one is favored?



3 **4**

Two limiting cases for alkene orientation in a trigonal planar complex.

First of all, we need to notice that these two complexes are **diastereomeric**. They have different energies as a result, so one must be favored over the other. Naive steric considerations suggest that complex **4** ought to be more stable (in most complexes, steric factors dictate alkene orientation). To dig a little deeper, let's consider any electronic factors that may influence the preferred geometry. We've already seen that electronic factors can overcome steric considerations when it comes to complex geometry! To begin, we need to consider the crystal field orbitals of the complex as a whole. Verify on your own that in this d10, Pt(0) complex, the crystal-field HOMOs are the dxy and dx2–y2 orbitals. Where are these orbitals located in space? In the xy-plane! Only the alkene in **3** can engage in efficient backbonding with the metal center. In cases when the metal is electron rich and/or the alkene is electron poor, complexes like **3** can sometimes be favored in spite of sterics. The thought process here is very similar to the one developed in an earlier post on geometry. However, please note that this situation is fairly rare—steric considerations often either match or dominate electronics where alkenes are concerned.

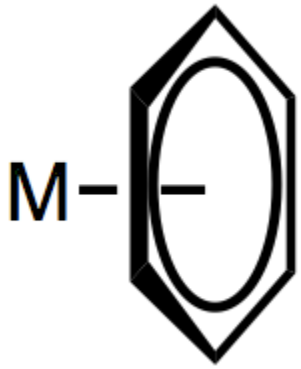
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13.5.2: Cyclic π systems

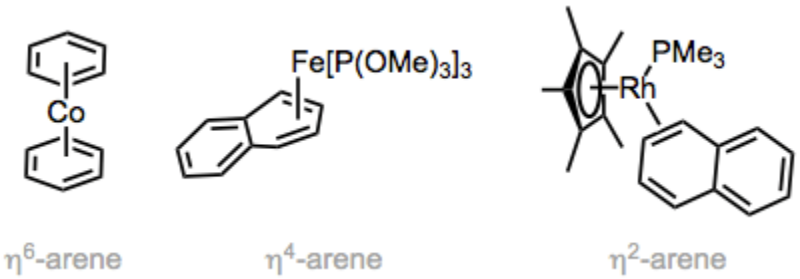
Arene or **aromatic ligands** are the subject of this post, the second in our series on π-system ligands. Arenes are dative, L-type ligands that may serve either as actors or spectators. Arenes commonly bind to metals through more than two atoms, although η2-arene ligands are known. Structurally, most η6-arenes tend to remain planar after binding to metals. Both "normal" bonding and backbonding are possible for arene ligands; however, arenes are stronger electron donors than CO and backbonding is less important for these ligands. The reactivity of arenes changes dramatically upon metal binding, along lines that we would expect for strongly electron-donating ligands. After coordinating to a transition metal, the arene usually becomes a better electrophile (particularly when the metal is electron poor). Thus, metal coordination can enable otherwise difficult **nucleophilic aromatic substitution** reactions.



General Properties

The coordination of an aromatic compound to a metal center through its aromatic π MOs removes electron density from the ring. I'm going to forego an in-depth orbital analysis in this post, because it's honestly not very useful (and overly complex) for arene ligands. π → dσ (normal bonding) and dπ → π* (backbonding) orbital interactions are possible for arene ligands, with the former being much more important, typically. To simplify drawings, you often see chemists draw "toilet-bowl" arenes involving a circle and single central line to represent the π → dσ orbital interaction. Despite the single line, it is often useful to think about arenes as L3-type ligands. For instance, we think of η6-arenes as six-electron donors.

Multiple coordination modes are possible for arene ligands. When all six atoms of a benzene ring are bound to the metal (η6-mode), the ring is flat and C–C bond lengths are slightly longer than those in the free arene. The ring is bent and non-aromatic in η4-mode, so that the four atoms bound to the metal are coplanar while the other π bond is out of the plane. η4-Arene ligands show up in both stable complexes (see the figure below) and reactive intermediates that possess an open coordination site. To generate the latter, the corresponding η6-arene ligand undergoes **ring slippage**—one of the π bonds "slips" off of the metal to create an open coordination site. We'll see ring slippage again in discussions of the aromatic cyclopentadienyl and indenyl ligands.



Arene ligands exhibit multiple coordination modes.

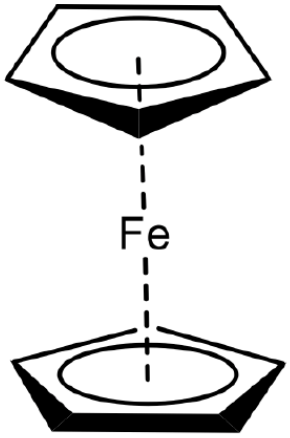
Even η2-arene ligands bound through one double bond are known. Coordination of one π bond results in **dearomatization** and makes η2-benzene behave more like butadiene, and furan act more like a vinyl ether. With naphthalene as ligand, there are multiple η2 isomers that could form; the isomer observed is the one that retains aromaticity in the free portion of the ligand. In fact, this result is general for polycyclic aromatic hydrocarbons: binding maximizes aromaticity in the free portion of the ligand. In the linked reference, the authors even observed the coordination of two different rhodium centers to naphthalene—a bridging arene ligand! Other bridging modes include σ, π-binding (the arene is an LX-type ligand, and one C–M bond is covalent, not dative) and L2-type bridging through two distinct π systems (as in biphenyl).

Arene ligands are usually hydrocarbons, not heterocycles. Why? Aromatic heterocycles, such as pyridine, more commonly bind using their basic lone pairs. That said, a few heterocycles form important π complexes. Thiophene is perhaps the most heavily studied, as the desulfurization of thiophene from fossil fuels is an industrially useful process.

Dr. Michael Evans (Georgia Tech)

Bonding in Ferrocene

Ferrocene was the first metallocene to be discovered and characterized. The structure of ferrocene is shown below.



Ferrocene

Figure 13.5.2.9: The sandwich structure of ferrocene

Can the stability of the ferrocene structure also be explained by molecular orbital theory? Let us check! First, we need to decide on the point group. We will make the simplification that the two C_p cyclopentadienyl rings are in eclipsed formation, and then the point group is D_{5h}. Actually, the rings are in staggered confirmation and the point group is D_{5d}, but the energy difference is minimal, and there is a very small activation barrier between the two conformers.



(13.5.2.1)

We can define the z-axis standing perpendicular to the Cp rings, and the xy plane to be coplanar with the Cp rings.

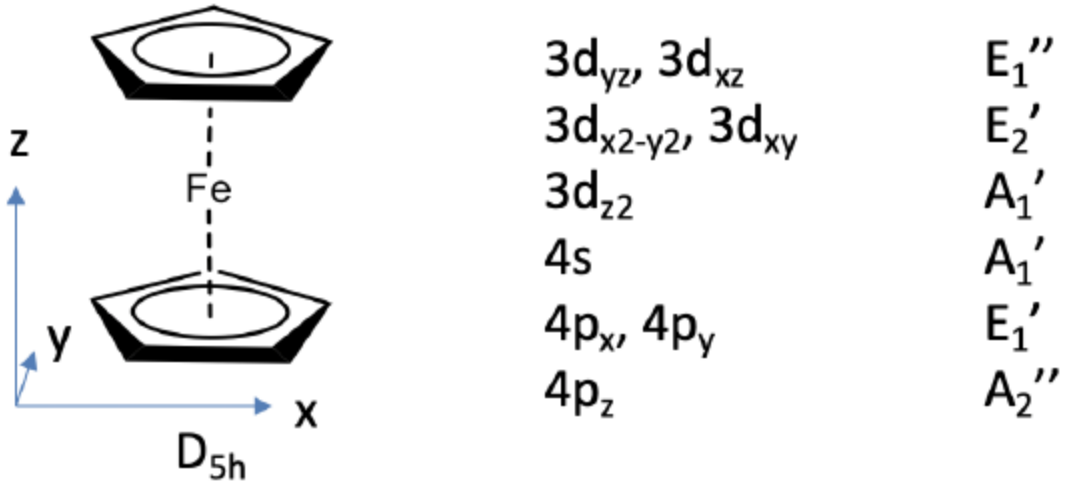


Figure 13.5.2.18: The coordinate system for ferrocene, Fe valence orbitals, and their symmetry types.

The Fe 3d, 4s and 4p orbitals will be our frontier orbitals and we can read their symmetry types from the character table of D_{5h}. The $3d_{xz}$ and $3d_{yz}$ have E_1'' symmetry, the $3d_{x^2-y^2}$ and the $3d_{xy}$ have E_2' symmetry, the $3d_{z^2}$ has A_1' symmetry, the 4s has A_1' symmetry, and the $4p_x$ and the $4p_y$ orbitals have E_1' symmetry, and the $4p_z$ has A_2'' symmetry.

Next, we need to determine the ligand group orbitals. We know that the π-ligand molecular orbitals are the ones that donate the electrons into the metal-orbitals, thus we have to have a closer look at these orbitals. The π-MOs of the ligand are made from the five $2p_z$ orbitals of the carbon atoms that stand perpendicular to the ring. This means that there are 5 MOs to consider.

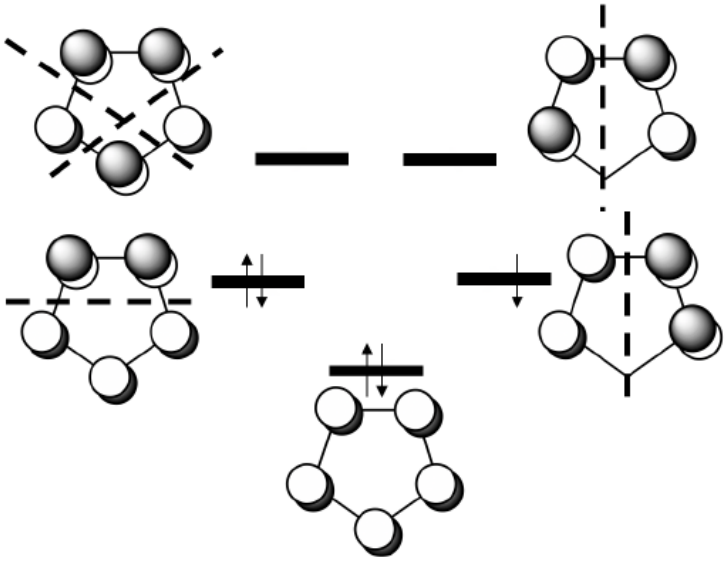


Figure 13.5.2.19: MOs of the cyclopentadienyl ligand and their relative energy

You can see the five MOs and their relative energy above. One is strongly bonding and has no node. Then, there are two double-generate weakly bonding ones that have one node, and finally there are two anti-bonding ones that have two nodes. Because the cyclopentadienyl anion has six π electrons, the bonding MO and the two weakly bonding MOs are full, the anti-bonding MOs are empty.

Because we have two Cp^- anions to consider we have overall 10 MOs to combine. We would therefore expect ten ligand group orbitals (LGOs). We can determine their symmetry type by determining the reducible and irreducible representations. The results are shown below.

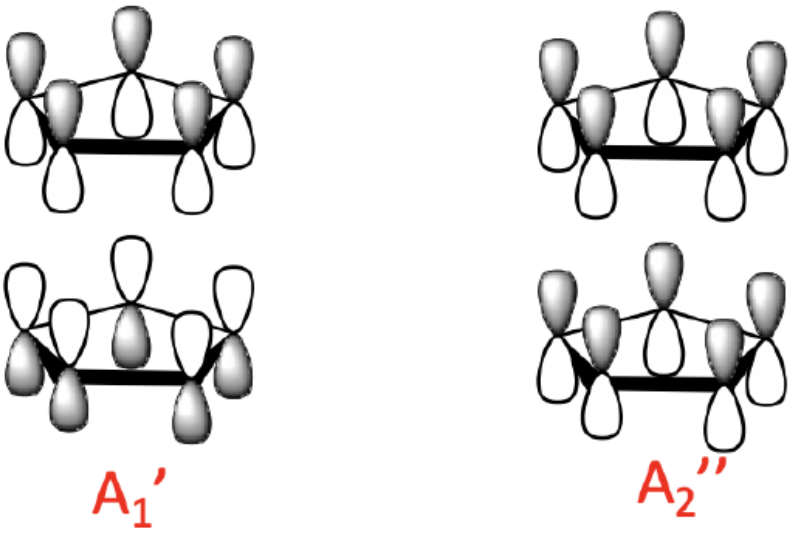


Figure 13.5.2.20: 0-node LGOs

We can generally divide the LGOs into three groups with a different number of nodes. There are two 0-node LGOs with A_1' and A_2'' symmetry. They are made from the 0-node MOs of the ligand. There is a bonding an anti-bonding combination possible. In the bonding combination the 0–node ligand MOs have the lobes with the same algebraic sign pointing toward each other. The anti-bonding combination has the lobes with opposite algebraic sign pointing toward each other.

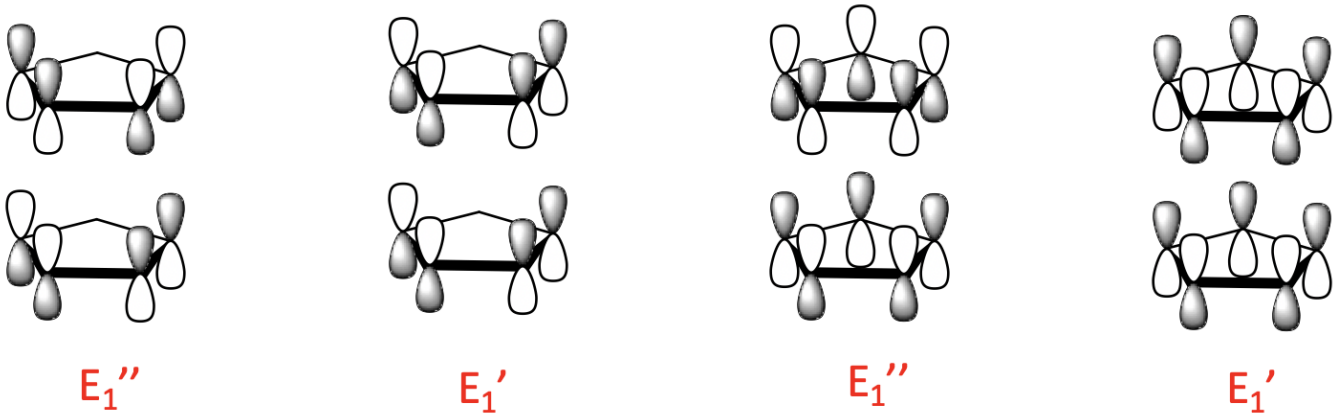


Figure 13.5.2.21: 1-node LGOs

There are four 1-node LGOs with E_1' and E_1'' symmetry. They are constructed from the two 1-node ligand MOs. Like for the 0-node orbitals, there is a bonding and an anti-bonding combination possible.

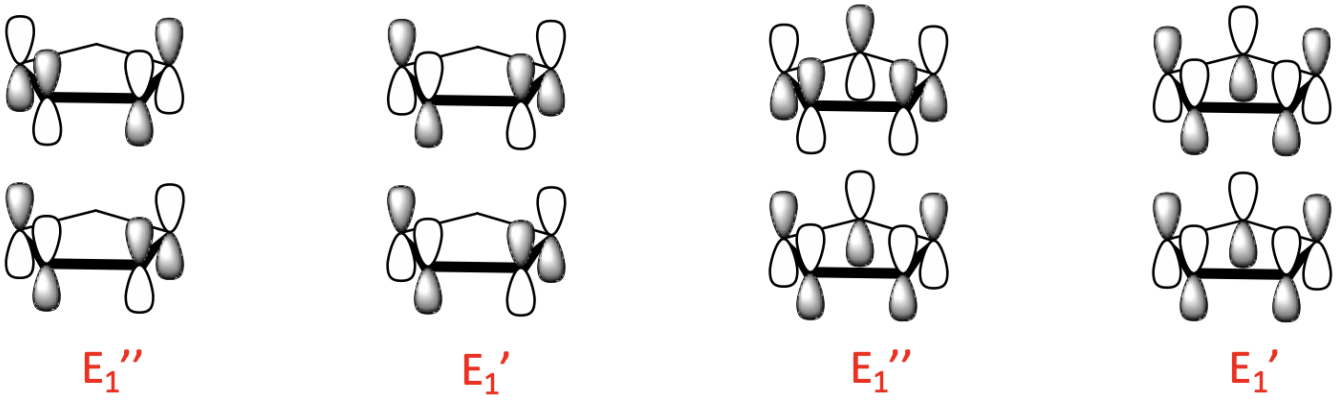


Figure 13.5.2.22: 2-node LGOs

Finally, there are four 2-node LGOs with E_2' and E_2'' symmetry. They are made from the 2-node ligand MOs and there is also a bonding and an anti-bonding combination possible.

The Molecular Orbital Diagram of Ferrocene

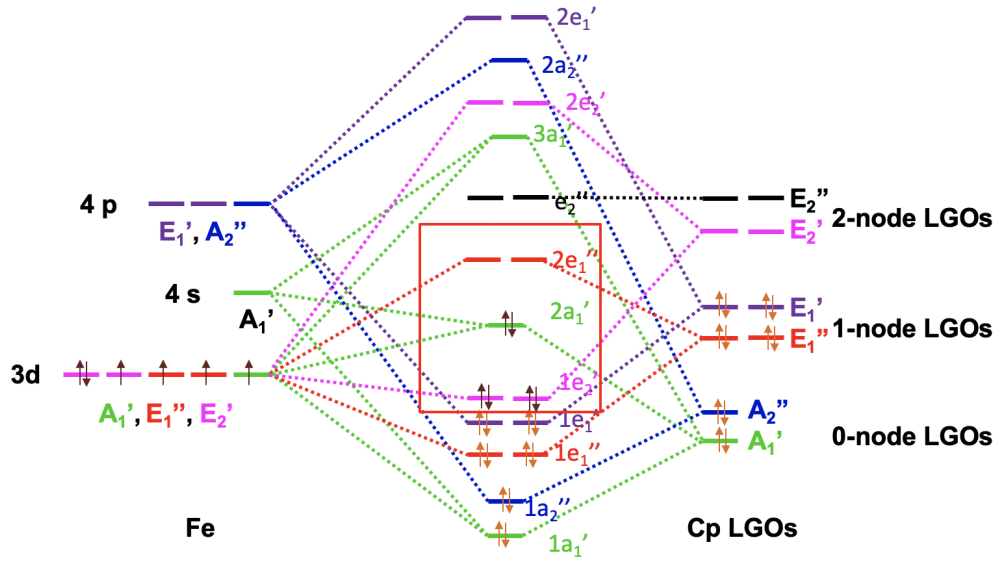


Figure 13.5.2.23: MO diagram of ferrocene

Now we have all the information to draw the molecular orbital diagram of ferrocene. As usual we plot the metal frontier orbitals on the left and label their symmetry. We plot the Cp LGOs on the right and also label the symmetry. We can order the LGOs according to energy with the 0-node LGOs having the lowest energy and the 2-node LGOs having the highest energy. Then, we can start to combine orbitals of the same symmetry type to form MOs. There are two metal AOs of the A_1' type and one A_1' LGO giving three MOs of this symmetry type, one bonding, one approximately non-bonding, and third one anti-bonding. We can connect AOs, LGOs, and MOs with dotted lines. Next, we can combine the A_2'' AO and the A_2'' LGO to form a bonding and an anti-bonding MO. We again connect the AOs, LGOs, and MOs with dotted lines. Then, we can produce two bonding e_1'' and two anti-bonding e_1'' MOs from the E_1'' metal AOs and the E_1'' LGOs and connect the orbitals with dotted lines. There are two E_1' LGOs and two E_1' AOs that can be combined to two bonding $1e_1$' and two anti-bonding $2e_1$' MOs and we again connect the orbitals with dotted lines. The two E_2' LGOs can be combined with the two E_2' d-orbitals to form a pair of bonding $1e_2$' and anti-bonding $2e_2$' molecular orbitals. Lastly, we notice that the E_2'' LGOs do not find a partner, and we have to write them as non-bonding with the same energy into the MO diagram.

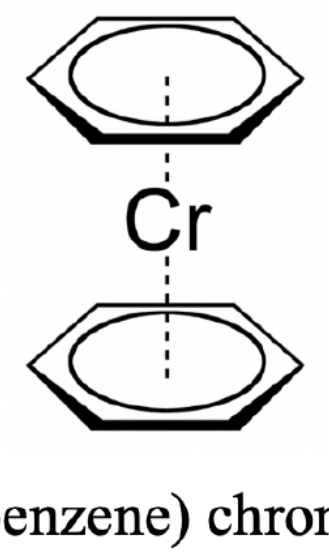
Now we need to fill the electrons into the orbitals. The ligands have twelve electrons overall. They can be filled into the six orbitals of the lowest energy. This fills the $1a_1$', the $1a_2$'', the $1e_1$'', the and $1e_1$' orbitals. We notice that all MOs are bonding which supports

the stability of the molecule. We still need to consider the metal d-orbitals. We have an Fe^{2+} ion and thus six metal d-electrons. They would go into the $1e_2$' orbital which is bonding and the $2a_1$' orbital which is weakly bonding. The $2a_1$ is the HOMO, and the next higher $2e_1$'' is the LUMO. We can see that we can fill all metal electrons into bonding MOs. The LUMO is an anti-bonding orbital, and thus overall all bonding MOs are filled, and no non-bonding and anti-bonding orbitals need to be filled. This is the ideal situation for a stable molecule. We can also see that the MO diagram explains the 18 electron rule. All 18 electrons are in bonding MOs.

We can consider the $1e_2$', the $2a_1$', and the $2e_1$'' metal d-orbitals in the ligand field produced by the Cp-ligands as these 5 orbitals can hold the maximum possible number of 10 d-electrons, have similar energy then the d-orbitals, and have contributions from them.

Metallocenes with other cyclic π-ligands

Is it possible to make metallocenes with other π-conjugated rings but the cylopentadienyl anion?



Bis-(benzene) chromium (0)

Figure 13.5.2.24: Bis-(benzene) chromium

The answer is yes, for instance benzene is known to act as a ligand bis-(benzene) chromium (0). In this case the ligand acts as a η^6-ligand because all six carbon atoms are involved in the bonding. Why does chromium give stable metallocene complex with benzene? We can explain this again with the 18 electron rule. In bis-(benzene) chromium (0), chromium is in the oxidation state 0 because the benzene ligand has no charge. Thus, chromium contributes six electrons. Adding the 12 π-electrons from the two benzene ligands gives 18 electrons.

Other cyclic π-ligands

Also cyclobutadiene can act as a cylic π-ligand in complexes. The cyclobutadiene is is different from the cyclopentadienyl anion and the benzene ligand in two ways. Firstly, it has much more ring strain then the previous two, and secondly it is not an aromatic, but an anti-aromatic ligand. Remember, we have an aromatic ring when there are 4n+2 π-electrons, whereby n is an inter number. This means that rings with two (n=0), six (n=1), and ten (n=2) π-electrons are aromatic. Anti-aromatic rings are those that have 4n electrons, such as four (n=1), eight (n=2) and so forth. Cyclobutadiene has four electrons, and thus it is anti-aromatic. Anti-aromatic rings are less stable than aromatic ones because not all π-electrons are in bonding molecular orbitals. Let us illustrate this by constructing the MO diagram for the π-system of the cyclobutadiene molecule (Figure 13.5.2.25)

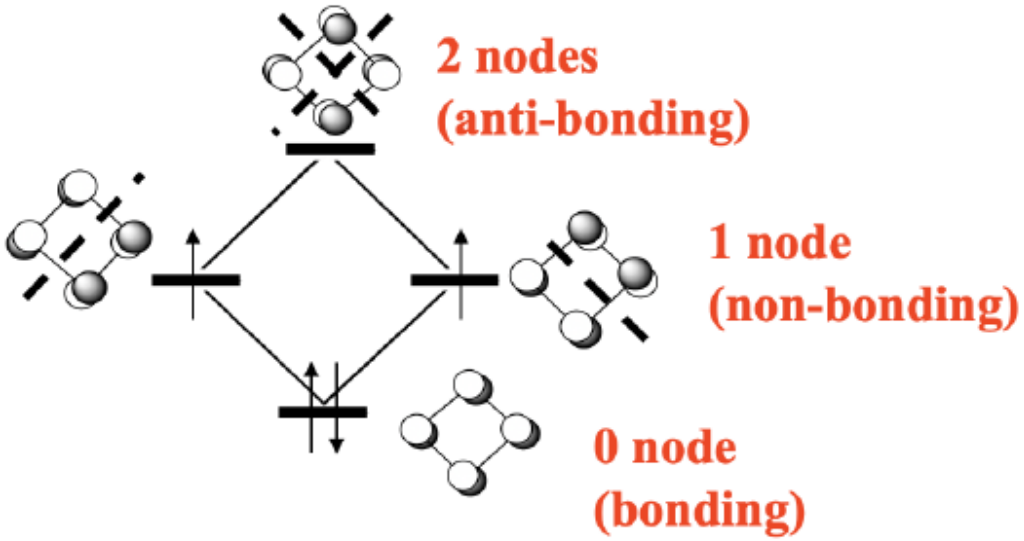


Figure 13.5.2.25: MO diagram for the π-system of the cyclobutadiene molecule

The π-system is made of four carbon atoms contributing a half-filled $2p_z$ orbital each (if we define the plane of the molecule as the xy plane). That makes four p-orbitals with four electrons that give four molecular orbitals. There is a bonding MO with no node, two doubly-degenerate non-bonding ones with one node, and one anti-bonding one with two nodes (Figure 13.5.2.25). There are four electrons. We can fill two electrons into the bonding MO, but the other two must go into the two non-bonding ones under obedience of Hund's rule.

Jahn-Teller distortion in cyclobutadiene

One may think that the cyclobutadiene is a square planar molecule because of complete delocalization of the π-electrons, but that is actually not the case. There are two shorter double-bonds and two longer single-bonds, and the shape of the molecules is a rectangle. This means that the two double bond are localized. We can view this effect as a Jahn-Teller distortion.

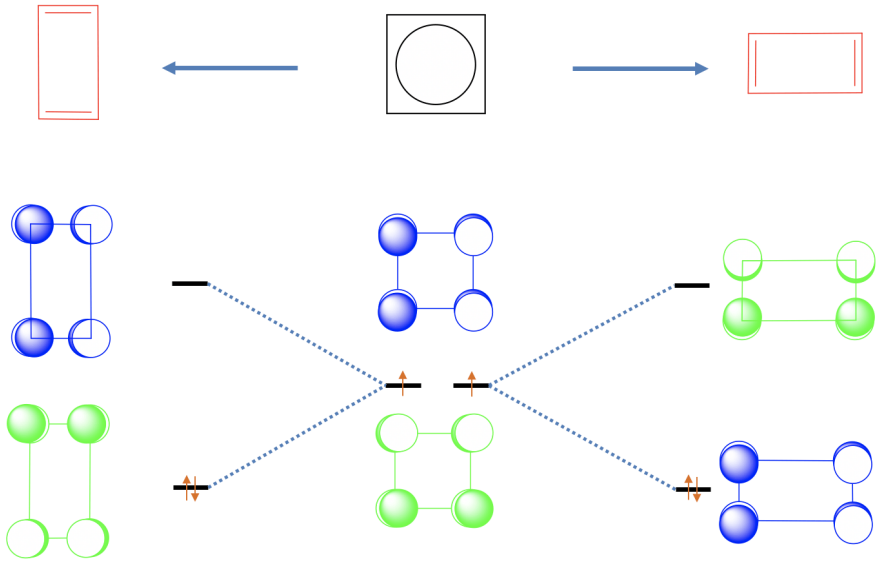


Figure 13.5.2.26: Jahn-Teller distortion in cyclobutadiene

The distortion of the square to form a rectangle is energetically favorable because it lowers the energy of the two non-bonding electrons. Why? Let us look at the non-bonding orbital 1 first and elongate in x-direction, and squeeze in y-direction (Figure 13.5.2.26). We can see that we bring the p-orbitals with bonding interactions further apart, and bring those with anti-bonding interactions closer together. This means that the energy of this orbital goes up and the orbital becomes anti-bonding. Let us do

the same with non-bonding orbital 2. We see that the opposite happens. The bonding interactions are enhanced and the anti-bonding interactions are weakened. Therefore, this orbital becomes bonding and the energy goes down. We can now fill the two electrons into the bonding MO. We see that we have lowered the energy of the electrons through the distortion.

We could also have squeezed in x-direction and elongated in y-direction. In this case orbital 1 would have become bonding and orbital 2 anti-bonding. However, this distortion is symmetry-equivalent to the previous one, and does not produce a new molecule. Both molecules can be superposed by a simple 90° rotation.

Cyclobutadiene as η^4-ligand

Cyclobutadiene (Cb) in its free form is not stable because of the high ring strain and the anti-aromaticity, but complexes with cyclobutadiene as a ligand are stable. We would expect that 18 electron complexes are most stable.

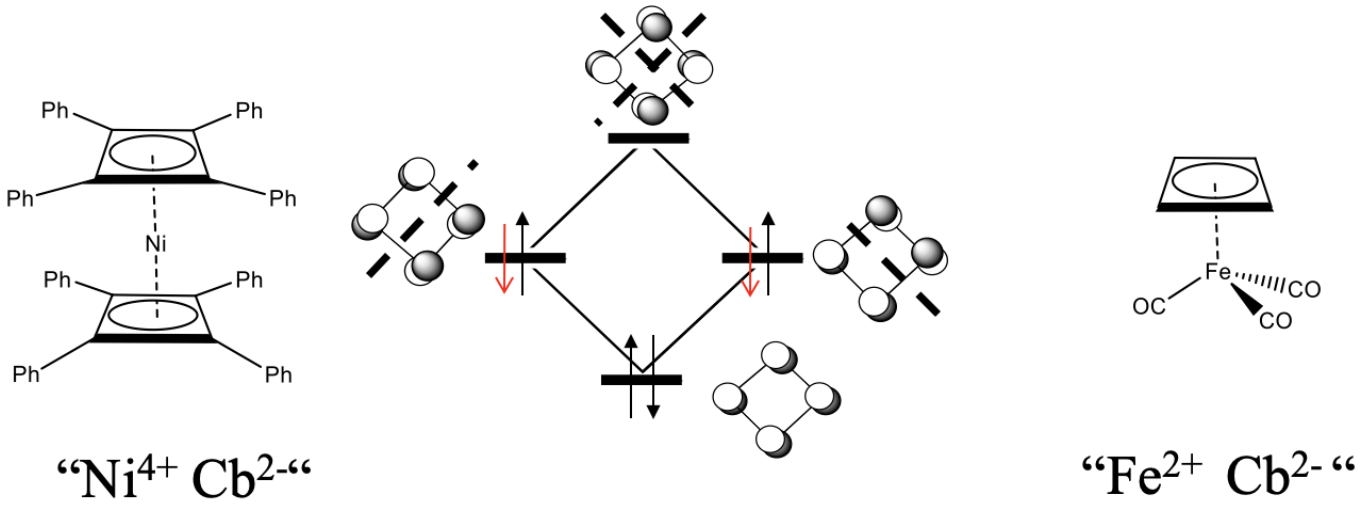
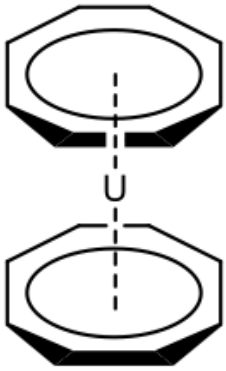


Figure 13.5.2.27: Complexes with cyclobutadiene

What would be an 18 electron sandwich complex with two cyclobutadiene ligands? Because each cyclobutadiene contributes four electrons, ten electrons would need to come from the metal, and we would expect a nickel cyclobutadienyl complex $Ni(Cb)_2$. This complex is not known, but derivatives are. For example a Ni complex with two tetraphenyl butadiene ligands are known (Figure 13.5.2.27). Another example is the butadienyl tricarbonyl iron (0) complex. Interestingly, when cyclobutadiene acts as a η^4-ligand, then it is not distorted, but square planar. An explanation is that we can formally treat the cyclobutadiene ligand as an Cb^{2-} ligand binding to a metal cation. For instance in $FeCb(CO)_3$ the Fe would be an Fe^{2+}, in the nickel complex, the nickel would be a Ni^{4+}. The Cb^{2-} anion would formally aromatic because it has 4n+2=6 electrons. The additional two electrons would be in the non-bonding orbitals. Because the two non-bonding orbitals are completely filled now, there would be no longer a driving force for the distortion. Note though that is is a formal view only, and there are arguments that speak against this view. One is that the addition of the two electrons to the ligand should further destabilize the ring because the added electrons are non-bonding. Aromaticity would rather be achieved by removing two electrons to form a Cb^{2+} cation that would have only two electrons in the bonding orbital.

Cyclooctetraene (cot) as a ligand

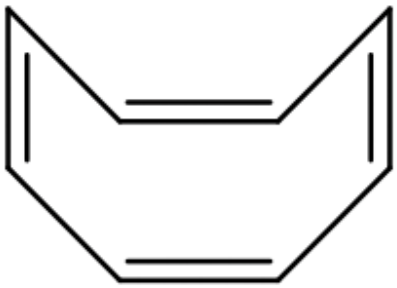
Also metallocenes with cyclooctatetraene (cot) acting as η^8-ligand is known. However, because of the large ring size only metals with large atomic radii, can make metallocenes with this ligand. For example uranium makes a uranocenes with two cyclooctatetraene ligands (Figure 13.5.2.28).



planar, formally aromatic (cot^{2-})

Figure 13.5.2.28: Aromatic Cot^{2-} ligand

Like cyclobutadiene, cyclooctatetraene is an anti-aromatic ligand with 4n=8 π-electrons (n=2). In the free cyclooctatetraene molecule is non-planar and the π-electrons are localized (Figure 13.5.2.29).



non-planar, antiaromatic

Figure 13.5.2.29: Free cyclooctatraene is non-planar, thus π electrons are localized.

In metallocenes however, the ring becomes planar (Figure 13.5.2.28). One can again formally explain that by assuming an aromatic *cot*$^{2-}$ ligand that binds to a metal 2+ cation, however one should keep in mind again that this is a formal view and not necessarily reflects the bonding situation in the compound.

Metals having smaller atomic radius can bind to *cot* in η^2, η^4, and less commonly in η^6-mode. The 18 electron rule holds in most cases. For instance, *cot* can make a η^4-complex in tricarbonyl cyclooctatetraene ruthenium (0) (Figure 13.5.2.30).

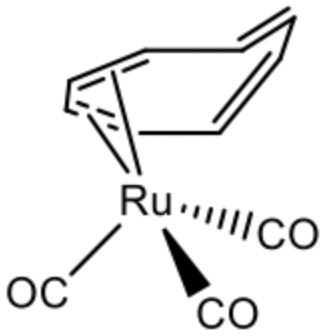


Figure 13.5.2.30: tricarbonyl cyclooctatetraene ruthenium (0)

Also two metals can bind to a single *cot*-ligand. This is for instance realize in μ-cyclooctetraene bis(tricarbonyl ruthenium (0) (Figure 13.5.2.31).

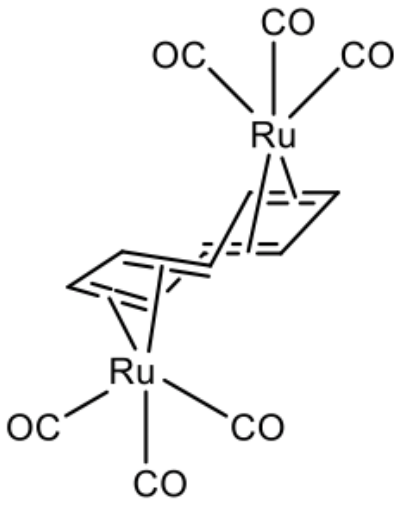


Figure 13.5.2.31: bis(tricarbonyl) cyclooctetraene ruthenium (0)

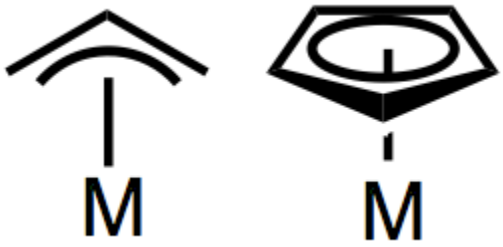
Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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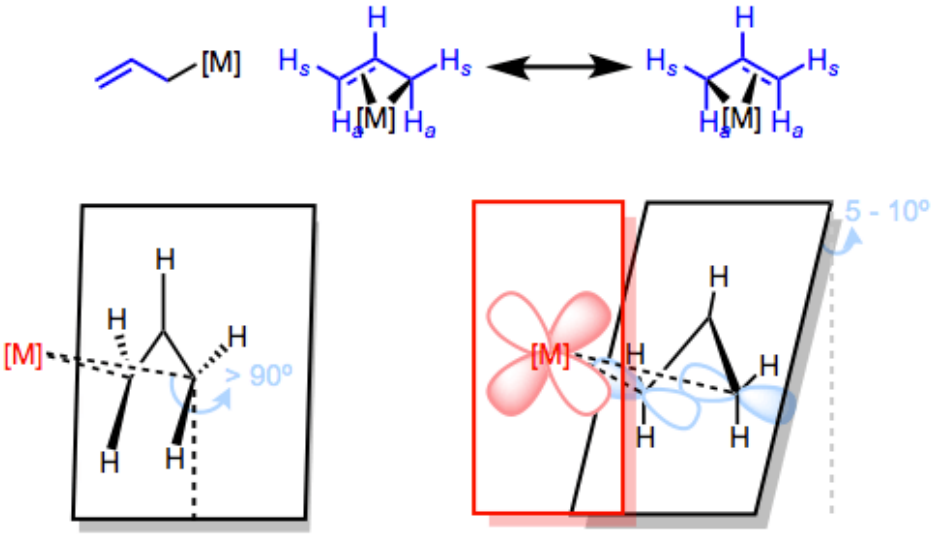
13.5.3: Odd-numbered π Systems

Odd-numbered π systems—most notably, the allyl and cyclopentadienyl ligands—are formally LnX-type ligands bound covalently through one atom (the “odd man out”) and datively through the others. This formal description is incomplete, however, as resonance structures reveal that multiple atoms within three- and five-atom π systems can be considered as covalently bound to the metal. To illustrate the plurality of equally important resonance structures for this class of ligands, we often just draw a curved line from one end of the π system to the other. Yet, even this form is not perfect, as it obscures the possibility that the datively bound atoms may dissociate from the metal center, forming σ-allyl or ring-slipped ligands. What do the odd-numbered π systems really look like, and how do they really behave?



General Properties

Allyls are often actor ligands, most famously in allylic substitution reactions. The allyl ligand is an interesting beast because it may bind to metals in two ways. When its double bond does not become involved in binding to the metal, allyl is a simple X-type ligand bound covalently through one carbon—basically, a monodentate alkyl! Alternatively, allyl can act as a bidentate LX-type ligand, bound to the metal through all three conjugated atoms. The LX or “trihapto” form can be represented using one of two resonance forms, or (more common) the “toilet-bowl” form seen in the general figure above. I don’t like the toilet-bowl form despite its ubiquity, as it tends to obscure the important dynamic possibilities of the allyl ligand.

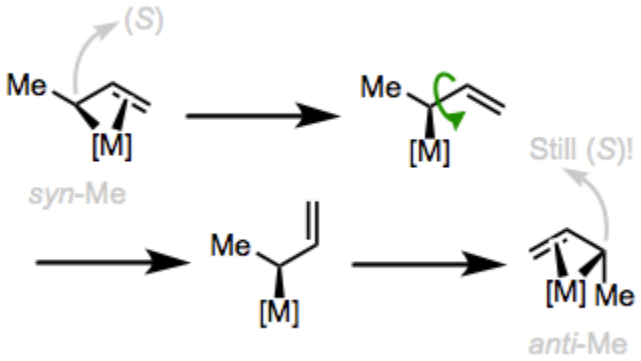


Can we use FMO theory to explain the wonky geometry of the allyl ligand?

The lower half of the figure above illustrates the slightly weird character of the geometry of allyl ligands. In a previous post on even-numbered π systems, we investigated the orientation of the ligand with respect to the metal and came to some logical

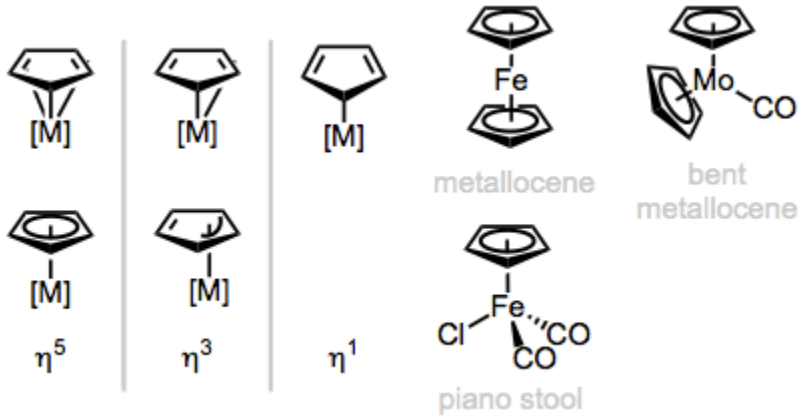
conclusions by invoking FMO theory and backbonding. A similar treatment of the allyl ligand leads us to similar conclusions: the plane of the allyl ligand should be parallel to the xy-plane of the metal center and normal to the z-axis. In reality, the allyl plane is slightly canted to optimize orbital overlap—but we can see at the right of the figure above that π2–dxy orbital overlap is key. Also note the rotation of the anti hydrogens (anti to the central C–H, that is) toward the metal center to improve orbital overlap.

Exchange of the syn and anti substituents can occur through σ,π-isomerization followed by bond rotation and formation of the isomerized trihapto form. Notice that the configuration of the stereocenter bearing the methyl group is unaffected by the isomerization! It should be noted that 1,3-disubstituted allyl complexes almost exclusively adopt a syn,syn configuration without danger of isomerization.



The methylene and central C–H simply change places!

Upon deconstruction, the cyclopentadienyl (Cp) ligand yields the aromatic cyclopentadienyl anion, an L2X-type ligand. Cp is normally an η5-ligand, but η3 (LX) and η1 (X) forms are known in cases where the other ligands on the metal center are tightly bound. η1-Cyclopentadienyl ligands can sometimes be fluxional—the metal has the ability to "jump" from atom to atom. Variations on the Cp theme include Cp* (C5Me5) and the monomethyl version (C5H4Me). Cp may be found as a loner alongside other ligands (in "half-sandwich" or "piano-stool" complexes), or paired up with a second Cp ligand in metallocenes. The piano-stool and bent metallocene complexes are most interesting for us, since these have potential for open coordination sites—plain vanilla metallocenes tend to be relatively stable and boring.

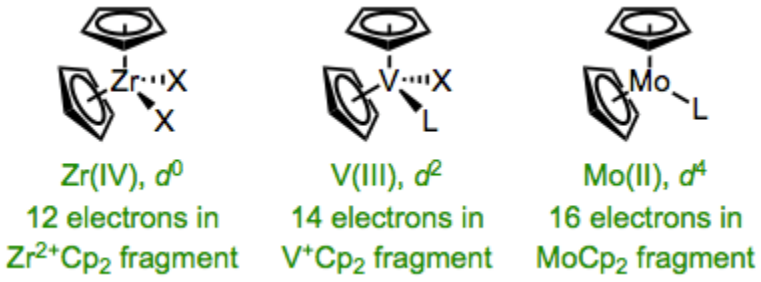


Binding modes of Cp and general classes of Cp complexes.

Research for this post has made me appreciate the remarkable electron-donating ability of the cyclopentadienyl (Cp) ligand, which renders its associated metal center electron rich. The LUMO of Cp is high in energy, so the ligand is a weak π-acid and is, first and foremost, a σ-donor. This effect is apparent in the strong backbonding displayed by Cp carbonyl complexes. Despite its strong donating ability, Cp is rarely an actor ligand unless another ligand shakes things up—check out the nucleophilic reactivity of doubly jazzed-up ferrocene for a nice example.

It's critical to recognize that η5-Cp is a six-electron ligand (!). Because Cp piles on electrons, the numbers of ligands bound to

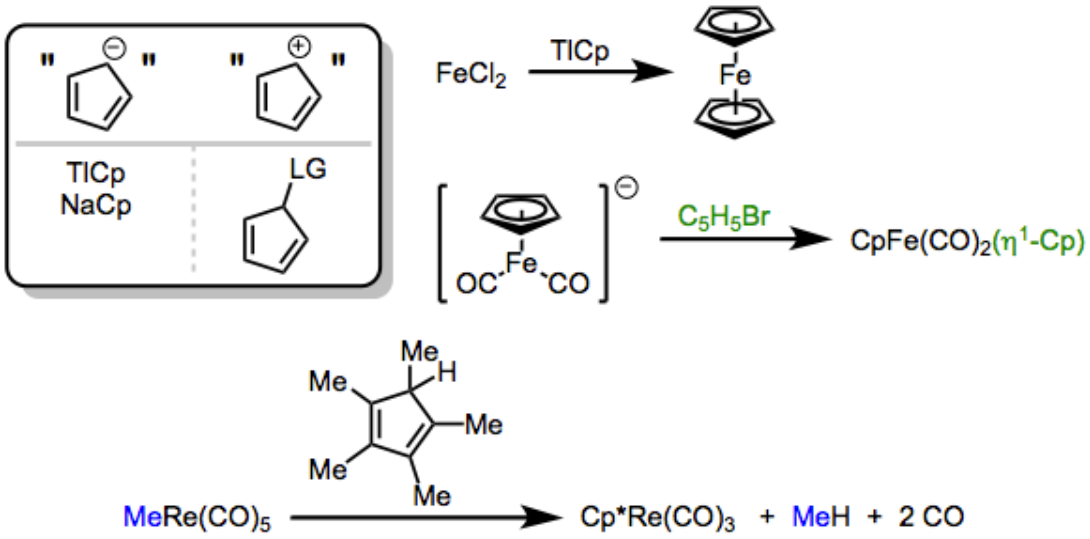
the metal in Cp complexes tend to be lower than we might be used to, especially in bent metallocenes containing two Cp's. Still, the number of ligands we'd expect on the metal center in these complexes is perfectly predictable. We just need to keep in mind that the resulting complexes are likely to contain 16 or 18 total electrons.



By considering the MCp2 fragment, we can predict the nature of ancillary ligands in bent metallocenes.

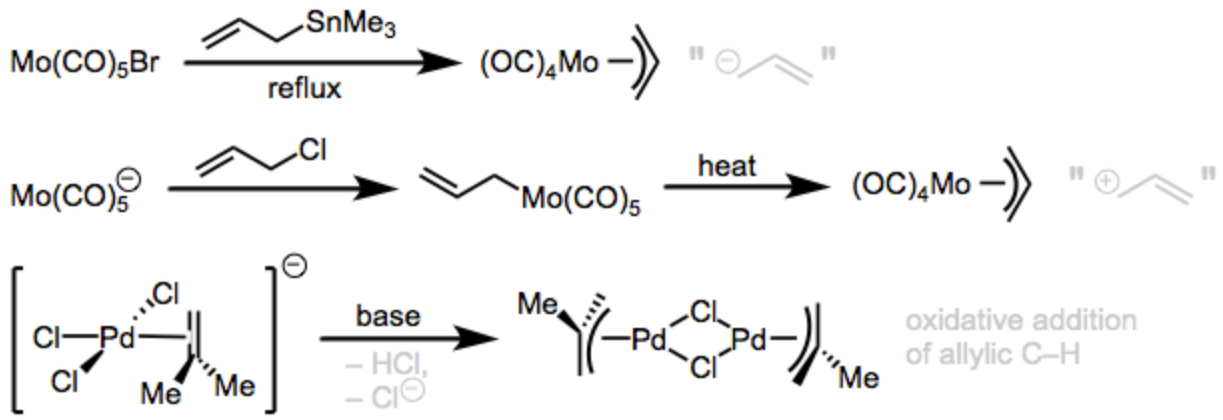
Synthesis

Crabtree cleanly divides methods for the synthesis of Cp complexes into those employing Cp+ equivalents, Cp– equivalents, and the neutral diene. Naturally, the first class of reagents are appropriate for electron-rich, nucleophilic complexes, while the second class are best used in conjunction with electron-poor, electrophilic complexes. The figure below provides a few examples.



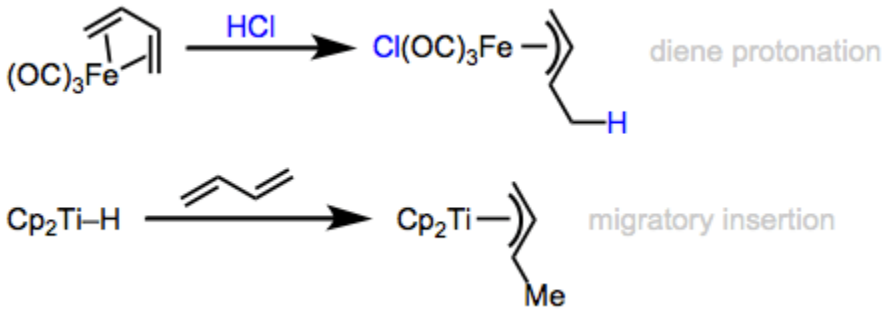
Methods for the synthesis of Cp complexes. The possibilities are exhausted by anionic, cationic, and neutral Cp equivalents!

Methods for synthesizing allyl complexes can also be classified according to whether the allyl donor is a cationic, anionic, or neutral allyl equivalent. In metal-catalyzed allylic substitution reactions, the allyl donor is usually a good electrophile bearing a leaving group displaced by the metal (an allyl cation equivalent). However, similar complexes may be obtained through oxidative addition of an allylic C–H bond to the metal, as in the synthesis of methallyl palladium chloride dimer below. Transmetalation of nucleophilic allyls from one metal to another, which we can imagine as nucleophilic attacks of an anionic allyl group, are useful when the metal is electron-poor.



Nucleophilic, electrophilic, and neutral allyl donors.

Complexes containing conjugated dienes are also viable precursors to allyl complexes. Migratory insertion of a diene into the M–H bond is a nice route to methyl-substituted allyl complexes, for example. Interestingly, analogous insertions of fulvenes do not appear to lead to Cp complexes, but some funky reductive couplings that yield ansa-metallocenes are known. External electrophilic attack (e.g., protonation) and nucleophilic attack on coordinated dienes also result in allyl complexes. In essence, one double bond of the diene becomes a part of the allyl ligand in the product; the other is used as a "handle" to establish the key covalent bond to the allyl ligand.

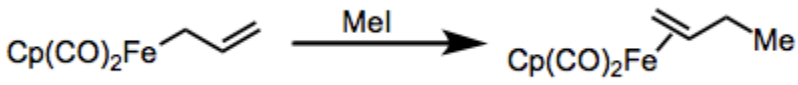


Dienes: brave crusaders in the quest for allyl complexes.

Reactions

Since the Cp ligand is typically a spectator, we'll focus in this section on the reactivity of allyl ligands. As usual, the behavior of the allyl ligand depends profoundly on the nature of its coordinated metal center, which depends in turn on the metal's ancillary ligands. Avoid "tunnel vision" as you study the examples below—depending on the issue at hand, the ancillary ligands may be as important as (or more important than) the actor ligand.

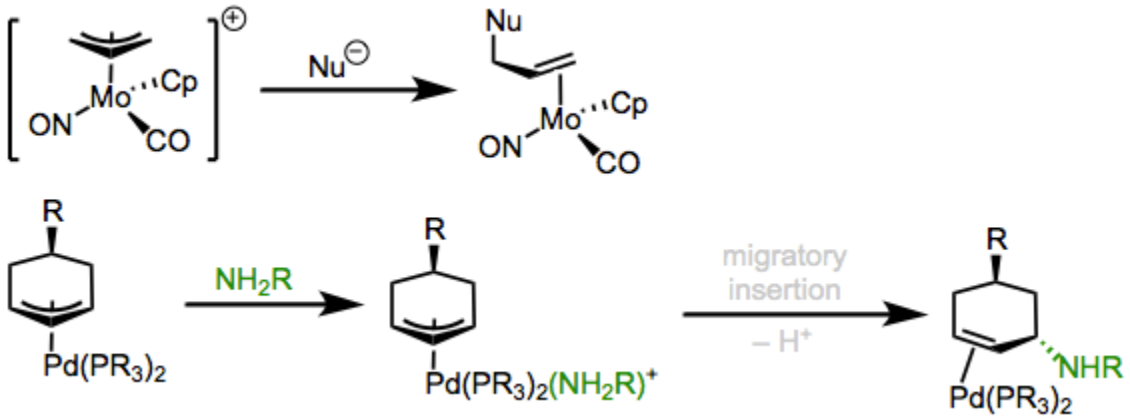
Nucleophilic allyl complexes react with electrophiles like H+, MeI, X+, and acylium ions to yield cationic alkene complexes.



Attack of electrophiles on nucleophilic allyl complexes. Notice the donating Cp ligand!

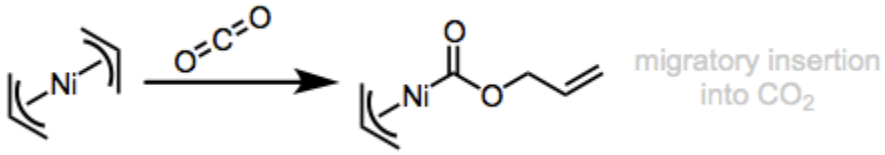
In a conceptually related process, nucleophiles can attack allyl ligands bound to electrophilic metals. This process is key in allylic substitution reactions. In some cases, the nucleophile is known to bind to the metal first, then transfer to the allyl ligand through reductive elimination. Alternatively, direct attack on the allyl ligand may occur on the face opposite the metal. The figure below

illustrates both possibilities.



External and internal attack of nucleophiles on coordinated allyl ligands.

Migratory insertion of allyl ligands is known, and is analogous to insertions involving alkyl ligands (see the figure below). Movement of the allyl ligand toward the coordination site of the dative ligand is assumed. Of course if oxidative addition to form allyl complexes is possible, reductive elimination of allyl ligands with other X-type ligands is also possible. We'll hit on these process in more detail in their dedicated posts.



Like alkyl ligands, allyls can migrate onto dative ligands like CO and π bonds.

One final post on σ-complexes will bring this series to a temporary close. In the next post, we'll look at ligands that, rather surprisingly, bind through their σ-electrons. These "non-classical" ligands behave like other dative ligands we've seen before, but are important for many reactions that involve main-group single bonds, such as oxidative addition. Before their discovery, the relevance of σ-ligands for reaction mechanisms went unappreciated by organometallic chemists.

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- 2.8: Odd-numbered π Systems by Michael Evans is licensed CC BY-NC-SA 4.0.

13.5.4: Fullerene Complexes

The π systems of fullerenes (eg buckmisterfullerene, C_{60}) also act as ligands for metal complexes. Most transition metal-fullerene complexes are derived from C_{60}. The structure of $C_{60}[IrCl(CO)(PMe_3)_2]_2$ is shown in Figure 13.5.4.1.

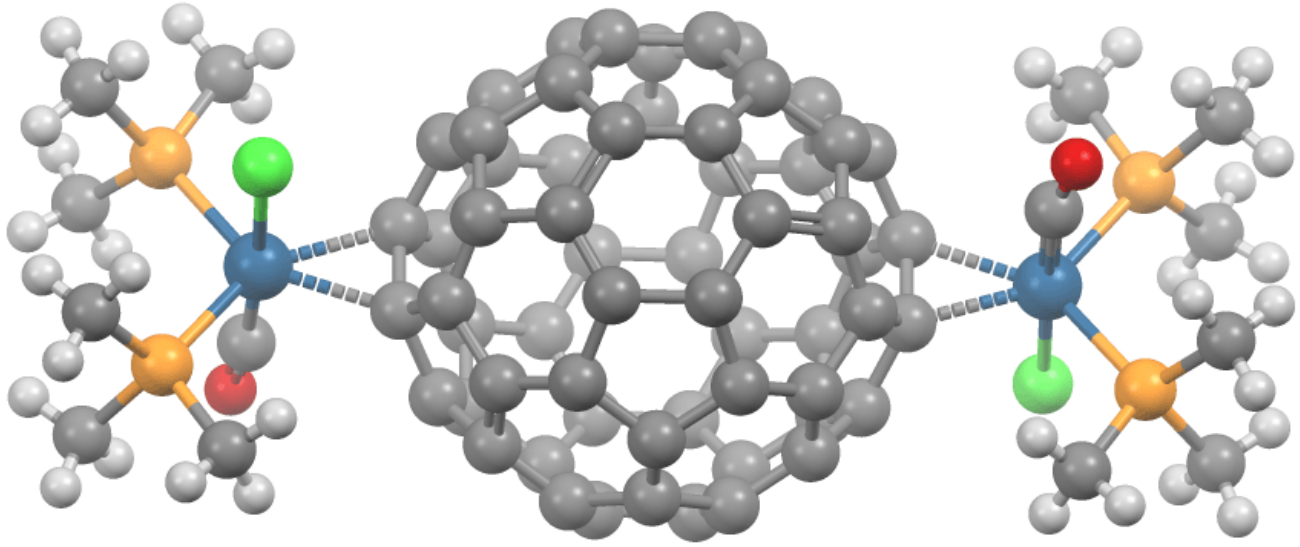


Figure 13.5.4.1: Structure of $C_{60}[IrCl(CO)(PMe_3)_2]_2$. doi=10.1021/ic00101a015. (Smokefoot, YEMVOB, CC BY-SA 4.0)

As ligands, fullerenes behave similarly to electron-deficient alkenes, and they prefer coordination to electron-rich metal centers (metal ions with softer character like those of the 4d and 5d transition metals). They almost always coordinate in a dihapto (η^2) fashion. The η^2 metal binding most often occurs on the junction of two 6-membered rings, as shown for $[[Ph_3P]_2Pt]_6(\eta^2\text{-}C_{60})$ on the left of Figure 13.5.4.2. In (\ce{Ru3(CO)9(C60)}\), the fullerene binds to the triangular face of the cluster as shown on the right in Figure 13.5.4.2.

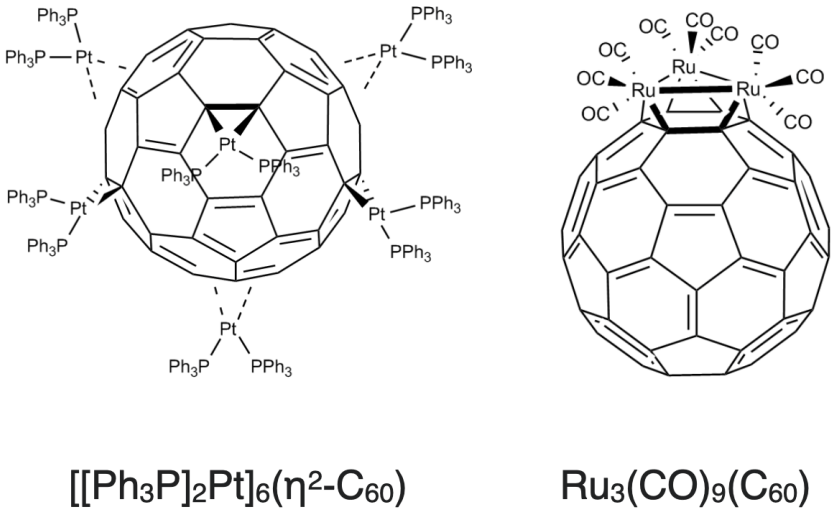


Figure 13.5.4.2: Structures of two η^2 fullerene complexes. Left, $[[Ph_3P]_2Pt]_6(\eta^2\text{-}C_{60})$. Right, $Ru_3(CO)_9(C_{60})$. (CMSherwood, Fullerene 4 and Fullerene 2, CC BY-SA 3.0)

Hexahapto and pentahato binding is possible, but is less common that dihapto coordination. Modification of the fullerene with phynyl substituents makes the fullerene a more electron rich ligand so that penta- and hexahapto coordination is more favorable.

For example, the pentaphenyl anion, $\mathrm{C_{60}Ph_5}^-$, binds to Fe in a pentahpto (η^5) fashion, similar to the interactions in ferrocene (Left, Figure $13.5.4.3$).

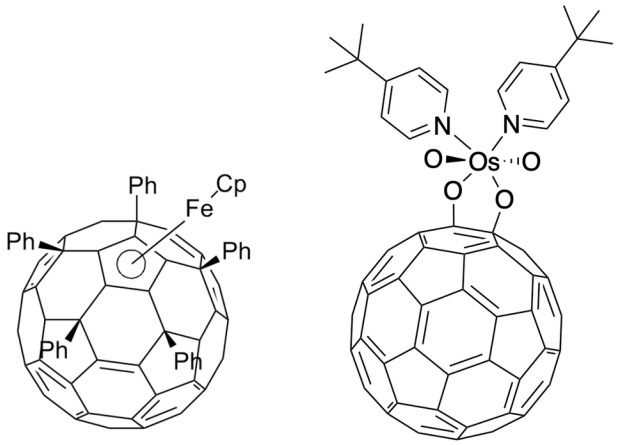


Figure $13.5.4.3$: Structures of two modified fullerenes. Left, a ferrocene-like complex of the pentaphynyl bucknisterfullerene anion (CMSherwood, Fullerene 3, CC BY-SA 3.0). Right, the structure of \(\ce{C60(OsO4)(4-*t*-butylpyridine)2}\), which was important for the original determination of the structure for $\mathrm{C_{60}}$
(CC-BY-SA; Kathryn Haas).

The first X-ray structure that gave insight into the spherical structure of fullerenes was derived from an oxygen adduct of osmium tetroxide (Right, Figure $13.5.4.3$).

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13.6: METAL-CARBON BONDS

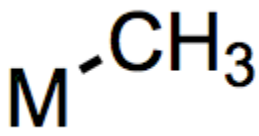
13.6.1: Metal Alkyls
13.6.2: Carbenes
13.6.3: Carbyne (Alkylidyne) Complexes
13.6.4: Carbido and Cumulene Complexes
13.6.5: Carbon Wires- Polyyne and Polyene Bridges

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13.6.1: Metal Alkyls

Part 1:

With this post we finally reach the defining ligands of organometallic chemistry, alkyls. Metal alkyls feature a metal-carbon σ bond and are usually actor ligands, although some alkyl ligands behave as spectators. Our aim will be to understand the general dependence of the behavior of alkyl ligands on the metal center and the ligand's substituents. Using this knowledge, we can make meaningful comparisons between related metal alkyl complexes and educated predictions about their likely behavior. Because alkyl ligands are central to organometallic chemistry, I've decided to spread this discussion across multiple posts. We'll deal first with the general properties of metal alkyls.



In the Simplifying the Organometallic Complex series, we decomposed the M–C bond into a positively charged metal and negatively charged carbon. This deconstruction procedure is consistent with the relative electronegativities of carbon and the transition metals. It can be very useful for us to imagine metal alkyls essentially as stabilized carbanions—but it's also important to understand that M–C bonds run the gamut from extremely ionic and salt-like ($NaCH_3$) to essentially covalent ($[HgCH_3]^+$). The reactivity of the alkyl ligand is inversely related to the electronegativity of the metal center.

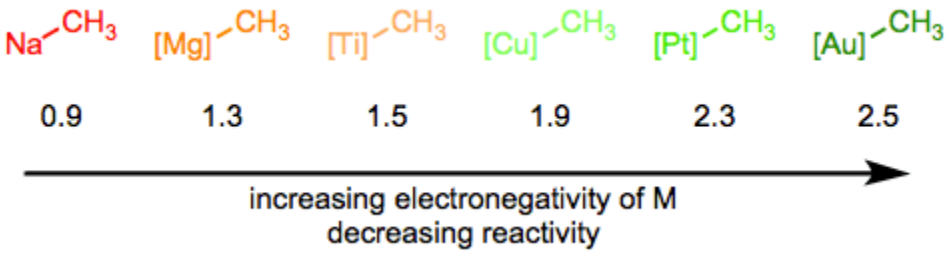


Figure 13.6.1.1: Reactivity decreases as the metal's electronegativity increases. Values given are Pauling electronegativities. (Michael Evans)

The hybridization of the carbon atom is also important, and the trend here follows the trend in nucleophilicity as a function of hybridization in organic chemistry. *sp*-Hybridized ligands are the least nucleophilic, followed by sp^2 and sp^3 ligands respectively.

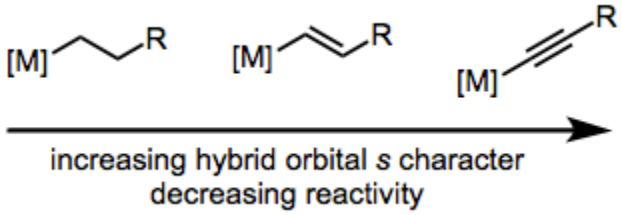


Figure 13.6.1.1: Note that this trend is similar to the nucleophilicity of carbanions as a function of hybridization. (Michael Evans)

The history of transition metal alkyls is an intriguing example of an incorrect scientific paradigm. After several unsuccessful attempts to isolate stable metal alkyls, organometallic chemists in the 1920s got the idea that metal-carbon bonds were weak in general. However, later studies showed that it was *kinetic instability*, not thermodynamic, that was to blame for our inability to isolate metal alkyls. In other words, most metal alkyls are susceptible to decomposition pathways with low activation barriers—the instability of the M–C bond *per se* is not to blame. Crabtree cites typical values of 30-65 kcal/mol for M–C bond strengths.

What are the major decomposition pathways of metal alkyl complexes? **β-hydride elimination** is the most common. Thermodynamically, the ubiquity of β-hydride elimination makes sense—M–C bonds run 30-65 kcal/mol, while M–H bonds tend to be stronger. The figure below summarizes the accepted mechanism and requirements of β-hydride elimination. We'll revisit this fundamental reaction of organometallic complexes in a future post.

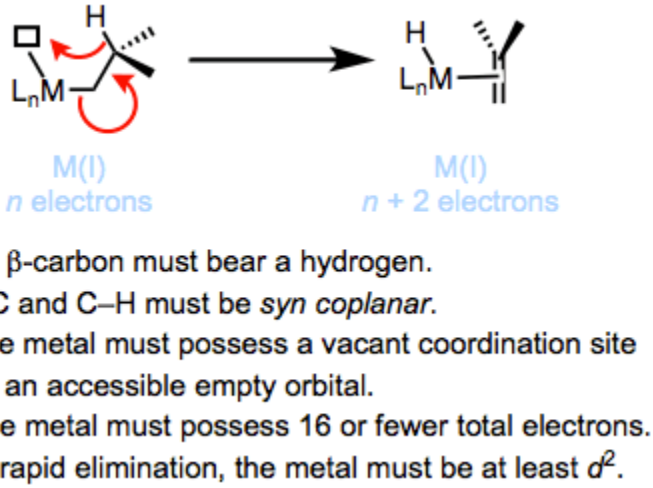


Figure 13.6.1.1: What kinds of metal alkyl complexes violate the requirements for beta-hydride elimination? (Copyright; author via source)

Kinetically stable metal alkyl complexes violate one of the requirements for β-hydride elimination. Methyl and neopentyl complexes lack β-hydrogens, violating requirement 1. Tightly binding, chelating ligands may be used to prevent the formation of an empty coordination site, violating requirements 3a and 3b. Titanium complexes are known that violate requirement 4 and eliminate only very slowly—back-donation from the metal to the σ^*_{C-H} is required for rapid elimination (see below).

Reductive elimination is a second common decomposition pathway. The alkyl ligand hooks up with a second X-type ligand on the metal, and the metal is reduced by two units with a decrease in the total electron count by two units. I've omitted curved arrows here because different mechanisms of reductive elimination are known. We'll discuss the requirements of reductive elimination in detail in a future post; for now, it's important to note that the thermodynamic stability of C–X versus that of (M–X + M–C) is a critical driving force for the reaction.

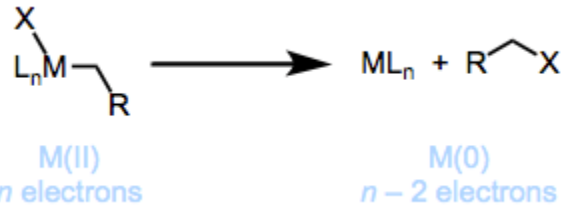


Figure 13.6.1.1: The thermodynamics of reductive elimination can present problems for some alkyl complexes. (Copyright; author via source)

When X = H, reductive elimination is nearly always thermodynamically favorable; thus, isolable alkyl hydride complexes are rare. This behavior is a feature, not a bug, when we consider that hydrogenation chemistry depends on it! On the other hand, when X = halogen reductive elimination is usually disfavored. Reductive elimination of C–C (X = C) can be favored thermodynamically, but is usually slower than the corresponding C–H elimination.

Complexes that cannot undergo β-hydride elimination are sometimes susceptible to **α-elimination**, a mechanistically similar process that forms a metal carbene. This process is particularly facile when the α-position is activated by an adjacent electron donor (Fischer carbenes are the result).

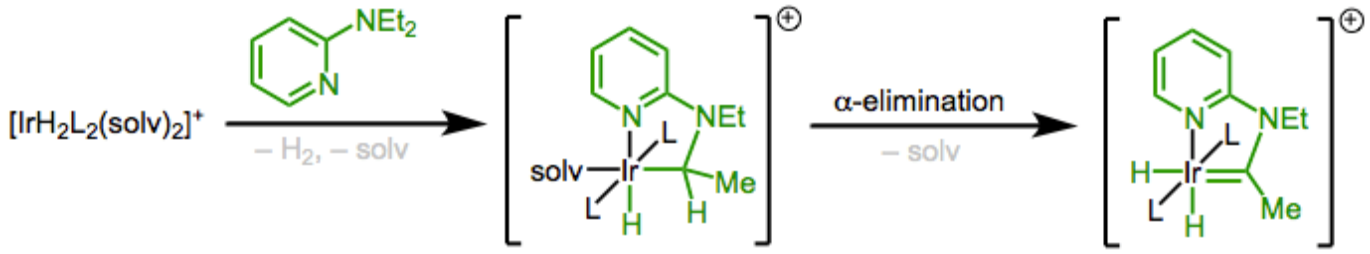


Figure 13.6.1.1: Oxidative addition followed by alpha-elimination, forming a Fischer carbene from an alkyl complex. (Copyright; author via source)

In some metal alkyl complexes, C–H bonds at the α, β, or even farther positions can serve as electron donors to the metal center. This idea is supported by crystallographic evidence and NMR chemical shifts (the donating hydrogens shift to high field). Such interactions are called **agostic interactions**, and they resemble an "interrupted" transition state for hydride elimination. Alkyl complexes that cannot undergo β-hydride elimination for electronic reasons (high oxidation state, d^0 metals) and vinyl complexes commonly exhibit this phenomenon. The fact that β-hydride elimination is slow for d^0 metals—agostic interactions are seen instead—suggests that back-donation from a filled metal orbital to the σ^*_{C-H} is important for β-hydride elimination. Here's an interesting, recent-ish review of agostic interactions.

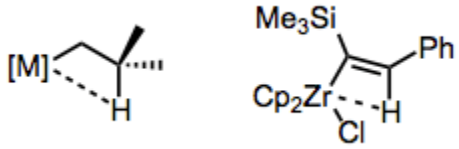


Figure 13.6.1.1: Copy and Paste Caption here. (Copyright; author via source)

In the next post in this series, we'll explore the synthesis of metal alkyl complexes in more detail, particularly clarifying the question: how can we conquer β-hydride elimination?

Part 2:

In this post, we'll explore the most common synthetic methods for the synthesis of alkyl complexes. In addition to enumerating the reactions that produce alkyl complexes, this post will also describe strategies for getting around β-hydride elimination when isolable alkyl complexes are the goal. Here we go!

Properties of Stable Alkyl Complexes

Stable alkyl complexes must be resistant to β-hydride elimination. In the last post we identified four key conditions necessary for elimination to occur:

1. The β-carbon must bear a hydrogen.
2. The M–C and C–H bonds must be able to achieve a *syn* coplanar orientation (pointing in the same direction in parallel planes).
3. The metal must bear 16 total electrons or fewer and possess an open coordination site.
4. The metal must be at least d^2.

Stable alkyl complexes must violate at least one of these conditions. For example, titanium(IV) complexes lacking *d* electrons β-eliminate very slowly. The complex below likely also benefits from chelation (see below).

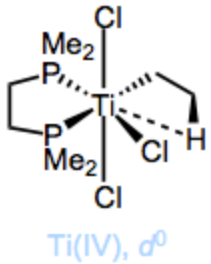


Figure 13.6.1.1: No d electrons here! (Michael Evans)

Complexes have been devised that are unable to achieve the *syn* coplanar orientation required for elimination, or that lack β-hydrogens outright. A few examples are provided below—one has to admire the cleverness of the researchers who devised these complexes. The metallacyclobutane is particularly striking!

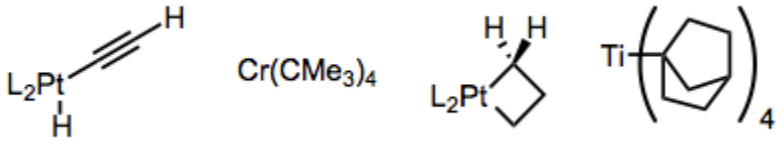


Figure 13.6.1.1: Complexes whose beta-C–H bonds cannot align in a syn coplanar manner with the M–C bond. (Copyright; author via source)

Using tightly binding, chelating ligands or a directing group on the substrate, the formation of 16-electron complexes susceptible to β-hydride elimination can be discouraged. Notice how the hyrdrogen-bonding L_2 ligands in the central complex below hold the metal center in a death grip.

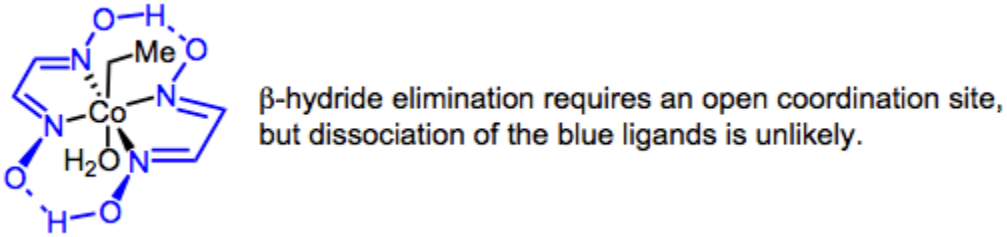


Figure 13.6.1.1: Tightly chelating ligands prevent the opening of a coordination site. (Copyright; author via source)

Finally, it's worth noting that complexes with an open coordination site—such as 16-electron, square-planar complexes of Ni, Pd, and Pt important for cross-coupling—are susceptible to reactions with solvent or other species at the open site. Bulky alkyl ligands help prevent these side reactions. In the example below, the methyl groups of the *o*-tolyl ligands extend into the space above and below the square plane, discouraging the approach of solvent molecules perpendicular to the plane.

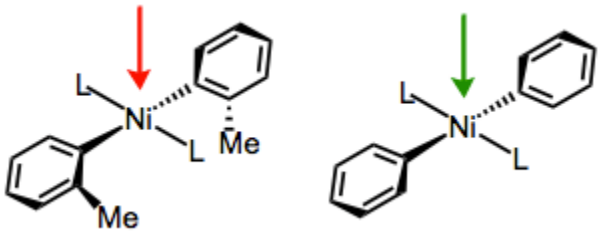


Figure 13.6.1.1: The approach of solvent perpendicular to the square plane is slowed by methyl groups on the aryl ligand. (Copyright; author via source)

Many transition metal complexes catalyze (*E*)/(*Z*) isomerization and the isomerization of terminal alkenes (α-olefins) to internal isomers via β-hydride elimination. This is a testament to the importance of this process for alkyl complexes. Of course, transient alkyl complexes may *appear* to be susceptible to β-hydride elimination, but if other processes are faster, elimination will not occur. Thus, the optimization of many reactions involving alkyl complexes as intermediates has involved speeding up other

processes at the expense of β-hydride elimination—hydrocyanation is a good example.

Synthesis of Alkyl Complexes

The dominant synthetic methods for alkyl complexes are based on nucleophilic attack, electrophilic attack, oxidative addition, and migratory insertion. The first two methods should be intuitive to the organic chemist; the second two are based on more esoteric (but no less important) reactions of organometallic complexes.

Metals bearing good leaving groups are analogous to organic electrophiles, and are susceptible to **nucleophilic attack** by organolithiums, Grignard reagents, and other polarized organometallics. These reactions can be viewed as a kind of **transmetalation**, as the alkyl ligand moves from one metal to another. Electron-withdrawing X-type ligands like –Cl and –Br should jump out as good leaving groups. On the other hand, clean substitution of L-type ligands by anionic nucleophiles is much more rare (anionic complexes would result).



Figure 13.6.1.1: Simple and straightforward: nucleophile attacks electrophilic metal. (Copyright; author via source)

Many anionic metal complexes are nucleophilic enough to attack electrophilic sources of carbon such as alkyl and acyl halides in an **electrophilic attack** mode. An available lone pair on the metal and open coordination site are prerequisites for this chemistry. The charge on the complex increases by one unit (in effect, negative charge is transferred to the electrophile's leaving group). We can classify these as oxidative ligation reactions—notice that the oxidation state of the metal increases by two units.

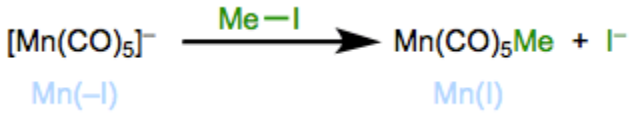


Figure 13.6.1.1: Oxidative ligation for the synthesis of alkyl complexes. Total electron count does not change. (Copyright; author via source)

Oxidative addition results in the cleavage of a W–Z bond and placement of two new X-type ligands (–W and –Z) on the metal center, with an increase in the oxidation state of the metal and the total electron count by two units. Organic halides are extremely common substrates for this reaction, the first step in the mechanism of cross-coupling reactions. The oxidized metal complex containing new alkyl and halide ligands is the final product. Notice that *two* open coordination sites are required (not necessarily simultaneously), the metal center must be amenable to two-electron oxidation, and the number of total electrons of the complex increases by two. In essence, the electrons of the W–Z bond join the complex's party. Take note that there are many known mechanisms for oxidative addition! We'll explore these different mechanisms in detail in a future post.

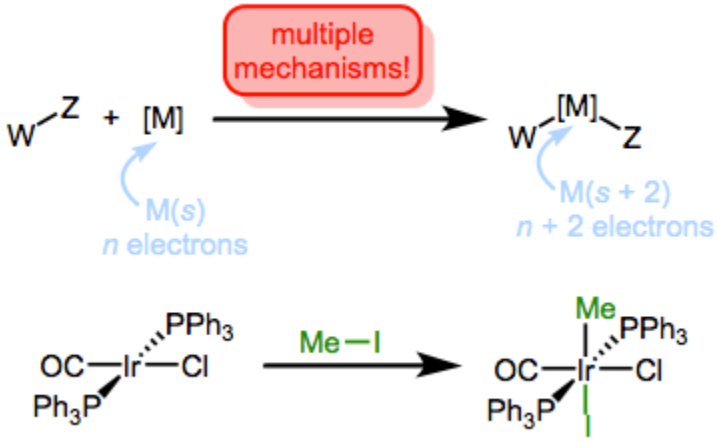


Figure 13.6.1.1: Oxidative addition, with a representative example, for the synthesis of metal alkyl complexes. (Copyright; author via source)

Finally, **migratory insertion** of unsaturated organic compounds is an important method for the synthesis of certain alkyl complexes, and an important step of organometallic reactions that result in addition across π bonds. Migratory insertion is the

microscopic reverse of β-hydride elimination. The clever among you may notice that the use of migratory insertion to synthesize alkyl complexes seems inconsistent with our observation that its reverse is ubiquitous for metal alkyls—shouldn't equilibrium favor the olefin hydride complex? In many cases this is the case; however, there are some notable exceptions. For example, perfluoroalkyl complexes are exceptionally stable (why?), so the insertion of fluoroalkenes is often favored over elimination.

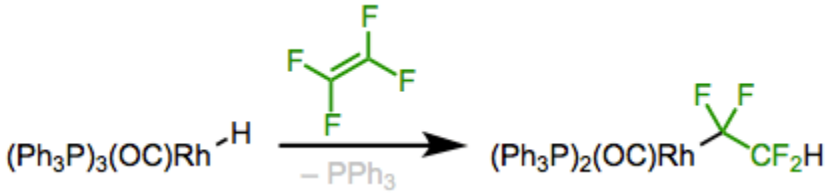


Figure 13.6.1.1: Why does this work? Thank fluorine! (Copyright; author via source)

As we noted above, we can still invoke kinetically stable alkyl complexes as *intermediates* in reactions provided subsequent steps are faster. In the next post, we'll examine the general classes of reactions in which alkyl complexes find themselves the major players, focusing on the specific mechanistic steps that involve the alkyl complex (reductive elimination, transmetalation, migratory insertion, and [naturally] β-hydride elimination).

Part 3:

In this last post on alkyl ligands, we'll explore the major modes of reactivity of metal alkyls. We've discussed β-hydride elimination in detail, but other fates of metal alkyls include reductive elimination, transmetallation, and migratory insertion into the M–C bond. In a similar manner to our studies of other ligands, we'd like to relate the steric and electronic properties of the metal alkyl complex to its propensity to undergo these reactions. This kind of thinking is particularly important when we're interested in controlling the relative rates and/or extents of two different, competing reaction pathways.

Reactions of Metal Alkyl Complexes

Recall that **β-hydride elimination** is an extremely common—and sometimes problematic—transformation of metal alkyls. Then again, there are reactions for which β-hydride elimination is desirable, such as the Heck reaction. Structural modifications that strengthen the M–H bond relative to the M–C bond encourage β-hydride elimination; the step can also be driven by trapping of the metal hydride product with a base (the Heck reaction uses this idea).

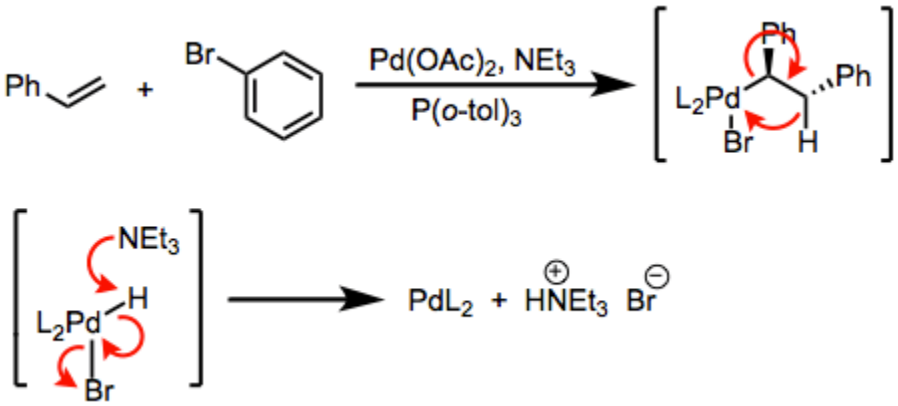


Figure 13.6.1.1: During the Heck reaction, beta-hydride elimination is driven by a base. (Copyright; author via source)

On the flip side, stabilization of the M–C bond discourages elimination and encourages its reverse: migratory insertion of olefins into M–H. Previously we saw the example of perfluoroalkyl ligands, which possess exceptionally stable M–C bonds. The fundamental idea here—that electron-withdrawing groups on the alkyl ligand stabilize the M–C bond—is quite general. Hartwig describes an increase in the "ionic character" of the M–C bond upon the addition of electron-withdrawing groups to the alkyl ligand (thereby strengthening the M–C bond, since ionic bonds are stronger than covalent bonds). Bond energies from organic chemistry bear out this idea to an extent; for instance, see the relative BDEs of Me–Me, Me–Ph, and Me–CCH in this reference. I still find this explanation a little "hand-wavy," but it serves our purpose, I suppose.

Metal alkyls are subject to **reductive elimination**, the microscopic reverse of oxidative addition. The metal loses two covalent ligands, its formal oxidation state decreases by two units, total electron count decreases by two units, and an R–X bond forms. Reductive elimination is favorable when the R–X bond in the organic product is more stable than the M–R and M–X bonds in the starting complex (a thermodynamic issue). It should be noted, however, that the kinetics of reductive elimination depend substantially on the steric bulk of the eliminating ligands. Concerted reductive elimination of R–H usually possesses a lower activation energy than R–R elimination.

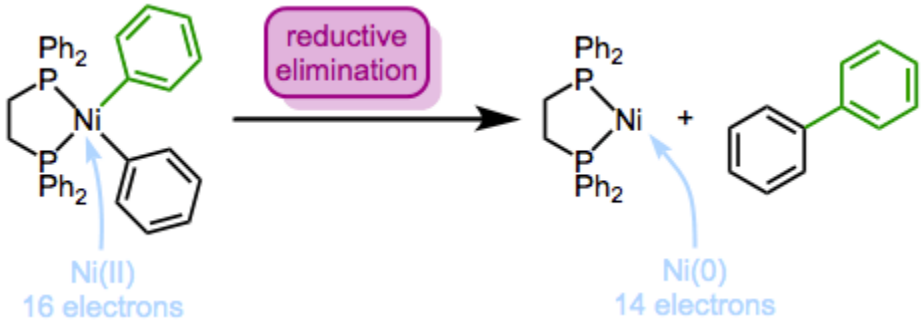


Figure 13.6.1.1: An example of reductive elimination. Intuitively, the electron density at the metal center increases as this step proceeds. (Copyright; author via source)

Transmetalation involves the transfer of an alkyl ligand from one metal to the other. An interesting problem concerns the relative reactivity of metal alkyls toward transmetalation. Assuming similar, uncomplicated ligand sets, which of two metal centers is more likely to hold on to an alkyl ligand? Consider the two situations below.

$$\mathrm{MR + M' \rightleftharpoons M + M'R}$$

$$\mathrm{MR + M'R' \rightleftharpoons MR' + M'R}$$

The first is a *bona fide* transmetalation; the second is really a double replacement reaction. The distinction is rarely drawn in practice, but it's important! The difference is that in the first case, a single-electron transfer of sorts must take place, while in the second case, no redox chemistry is necessary. Favorability in the first case is governed by the relative reduction potentials of M and M' (the reaction goes forward when M' is more easily oxidized than M); in the second case, the relative electropositivities of the metals is key, and other factors like lattice energies may be important. The distinction between transmetalation *per se* and double replacement explains the paradoxical synthetic sequence in the figure below. In practice, both are called "transmetalation." See these slides (page 6) for a summarizing reference.

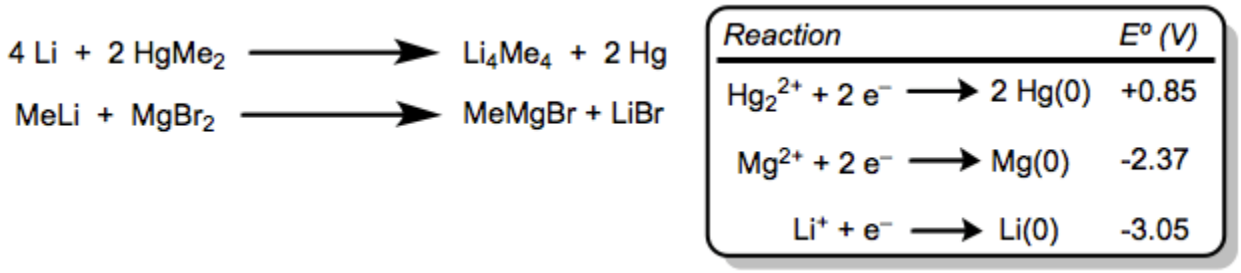


Figure 13.6.1.1: How are both of these reactions favorable? The first is a true transmetalation; the second is a double replacement. (Copyright; author via source)

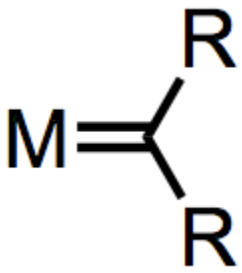
This brings our extended look at metal alkyl complexes to a temporary close. Of course, metal alkyls are *everywhere* in organometallic chemistry...so seeing them again is pretty much inevitable! The next installment in the Epic Ligand Survey series concerns allyl, cyclopentadienyl, and other odd-membered pi systems. These L_nX-type ligands can, like arenes, pile as many as six electrons on the metal center at once.

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- 2.5: Metal Alkyls by Michael Evans is licensed CC BY-NC-SA 4.0.

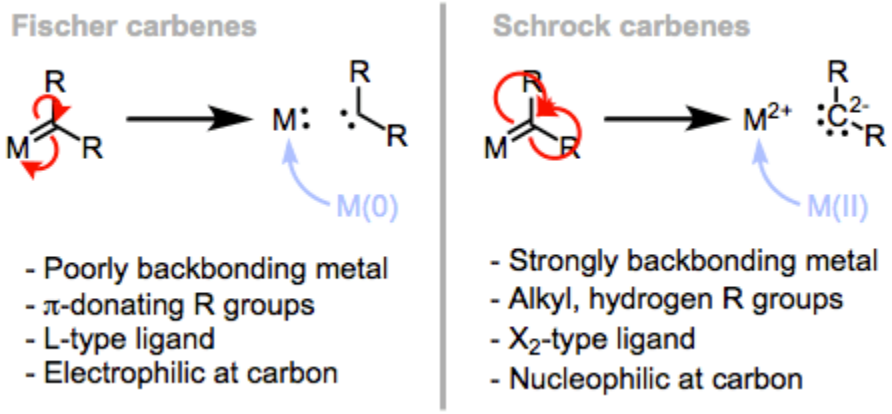
13.6.2: Carbenes

In a previous post, we were introduced to the N-heterocyclic carbenes, a special class of carbene best envisioned as an L-type ligand. In this post, we'll investigate other classes of carbenes, which are all characterized by a metal-carbon double bond. Fischer carbenes, Shrock carbenes, and vinylidenes are usually actor ligands, but they may be either nucleophilic or electrophilic, depending on the nature of the R groups and metal. In addition, these ligands present some interesting synthetic problems: because free carbenes are quite unstable, ligand substitution does not cut the mustard for metal carbene synthesis.



General Properties

Metal carbenes all possess a metal-carbon double bond. That's kind of a given. What's interesting for us about this double bond is that there are multiple ways to deconstruct it to determine the metal's oxidation state and number of d electrons. We could give one pair of electrons to the metal center and one to the ligand, as we did for the NHCs. This procedure nicely illustrates why compounds containing M=C bonds are called "metal carbenoids"—the deconstructed ligand is an L-type carbenoid. Alternatively, we could give both pairs of electrons to the ligand and think of it as an X2-type ligand. The appropriate procedure depends on the ligand's substituents and the electronic nature of the metal. The figure below summarizes the two deconstruction procedures.

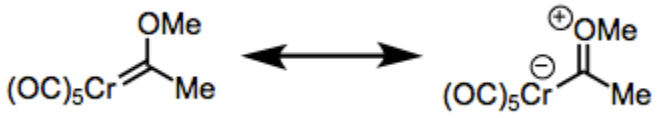


The proper method of deconstruction depends on the electronic nature of the ligand and metal.

When the metal possesses π-acidic ligands and the R groups are π-basic, the complex is best described as an L-type Fischer carbene and the oxidation state of the metal is unaffected by the carbene ligand. When the ligands are "neutral" (R = H, alkyl) and the metal is a good backbonder—that is, in the absence of π-acidic ligands and electronegative late metals—the complex is best described as an X2-type Schrock carbene. Notice that the oxidation state of the metal depends on our deconstruction method! Thus, we see that even the oxidation state formalism isn't perfect.

Deconstruction reveals the typical behavior of the methylene carbon in each class of complex. The methylene carbon of Schrock carbenes, on which electron density is piled through backbonding, is nucleophilic (the 2– charge screams nucleophilic!). On the other hand, the methylene carbon of Fischer carbons is electrophilic, because backbonding is weak and does not compensate for σ-donation from the ligand to the metal. To spot a Fischer carbene, be on the lookout for reasonable zwitterionic resonance

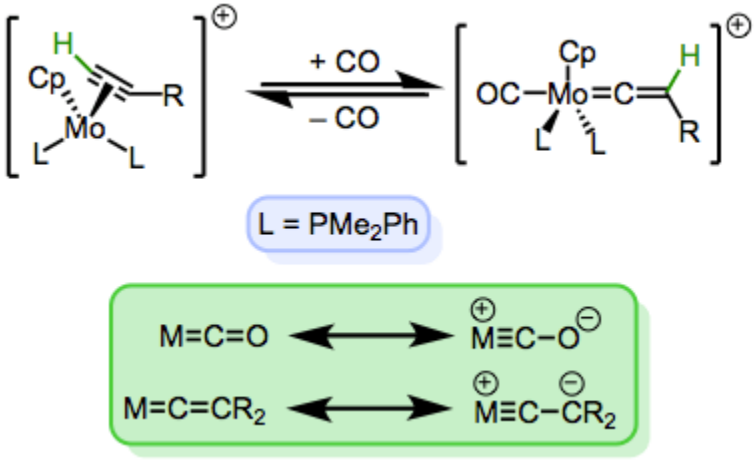
structures like the one at right below.



Thanks to the pi-accepting CO ligands, the metal handles the negative charge well. This is a Fischer carbene.

The clever reader may notice that we haven't mentioned π-acidic R groups, such as carbonyls. Complexes of this type are best described as Fischer carbenes as well, as the ligand is still electrophilic. However, complexes of this type are difficult to handle and crazy reactive (see below) without a π-basic substituent to hold them in check.

Vinylidenes are the organometallic analogues of allenes, and are best described as intermediate in behavior between Fischer and Schrock carbenes. They are electrophilic at the α carbon and nucleophilic at the β carbon—in fact, a nice analogy can be made between vinylidenes and carbon monoxide. Tautomerization to form alkyne π-complexes is common, as the vinylidene and alkyne complexes are often comparable in stability.



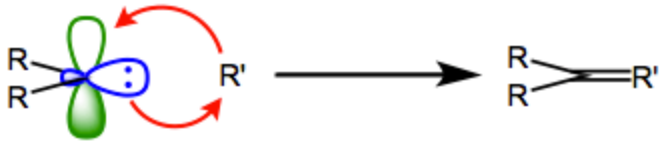
Vinylidene tautomerization, and an analogy between vinylidenes and CO.

Take care when diagnosing the behavior of metal carbenes. In these complexes, there is often a subtle interplay between the R groups on the carbene and other ligands on the metal. In practice, many carbenes are intermediate between the Fischer and Schrock ideals.

Synthesis

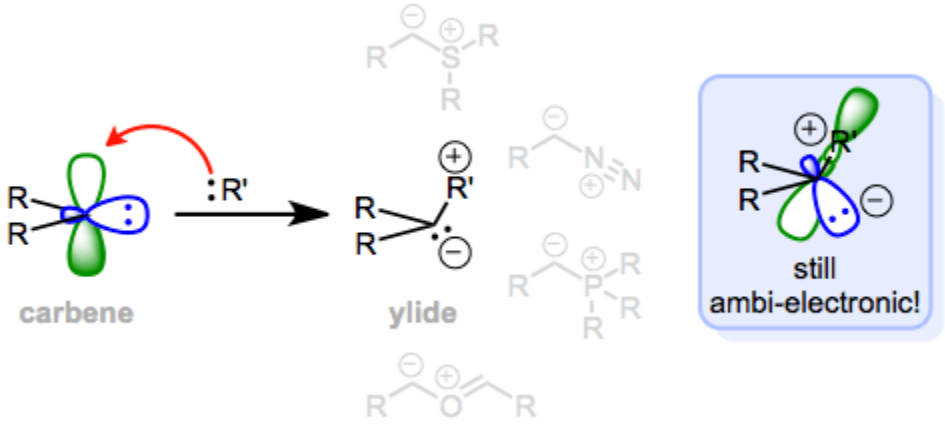
Metal carbenes present a fascinating synthetic problem. A cursory look at the deconstruction procedures above reveals that these complexes cannot be made using ligand substitution reactions, because the free ligands are far too unstable. Although the synthetic methods introduced here will be new for us, the attuned organic chemist will find them familiar. The conceptual foundations of metal carbene synthesis are similar to methods for the synthesis of alkenes in organic chemistry.

In the post on NHCs, we saw that the free carbene is both nucleophilic (via the lone pair in its σ system) and electrophilic (via its empty 2pz orbital). Organic precursors to metal carbenes and alkenes also possess this property—they can act both as nucleophiles and electrophiles. Fundamentally, this "ambi-electronic" behavior is useful for the creation of double bonds. One bond comes from "forward flow," and the other from "reverse flow." Naturally, the other reacting partner also needs to be ambi-electronic for this method to work.



A fundamental paradigm for double bond synthesis: ambi-electronic compounds doing what they do.

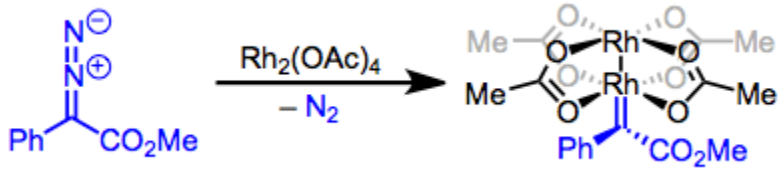
What sets carbene precursors apart from free carbenes? What other kinds of molecules may act as both nucleophiles and electrophiles at the same atom? Watch what happens when we tack a third group onto the free carbene...the figure below shows the result in general and a few specific examples in gray.



A "dative ligand" R' is the difference between a carbene and an ylide. Both are ambi-electronic.

An ylide, which contains adjacent positive and negative charges, results from this purely hypothetical process. Ylides (diazo compounds, specifically) are the most common precursors to metal carbene complexes. Like free carbenes, ylides are ambi-electronic. The electrophilic frontier orbital of an ylide is just the σ* orbital of the bond connecting the charged atoms, which makes sense if we consider the positively charged fragment as a good leaving group (it always is). The lone pair is still nucleophilic. The figure above depicts some of the most famous ylides of organic chemistry, including those used for alkene synthesis (Corey-Chaykovsky and Wittig) and cycloaddition reactions (the carbonyl ylide).

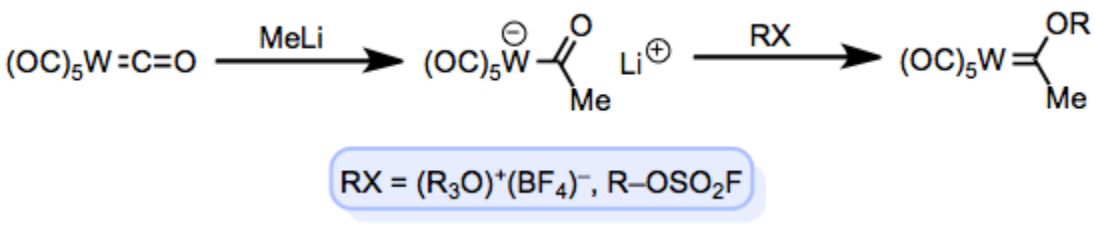
Although diazo compounds are most commonly drawn with charges on the two nitrogen atoms, the diazo carbon is a good nucleophile and can attack electrophilic metal centers to initiate metal carbene formation. A slick 15N kinetic isotope effect study showed that C–N bond cleavage is the rate-limiting step of the reaction below. Visualize the carbanionic resonance structure to kick off the mechanism! Don't think too hard about the structure of rhodium(II) acetate here. Rhodium, copper, ruthenium, and iridium all form carbene complexes with diazo compounds in a similar way.



After association of the nucleophilic carbon to Rh, elimination with loss of nitrogen gas is the slow step of this reaction.

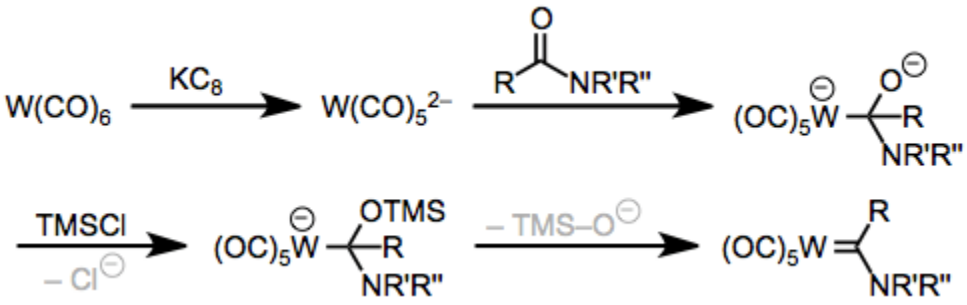
Diazo compounds work well for metal carbene formation when they possess an electron-withdrawing group, which stabilizes the ylide through conjugation. What about Fischer carbenes, which possess electron-donating groups on the carbene carbon? An interesting method that still involves a "push-and-pull" of electron flow (but not ylides) employs metal-CO complexes. Upon addition of a strong nucleophile ("forward flow") to the carbonyl carbon, a metalloenolate of sorts is produced. Treatment with an electrophile RX that prefers oxygen over the metal ("reverse flow") results in an OR-substituted Fischer carbene. Reactions reminiscent of transesterification trade out the OR group for an –SR group (using a thiol) or an –NR2 group (using a secondary

amine).



Fischer's classical route to L-type carbenes.

As counterintuitive as it may seem, it's possible to use metal dianions for the synthesis of Fischer carbenes via a method pioneered by Hegedus and Semmelhack. Potassium intercalated in graphite—the mysterious "KC8"—reduces group 6 metal carbonyl complexes to the corresponding dianions, which subsequently unleash a deluge of electrons on a poor, unsuspecting amide to afford NR2-substituted Fischer carbenes after treatment with trimethylsilyl chloride.

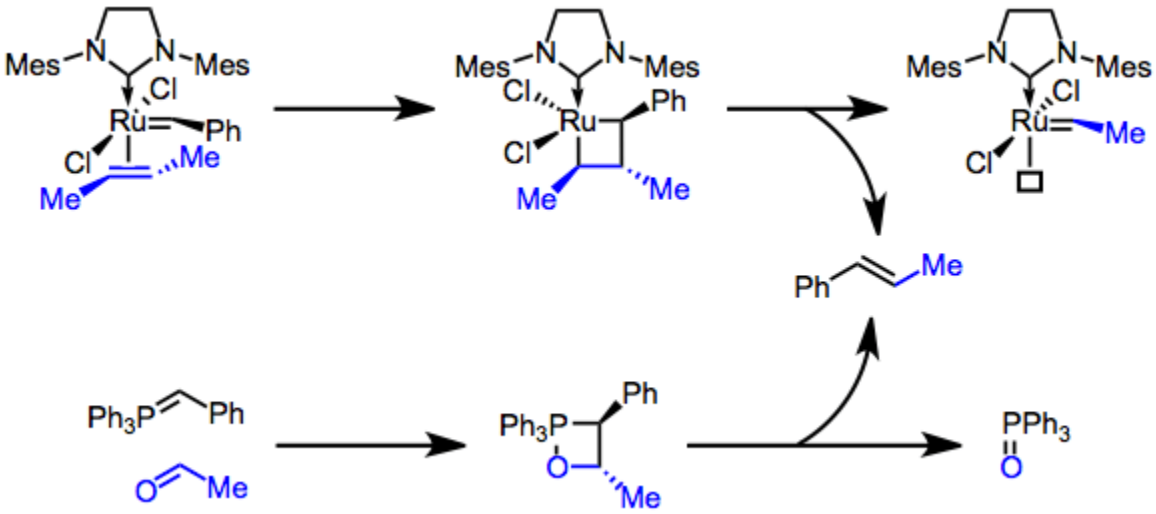


One-directional electron flow for Fischer carbene synthesis: the Hegedus-Semmelhack approach.

For other methods for the synthesis of Fischer carbenes, check out this nice review from the Baran group.

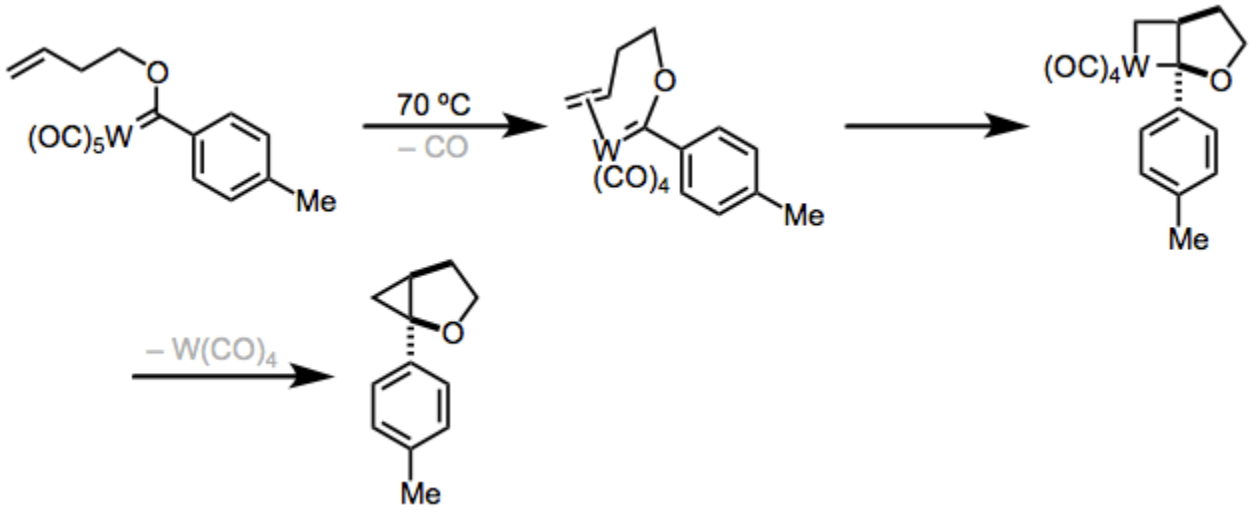
Reactions

In many ways, the reactivity of metal carbenes parallels that of ylides. Olefin metathesis catapulted metal carbenes to international stardom, but in many ways, metathesis is conceptually similar to the Wittig reaction, which employs phosphorus ylides. During both mechanisms, an ylide/carbene hooks up with another doubly bound molecule to form a four-membered ring. This step is followed by what we might call "orthogonal breakdown" to yield two new double bonds.



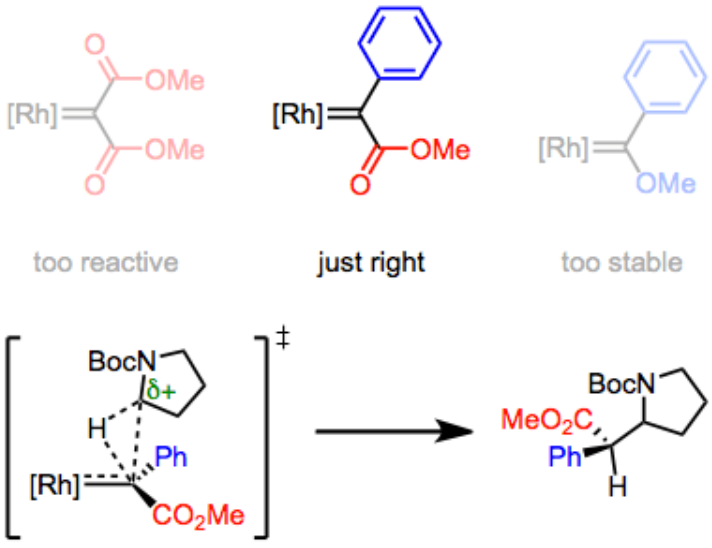
Wittig, Grubbs, and Schrock: Lords of the Chemical Dance. Ambi-electronic molecules are the dancers!

In my opinion, bond insertion reactions are the most interesting processes in which carbenes regularly engage. Bond insertions may be subdivided into cyclopropanation (π-bond insertion) and σ-bond insertion. Evidence suggests that most cyclopropanations take place by a mechanism that overlaps with metathesis—instead of orthogonal breakdown, reductive elimination occurs to release the three carbon atoms as a cyclopropane.



The metallacyclobutane mechanism of cyclopropanation.

σ-Bond insertion involves electron-rich C–H bonds most prominently, suggesting that electrophilic Fischer carbenes should be best for this chemistry. Fischer carbenes incorporating electron-withdrawing groups love to dimerize to form olefins and/or cyclopropanate olefins—how might we put the brakes on this behavior? If we simply tack a π-basic substituent onto the carbene carbon, the reactivity of these complexes is "just right" for C–H insertion. Notably, no covalent organometallic intermediates are involved; the electrophilic carbene carbon snuggles in between C and H in a single step. The transition state of this step resembles the transfer of a hydride from the organic substrate to the carbene, with "rebound" of electron density toward the partial positive charge.



Donor-acceptor carbenoids are the "Goldilocks complexes" of C–H insertion.

Let's end with a nod to the similarity between Fischer carbenes and carboxylic acid derivatives (esters and amides).

Transesterification-type reactions allow the chemist to swap out heteroatomic substituents on the carbene carbon at will (see above). Alkyl substitutents can even be deprotonated at the α carbon, just like esters! When we see the electronic similarities between the M=C bond of a Fischer carbene and the O=C bond of carboxylic acid derivatives, the similar behavior is only natural.

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13.6.3: Carbyne (Alkylidyne) Complexes

Learning Objectives

In this lecture you will learn the following

- The metal–ligand multiple bonding and their relevance in.
- The Fischer type carbyne complexes.
- The Schrock type carbyne complexes.

The metal–ligand multiply bonded systems even extended beyond the doubly bonded Fischer and the Schrock carbenes to the triply bonded $L_nM{\equiv}CR$ type Fischer carbyne and the Schrock carbyne complexes. Similar to carbene that exists in a singlet and a triplet spin state, the carbyne also exists in two other spin states *i.e* in a doublet and a quartet form.

Upon binding to the metal in its doublet spin state as in the Fischer carbene system, the carbyne moiety donates two electrons *via* its *sp* hybridized lone pair containing orbital to an empty metal *d* orbital to yield a $L_nM \leftarrow CR$ type ligand to metal dative bond. It also makes a covalent π–bond through one of its singly occupied p_z orbital with one of the metal *d* orbitals. The carbyne–metal interaction consist of two ligand to metal interactions namely a dative one and a covalent one that together makes the carbyne moiety a LX type of a ligand. In addition to these two types of ligand to metal bonding interactions, there remains an empty p_y orbital on the carbyne–C atom that can accommodate electron donation from a filled metal *d* orbital to give a metal to ligand π–back bonding interaction (Figure 13.6.3.1).

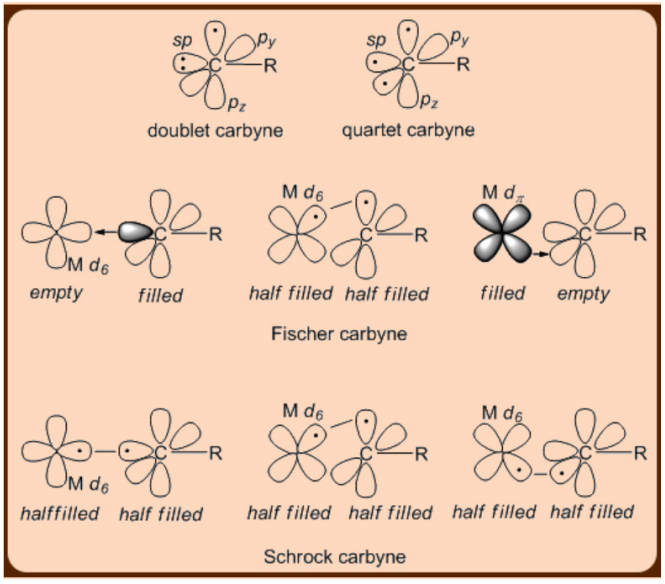


Figure 13.6.3.1: Metal–ligand multiple bonding in the Fischer and Schrock carbyne system

Analogously, in the quartet carbyne spin state in the Schrock carbyne systems three covalent bonds occur between the singly occupied *sp*, $p_y$and p_z orbitals of carbyne–C moiety with the respective singly occupied metal *d* orbitals (Figure 13.6.3.1).

Similar to what has been observed earlier in the case of the Fischer carbenes and Schrock carbenes, the Fischer carbyne complexes are formed with metal centers in lower oxidation states for *e.g.* as in $Br(CO)_4W{\equiv}CMe$, while the Schrock carbyne complexes are formed with metals in higher oxidation state, *e.g.* as in $(t\text{–BuO})_3W{\equiv}Ct\text{–Bu}$.

Carbyne complexes can be prepared by the following methods.

i. The Fischer carbyne complexes can be prepared by the electrophilic abstraction of a methoxy group from a methoxy methyl substituted Fischer carbene complex.

$$\mathrm{L(CO)_4M{=}C(OMe)Me + 2\,BX_3 \longrightarrow [L(CO)_4M{\equiv}CMe]^+BX_4^- + BX_2(OMe) \longrightarrow X(CO)_4M{\equiv}CMe}$$

ii. Schrock carbynes can be prepared by the deprotonation of a α–CH bond of a metal–carbene complex.

$$\mathrm{CPCl_2Ta{=}CHR \xrightarrow[(ii)Ph_3P{=}CH_2]{(i)PMe_3} Cp(PMe_3)ClTa{\equiv}CR}$$

iii. by an α–elimination reaction on a metal–carbene complex

$$\mathrm{Cp \cdot Br_2Ta{=}CHt{-}Bu \xrightarrow[(ii)Na/Hg]{(i)dmpe} Cp \cdot (dmpe)HTa{\equiv}Ct{-}Bu}$$

iv. by metathesis reaction

$$\mathrm{(\mathit{t}\text{-}BuO)_3W{\equiv}W(Ot{-}Bu)_3 + \mathit{t}\text{-}BuC{\equiv}Ct{-}Bu \longrightarrow 2\,(\mathit{t}\text{-}BuO)_3W{\equiv}Ct{-}Bu}$$

The reactivities of Fischer and the Schrock carbynes mirror that of the Fischer and Schrock carbenes. For example, the Fischer carbyne undergo nucleophilic attack at the carbyne–C atom while the Schrock carbyne undergo electrophilic attack at the carbyne–C atom.

Summary

The theme of metal–ligand multiple bonding extends beyond the doubly bonded Fischer and the Schrock carbene systems to even triply bonded Fischer and the Schrock carbyne systems. The carbyne moieties in these Fischer and the Schrock carbyne systems respectively exist in a doublet and a quartet spin state. The carbyne complexes are generally prepared from the respective carbene analogues by the abstraction of alkoxy (OR), proton (H^+), hydride (H^-) moieties, the α–elimination reactions and the metathesis reactions. The reactivity of the Fischer and the Schrock carbyne complexes parallel the corresponding Fischer and the Schrock carbene counterparts with regard to their reactivities toward electrophiles and nucleophiles.

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- 13.2: Metal-Carbynes by M. S. Balakrishna and Prasenjit Ghosh is licensed CC BY-NC-SA 4.0. Original source: https://nptel.ac.in/courses/104101006.

13.6.4: Carbido and Cumulene Complexes

Carbido ligand: One single carbon

A metal carbido (aka carbide, or simply carbon) complex is a metal complex that contains the ligand, carbon (C). Most molecular carbido complexes are clusters, usually featuring carbide as a six-fold bridging ligand. Examples include $[\mathrm{Rh_6C(CO)_{15}}]^{2-}$, and $[\mathrm{Ru_6C(CO)_{16}}]^{2-}$. The iron carbonyl carbides exist not only in the encapsulated carbon ($[\mathrm{Fe_6C(CO)_{16}}]^{2-}$) but also with exposed carbon centres as in $\mathrm{Fe_5C(CO)_{15}}$ and $\mathrm{Fe_4C(CO)_{13}}$.

Figure 13.6.4.1: Structure of $\mathrm{Fe_5C(CO)_{15}}$ containing a carbido bridging five iron centers. (Public domain)

In rare cases, carbido ligands are terminal ligands (Figure 13.6.4.2, left). Although it is tempting to extend the model of metal-carbon bonds from the alkyl ($\mathrm{M-C}$), carbene ($\mathrm{M=C}$, and carbyne ($\mathrm{M \equiv C}$) ligands and evoke the idea of a quadruple bond between metal and carbon in the case of a carbido, experimental data is more consistent with a triple bonded to a metal ion (($\mathrm{M \equiv C_1}$)). For example, the metal-carbon bond in the $\mathrm{RuC(PCy_3)_2Cl_2}$ complex is similar to the bond length of other complexes with $\mathrm{C \equiv M}$ (Figure 13.6.4.2).

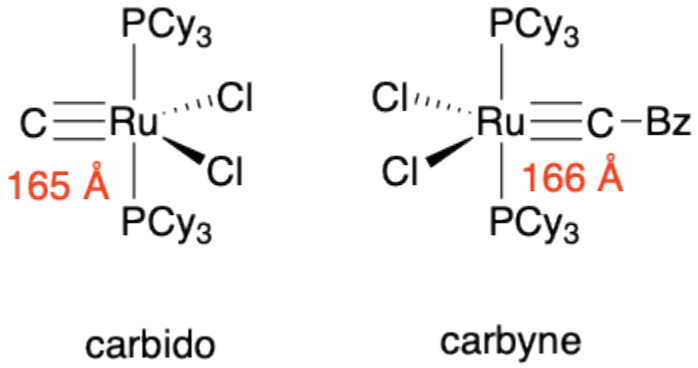


Figure 13.6.4.2: Carbido-metal bonds are similar in length to the $\mathrm{C \equiv M}$ of metal carbynes. Cy = cyclohexane, Bz = benzyl. (CC-BY-SA; Kathryn Haas)

Source: https://en.Wikipedia.org/wiki/Metal_carbido_complex

Cumulene ligands: Chains of carbon atoms with consecutive double bonds

Chains of carbon atoms that have consecutive (cumulated) double bonds are intriguing ligands for metal complexes due to their potential utility as molecular wires in nano or optical devices. The first reported complex containing a vinylidene ligand was $\mathrm{Ph_2C_2Fe_2(CO)_8}$. The first monometallic vinylidene complex was $\mathrm{(C_5H_5)Mo(P(C_6H_5)_3)(CO)_2[C{=}C(CN)_2]Cl}$. Just as in the case of conjugated pi systems, the longer the length of a cumulated diene, the closer the HOMO/LUMO gap, and thus the more conductive. To date, the longest cumulenylidene ligand reported is heptahexaenylidene (Figure 13.6.4.3).

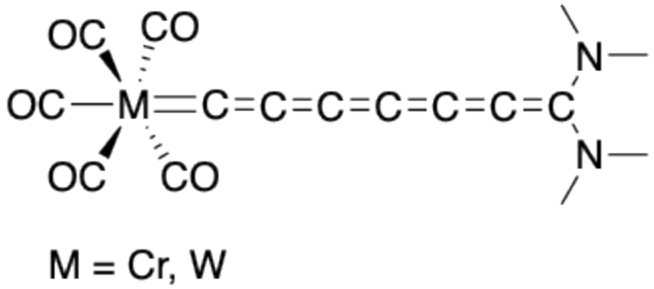


Figure 13.6.4.3: Structure of a metal complex with a heptahexaenylidene ligand. (CC-BY-SA; Kathryn Haas)

Source: https://en.Wikipedia.org/wiki/Cumule...ply%20cumulene.

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13.6.5: Carbon Wires- Polyyne and Polyene Bridges

Organic molecules with conjugated π systems are known to have interesting optical and electronic properties. When ligands with conjugated π systems are used to bridge two metal centers, the two metals can behave in a cooperative way because the electronic state of one metal ion is conjugated to the other. The most intensely investigated complexes are bimetallic metal complexes (two metal ions) that are bridged by long carbon chains with alternating single and double bonds. Some examples are given below. (This topic is reviewed in Aguirre-Etcheverry D. O'Hare, *Chem. Rev.*, **2010**, *110*, 4839, doi: 10.1021/cr9003852)

Polyene

Polyenes are organic molecules with alternating double and single bonds. In other words, they contain a series of consecutive \(\ce{(-C= C-)_{n}}\) with $n > 1$. Aromatic and cyclic polyenes were discussed in a previous section. One of the longest ligands reported as of 2010 was a $\mathrm{Ru{-}(CH)_{14}{-}Ru}$ complex (shown in Figure 13.6.5.1).

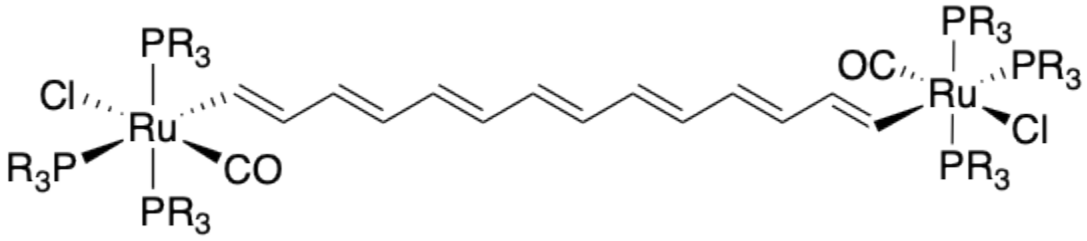


Figure 13.6.5.1: Structure of linear polyene complex of Ru with and 14-carbon polyene. (CC-BY-SA; Kathryn Haas)

Source: Aguirre-Etcheverry D. O'Hare, *Chem. Rev.*, **2010**, *110*, 4839, doi: 10.1021/cr9003852

Polyyne ligands

Polyynes are organic molecules with alternating single and double bonds. In other words, they contain a series of consecutive $(-\mathrm{C} \equiv \mathrm{C}-)_n$ with $n > 1$.

Organometallic polyynes capped with metal complexes are well characterized. As of the mid-2010s, the most intense research had concerned rhenium (ReC_nRe, n=6-20), ruthenium ($RuRuC_nRuRu$, n = 8–20), iron ($FeC_{12}CFe$), platinum (PtC_nPt, n = 16–28), palladium (ArC_nPd, n = 6–10), and cobalt ($Co_3C_nCo_3$, n = 14–26) complexes (Figure 13.6.5.1).

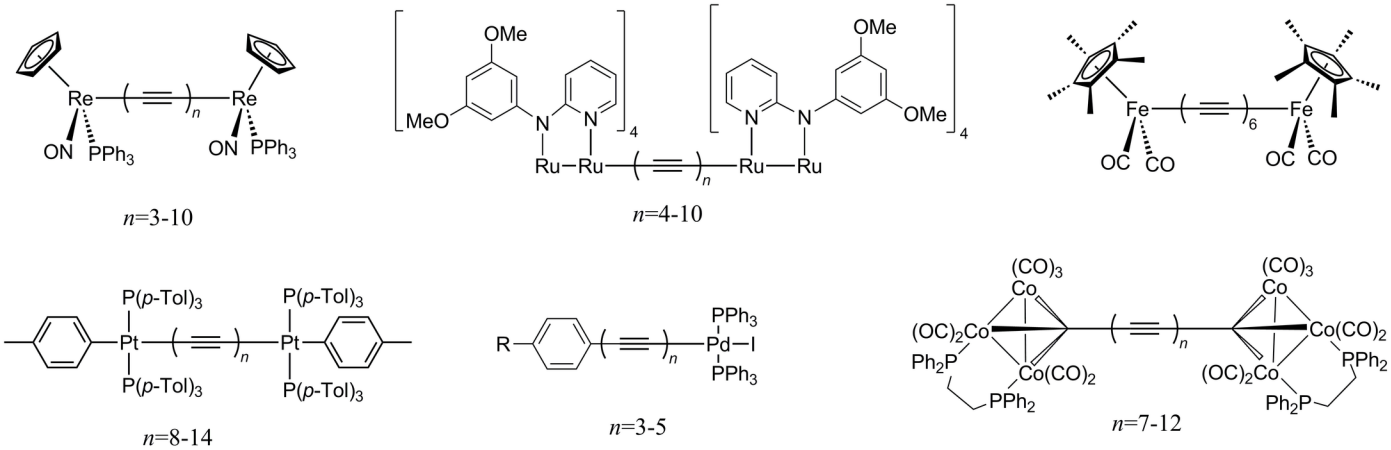


Figure 13.6.5.1: Examples of known polyyne organometallic complexes. (Pigulski, Organometallic polyynes, CC BY-SA 4.0)

Source: https://en.Wikipedia.org/wiki/Polyyne

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13.7: Characterization of Organometallic Complexes

Learning Objectives

In this lecture you will learn the following

- The characterization techniques of organometallic compounds.
- The NMR analysis of these compounds.
- The IR analysis of these compounds.
- The X-ray single crystal diffraction studies of these compounds.

The characterization of an organometallic complex involves obtaining a complete understanding of the same right from its identification to the assessment of its purity content, to even elucidation of its stereochemical features. Detailed structural understanding of the organometallic compounds is critical for obtaining an insight on its properties and which is achieved based on the structure-property paradigm.

Synthesis and isolation

Synthesis and isolation are two very important experimental protocols in the overall scheme of things of organometallic chemistry and thus these needs to be performed carefully. The isolation of the organometallic compounds is essential for their characterization and reactivity studies. Fortunately, many of the methods of organic chemistry can be used in organometallic chemistry as the organometallic compounds are mostly nonvolatile crystalline solids at room temperature and atmospheric pressure though a few examples of these compounds are known to exist in the liquid [$(CH_3C_5H_4Mn(CO)_3$] and even in the vapor [$Ni(CO)_4$] states. The organometallic compounds are comparatively more sensitive to aerial oxygen and moisture, and because of which the manipulation of these compounds requires stringent experimental skills to constantly provide them with anaerobic environment for their protection. All of these necessities led to the development of the so-called special Schlenk techniques, requiring special glasswares and which in conjunction with a high vacuum line and a dry box allow the lab bench-top manipulation of these compounds. Successful isolation of organometallic compounds naturally points to the need for various spectroscopic techniques for their characterizations and some of the important ones are discussed below.

1H NMR spectroscopy

The ^{1}H NMR spectroscopy is among the extensively used techniques for the characterization of organometallic compounds. Of particular interest is the application of ^{1}H NMR spectroscopy in the characterization of the metal hydride complexes, for which the metal hydride moiety appear at a distinct chemical shift range between 0 ppm to −40 ppm to the high field of tetramethyl silane (TMS). This upfield shift of the metal hydride moiety is attributed to a shielding by metal *d*–electrons and the extent of the upfield shift increases with higher the d^n configuration. Chemical shifts, peak intensities as well as coupling constants from the through-bond couplings between adjacent nuclei like that of the observation of $J_{P\text{-}H}$, if a phosphorous nucleus is present within the coupling range of a proton nucleus, are often used for the analysis of these compounds. The ^{1}H NMR spectroscopy is often successfully employed in studying more complex issues like fluxionality and diastereotopy in organometallic molecules (Figure 13.7.1).

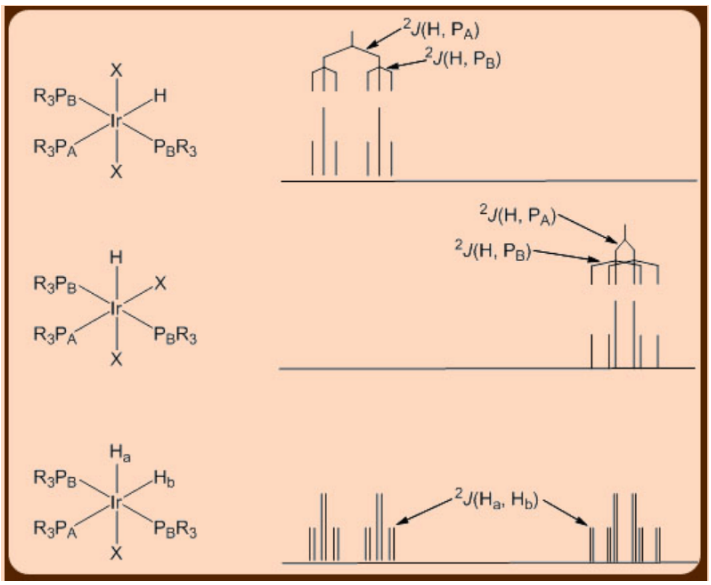


Figure 13.7.1: Different phosphorous-proton coupling patterns in various iridium hydride complexes.

The paramagnetic organometallic complexes show a large range of chemical shifts, for example, $(\eta^6\text{–}C_6H_6)_2V$ exhibits proton resonances that extend even up to 2900 ppm.

13C NMR spectroscopy

Although the natural abundance of NMR active ^{13}C (I = ½) nuclei is only 1 %, it is possible to obtain a proton decoupled $^{13}C\{^1H\}$ NMR spectra for most of the organometallic complexes. In addition, the off–resonance ^1H decoupled ^{13}C experiments yield $^1J_{C\text{-}H}$ coupling constants, which contain vital structural information, and hence are very critical to the ^{13}C NMR spectral analysis. For example, the $^1J_{C\text{-}H}$ coupling constants directly correlate with the hybridization of the C–H bonds with *sp* center exhibiting a $^1J_{C\text{-}H}$ coupling constant of ~250 Hz, a sp^2 center of 160 Hz and a sp^3 center of 125 Hz. Similar to what is seen in ^1H NMR, a phosphorous–carbon coupling is also observed in a ^{13}C NMR spectrum with the *trans* coupling (~100 Hz) being larger than the *cis* coupling (~10 Hz).

^{31}P NMR spectroscopy

The ^{31}P NMR spectroscopy, which in conjunction with ^1H and ^{13}C NMR spectroscopies, is a useful technique in studying the phosphine containing organometallic complexes. The ^{31}P NMR experiments are routinely run under ^1H decoupled conditions for simplification of the spectral features that allow convenience in spectral analysis. Thus, for this very reason, many mechanistic studies on catalytic cycle are conveniently undertaken by ^{31}P NMR spectroscopy whenever applicable.

IR spectroscopy

Qualitative to semi-quantitative analysis of organometallic compounds using IR spectroscopy are performed whenever possible. In general the signature stretching vibrations for chemical bonds are more conveniently looked at in these studies. The frequency (ν) of a stretching vibration of a covalent bond is directly proportional to the strength of the bond, usually given by the force constant (*k*) and inversely proportional to the reduced mass of the system, which relates to the masses of the individual atoms.

$$\nu = \frac{1}{2\pi C}\sqrt{\frac{k}{m_r}}$$

$$m_r = \frac{m_1 m_2}{m_1 + m_2}$$

The organometallic compounds containing carbonyl groups are regularly studied using IR spectroscopy, and in which the CO peaks appear in the range between 2100–1700 cm^{-1} as distinctly intense peaks.

Crystallography

The solid state structure elucidation using single crystal diffraction studies are extremely useful techniques for the characterization of the organometallic compounds and for which the X-ray diffraction and neutron diffraction studies are often undertaken. As these methods give a three dimensional structural rendition at a molecular level, they are of significant importance among the various available characterization methods. The X-ray diffraction technique is founded on Bragg's law that explains the diffraction pattern arising out of a repetitive arrangement of the atoms located at the crystal lattices.

$$2d \sin \theta = n\lambda$$

A major limitation of the X-ray diffraction is that the technique is not sensitive enough to detect the hydrogen atoms, which appear as weak peaks as opposed to intense peaks arising out of the more electron rich metal atoms, and hence are not very useful for metal hydride compounds. Neutron diffraction studies can detect hydrogens more accurately and thus are good for the analysis of the metal hydride complexes.

Summary

Along with the synthesis, the isolation and the characterization protocols are also integral part of the experimental organometallic chemistry. Because of their air and moisture sensitivities, specialized experimental techniques that succeed in performing the synthesis, isolation and storage of these compounds in an air and moisture-free environment are often used. The organometallic compounds are characterized by various spectroscopic techniques including the ^{1}H NMR, ^{13}C NMR and IR spectroscopies and the X-ray and the neutron diffraction studies.

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14: ORGANOMETALLIC REACTIONS AND CATALYSIS

Introduction

This chapter is a survey of common organometallic reactions and catalytic cycles. The reactions of organometallic complexes are divided into two main categories: (1) Reactions that involve gain or loss of ligands, and (2) Reactions involving modification of ligands.

14.1: Reactions Involving Gain or Loss of Ligands

14.1.1: Ligand Dissociation and Substitution

14.1.2: Oxidative Addition

14.1.3: Reductive Elimination

14.1.4: Sigma Bond Metathasis

14.1.5: Application of Pincer Ligands

14.2: Reactions Invloving Modification of Unsaturated Ligands

14.2.1: Introduction to Insertion

14.2.2: CO Insertions (Alkyl Migration)

14.2.3: Migratory Insertion-1,2-Insertions

14.2.4: β-Elimination Reactions

14.2.5: Abstraction and Addition

14.3: Organometallic Catalysts

14.3.1: Catalytic Deuteration

14.3.2: Hydroformylation

14.3.3: Monsanto Acetic Acid Process

14.3.4: Wacker (Smidt) Process

14.3.5: Hydrogenation by Wilkinson's Catalyst

14.3.6: Olefin Metathesis

14.4: Heterogeneous Catalysts

14.4.1: Ziegler-Natta Polymerizations

14.4.2: Water-Gas Shift Reaction

14.5: Problems

14.5.1: Concept Review Questions Chapter 12

14.5.2: Homework Problems Chapter 12

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- 12.1: Organometallic reactions by Kai Landskron is licensed CC BY 4.0.

14.1: REACTIONS INVOLVING GAIN OR LOSS OF LIGANDS

Many reactions of organometallic complexes involve change in coordination number. In a dissociation reaction, one or more ligands are eliminated from the complex and the coordination number decreases. In an association, one or more ligands are added to the complex and the coordination number increases. If the coordination number changes while the metal oxidation state remains constant, the reactions are considered **association/addition** reactions or **dissociation** reactions. Reactions can also occur where the coordination number changes while the metal oxidation state also changes. These reactions are considered **reductive eliminations** or **oxidative additions** (or a combination of these).

Types of reactions involving gain or loss of ligands

- **Association or Addition Reaction**: a reaction in which the coordination number increases; metal oxidation state is unchanged.
- **Dissociation Reaction**: a reaction in which the coordination number decreases; metal oxidation state is unchanged.
- **Oxidative Addition**: a reaction in which coordination number increases while metal oxidation state increases.
- **Reductive Elimination**: a reaction in which coordination number decreases while metal oxidation state decreases.

14.1.1: Ligand Dissociation and Substitution

14.1.2: Oxidative Addition

14.1.3: Reductive Elimination

14.1.4: Sigma Bond Metathasis

14.1.5: Application of Pincer Ligands

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14.1.1: Ligand Dissociation and Substitution

As discussed in Chapter 13, ligand substitution is characterized by a continuum of mechanisms bound by associative (A) and dissociative (D) extremes. At the associative extreme, the first step is an Associative reaction; the incoming ligand forms a bond to the metal and creates an intermediate of higher coordination number. Then the departing ligand takes its lone pair and leaves. At the dissociative extreme, the fist step is a Dissociative reaction and the order of events is opposite; a ligand departs and a new complex with lower coordination number forms. Then, a new ligand associates with the complex in the second step. Sometimes, instead of reacting, the "intermediate" is simply a stable complex with a different coordination number than the reactant.

The most common reactions that are used to create new complexes are Dissociations and Substitutions (involving both Dissociation and Association steps). Associative substitution is common for 16-electron complexes (like d^8 complexes of Ni, Pd, and Pt), while both Dissociation and Dissociative Substitution are the norm for 18-electron complexes. Then again, reality is often more complicated than these extremes. In some cases, evidence is available for interchange (I_a or I_d).

In this subsection, we'll explore ligand substitution reactions and mechanisms in the context of organometallic chemistry. We'd like to be able to (a) predict whether a mechanism is likely to be associative or dissociative; (b) propose a reasonable mechanism from given experimental data; and (c) describe the results we'd expect given a particular mechanism. Keep these goals in mind as you learn the theoretical and experimental nuts and bolts of substitution reactions.

Dissociation

Carbonyl compounds are known to undergo dissociation reactions upon heating or irradiation with light. For example, upon heating, the the cyclopentadienylmolybdenum tricarbonyl dimer ($\mathrm{Cp_2Mo_2(CO)_6}$), where Cp is the cyclopentadienyl ligand) loses a CO ligand from each Mo ion, and a triple bond between the Mo ions is formed (Top, Figure 14.1.1.1). An example of a photoactivated dissociation of CO is the case of neutral iron pentacarbonyl, $\mathrm{Fe(CO)_5}$. Irradiation of $\mathrm{Fe(CO)_5}$ with UV produces $\mathrm{Fe(CO)_4}$ (Bottom, Figure 14.1.1.1).

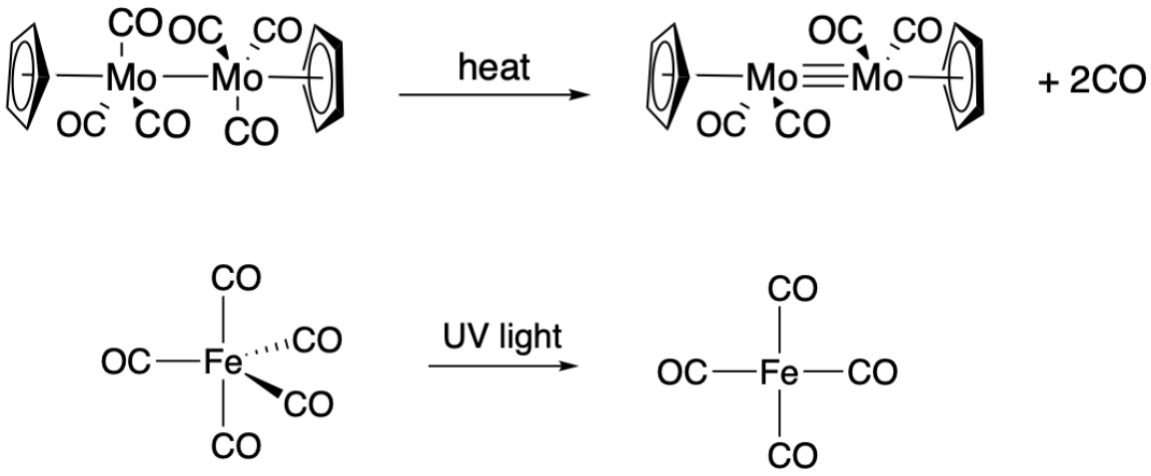


Figure 14.1.1.1: Dissociation reactions: Top, the thermally-activated dissociation of CO from cyclopentadienylmolybdenum tricarbonyl dimer. Bottom, the photochemically-activated dissociation of CO from ironpentacarbonyl. (CC-BY-SA; Kathryn Haas)

However, in each of the cases shown above, the product complex is reactive toward ligand association, usually resulting in an overall substitution. The cyclopentadienylmolybdenum dicarbonyl dimer shown on the top of Figure 14.1.1.1 binds a variety of substrates across the metal-metal triple bond. And the iron tetracarbonyl complex shown on the bottom in Figure 14.1.1.1 readily captures a variety of ligands to result in an overall substitution (example given below); when a ligand doe not associate with it, $\mathrm{Fe_2(CO)_9}$ is produced.

Sources: Iron Pentacarbonyl and Cyclopentadienylmolybdenum tricarbonyl dimer articles from Wikipedia.

Dissociative Substitution

Associative substitution is unlikely for saturated, 18-electron complexes—coordination of another ligand would produce a 20-electron intermediate. For 18-electron complexes, dissociative substitution mechanisms involving 16-electron intermediates are more likely. In a slow step with positive entropy of activation, the departing ligand leaves, generating a coordinatively unsaturated intermediate. The incoming ligand then enters the coordination sphere of the metal to generate the product. For the remainder of this post, we'll focus on the kinetics of the reaction and the nature of the unsaturated intermediate (which influences the stereochemistry of the reaction). The reverse of the first step, re-coordination of the departing ligand (rate constant k–1), is often competitive with dissociation.

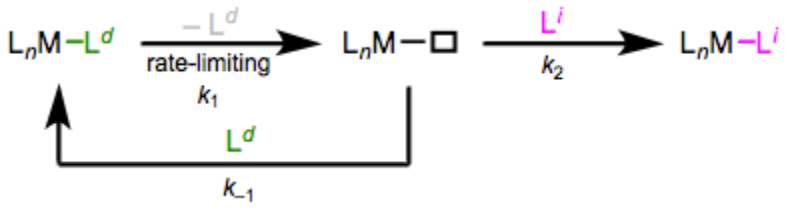


Figure 14.1.1.7: A general scheme for dissociative ligand substitution. There's more to the intermediate than meets the eye! (Michael Evans)

Reaction Kinetics

Let's begin with the general situation in which k_1 and k_{-1} are similar in magnitude. Since k_1 is rate limiting, k_2 is assumed to be much larger than k_1 and k_{-1}. Most importantly, we need to assume that variation in the concentration of the unsaturated intermediate is essentially zero. This is called the steady state approximation, and it allows us to set up an equation that relates reaction rate to observable concentrations Hold onto that for a second; first, we can use step 2 to establish a preliminary rate expression.

$$\text{rate} = k_2[L_nM{-}\Diamond][Li] \tag{1}$$

Of course, the unsaturated complex is present in very small concentration and is unmeasurable, so this equation doesn't help us much. We need to remove the concentration of the unmeasurable intermediate from (1), and the steady state approximation helps us do this. We can express variation in the concentration of the unsaturated intermediate as (processes that make it) minus (processes that destroy it), multiplying by an arbitrary time length to make the units work out. All of that equals zero, according to the SS approximation. The painful math is almost over! Since Δt must not be zero, the other factor, the collection of terms, must equal zero.

$$\Delta[L_nM{-}\Diamond] = 0 = (k1[L_nM{-}L^d]{-}k{-}1[L_nM{-}\Diamond][L^d]{-}k_2[L_nM{-}\Diamond][Li])\Delta t \tag{2}$$

$$0 = k_1[L_nM{-}Ld]{-}k_{-1}[L_nM{-}\Diamond][Ld]{-}k_2[L_nM{-}\Diamond][Li] \tag{3}$$

Rearranging to solve for $[L_nM{-}\Diamond]$, we arrive at the following.

$$[L_nM{-}\Diamond] = k_1\frac{[L_nM{-}L_d]}{(k_{-1}[L_d] + k_2[Li]} \tag{4}$$

Finally, substituting into equation (1) we reach a verifiable rate equation.

$$\text{rate} = k_2k_1\frac{[L_nM{-}Ld][Li]}{(k_{-1}[L_d] + k_2[Li]} \tag{5}$$

When k_{-1} is negligibly small, (5) reduces to the familiar equation (6), typical of dissociative reactions like S_N1.

$$\text{rate} = k_1[L_nM{-}L_d] \tag{6}$$

Unlike the associative rate law, this rate does not depend on the concentration of incoming ligand. For reactions that are better described by (5), we can drown the reaction in incoming ligand to make $k_2[Li]$ far greater than $k_{-1}[Ld]$, essentially forcing the

reaction to fit equation (6).

The Unsaturated Intermediate & Stereochemistry

Dissociation of a ligand from an octahedral complex generates an usaturated ML5 intermediate. When all five of the remaining ligands are L-type, as in Cr(CO)5, the metal has 6 d electrons for a total electron count of 16. The trigonal bipyramidal geometry presents electronic problems (unpaired electrons) for 6 d electrons, as the figure below shows. The orbital energy levels come from crystal field theory. Distortion to a square pyramid or a distorted TBP geometry removes the electronic issue, and so five-coordinate d6 complexes typically have square pyramidal or distorted TBP geometries. This is just the geometry prediction process in action!

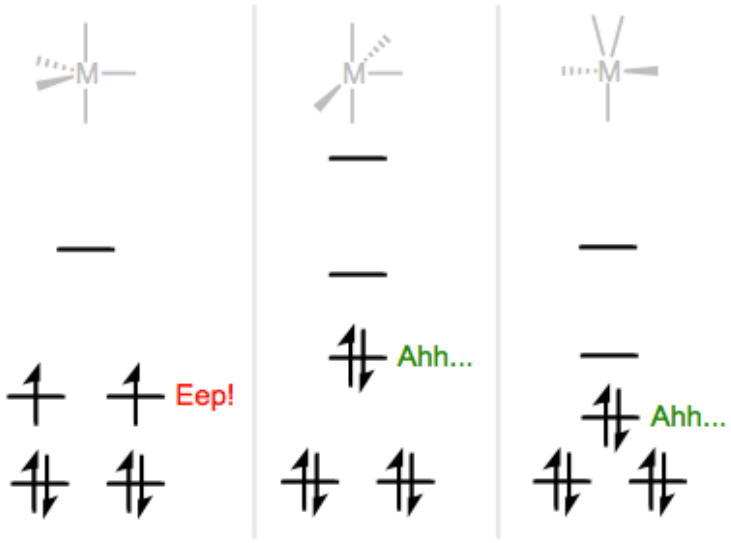


Figure 14.1.1.8: TBP geometry is electronically disfavored for d6 metals. Distorted TBP and SP geometries are favored. (Michael Evans)

When the intermediate adopts square pyramidal geometry (favored for good π-acceptors and σ-donors...why?), the incoming ligand can simply approach where the departing ligand left, resulting in retention of stereochemistry. Inversion is more likely when the intermediate is a distorted trigonal bipyramid (favored for good π-donors). As we've already seen for associative substitution, fluxionality in the five-coordinate intermediate can complicate the stereochemistry of the reaction.

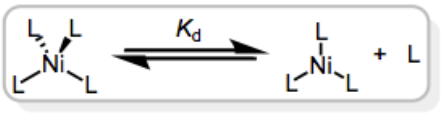
Encouraging Dissocative Substitution

In general, introducing structural features that either stabilize the unsaturated intermediate or destabilize the starting complex can encourage dissociative substitution. Both of these strategies lower the activation barrier for the reaction. Other, quirky ways to encourage dissociation include photochemical methods, oxidation/reduction, and ligand abstraction.

Let's begin with features that stabilize the unsaturated intermediate. Electronically, the intermediate loves it when its d electron count is nicely matched to its crystal field orbitals. As you study organometallic chemistry, you'll learn that there are certain "natural" d electron counts for particular geometries that fit well with the metal-centered orbitals predicted by crystal field theory. Octahedral geometry is great for six d electrons, for example, and square planar geometry loves eight d electrons. Complexes with "natural" d electron counts—but bearing one extra ligand—are ripe for dissociative substitution. The classic examples are d8 TBP complexes, which become d8 square planar complexes (think Pt(II) and Pd(II)) upon dissociation. Similar factors actually stabilize starting 18-electron complexes, making them less reactive in dissociative substitution reactions. d6 octahedral complexes are particularly happy, and react most slowly in dissociative substitutions. The three most common types of 18-electron complexes, from fastest to slowest at dissociative substitution, are:

$$d^8 \text{ TBP} > d^10 \text{ tetrahedral} > d^6 \text{ octahedral}$$

Destabilization of the starting complex is commonly accomplished by adding steric bulk to its ligands. Naturally, dissociation relieves steric congestion in the starting complex. Chelation has the opposite effect, and tends to steel the starting complex against dissociation.



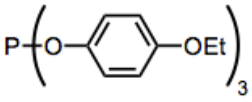
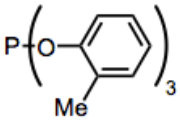
L	Cone Angle	K_d
$P(OEt)_3$	109	$< 10^{-10}$
	128	$6 * 10^{-10}$
$P(O\textit{i}\text{-}Pr)_3$	130	$2.7 * 10^{-5}$
	141	$4 * 10^{-2}$
PPh_3	145	huge

Figure 14.1.1.9: As steric bulk on the ligand increases, dissociation becomes more favorable. (Michael Evans)

I plan to cover the "quirky" methods in a post of their own, but these include strategies like N-oxides for CO removal, photochemical cleavage of the metal–departing ligand bond, and the use of silver cation to abstract halide ligands. Oxidation and reduction can also be used to encourage substitution: 17- and 19-electron complexes are much more reactive toward substitution than their 18-electron analogues.

Associative Substitutions

Despite the sanctity of the 18-electron rule in organometallic chemistry, a wide variety of stable complexes possess fewer than 18 total electrons at the metal center. Perhaps the most famous examples of these complexes are 14- and 16-electron complexes of group 10 metals (Ni, Pt, Pd). Ligand substitution in complexes of this class typically occurs via an associative mechanism, involving approach of the incoming ligand to the complex before departure of the leaving group. If we keep this principle in mind, it seems easy enough to predict when ligand substitution is likely to be associative. But how can we spot an associative mechanism in experimental data, and what are some of the consequences of this mechanism?

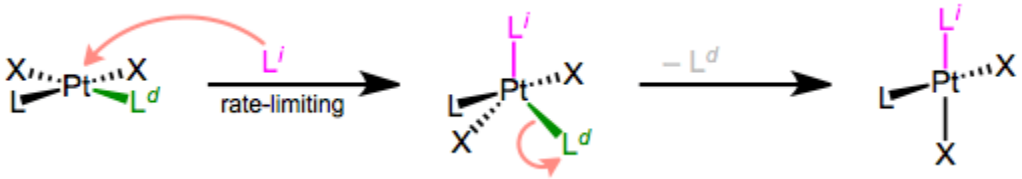


Figure 14.1.1.2: Associative substitution. (Michael Evans)

The prototypical mechanism of associative ligand substitution. The first step is rate-determining. A typical mechanism for associative ligand substitution is shown above. It should be noted that square pyramidal geometry is also possible for the intermediate, but is less common. Let's begin with the kinetics of the reaction.

Reaction Kinetics for Associative Reactions

Reaction kinetics are commonly used to elucidate organometallic reaction mechanisms, and ligand substitution is no exception. Different mechanisms of substitution may follow different rate laws, so plotting the dependence of reaction rate on concentration often allows us to distinguish mechanisms. Associative substitution's rate law is analogous to that of the S_N2 reaction—rate depends on the concentrations of both starting materials.

$$L_nM\text{–}L^d + L_i \rightarrow L_nM\text{–}L_i + L^d \tag{14.1.1.1}$$

$$\frac{d[L_nM–L^i]}{dt} = rate = k_1[L_nM–L^d][L^i] \tag{14.1.1.2}$$

The easiest way to determine this rate law is to use pseudo-first-order conditions. Although the rate law is second order overall, if we could somehow render the concentration of the incoming ligand unchanging, the reaction would appear first order. The observed rate constant under these conditions reflects the constancy of the incoming ligand's concentration ($k_{obs} = k_1[L^i]$, where both k_1 and $[Li]$ are constants). How can we make the concentration of the incoming ligand invariant, you ask? We can drown the reaction in ligand to achieve this. The teensy weensy bit actually used up in the reaction has a negligible effect on the concentration of the "sea" of starting ligand we began with. The observed rate is equal to $k_{obs}[L_nM–L^d]$, as shown by the purple trace below. By determining k_{obs} at a variety of $[L^i]$ values, we can finally isolate k_1, the rate constant for the slow step. The red trace below at right shows the idea.

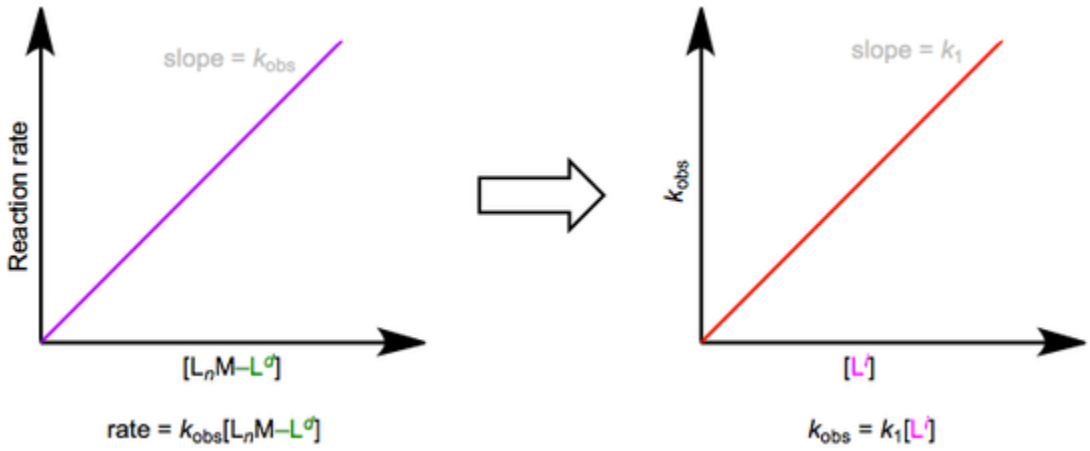


Figure 14.1.1.3: Associative substitution under pseudo-first-order conditions. The reaction is "swamped out" with incoming ligand. (Michael Evans)

In many cases, the red trace ends up with a non-zero y-intercept...curious, if we limit ourselves to the simple mechanism shown in the first figure of this post. A non-zero intercept suggests a more complex mechanism. We need to add a new term (called k_s for reasons to become clear shortly) to our first set of equations:

$$rate = (k_1[L_i] + k_s)[L_nM–L^d] \tag{14.1.1.3}$$

$$k_{obs} = k_1[L_i] + k_s \tag{14.1.1.4}$$

The full rate law suggests that some other step (with rate ks[LnM–Ld]) independent of incoming ligand is involved in the mechanism. To explain this observation, we can invoke the solvent as a reactant. Solvent can associate with the complex first in a slow step, then incoming ligand can displace the solvent in a fast step. Solvent concentration doesn't enter the rate law because, well, it's drowning the reactants and its concentration undergoes negligible change! An example of this mechanism in the context of Pt(II) chemistry is shown below.

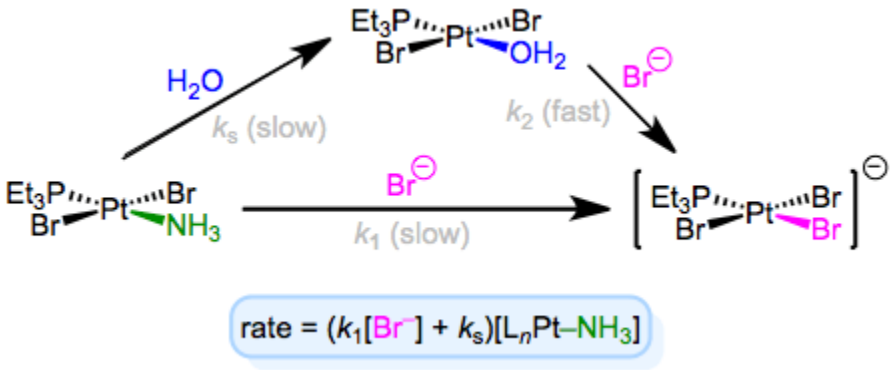


Figure 14.1.1.4: Associative substitution with solvent participation—a head-scratching mechanism for many an organometallic grad student! (Michael Evans)

As an aside, it's worth mentioning that the entropy of activation of associative substitution is typically negative. Entropy decreases as the incoming ligand and complex come together in the rate-determining step. Dissociative substitution shows the opposite behavior: loss of the departing ligand in the RDS increases entropy, resulting in positive entropy of activation.

Stereochemistry of Associative Substitution

As we saw in discussions of the trans effect, the entering and departing ligands both occupy equatorial positions in the trigonal bipyramidal intermediate. Microscopic reversibility is to blame: the mechanism of the forward substitution (displacement of the leaving by the incoming ligand) must be the same as the mechanism of the reverse reaction (displacement of the incoming by the leaving ligand). This can be a confusing point, so let's examine an alternative mechanism that violates microscopic reversibility.

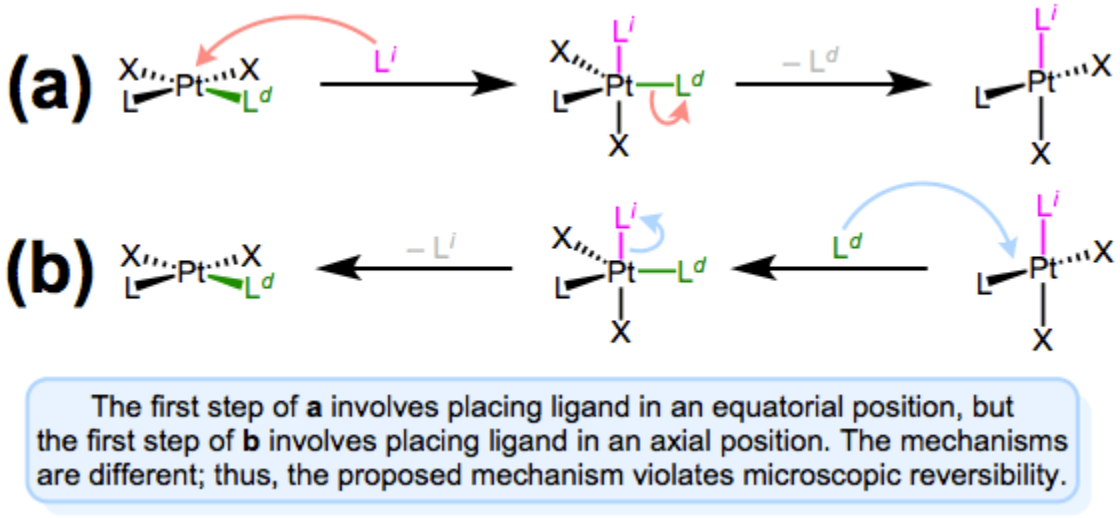


Figure 14.1.1.5: A mechanism involving approach to an axial position and departure from an equatorial position violates microscopic reversibility. Forward and reverse reactions a and b differ! (Michael Evans)

The figure above shows why a mechanism involving axial approach and equatorial departure (or vice versa) is not possible. The forward and reverse reactions differ, in fact, in both steps. In forward mechanism a, the incoming ligand enters an axial site. But in the reverse reaction, the incoming ligand (viz., the departing ligand in mechanism a) sits on an equatorial site. The second steps of each mechanism differ too—a involves loss of an equatorial ligand, while b involves loss of an axial ligand. Long story short, this mechanism violates microscopic reversibility. And what about a mechanism involving axial approach and axial departure? Such a mechanism is unlikely on electronic grounds. The equatorial sites are more electron rich than the axial sites, and σ bonding to the axial d_{z^2} orbital is expected to be strong. Intuitively, then, loss of ligand from an axial site is less favorable than loss from an equatorial site.

I know what you're thinking: what the heck does all of this have to do with stereochemistry? Notice that, in the equatorial-equatorial mechanism (first figure of this post), the axial ligands don't move at all. The configuration of the starting complex is thus retained in the product. Although retention is "normal," complications often arise because five-coordinate TBP complexes—like other odd-coordinate organometallic complexes—are often fluxional. Axial and equatorial ligands can rapidly exchange through a process called Berry pseudorotation, which resembles the axial ligands "cutting through" a pair of equatorial ligands like scissors (animation!). Fluxionality means that all stereochemical bets are off, since any ligand can feasibly occupy an equatorial site. In the example below, the departing ligand starts out cis to L, but the incoming ligand ends up trans to L.

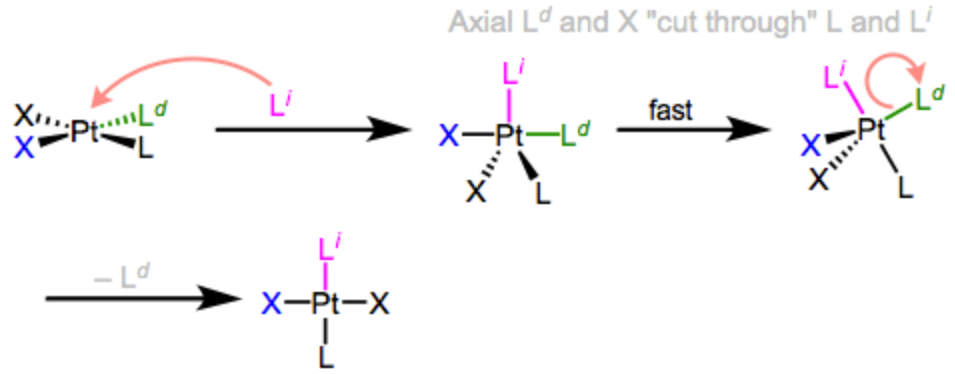


Figure 14.1.1.6: Berry pseudorotation in the midst of associative ligand substitution. (Michael Evans)

Associative Substitution in 18-electron Complexes?

Associative substitution can occur in 18-electron complexes if it's preceded by the dissociation of a ligand. For example, changes in the hapticity of cyclopentadienyl or indenyl ligands may open up a coordination site, which can be occupied by a new ligand to kick off associative substitution. An allyl ligand may convert from its π to σ form, leaving an open coordination site where the π bond left. A particularly interesting case is the **nitrosyl ligand**—conversion from its linear to bent form opens up a site for coordination of an external ligand.

Summary of Associative Substitution

Associative ligand substitution is common for complexes with 16 total electrons or fewer. The reaction is characterized by a second-order rate law, the possibility of solvent participation, and a trigonal bipyramidal intermediate that is often fluxional. An open coordination site is essential for associative substitution, but such sites are often hidden in the dynamism of 18-electron complexes with labile ligands.

Dr. Michael Evans (Georgia Tech)

Quirky Substitutions

Over the years, a variety of "quirky" substitution methods have been developed. All of these have the common goal of facilitating substitution in complexes that would otherwise be inert. It's an age-old challenge: how can we turn a stable complex into something unstable enough to react? Photochemical excitation, oxidation/reduction, and radical chains all do the job, and have all been well studied. We'll look at a few examples in this post—remember these methods when simple associative or dissociative substitution won't get the job done.

Photochemical Substitution

Substitution reactions of dative ligands—most famously, CO—may be facilitated by photochemical excitation. We just discussed the photochemically-activated dissociation of CO from ironpentacarbonyl above; that reaction is often used to accomplish substitution of a CO ligand. Other CO complexes also undergo photochemically-activated CO substitution reactions. Two examples are shown below. The first reaction yields only monosubstituted product without ultraviolet light, even in the presence of a strongly donating phosphine.

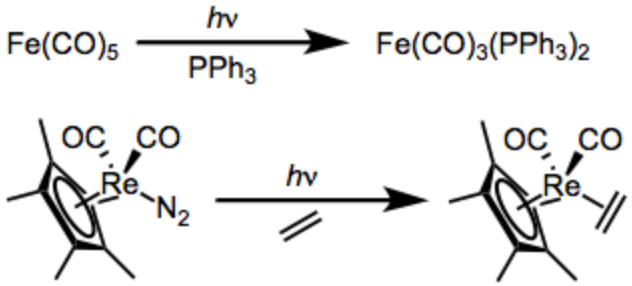


Figure 14.1.1.10:Dissociative photochemical substitutions of CO and dinitrogen. (Michael Evans)

All signs point to dissociative mechanisms for these reactions (the starting complexes have 18 total electrons each). Excitation, then, must increase the M–L antibonding character of the complex's electrons; exactly how this increase in antibonding character happens has been a matter of some debate. Originally, the prevailing explanation was that the LUMO bears M–L antibonding character, and excitation kicks an electron up from the HOMO to the LUMO, encouraging cleavage of the M–L bond. A more recent, more subtle explanation backed by calculations supports the involvement of a metal-to-ligand charge-transfer state along with the "classical" ligand-field excited state.

Oxidation/Reduction

Imagine a screaming baby without her pacifier—that's a nice analogy for an odd-electron organometallic complex. Complexes bearing 17 and 19 total electrons are much more reactive toward substitution than their even-electron counterparts. Single-electron oxidation and reduction ("popping out the pacifier," if you will) can thus be used to efficiently turn on substitution. As you might expect, oxidation and reduction work best on electron-rich and electron-poor complexes, respectively. The Mn complex in the oxidative example below, for instance, includes a strongly donating MeCp group (not shown).

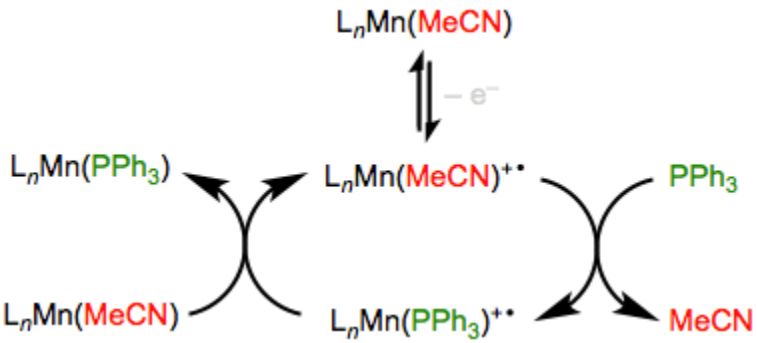


Figure 14.1.1.11: Oxidation accelerates substitution in electron-rich complexes through a chain process. (Michael Evans)

Reduction works well for electron-poor metal carbonyl complexes, which are happy to accept an additional electron.

There is a two-electron oxidation method that's also worth knowing: the oxidation of CO with amine oxides. This nifty little method releases carbon dioxide, amine, and an unsaturated complex that may be quenched by a ligand hanging around. The trick is addition to the CO ligand followed by elimination of the unsaturated complex. As the oxidized CO2 and reduced amine float away, the metal complex finds another ligand.

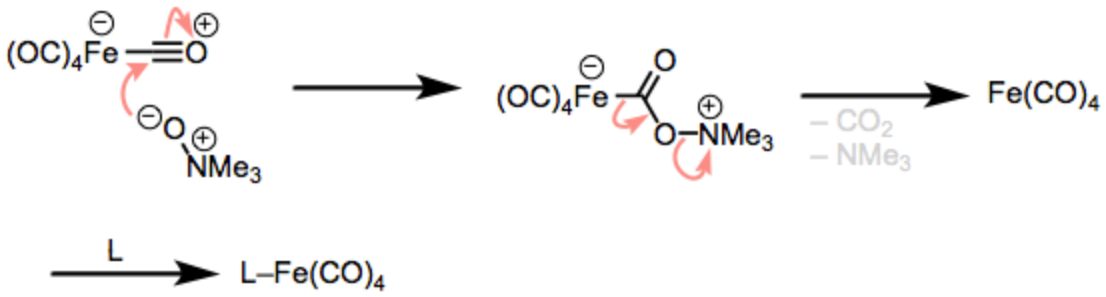


Figure 14.1.1.12: Oxidation of CO with amine oxides. A fun method for dissociative substitution of metal carbonyls! (Michael Evans)

Radical Chain Processes

Atom abstraction from 18-electron complexes produces neutral 17-electron intermediates, which are susceptible to ligand substitution via radical chain mechanisms. The fact that the intermediates are neutral distinguishes these methods from oxidation-based methods. First-row metal hydrides are great for these reactions, owing to their relatively weak M–H bonds. One example is shown below.

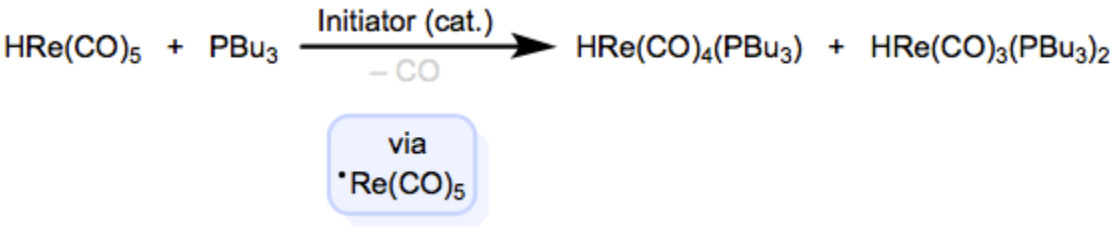


Figure 14.1.1.13: Radical-chain substitution involving atom abstraction. (Michael Evans)

After abstraction of the hydrogen atom by initiator, substitution is rapid and may occur multiple times. Propagation begins anew when the substituted radical abstracts hydrogen from the starting material to regenerate the propagating radical and form the product. These quirky methods are nice to have in your back pocket when you're backed into a synthetic corner—sometimes, conventional associative and dissociative substitution just won't do the job. In the next post, we'll press on to oxidative addition.

Template:Evans

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14.1.2: Oxidative Addition

An **oxidative addition** is a reaction in which the coordination number and the oxidation state of the metal ion both increase by 2. In other words, the metal becomes oxidized by two electrons as the coordination number increases by 2 ligands. The microscopic reverse of oxidative addition is reductive elimination (discussed in the next section).

Oxidative addition can occur in a cis- or trans-fashion. A cis-addition means that two ligands are added so that they have cis-orientation to each other after the reaction is complete. A trans-addition implies that two new ligands are in opposite, trans-position after they have been added. We can further distinguish between mononuclear and dinuclear additions. Mononuclear addition involves a complex with a single metal. Dinuclear additions are additions to a metal-metal bond. The addition cleaves the metal-metal bond and adds one ligand to each fragment.

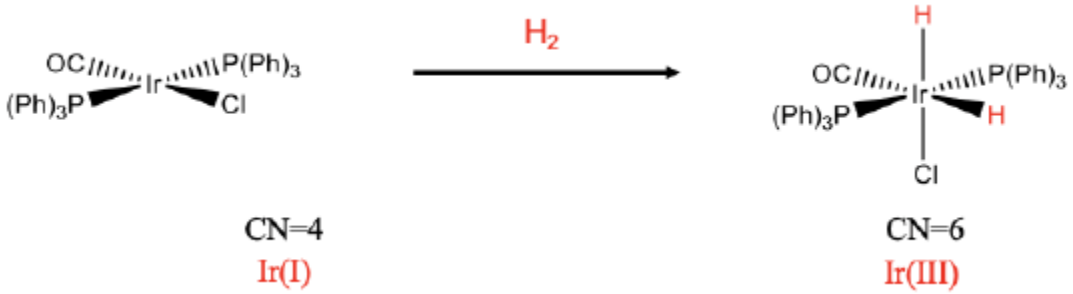


Figure 14.1.2.1: Mononuclear oxidative cis-addition (Attribution: A. Vedernikov, U Maryland (modified))

Let's explore a few examples. The first example is a mononuclear cis-addition (Fig. 14.1.2.1). In the reaction we add dihydrogen to a square planar iridium complex. After the reaction there are two additional hydrido ligands, and the coordination number has increased from 4 to 6. We can see that the two hydrido ligands are oriented in cis-fashion relative to each other. We can verify that the addition of the hydrido ligands oxidized the metal by determining the oxidation number of the metal before and after the reaction. There are three neutral ligands and one negatively charged chloro ligand. There is no overall charge at the complex. This means that the oxidation number of Ir is +1. After the reaction, there are the two hydrido ligands that have both a -1 charge. Remember, we get the charge at a ligand by cleaving the metal-ligand bond so that all electrons in the bond get assigned to the ligand. This means the oxidation number must be increased by +2, and is +3 after the reaction.

We can rationalize why the addition occurs in cis-fashion and not in trans-fashion. The two hydrido ligands are the smallest ligands, therefore, steric repulsion is minimized in the complex is minimized when the two hydrido ligands are in cis-position.

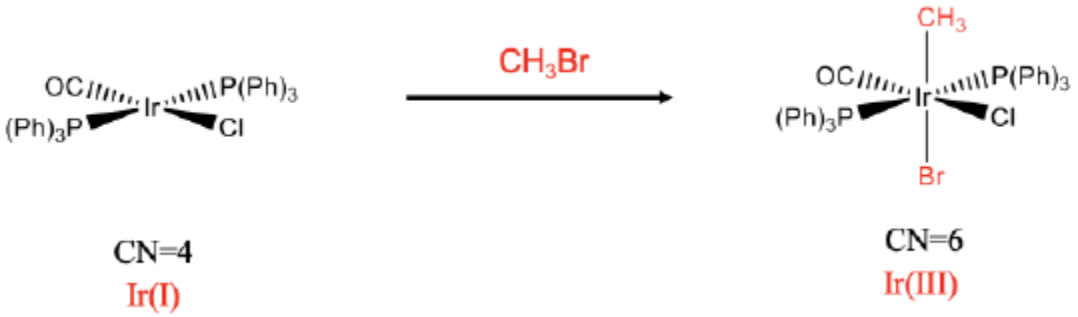


Figure 14.1.2.2: Mononuclear oxidative trans-addition (Attribution: A. Vedernikov, U Maryland (modified))

The second example is a mononuclear trans-addition (Fig. 14.1.2.2). In this reaction CH_3Br is added to the iridium complex. In this case the two new ligands, a CH_3 and the Br group are in opposite position. Again, the coordination number increases from four to six. We can again verify that an oxidation has occurred by analyzing the oxidation number of Ir. As previously determined, the oxidation number of iridium in the reactant complex is +1. Let us analyze the product complex. The chloro ligand and the bromo ligand have a 1- charge. In addition to that also the CH_3 ligand has a 1- charge assuming that we treat the Ir-C bond as a dative bond. Thus, the oxidation number of Ir must be +3 to give a neutral complex.

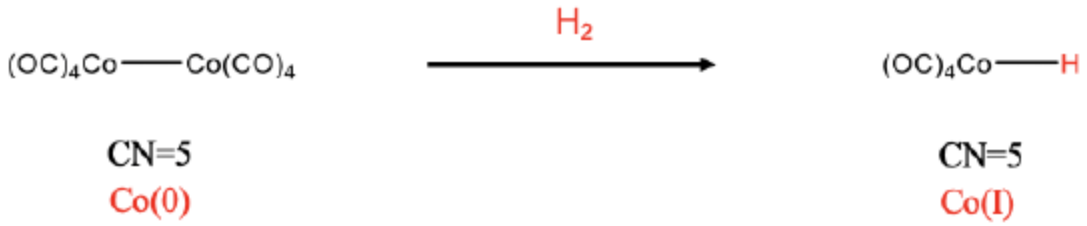


Figure 14.1.2.3: Dinuclear addition (Attribution: A. Vedernikov, U Maryland (modified))

The third example is a dinuclear addition (Fig. 14.1.2.3). This addition is neither cis nor trans because it cleaves a metal-metal bond, and the one new ligand is added to each fragment. In the example the Co-Co bond of the dicobalt octacarbonyl gets cleaved upon the reaction with dihydrogen, and two $HCo(CO)_4$ complexes with Co-H bonds form. In this case the coordination number does not increase. Both the reactant and the products have the coordination number 5. We can see that an oxidation of Co has occurred by comparing the oxidation numbers. In the reactant the oxidation number of Co is zero because all CO ligands are neutral and the complex is overall neutral. In the carbonyl hydride product, Co has the oxidation number +1, because the hydrido ligand has a 1- charge.

Oxidative Additions with Intact Ligands

In the previous examples, the ligands that reacted with the complexes lost their integrity. The H-H bond in the H_2 molecule cleaved to form the hydrido ligands, and the C-Br bond in CH_3Br was cleaved to form separate Br and methyl ligands. Not all ligands lose their integrity upon their addition, in particular when they contain multiple bonds. These ligands are called intact ligands. In these cases the bond order *between two atoms in the ligand* is decreased, but the bond order is still at least 1. For example, the alkyne ligand shown belo decreases from a carbon-carbon bond order of three to a bond order of two after it binds to Pt.

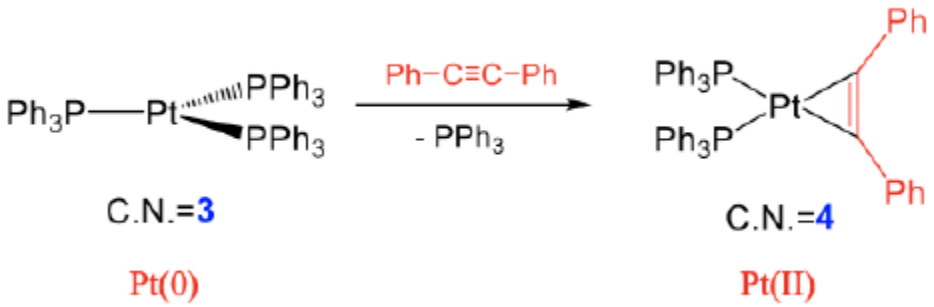


Figure 14.1.2.4: Oxidative addition with intact ligands (Attribution: A. Vedernikov, U Maryland (modified))

Examples for intact ligands are are alkenes, alkynes, O_2, etc. In an oxidative addition with an alkyne for example, the alkyne binds side-on to the transition metal under the formation of two metal-C single bonds, and the reduction of the bond order within the alkyne from 3 to 2 (Fig. 14.1.2.4). In the shown reaction, a diphenyl ethine molecule adds to tris(triphenyl phosphine) platinum under the formation of two Pt-C single bonds. The C-C triple bond in the ligand becomes a double bond. This reaction occurs under loss of one of the three triphenyl phosphine ligands. The coordination number at the metal increases from 3 to 4. We can again show that the reaction is oxidative by comparing the oxidation numbers of the metal. In the reactant, Pt has the oxidation number 0 because the three triphenyl phosphine ligands have no charge and the complex has overall no charge. After the reaction, the oxidation number of Pt is +2. This is because when we assign the four electrons of the two Pt-C single bonds to the ligand, the ligand becomes a $(Ph\text{-}C{=}C\text{-}Ph)^{2-}$ ligand with each C atom carrying a 1- charge. Because the product complex is overall neutral, the oxidation number of Pt is +2.

Nucleophilic Displacement Reactions

Another important reaction is the nucleophilic displacement reaction. This type of reaction can be classified as an oxidative addition although it does not strictly meet the definnition. In these reactions a metal complex (typically an anion) acts as a

nucleophile. A ligand is added, but no electrons are added to the complex. The reactions can be extremely useful for the synthesis of organic compounds. The utility results mostly from the fact that an organic electrophile is turned into a nucleophile.

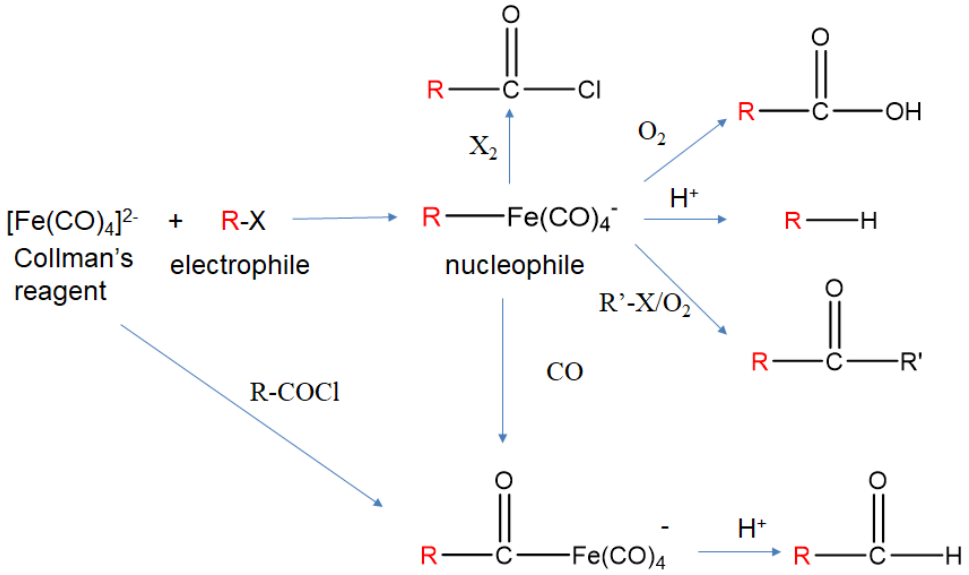


Figure 14.1.2.5: Mononuclear oxidative trans-addition (Attribution: A. Vedernikov, U Maryland (modified)): Examples of nucleophilic displacement reactions

For example, tetracarbonyl ferrate (2-), also known as Collman's reagent reacts with alkyl halides to form alkyl tetracarbonyl ferrate (-) (Fig. 14.1.2.5). We can check that the addition of the alkyl group did not add any electrons by counting the electrons before and after the reaction. The $Fe(CO)_4^{2-}$ anion is an 18e complex. Applying the neutral atom method to the electron counting in $[R\text{-}Fe(CO)_4]^-$ means that Fe contributes 8e, the 1- charge adds 1e, the CO ligands 4x2=8 electrons and the alkyl ligand 1e. This gives 8+1+8+1=18 electrons. Also the oxidation number of Fe has not changed upon the addition of the ligand. It is -2 before and after the reaction.

In the alkyltetracarbonyl ferrate (1-) anion, the group R which was formerly an electrophile in R-X, can now act as a nucleophile due to the fact that the Fe-C bond is polarized toward the C-atom. As a nucleophile it can for instance react with protons to form an alkane. It can also react with oxygen to form a carboxylic acid. In the presence of another alkyl halide R'-X it can form a ketone R-C(O)-R'. It can also insert CO into the Fe-C bonding in a so-called migratory insertion reaction, and the reaction product can react with acid to form an aldehyde. With dihalogens X_2 it can form acyl chloride. Collman's reagent cannot only add alkyl halides by also acyl halides to form acyl tetracarbonyl ferrates (-).

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14.1.3: Reductive Elimination

Reductive Elimination Reactions

Reductive elimination is the microscopic reverse of oxidative addition. The reductive elimination can only occur when the two ligands to be eliminated are in cis-position.

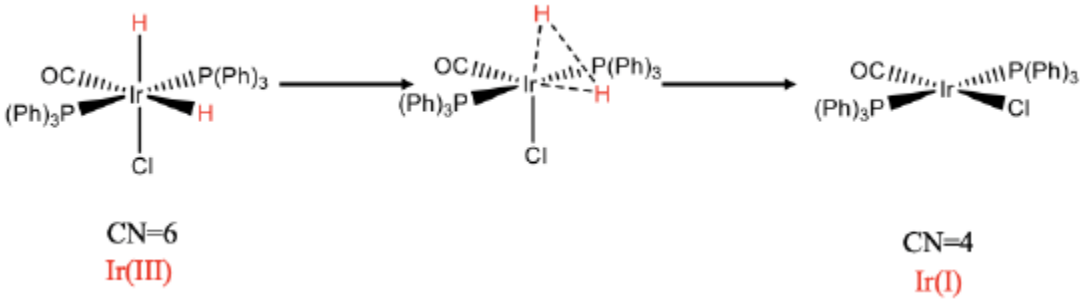


Figure 14.1.3.1: Reductive elimination (Attribution: A. Vedernikov, U Maryland.)

For instance the previously discussed oxidative cis-addition of H_2 to the iridium complex is reversible, and the reverse is called the reductive elimination (Fig. 14.1.3.1). The cis-orientation of the two hydrido ligands is necessary to form an H-H bond. The reaction can be thought of going along a reaction path in which the Ir-H bonds become gradually larger and and the H-H distance gradually smaller until the H_2 molecule is eliminated from the complex.

During reductive elimination, the electrons in the M–X bond head toward ligand Y, and the electrons in M–Y head to the metal. The eliminating ligands are always X-type! On the whole, the oxidation state of the metal decreases by two units, two new open coordination sites become available, and an X–Y bond forms. What does the change in oxidation state suggest about changes in electron density at the metal? As suggested by the name “reductive,” the metal gains electrons. The ligands lose electrons as the new X–Y bond cannot possibly be polarized to both X and Y, as the original M–X and M–Y bonds were. Using these ideas, you may already be thinking about reactivity trends in reductive elimination...hold that thought.

It’s been observed in a number of cases that a ligand dissociates from octahedral complexes before concerted reductive elimination occurs. Presumably, dissociation to form a distorted TBP geometry brings the eliminating groups closer to one another to facilitate elimination.

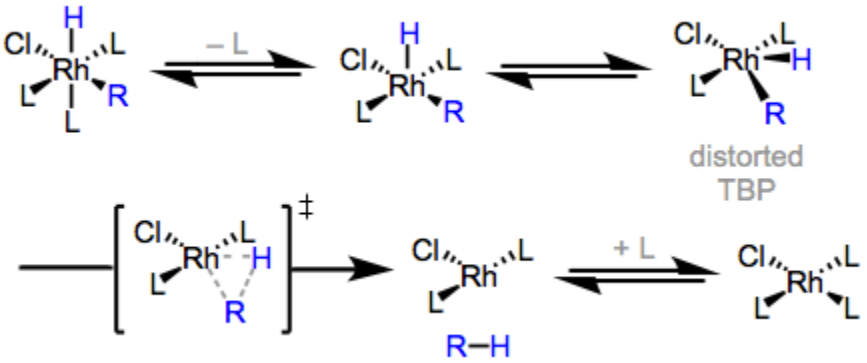


Figure 14.1.3.2: Reductive elimination is faster from five-coordinate than six-coordinate complexes. (Michael Evans)

Square planar complexes may either take on an additional fifth ligand or lose a ligand to form an odd-coordinate complex before reductive elimination. Direct reductive elimination without dissociation or association is possible, too.

Reactivity trends in reductive elimination are opposite those of oxidative addition. More electron-rich ligands bearing electron-donating groups react more rapidly, since the ligands lose electron density as the reaction proceeds. More electron-poor metal

centers—bearing π-acidic ligands and/or ligands with electron-withdrawing groups—react more rapidly, since the metal center gains electrons. Sterically bulky ancillary ligands promote reductive elimination since the release of X and Y can "ease" steric strain in the starting complex. Steric hindrance helps explain, for example, why coordination of a fifth ligand to a square planar complex promotes reductive elimination even though coordination increases electron density at the metal center. A second example: trends in rates of reductive eliminations of alkanes parallel the steric demands of the eliminating ligands: C–C > C–H > H–H.

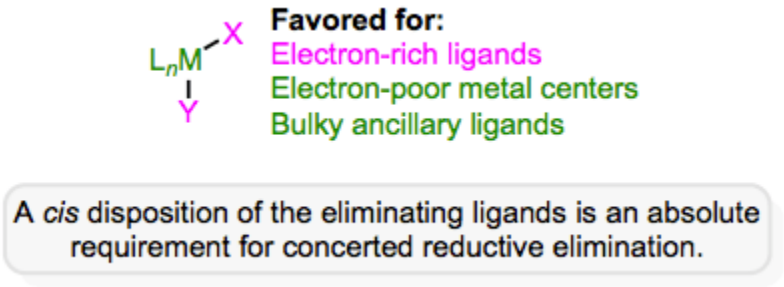


Figure 14.1.3.3: Reactivity trends for reductive eliminations. (Michael Evans)

Mechanistic trends for reductive elimination actually parallel trends in mechanisms of oxidative addition, since these two reactions are the microscopic reverse of one another. Non-polar and moderately polar ligands react by concerted or radical mechanisms; highly polarized ligands and/or very electrophilic metal complexes react by ionic (S_N2) mechanisms. The thermodynamics of reductive elimination must be favorable in order for it to occur! Most carbon–halogen reductive eliminations, for example, are thermodynamically unfavorable (this has turned out to be a good thing, especially for cross-coupling reactions).

Reductive elimination is an important step in many catalytic cycles—it usually comes near the "end" of catalytic mechanisms, just before product formation. For some catalytic cycles it's the turnover-limiting step, making it very important to consider! Hydrocyanation is a classic example; in the mechanism of this reaction, reductive elimination of C–CN is the slow step. Electron-poor alkyl ligands, derived from electron-poor olefins like unsaturated ketones, are bad enough at reductive elimination to prevent turnover altogether! Of course, the electronegative CN ligand is not helping things either...how would you design the ancillary ligands L to speed up this step?

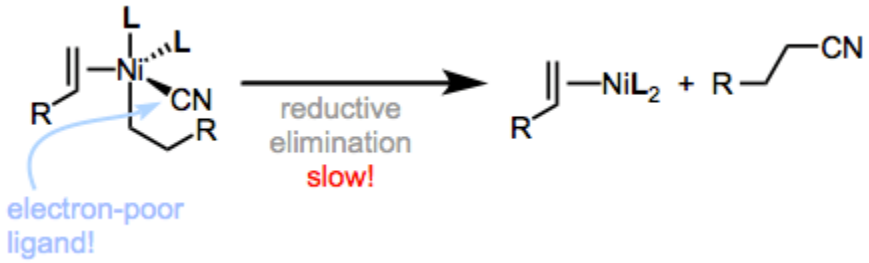


Figure 14.1.3.4: Reductive elimination is the turnover-limiting step of hydrocyanation. How would you design L to speed it up? (Michael Evans)

Dr. Michael Evans (Georgia Tech)

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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14.1.4: Sigma Bond Metathasis

Metal compounds with d^0 electron count are able to activate C-H bonds through σ bond metathesis reactions. **σ-bond metathesis** is a chemical reaction wherein a metal-ligand σ bond undergoes metathesis (exchange of parts) with the sigma bond in some other reagent. The reaction is illustrated by the exchange of lutetium(III) methyl complex with a hydrocarbon (R-H) (Figure 14.1.4.1). The oxidation state of the metal ion does not change during the reaction. This reactivity was first observed by Patricia L. Watson, a researcher at duPont.

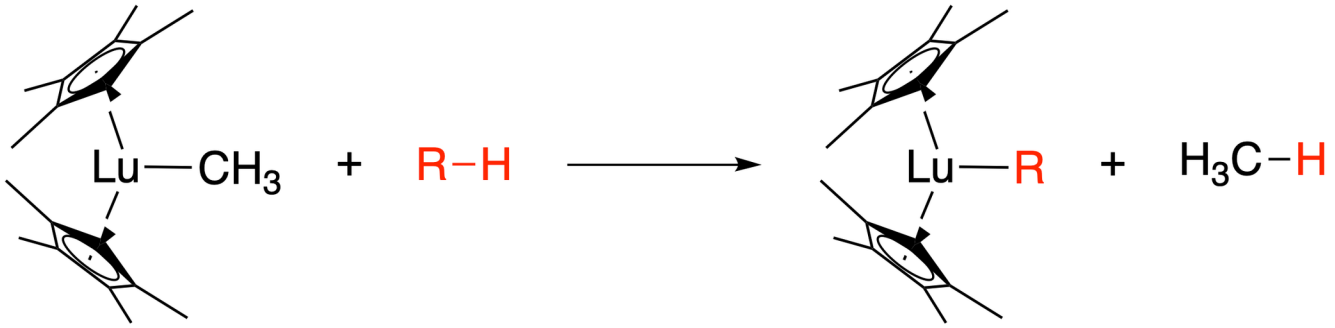


Figure 14.1.4.1: Example of σ bond metathesis; exchange of lutetium(III) methyl complex with a hydrocarbon. The R-H bond is activated and a new C-H bond is created. (CC-BY-SA; Kathryn Haas)

The reaction is mainly observed for complexes of metals with d^0 electron configuration, e.g. complexes of Sc(III), Zr(IV), Nb(IV), Ta(V), etc. Complexes of the f-block elements also participate, regardless of the number of f-electrons. For metals unsuited for redox, sigma bond metathesis provides a pathway for introducing substituents.

The details of the reaction mechanism are somewhat a matter of debate, however a currently accepted model is that it precedes through a cycloaddition and via a "kite-shaped" transition state (Figure 14.1.4.2). Indeed, the rate of the reaction is characterized by a highly negative entropy of activation, indicating an ordered transition state.

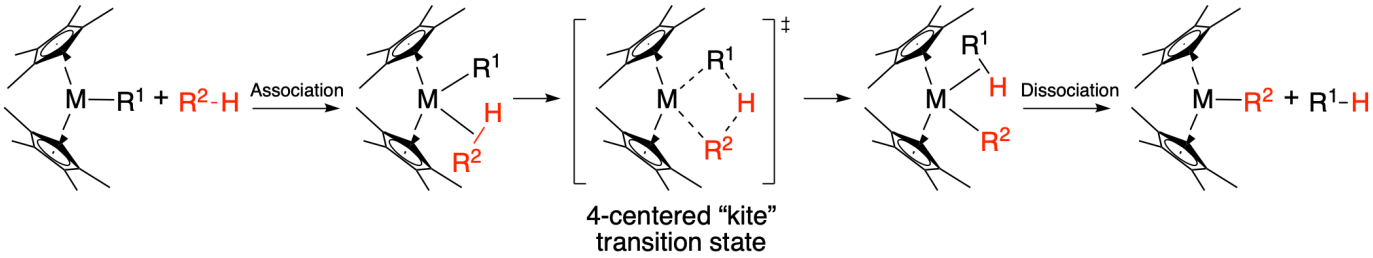


Figure 14.1.4.2: The currently accepted mode for the mechanism of σ bond metathesis involving a kite-like transition state. (CC-BY-SA; Kathryn Haas)

The reaction attracted much attention because hydrocarbons are normally unreactive substrates, whereas some sigma-bond metatheses are facile. Unfortunately the reaction does not readily allow the introduction of functional groups. It has been suggested that dehydrocoupling reactions proceed via sigma-bond metathesis.

Sources:

- https://en.Wikipedia.org/wiki/Sigma-bond_metathesis
- *Waterman, Rory (2013). "σ-Bond Metathesis: A 30-Year Retrospective". Organometallics.* ***32****: 7249–7263. doi:10.1021/om400760k.*

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14.1.5: Application of Pincer Ligands

Pincer ligands are chelating agents that bind tightly to three adjacent coplanar sites of a metal complex. Stoichiometric and catalytic applications of pincer complexes have been studied at an accelerating pace since the mid-1970s.

Pincers often include one anionic, two-electron donor flanked by two neutral, two-electron donor groups. It consists of a rigid, planar backbone, usually consisting of aryl frameworks. The inflexibility of the pincer-metal interaction confers high thermal stability to the resulting complexes. This stability is in part ascribed to the constrained geometry of the pincer, which inhibits ligand exchange and cyclometallation of the pincer. In contrast, cyclometallation is often a significant deactivation process in the case of other types of chelates, in particular limiting their ability to effect C-H bond activation. The pincer ligand also creates a hydrophobic pocket around the reactive coordination site.

There are various types of pincer ligands that are used in transition metal catalysis. Often, they have the same two-electron donor flanking the metal centre, but this is not a requirement. Early examples of pincer ligands were anionic with a carbanion as the central donor site and flanking phosphine donors; these compounds are referred to as **PCP pincers**. Although the most common class of pincer ligands features PCP donor sets, variations have been developed where the phosphines are replaced by thioethers and tertiary amines. Many pincer ligands also feature nitrogenous donors at the central coordinating group position (see figure), such as pyridines. By altering the properties of the pincer ligands, it is possible to significantly alter the chemistry at the metal centre. Changing the hardness/softness of the donor, using electron-withdrawing groups (EWGs) in the backbone, and the altering the steric constraints of the ligands are all methods used to tune the reactivity at the metal centre.

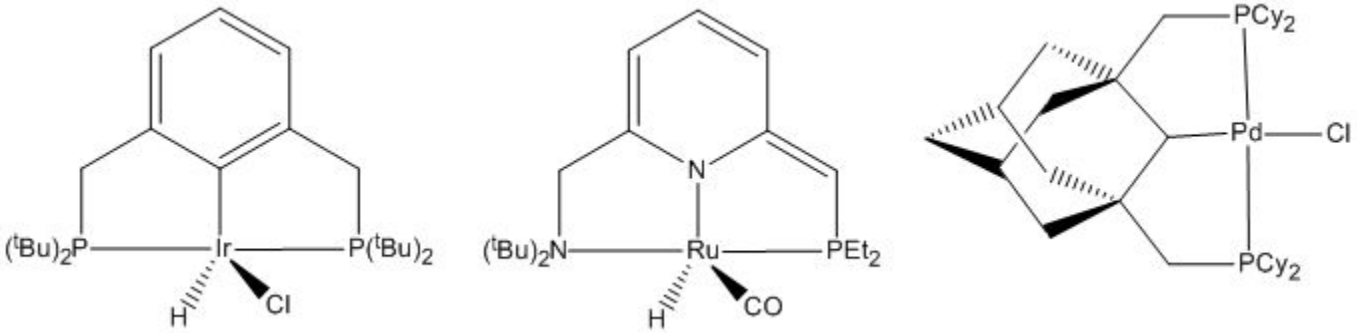
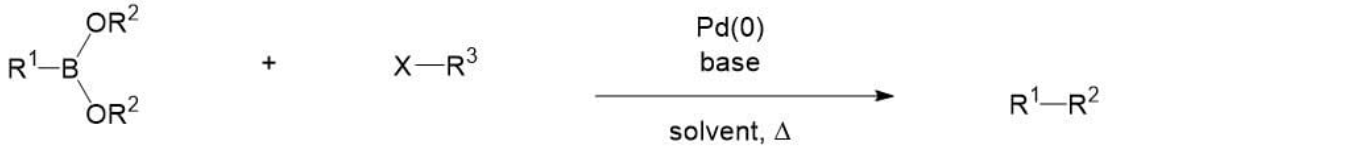


Figure 14.1.5.1: Examples of transition metal pincer complexes. (Scott, Examples pincer complexes, CC BY-SA 3.0)

The Role of Pincer Complexes in Catalysis

Suzuki-Miyaura coupling

Pincer complexes have been shown to catalyse Suzuki-Miyaura coupling reactions, a versatile carbon-carbon bond forming reaction. Suzuki-Miyaura coupling (or Suzuki coupling) is a metal catalyzed reaction, typically with Pd, between an alkenyl (vinyl), aryl, or alkynyl organoborane (boronic acid or boronic ester, or special cases with aryl trifluoroborane) and halide or triflate under basic conditions. This reaction is used to create carbon-carbon bonds to produce conjugated systems of alkenes, styrenes, or biaryl compounds (Scheme 1).



R^1= aryl, alkene (vinyl), alkyne **R**^{2}= H (boronic acid), alkyl (boronic ester) **R**^{3}= aryl, alkene (vinyl), alkyne

X = halide (I, Br, Cl*) triflate (-OTf) *Cl requires special conditions for activation

Scheme 14.1.5.2: General reaction scheme of Suzuki cross coupling reaction. (Suzuki-Miyaura Coupling)

Modified conditions have demonstrated reactivity with less reactive substrates such as alkyl boranes (BR_3) or aryl or alkenyl chlorides by amending the base and ligands employed.

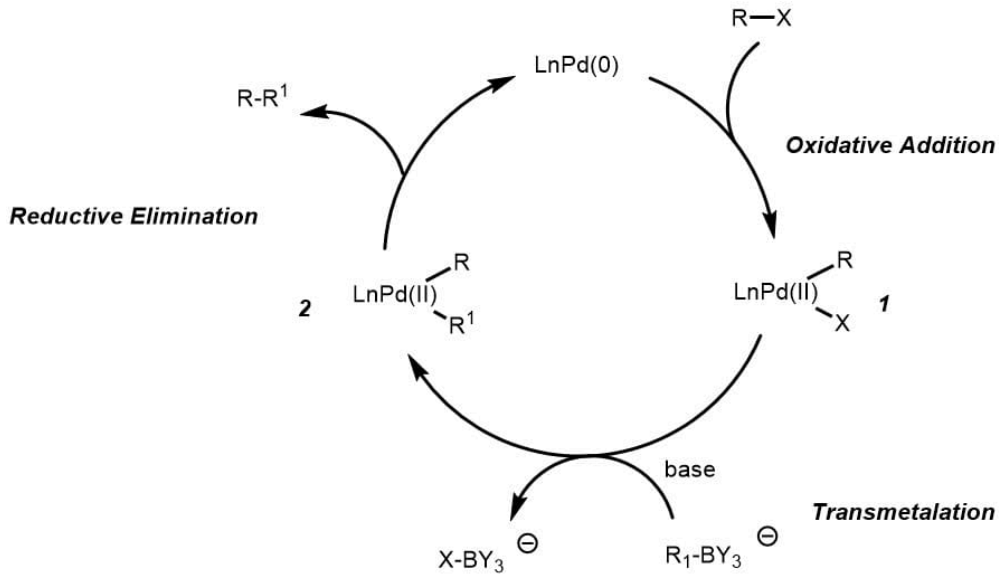
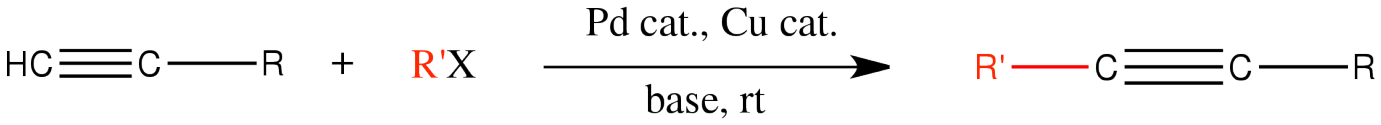


Figure 14.1.5.3: Suzuki coupling proceeds via three basic steps: oxidative addition, transmetallation, and reductive elimination. (Suzuki-Miyaura Coupling)

Sonogashira Coupling

The Sonogashira reaction (also called the Sonogashira-Hagihara reaction) is the cross coupling of aryl or vinyl halides with terminal alkynes to generate conjugated enynes and arylalkynes (Scheme 1). The reaction typically proceeds in the presence of a palladium(0) catalyst, a copper(I) cocatalyst, and an imine base. Alternative procedures describe Sonogashira coupling reactions performed without the Cu(I) cocatalyst.



R' = Aryl, Vinyl

X = I, Br, Cl, OTf

Scheme 14.1.5.4: *General reaction for Sonogashira Coupling*. (Jcap17, Sonogashira Cross-Coupling Reaction, CC BY-SA 3.0)

Dehydrogenation of alkanes

Alkanes undergo dehydrogenation at high temperatures. Typically this conversion is promoted heterogeneously because typically homogeneous catalysts do not survive the required temperatures (~200 °C) The corresponding conversion can be catalyzed homogeneously by pincer catalysts, which are sufficiently thermally robust. Proof of concept was established in 1996 by Jensen and co-workers. They reported that an iridium and rhodium pincer complex catalyze the dehydrogenation of cyclooctane with a turnover frequency of 12 min^{-1} at 200 °C. They found that the dehydrogenation was performed at a rate two orders of magnitude greater than those previously reported. The iridium pincer complex was also found to exhibit higher activity than the rhodium complex. This rate difference may be due to the availability of the Ir(V) oxidation state which allows stronger Ir-C and Ir-H bonds.

The homogeneously catalyzed process can be coupled to other reactions such as alkene metathesis. Such tandem reactions have

not been demonstrated with heterogeneous catalysts.

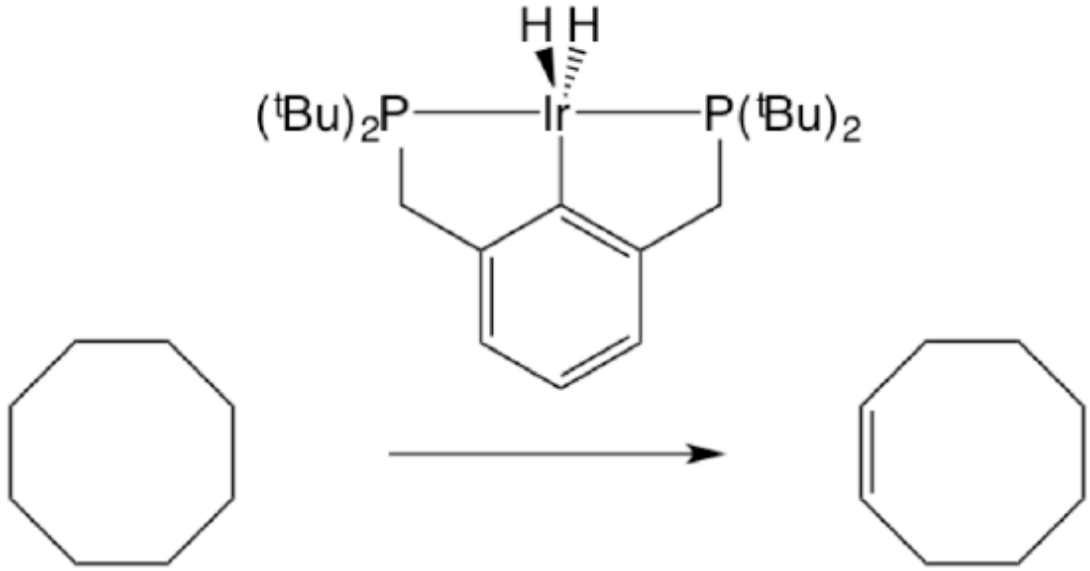


Figure 14.1.5.5: Iridium pincer complex catalyzing the dehydrogenation of cyclooctane to cyclooctene. (Paul Gray, Iridium Pincer Catalysis, CC BY-SA 3.0)

Sources:

- https://en.Wikipedia.org/wiki/Transi...pincer_complex
- Sonogashira Coupling
- Suzuki-Miyaura Coupling

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14.2: REACTIONS INVLOVING MODIFICATION OF UNSATURATED LIGANDS

This section will describe organometallic reactions that involve modification of unsaturated ligands.

14.2.1: Introduction to Insertion

14.2.2: CO Insertions (Alkyl Migration)

14.2.3: Migratory Insertion-1,2-Insertions

14.2.4: β-Elimination Reactions

14.2.5: Abstraction and Addition

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14.2.1: Introduction to Insertion

We've seen that the metal-ligand bond is generally polarized toward the ligand, making the ligand nucleophilic. The ligand is especially nucleophilic in the case of X-type (anionic) ligands. When a nucleophilic, X-type ligand is positioned *cis* to a neutral, unsaturated ligand (L) in an organometallic complex, a migratory insertion reaction can occur. In a **migratory insertion reaction**, an anionic ligand (X^{-}) and a neutral unsaturated ligand (L) couple to form a new anionic ligand ($^{-}\mathrm{LX})thatisattachedtothesamemetal(Figure\ (14.2.1.1)$. The overall result is that an M-X bond is broken and M and X are added across a π bond of L. There is no change in oxidation state at the metal (unless the ligand is an alkylidene/alkylidyne), but the total electron count of the complex decreases by two during the actual insertion event.

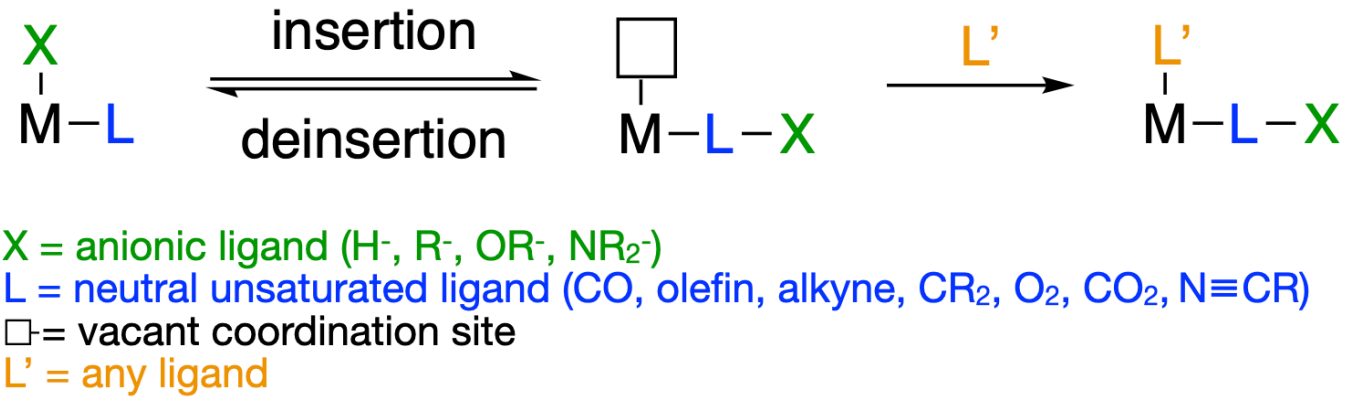


Figure 14.2.1.1: Migratory insertion (CC-BY-SA; Kathryn Haas)

The migratory insertion results in a decrease in coordination number and the creation of an open coordination site on the complex. The open coordination site can be filled by an added ligand (L') (Figure 14.2.1.1). The reverse of the insertion reaction is called a **deinsertion**. To drive the chemical equilibrium in the forward (insertion) direction, the reactant neutral ligand (or another neutral ligand) can be added in excess so that the neutral ligand fills the vacancy in the product complex and prevents the reverse (deinsertion) reaction. Typical neutral, unsaturated ligands are CO, olefins, alkynes, carbenes, dioxygen, carbon dioxide, and nitriles. Typical anionic ligands are hydrido, alkyl, aryl, alkoxy, and amido-ligands Figure 14.2.1.1.

The open site may appear where the unsaturated ligand was *or* where the X-type ligand was, depending on which group actually moved (see below). It is more common that the anionic X ligand moves (Figure 14.2.1.2).

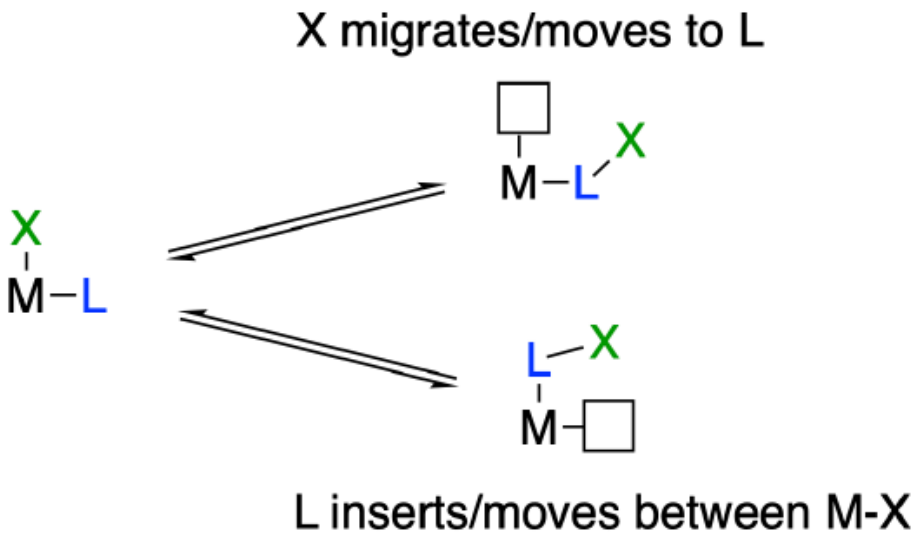


Figure 14.2.1.2: X can migrate onto unsaturated ligand L, or L can move to the original position of X. The former is more common for CO insertions. (CC-BY-SA; Kathryn Haas)

We can distinguish between two types of insertions, which differ in the number of atoms in the unsaturated ligand involved in the step. Insertions of CO, carbenes, and other η^1 unsaturated ligands are called **1,1-insertions** because the X-type ligand moves from its current location on the metal to one spot over, on the atom bound to the metal. η^2 ligands like alkenes and alkynes can also participate in migratory insertion; these reactions are called **1,2-insertions** because the X-type ligand slides two atoms over, from the metal to the distal atom of the unsaturated ligand (Figure 14.2.1.4).

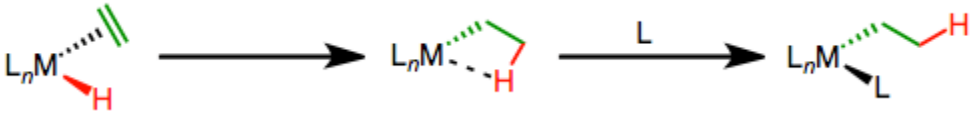


Figure 14.2.1.4: 1,2-insertion of an alkene and hydride. In some cases, an agostic interaction has been observed in the unsaturated intermediate. (Michael Evans)

This is really starting to look like the addition of M and X across a π bond! However, we should take care to distinguish this completely intramolecular process from the attack of a nucleophile or electrophile on a coordinated π system, which is a different beast altogether. Confusingly, chemists often jumble up all of these processes using words like “hydrometalation,” “carbometalation,” “aminometalation,” etc. Another case of big words being used to obscure ignorance! We’ll look at nucleophilic and electrophilic attack on coordinated ligands in separate posts.

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14.2.2: CO Insertions (Alkyl Migration)

One of the most common types of migratory insertions is carbonyl insertion (Figure 14.2.2.3). The carbonyl insertion produces an acyl group. Notice in the example below that the complex goes from 18 to 16 total electrons after insertion. A dative ligand comes in to fill the empty coordination site. L can be a neutral or anionic ligand, and it can even be the carbonyl oxygen itself. To drive the reaction, the reaction can be carried out in the presence of a neutral ligand like free CO, which occupies the vacant site.

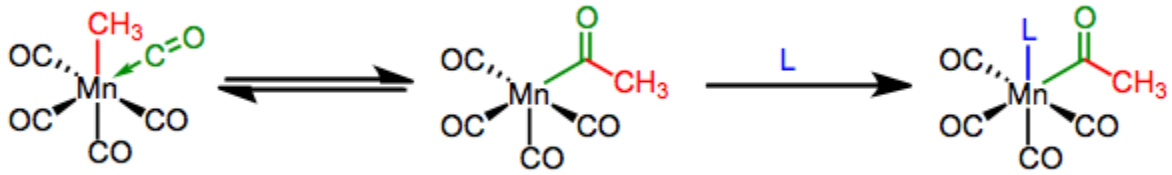


Figure 14.2.2.1: Migratory insertion into a metal-carbon bond. (Michael Evans)

Reactivity Trends in CO Insertions

Certain conditions *must* be met for migratory insertion to occur: the two ligands undergoing the process must be *cis*, and the complex must be stable with two fewer total electrons. Thermodynamically, the formed Y–X and covalent M–Y bonds must be more stable than the broken M–X and dative M–Y bonds for insertion to be favored. When the opposite is true, the microscopic reverse (**elimination** or **deinsertion**) will occur spontaneously.

Migratory aptitudes for insertion into CO have been studied extensively, and the general conclusion here is “it’s complicated.” A few ligands characterized by remarkably stable metal-ligand bonds don’t undergo insertion for thermodynamic reasons—the M–X bond is just too darn strong. Perfluoroalkyl complexes and metal hydrides are two notable examples. Electron-withdrawing groups on the X-type ligand, which strengthen the M–X bond, slow down insertion (likely for thermodynamic reasons though…Hammond’s postulate in action).

What factors affect the relative speed (kinetics) of favorable insertions? Sterics is one important variable. Both 1,1- and 1,2-insertions can relieve steric strain at the metal center by spreading out the ligands involved in the step. In 1,2-insertions, the X-type ligand removes itself completely from the metal! Unsurprisingly, then, bulky ligands undergo insertions more rapidly than smaller ligands. Complexes of the first-row metals tend to react more rapidly than analogous second-row metal complexes, and second-row metal complexes react faster than third-row metal complexes. This trend fits in nicely with the typical trend in M–C bond strengths: first row < second row < third row. Lewis acids help accelerate insertions into CO by coordinating to CO and making the carbonyl carbon more electrophilic. For a similar reason, CO ligands bound to electron-poor metal centers undergo insertion more rapidly than CO’s bound to electron-rich metals. Finally, for reasons that are still unclear, one-electron oxidation often increases the rate of CO insertion substantially.

Although the thermodynamics of alkene 1,2-insertion are more favorable for metal-carbon than metal-hydrogen bonds, M–H bonds react *much* more rapidly than M–C bonds in 1,2-insertions. This fact has been exploited for olefin hydrogenation, which would be much less useful if it had to complete with olefin polymerization (the result of repeated insertion of C=C into M–C) in the same reaction flask! More on that in the next post.

Stereochemistry in CO Insertions

Migratory insertion steps are full of stereochemistry! Configuration at the migrating alkyl group is retainedduring insertion—a nice piece of evidence supporting a concerted, intramolecular mechanism of migration.

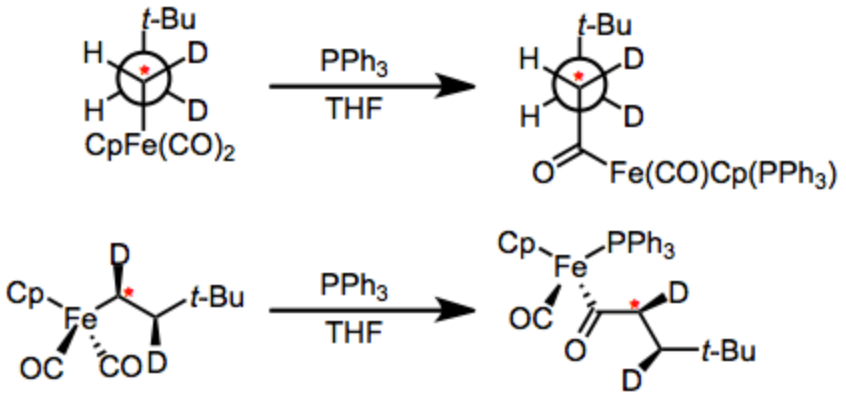


Figure 14.2.2.2: Migratory insertion occurs with retention of configuration at the migrating alkyl group. Two different views of the same reaction are shown here. (Michael Evans)

What about stereochemistry at the metal center? Migratory insertion may create a stereogenic center at the metal—see the iron example above. Whether the X-type ligand moves onto the unsaturated ligand or *vice versa* will impact the configuration of the product complex. Calderazzo's study of this issue is one of my favorite experiments in all of organometallic chemistry! He took the simple labeled substrate in the figure below and treated it with dative ligand, encouraging insertion. Four products of insertion are possible, corresponding to reaction of the four CO ligands *cis* to the methyl ligand. Try drawing a few curved arrows to wrap your mind around the four possibilities, and consider both CO migration and Me migration as possible at this point.

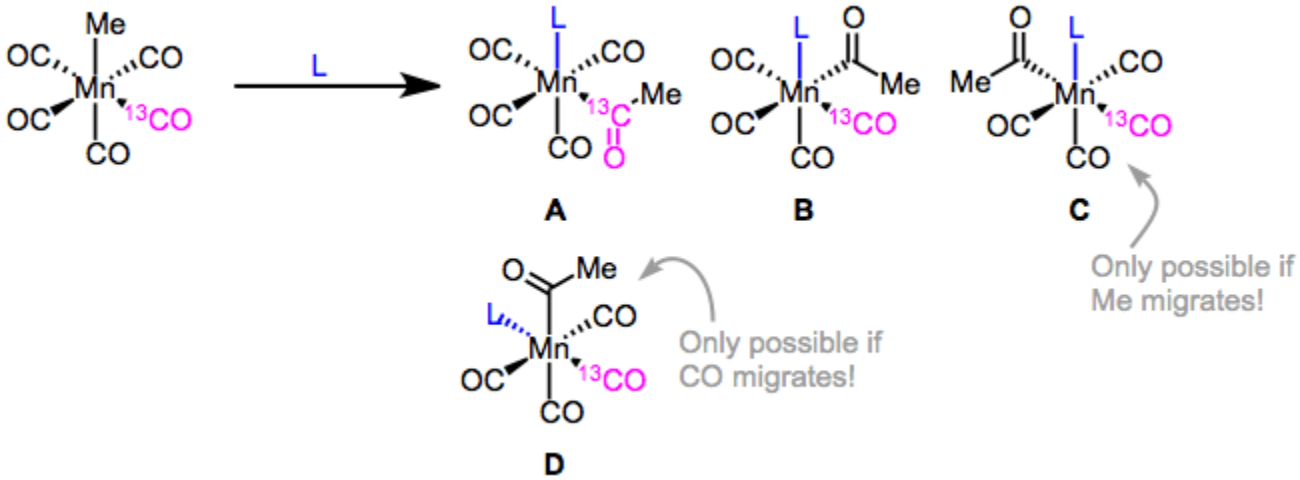


Figure 14.2.2.3: Insertion of the labeled complex shown could produce four products. Calderazzo did not observe product **D**, supporting a mechanism involving Me migration to CO. (Michael Evans)

Note that product **D** is impossible if we only allow the Me group to migrate—the spot *trans* to the labeled CO is another CO ligand, so that spot can only pick up L if CO migrates (not if Me migrates). On the other hand, product **C** must have come from the migration of Me, since the Me group has moved from a *cis* to a *trans*position relative to the labeled CO in product **C**. Calderazzo observed products **A**, **B**, and **C**, but not **D**, supporting a mechanism involving Me migration. Other experiments since support the idea that most of the time, the alkyl group migrates onto CO. Slick, huh?

I won't address insertions into alkylidenes, alkylidynes, and other one-atom unsaturated ligands in this post, as insertions into CO are by far the most popular 1,1 insertions in organometallic chemistry. In the next post, we'll dig more deeply into 1,2-insertions of alkenes and alkynes. Thanks for reading!

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14.2.3: Migratory Insertion-1,2-Insertions

Insertions of π systems into M-X bonds are appealing in the sense that they establish two new σ bonds in one step, in a stereocontrolled manner. As we saw in the last post, however, we should take care to distinguish these fully intramolecular migratory insertions from intermolecular attack of a nucleophile or electrophile on a coordinated π-system ligand. The reverse reaction of migratory insertion, β-elimination, is not the same as the reverse of nucleophilic or electrophilic attack on a coordinated π system.

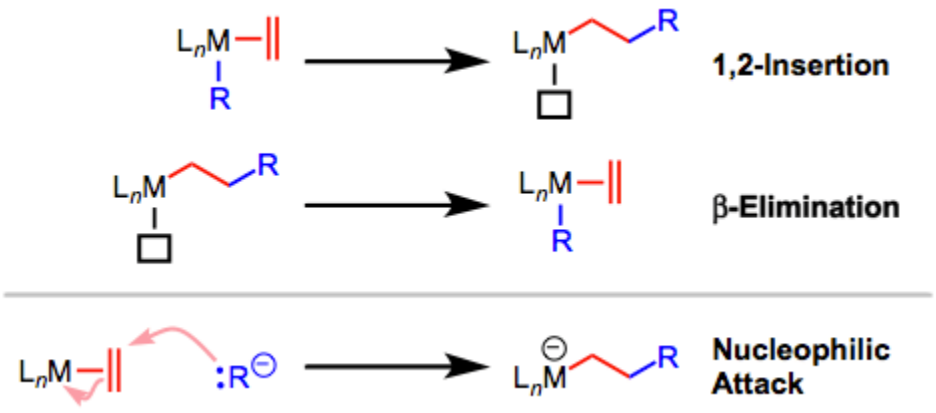


Figure 14.2.3.1: 1,2-Insertion is dinstinct from nucleophilic/electrophilic attack on coordinated ligands. (Michael Evans)

Like 1,1-insertions, 1,2-insertions generate a vacant site on the metal, which is usually filled by external ligand. For unsymmetrical alkenes, it's important to think about site selectivity: which atom of the alkene will end up bound to metal, and which to the other ligand? To make predictions about site selectivity we can appeal to the classic picture of the M–X bond as M + X^-. Asymmetric, polarized π ligands contain one atom with excess partial charge; this atom hooks up with the complementary atom in the M–R bond during insertion. Resonance is our best friend here!

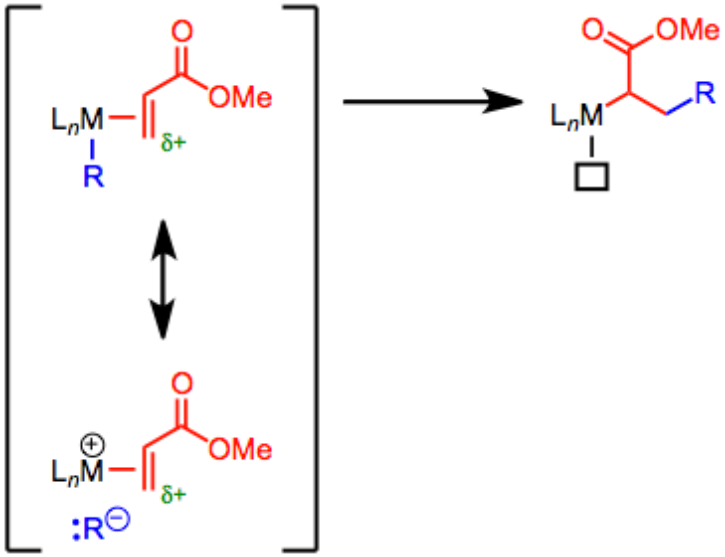


Figure 14.2.3.2: The site selectivity of 1,2-insertion can be predicted using resonance forms and partial charges. (Michael Evans)

A nice study by Yu and Spencer illustrates these effects in homogeneous palladium- and rhodium-catalyzed hydrogenation reactions. Unactivated alkenes generally exhibit lower site selectivity than activated ones, although steric differences between the two ends of the double bond can promote selectivity.

Reactivity Trends in 1,2-Insertions

The thermodynamics of 1,2-insertions of alkenes depend strongly on the alkene, but we can gain great insight by examining the structure of the product alkyl. Coordinated alkenes that give strong metal-alkyl bonds after migratory insertion tend to undergo the process. Hence, electron-withdrawing groups, such as carbonyls and fluorine atoms, tend to encourage migratory insertion—remember that alkyl complexes bearing these groups tend to have stable M–C bonds.

Insertions of alkenes into both M–H and M–R (R = alkyl) are favored thermodynamically, but the kinetics of M–R insertion are much slower. This observation reflects a pervasive trend in organometallic chemistry: M–H bonds react more rapidly than M–R bonds. The same is true of the reverse, β-elimination. Even in cases when both hydride and alkyl elimination are thermodynamically favored, β-hydride elimination is much faster. Although insertion into M–R is relatively slow, this elementary step is critical for olefin polymerizations that form polyalkenes (Ziegler-Natta polymerization). This reaction deserves a post all its own!

As the strength of the M–X bond increases, the likelihood that an L-type π ligand will insert into the bond goes down. Hence, while insertions into M–H and M–C are relatively common, insertions into M–N and M–O bonds are more rare. Lanthanides and palladium are known to promote insertion into M–N in some cases, but products with identical connectivity can come from external attack of nitrogen on a coordinated π ligand. The diastereoselectivity of these reactions provides mechanistic insight—since migratory insertion is syn (see below), a syn relationship between Pd and N is to be expected in the products of migratory insertion. An anti relationship indicates external attack by nitrogen or oxygen.

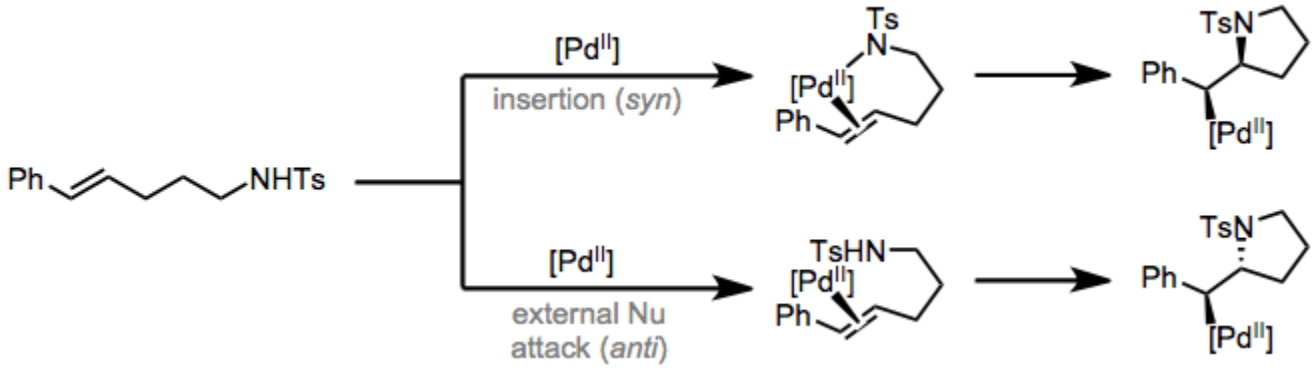


Figure 14.2.3.3: The diastereoselectivity of formal insertions provides insight about their mechanisms. (Michael Evans)

Stereochemistry of 1,2-Insertions

1,2-Insertion may establish two stereocenters at once, so the stereochemistry of the process is critical! Furthermore, 1,2-insertions and β-eliminations are bound by important stereoelectronic requirements. An analogy can be made to the E2 elimination of organic chemistry, which also has strict stereoelectronic demands. For migratory insertion to proceed, the alkene and X-type ligand must be syncoplanar during insertion; as a consequence of this alignment, X and MLn end up on the same face of the alkene after insertion. In other words, insertions into alkenes take place in a syn fashion. Complexes that have difficulty achieving a coplanar arrangement of C=C and M–X undergo insertion very slowly, if at all.

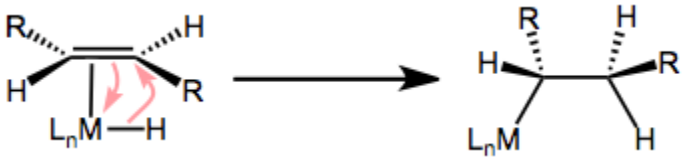


Figure 14.2.3.4: 1,2-Insertions take place in a syn fashion. The metal and X end up bound to the same face of the alkene. (Michael Evans)

This observation has important implications for β-elimination, too—the eliminating X and the metal must have the ability to align syn.

Insertions of Other π Systems

To close this post, let's examine insertions into π ligands other than alkenes briefly. Insertions of alkynes into metal-hydride bonds are known, and are sometimes involved in reactions that I refer to collectively as "hydrostuffylation": hydrosilylation, hydroesterification, hydrogenation, and other net H–X additions across the π bond. Strangely, some insertions of alkynes yield trans products, even though cis products are to be expected from syn addition of M–X. The mechanisms of these processes involve initial syn addition followed by isomerization to the trans complex via an interesting resonance form. The cis complex is the kinetic product, but it isomerizes over time to the more thermodynamically stable trans complex.

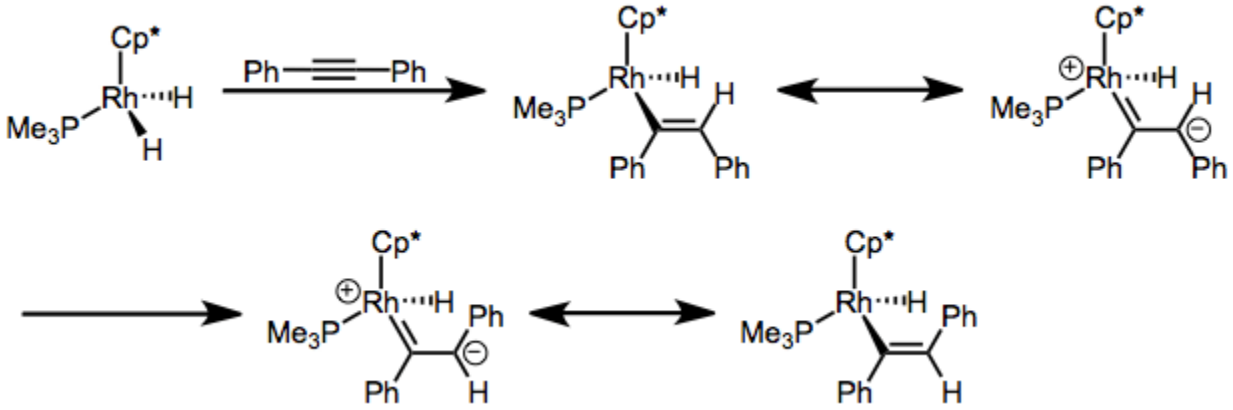


Figure 14.2.3.5: Migratory insertions of alkynes into M–H produce alkenyl complexes, which have been known to isomerize. (Michael Evans)

The strongly donating Cp* ligand supports the legitimacy of the zwitterionic resonance form—and suggests that the C=C bond may be weaker than it first appears!

Polyenes can participate in migratory insertion, and insertions of polyenes are usually quite favored because stabilized π-allyl complexes result. In one mind-bending case, a coordinated arene inserts into an M–Me bond in a syn fashion!

Have you ever stopped to consider that the addition of methyllithium to an aldehyde is a formal insertion of the carbonyl group into the Li–Me bond? It's true! We can think of these as (very) early-metal "insertion" reactions. Despite this precedent, migratory insertion reactions of carbonyls and imines into late-metal hydride and alkyl bonds are surprisingly hard to come by. Rhodium is the most famous metal that can make this happen—rhodium has been used in complexes for arylation and vinylation, for example. Insertion of X=C into the M–R bond is usually followed by β-hydride elimination, which has the nifty effect of replacing H in aldehydes and aldimines with an aryl or vinyl group.

Contributors and Attributions

Dr. Michael Evans (Georgia Tech)

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14.2.4: β-Elimination Reactions

In organic chemistry class, one learns that elimination reactions involve the cleavage of a σ bond and formation of a π bond. A nucleophilic pair of electrons (either from another bond or a lone pair) heads into a new π bond as a leaving group departs. This process is called β-elimination because the bond β to the nucleophilic pair of electrons breaks. Transition metal complexes can participate in their own version of β-elimination, and metal alkyl complexes famously do so. Almost by definition, metal alkyls contain a nucleophilic bond—the M–C bond! This bond can be so polarized toward carbon, in fact, that it can promote the elimination of some of the world's worst leaving groups, like –H and –CH3. Unlike the organic case, however, the leaving group is not lost completely in organometallic β-eliminations. As the metal donates electrons, it receives electrons from the departing leaving group. When the reaction is complete, the metal has picked up a new π-bound ligand and exchanged one X-type ligand for another.

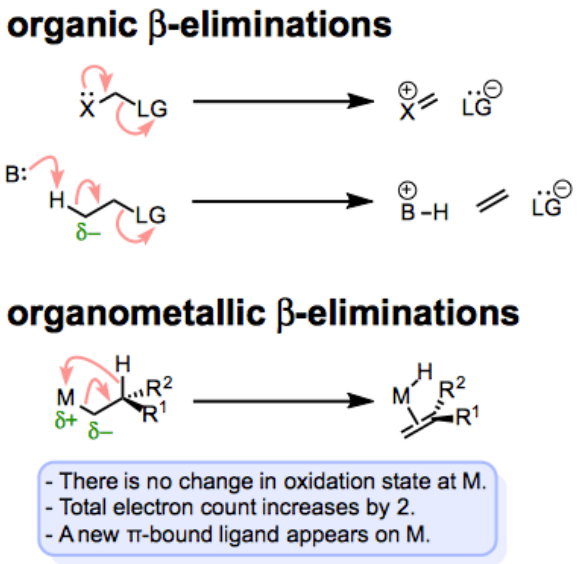


Figure 14.2.4.1: Comparing organic and organometallic β-eliminations. A nucleophilic bond or lone pair promotes loss or migration of a leaving group. (Michael Evans)

In this post, we'll flesh out the mechanism of β-elimination reactions by looking at the conditions required for their occurrence and their reactivity trends. Many of the trends associated with β-eliminations are the opposite of analogous trends in 1,2-insertion reactions. A future post will address other types of elimination reactions.

β-Hydride Elimination

The most famous and ubiquitous type of β-elimination is **β-hydride elimination**, which involves the formation of a π bond and an M–H bond. Metal alkyls that contain β-hydrogens experience rapid elimination of these hydrogens, provided a few other conditions are met.

The complex must have an open coordination site and an accessible, empty orbital on the metal center. The leaving group (–H) needs a place to land. Notice that after β-elimination, the metal has picked up one more ligand—it needs an empty spot for that ligand for elimination to occur. We can envision hydride "attacking" the empty orbital on the metal center as an important orbital interaction in this process.

The M–C_α and C_β–H bonds must have the ability to align in a syn coplanar arrangement. By "syn coplanar" we mean that all four atoms are in a plane and that the M–C_α and C_β–H bonds are on the same side of the C_α–C_β bond (a dihedral angle of 0°). You can see that conformation in the figure above. In the syn coplanar arrangement, the C–H bond departing from the ligand is optimally lined up with the empty orbital on the metal center. Hindered or cyclic complexes that cannot achieve this conformation do not undergo β-hydride elimination. The need for a syn coplanar conformation has important implications for eliminations that may establish diastereomeric olefins: β-elimination is stereospecific. One diastereomer leads to the (E)-olefin, and the other leads to

the (Z)-olefin.

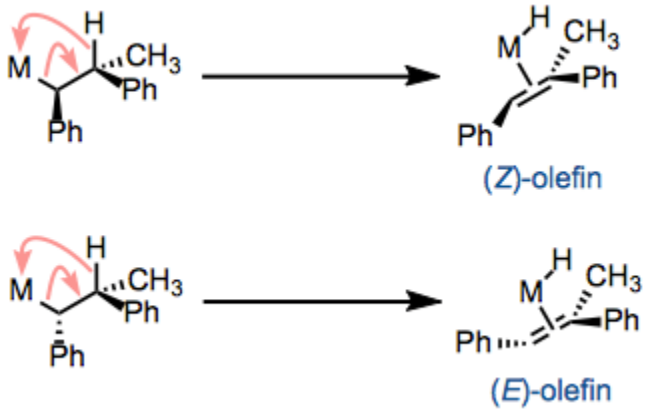


Figure 14.2.4.2: β-elimination is stereospecific. One diastereomer of reactant leads to the (Z)-olefin and the other to the (E)-olefin. (Michael Evans)

The complex must possess 16 or fewer total electrons. Examine the first figure one more time—notice that the total electron count of the complex increases by 2 during β-hydride elimination. Complexes with 18 total electrons don't undergo β-elimination because the product would end up with 20 total electrons. Of course, dissociation of a loose ligand can produce a 16-electron complex pretty easily, so watch out for ligand dissociation when considering the possibility of β-elimination in a complex. Ligand dissociation may be reversible, but β-Hydride elimination is almost always irreversible.

The metal must bear at least 2 d electrons. Now this seems a bit strange, as the metal has served as nothing but an empty bin for electrons in our discussion so far. Why would the metal center need electrons for β-hydride elimination to occur? The answer lies in an old friend: backbonding. The $\sigma_{C-H} \rightarrow$ M orbital interaction mentioned above is not enough to promote elimination on its own; an M $\rightarrow \sigma^*_{C-H}$ interaction is also required! I've said it before, and I'll say it again: backbonding is everywhere in organometallic chemistry. If you can understand and articulate it, you'll blow your instructor's mind.

Other β-Elimination Reactions

The leaving group does not need to be hydrogen, of course, and a number of more electronegative groups come to mind as better candidates for leaving groups. β-Alkoxy and β-amino eliminations are usually thermodynamically favored thanks to the formation of strong M–O and M–N bonds, respectively. These reactions are so favored in β-alkoxyalkyl "complexes" of alkali and alkaline earth metals (R–Li, R–MgBr, etc.) that using these as σ-nucleophiles at carbon is untenable. Such compounds eliminate immediately upon their formation. I had an organic synthesis professor in undergrad who was obsessed with this—using a β-alkoxyalkyl lithium or β-alkoxyalkyl Grignard reagent in a synthesis was a recipe for red ink. β-Haloalkyls were naturally off limits too.

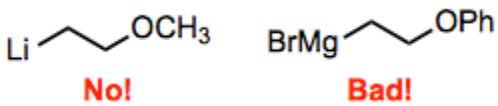


Figure 14.2.4.3: Watch out...these are not stable compounds! (Michael Evans)

The atom bound to the metal doesn't have to be carbon. β-Elimination of alkoxy ligands affords ketones or aldehydes bound at oxygen or through the C=O π bond (this step is important in many transfer hydrogenations, and an analogous process occurs in the Oppenauer oxidation). Amido ligands can undergo β-elimination to afford complexes of imines; however, this process tends to be slower than β-alkoxy elimination.

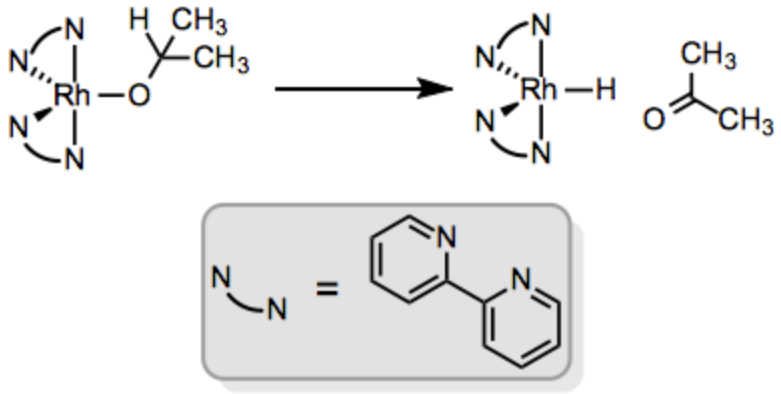


Figure 14.2.4.4: β-Elimination helps transfer the elements of dihydrogen from one organic compound to another.. (Michael Evans)

Incidentally, I haven't seen any examples in which the β atom is not carbon, but would be interested if anyone knows of an example!

Applications of β-Eliminations

As with many concepts in organometallic chemistry, there are two ways to think about applications of β-elimination. One can take either the "inorganic" perspective, which focuses on the metal center, or the "organic" perspective, which focuses on the ligands.

With the metal center in focus, we can recognize that β-hydride elimination has the wonderful side effect of establishing an M–H bond—a feat generally difficult to achieve in a selective manner via oxidative addition of X–H. If the ligand from which the hydrogen came displaced something more electronegative, the whole process represents reduction at the metal center. For example, imagine rhodium(III) chloride is mixed with sodium isopropoxide, $NaOCH(CH_3)_2$. The isopropoxide easily displaces chloride, and subsequent β-hydride elimination affords a rhodium hydride, formally reduced with respect to the chloride starting material. See p. 236 of this review for more.

With the ligand in focus, we see that the organic ligand is oxidized in the course of β-hydride elimination. Notice that the metal is reduced and the ligand oxidized! A π bond replaces a σ bond in the ligand, and if the conditions are right, this represents a bona fide oxidation (as opposed to a mere elimination). For example, oxidative addition into a C–H bond followed by β-hydride elimination at a C–H bond next door sets up an alkene where two adjacent C–H bonds existed before, an oxidation process. These dehydrogenation reactions are incredibly appealing in a theoretical sense, but still at an early stage when it comes to scope and practicality.

Summary

We already encountered β-hydride elimination in an earlier series of posts on metal alkyl complexes, where we noted that it's a very common decomposition pathway for metal alkyls. β-Hydride elimination isn't all bad, however, as it can be an important step in catalytic reactions that result in the oxidation of organic substrates (dehydrogenations and transfer hydrogenations) and in reactions that reduce metal halides to metal hydrides. The general idea of β-elimination involves the transfer of a leaving group from a ligand to the metal center with simultaneous formation of a π bond in the ligand. β-Elimination requires an open coordination site and at least two d electrons on the metal center, and eliminations of chiral complexes are stereospecific. The leaving group is commonly hydrogen, but need not be—the more electronegative the leaving group, the more favorable the elimination. Stronger π bonds in the product also encourage β-elimination, so eliminations that form carbonyl compounds or imines are common.

In the next post, we'll explore other types of organometallic elimination reactions, which establish π bonds at different positions in metal alkyl or other complexes. α-Eliminations, for example, establish metal-carbon, -oxygen, or -nitrogen multiple bonds, which are generally difficult to forge through other means

Contributors and Attributions

- Dr. Michael Evans (Georgia Tech)

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14.2.5: Abstraction and Addition

The nucleophilic and electrophilic addition and abstraction reactions can be viewed as ways of activating a ligand toward reaction with an external reagent. The external reagent reacts directly with the ligand, not with the metal center. The external reagent may be a nucleophile (Lewis Base) or an electrophile (Lewis acid).

Nucleophilic Addition and Abstraction

The reaction of an activated ligand with a nucleophilic reagent is favored if the activated ligand is electron poor. When the metal complex is either cationic and/or has spectator ligands that are are electron withdrawing, the reactive ligand becomes activated by being depleted of electron density. The attack of the nucleophile may result in the formation of a new bond between the nucleophile and the activated unsaturated substrate, in which case it is called nucleophilic addition. Alternatively, the reaction may result in an abstraction of a part or the whole of the activated ligand, in which case it is called the nucleophilic abstraction. Some examples of nucleophilic addition and the abstraction reactions are discussed below.

Nucleophilic Addition

An example of a nucleophilic addition reaction is shown in Figure 14.2.5.1. The olefin is activated by its interaction with platinum. Pyridine is the nucleophile, and the result is a new C—N bond.

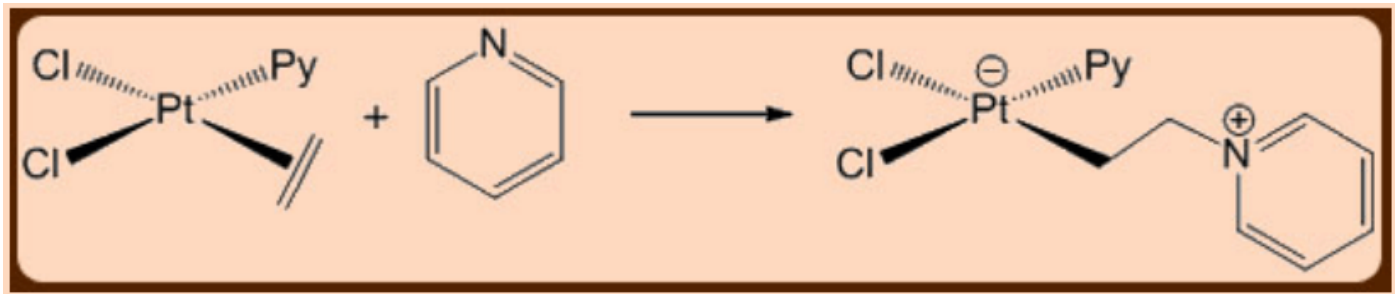


Figure 14.2.5.1: An example of addition of a nucleophile to an activated ligand.

Nucleophilic Abstraction

An example of a nucleophilic abstraction reaction is shown in Figure 14.2.5.2.

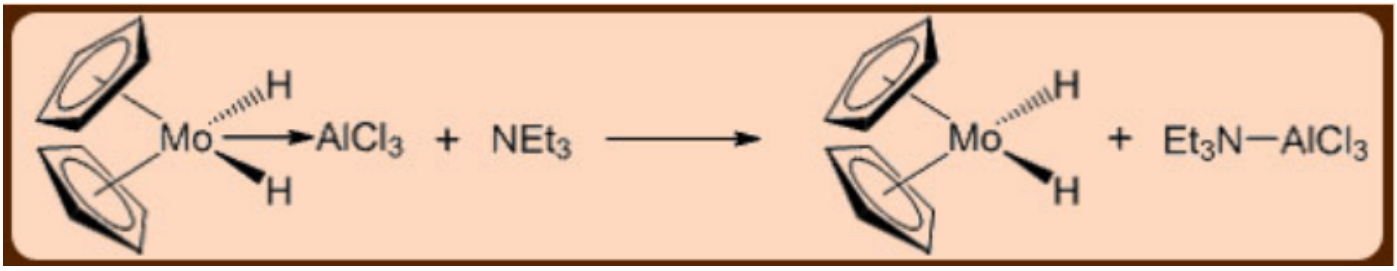


Figure 14.2.5.2: An example of abstraction by a nucleophile.

Electrophilic Addition and Abstraction

Similar to the nucleophilic addition and abstraction reactions, the electrophilic counterparts of these reactions also exist. An electrophilic attack is favored if the ligand-metal fragment is more electron rich. When the complex is anionic, the metal center is at low oxidation state, and/or when the spectator ligands are electron donating, the ligand becomes activated toward reaction with an electrophile. The reaction of activated ligands with electrophilic substrates may result in the formation of a new bond between the electrophile and the activated unsaturated substrate, in which case it is called electrophilic addition, or may result in

an abstraction of a part or the whole of the activated ligand, in which case it is called the electrophilic abstraction.

Electrophilic Addition

An example of an electrophile being added to an activated ligand is shown in Figure 14.2.5.3. The allylic anion ligand uses its π electrons to react with hydrogen ion. This adds a hydrogen to the ligand, converting it from an anionic X-type ligand to a neutral L-type ligand .

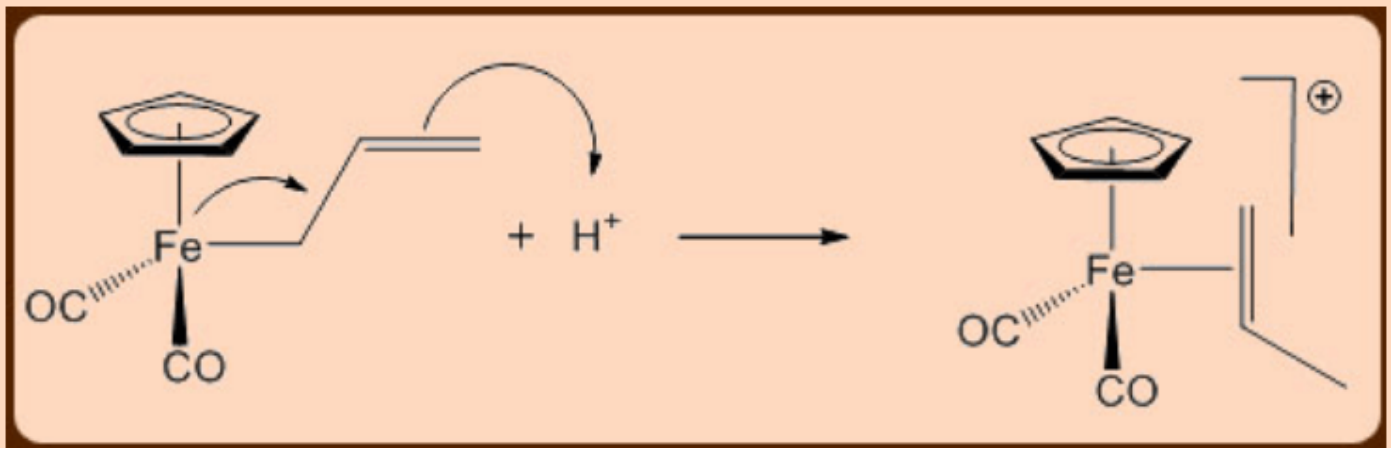


Figure 14.2.5.3: An example of electrophilic addition to an activated ligand.

Electrophilic Abstraction

Depending on whether the abstraction occurs at the α or β position with respect to the metal ion, the reaction is either classified as an α-abstraction or a β-abstraction.

An example of an α electrophilic abstraction reaction is shown in Figure 14.2.5.4.

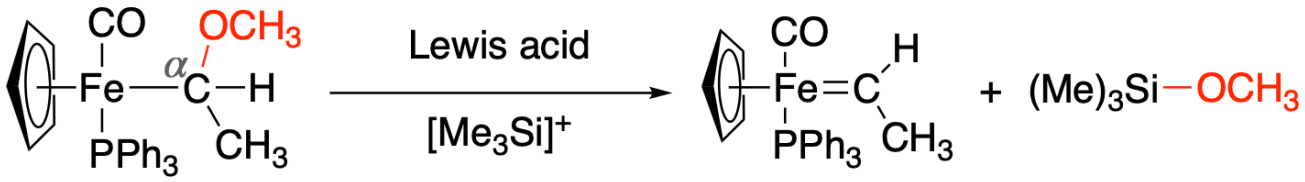


Figure 14.2.5.4: An example of an electrophilic α-abstraction. (CC-BY-SA; Kathryn Haas)

Two examples of a β electrophilic abstraction are shown in Figure 14.2.5.5.

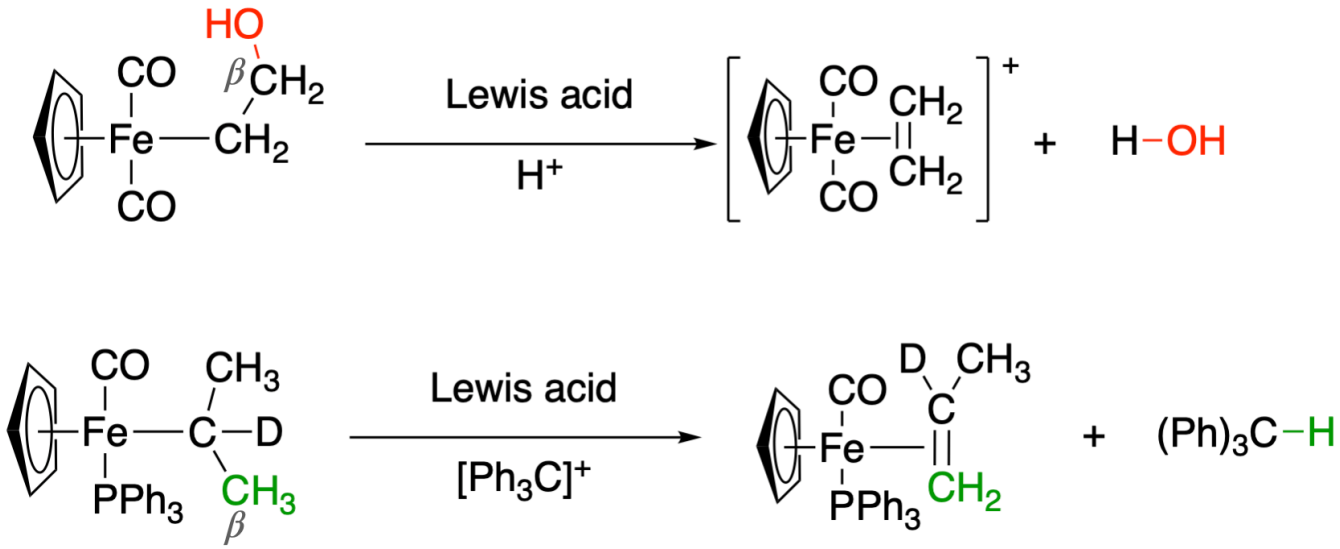


Figure 14.2.5.5: Two examples of electrophilic β-abstraction. (CC-BY-SA; Kathryn Haas)

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14.3: ORGANOMETALLIC CATALYSTS

One of the most important uses of organometalic complexes is in the catalysis of chemical reactions. In this section, we will apply knowledge of reaction types and the skill of electron counting to understand organometalic catalytic cycles.

14.3.1: Catalytic Deuteration

14.3.2: Hydroformylation

14.3.3: Monsanto Acetic Acid Process

14.3.4: Wacker (Smidt) Process

14.3.5: Hydrogenation by Wilkinson's Catalyst

14.3.6: Olefin Metathesis

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14.3.1: Catalytic Deuteration

Catalytic Deuteration of Benzene

Combinations of oxidative additions and reductive eliminations have many applications in the synthesis of organic molecules using an organometallic reactant.

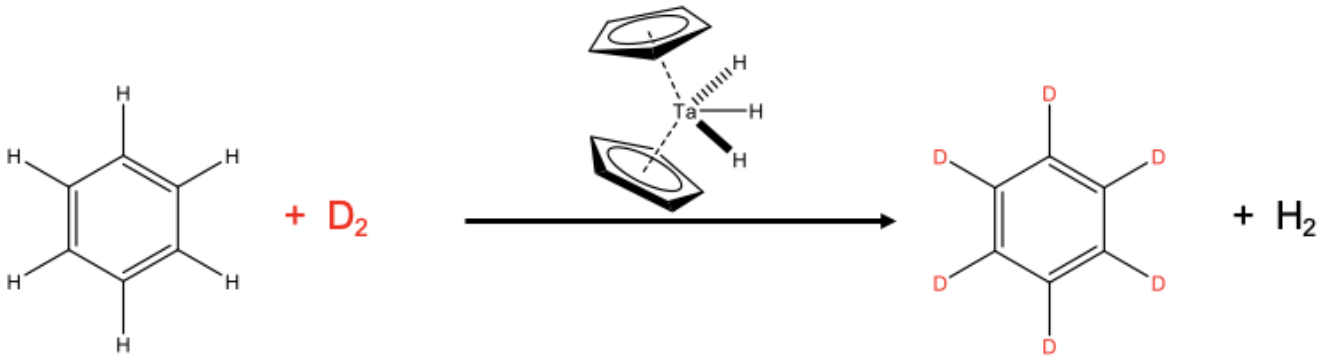


Figure 14.3.1.1 Deuteration of benzene

An example is the deuteration of benzene (Fig. 14.3.1.1). Deuterated benzene is an important solvent in NMR spectroscopy. Industrially, the deuteration is done using a dicyclopentadienyltrihydridotantalum(V) catalyst starting out from benzene and D_2. The D_2 is provided in excess to drive the chemical equilibrium to the right side.

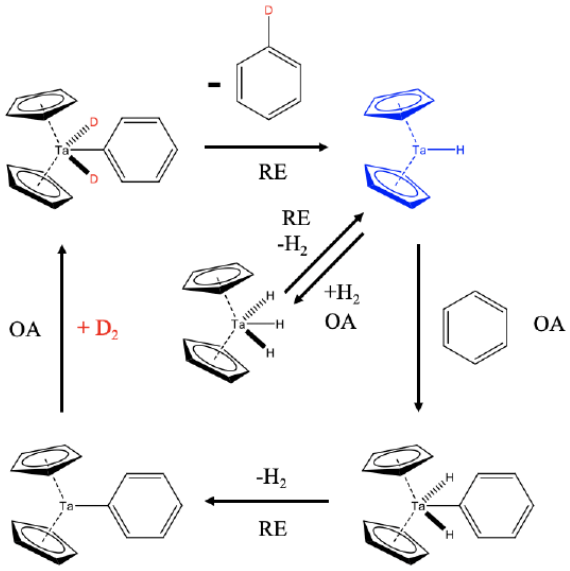


Figure 14.3.1.2 Mechanism of the catalytic deuteration of benzene

How does this reaction work mechanistically? This 18e Cp_2TaH_3 is actually a precatalyst that is in chemical equilibrium with H_2 and the 16e dicyclopentadienylhydrido tantalum(III) which is the actual catalyst (Fig. 14.3.1.2). Elimination of H_2 from the Ta(V) catalyst is a reductive elimination (RE) and the re-addition of H_2 to the Ta(III) species an oxidative addition (OA). In the presence of benzene, the Ta(III) species can oxidatively add benzene to form an 18e Ta(V) complex. This complex can reductively eliminate H_2 to form a 16e Cp_2Ta(III)-Ph complex. In the presence of deuterium this complex can add D_2 oxidatively to form an 18e Cp_2D_2Ta(V)-Ph complex. This species can then reductively eliminate a monodeuterated benzene molecule under formation

of $Cp_2Ta(III)$-D. In the presence of enough D_2 this monodeuterated benzene can be further deuterated in subsequent catalytic cycles.

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14.3.2: Hydroformylation

Catalytic Olefin Hydroformylation

An important industrial reaction is the catalytic hydroformylation reaction, also known as oxo-process (Figure 14.3.2.1). It was discovered in 1938 by Otto Roelen at BASF. In the hydroformylation reaction an H atom and a formyl group are added to an alkene to form aldehydes. The reaction can produce both branched an linear aldehydes from terminal alkenes, CO, and H_2 using a carbonyl hydrides such as $HCo(CO)_4$ as a catalyst. The reaction is performed at about 100°C at a pressure of up to 100 atm.

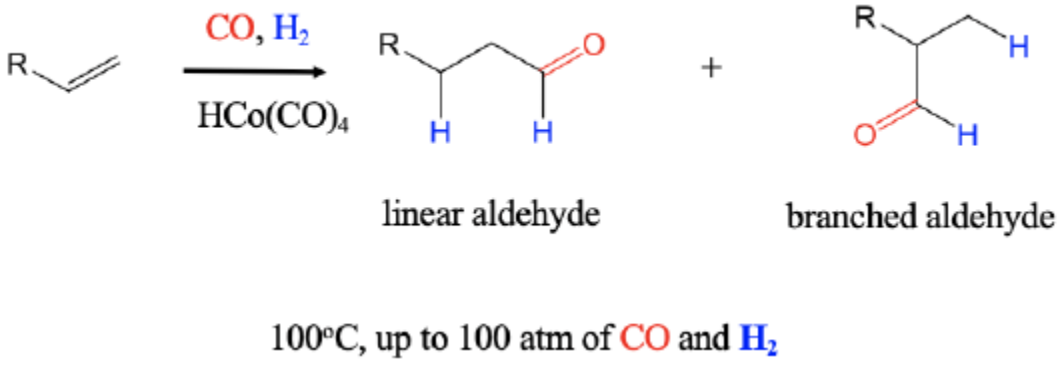


Figure 14.3.2.1: Catalytic olefin hydroformylation

Mechanism of the Catalytic Olefin Hydroformylation by $HCo(CO)_4$

How does the hydroformylation work mechanistically?

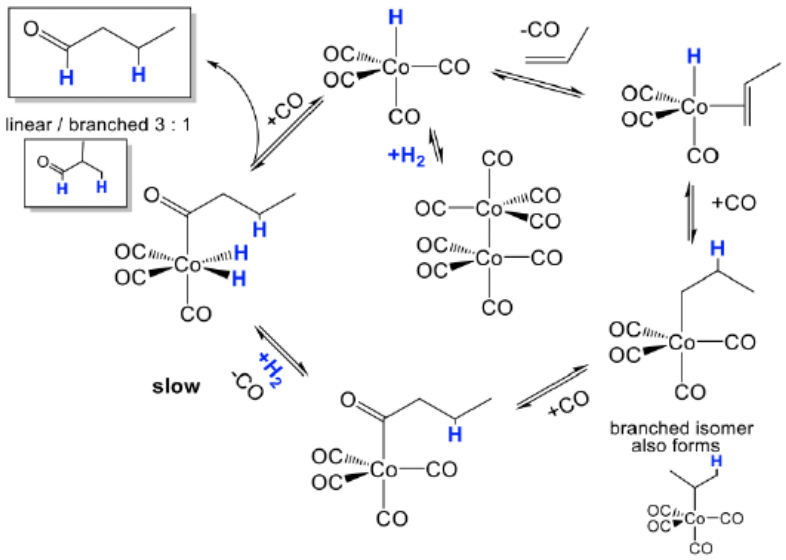


Figure 14.3.2.2: Mechanism of the catalytic olefin hydroformylation by $HCo(CO)_4$ (Attribution: A. Vedernikov, U Maryland (modified).)

The mechanism is illustrated for the hydroformylation of propene (Fig. 14.3.2.2:). The actual catalyst $HCo(CO)_4$ is first formed from its precatalyst $Co_2(CO)_8$ in the presence of H_2 in a dinuclear oxidative addition reaction. The catalyst can undergo a substitution reaction in which a CO ligand is replaced by the olefin that binds side-on to the cobalt. This species can then undergo a migratory olefin insertion reaction. This leads to a mixture of linear and branched alkyl groups attached to the Co. A new CO ligand can add to the vacant site. The alkyl group can then insert into a carbonyl group in another migratory insert step, and the vacant site can

be reoccupied by a new CO molecule. Then, H_2 is added in an oxidative addition. This is the slowest and rate-limiting step in the catalytic cycle. From the addition product the aldehyde can then be eliminated in a reductive elimination reaction. Addition of CO regenerates the catalyst, and the catalytic cycle can begin again.

Hydrocarbonylations

After the hydroformylation, a number of other hydrocarbonylations were developed, and industrially deployed.

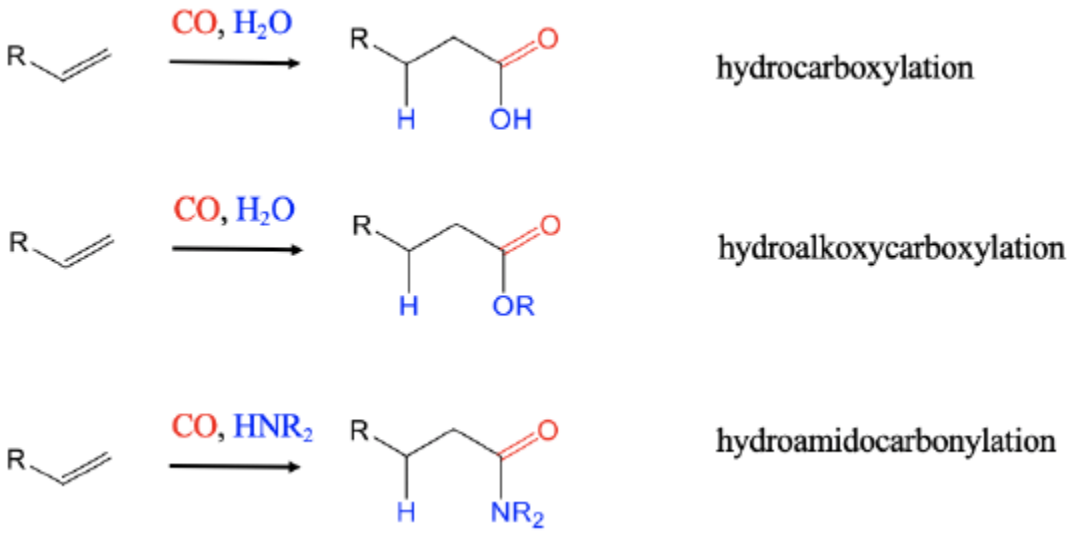


Figure 14.3.2.3: Hydrocarbonylation reactions

When hydrogen is replaced by H_2O hydrocarboxylations of alkenes lead to carboxylic acids (Fig. 14.3.2.3:). With an alcohol instead of H_2 hydroalkoxycarbonylcations lead to esters. The employment of amines instead of H_2 leads to amides in hydroamidocarbonylation reactions.

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14.3.3: Monsanto Acetic Acid Process

The Monsanto Acetic Acid Process

Another carbonylation reaction involving an organometallic catalyst is the Monsanto acetic acid process (Figure 14.3.3.1). It has been introduced by Monsanto in the 1970s for the industrial production of acetic acid from methanol. The reaction involves dual catalysis with HI and $[RhI_2(CO)_2]^-$ as a co-catalysts. How does this reaction work?

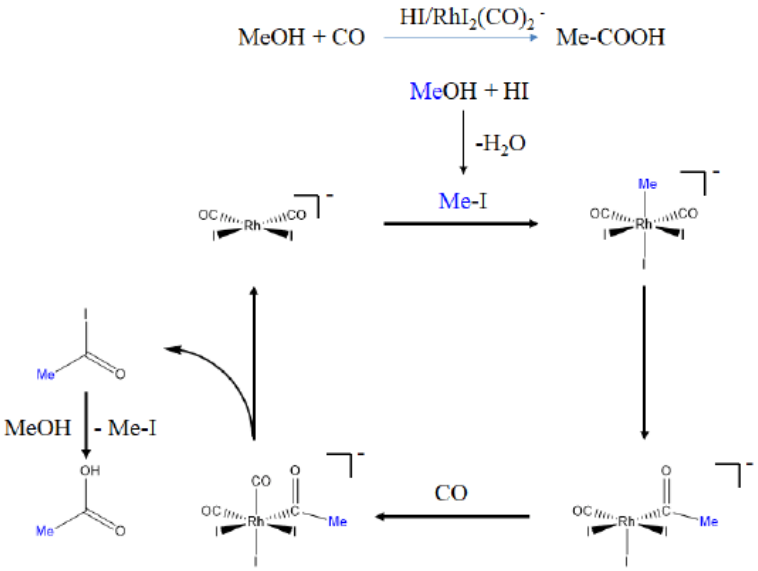


Figure 14.3.3.1: The catalytic cycle in the Monsanto acetic acid process

In the first step methanol reacts with HI to form methyl iodide. The methyl iodide then reacts with the Rh-catalyst in an oxidative addition reaction in which a methyl and an iodo group are added in trans-fashion to the square-planar Rh-complex to give an octahedral complex. The octahedral complex then undergoes a migratory insertion reaction with CO producing an acyl group and a vacant site. A CO molecule can then add to the vacant site. The acetyl iodide can then be eliminated in a reductive elimination to reform the Rh-catalyst thereby closing the catalytic cycle. The acetyl iodide can then react with methanol to form new methyl iodide and acetic acid. The methyl iodide can start a new catalytic cycle with the Rh-catalyst.

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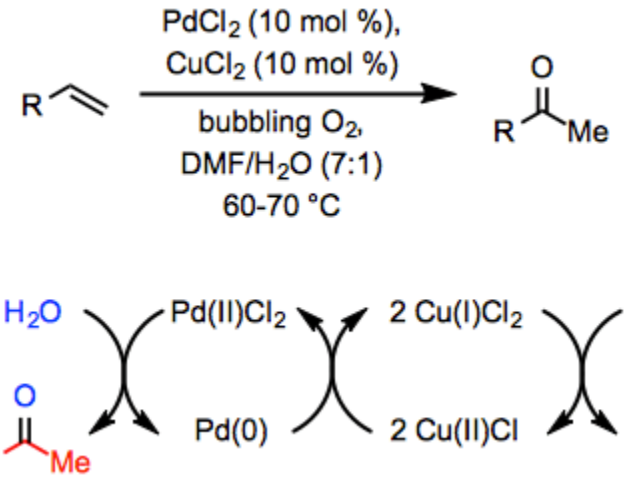
14.3.4: Wacker (Smidt) Process

See also Wacker Oxidation (Wikipedia)

The **Wacker oxidation** refers generally to the transformation of a terminal or 1,2-disubstituted alkene to a ketone through the action of catalytic palladium(II), water, and a co-oxidant. Variants of the reaction yield aldehydes, allylic/vinylic ethers, and allylic/vinylic amines. Because of the ease with which terminal alkenes may be prepared and the versatility of the methyl ketone group installed by the reaction, the Wacker oxidation has been employed extensively in organic synthesis.[1]

Introduction

The stoichiometric conversion of ethylene to acetaldehyde by an acidic, aqueous solution of $PdCl_2$ was discovered over a century ago,[2] but fifty years passed between the discovery of this reaction and the development of a catalytic method. In 1959, researchers at Wacker Chemie reported that a similar transformation takes place in an aqueous, acidic solution of catalytic $PdCl_2$ and a stoichiometric amount of $CuCl_2$ through which oxygen is bubbled (Equ. 14.3.4.1).[3]



Equation 14.3.4.1

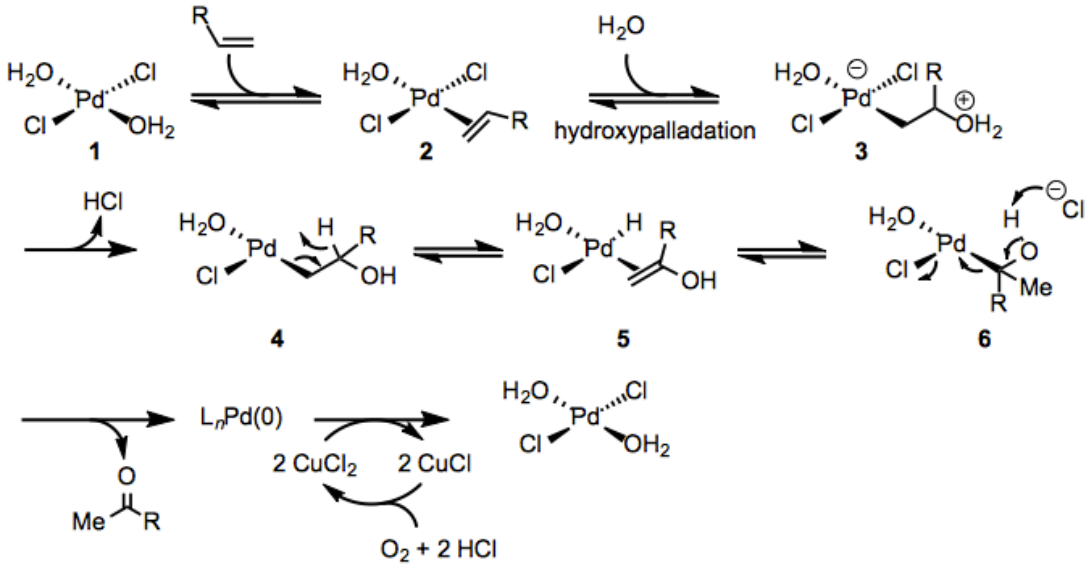
Since this initial report, the Wacker process has been widely applied in organic synthesis and has been extended to other classes of substrates and products. To encourage mixing of the organic reactants with the aqueous phase, a co-solvent is generally employed along with water. Dimethylformamide (DMF) is a common choice; when DMF is used as a co-solvent with a stoichiometric amount of CuCl under balloon pressure of oxygen, the reaction is called the "Tsuji-Wacker oxidation."[4] Applications of the Wacker oxidation to organic synthesis typically involve the installation of a methyl ketone moiety, which may subsequently undergo nucleophilic addition or deprotonation to form an enolate.

Mechanism and Stereochemistry

Prevailing Mechanism: Water Nucleophile

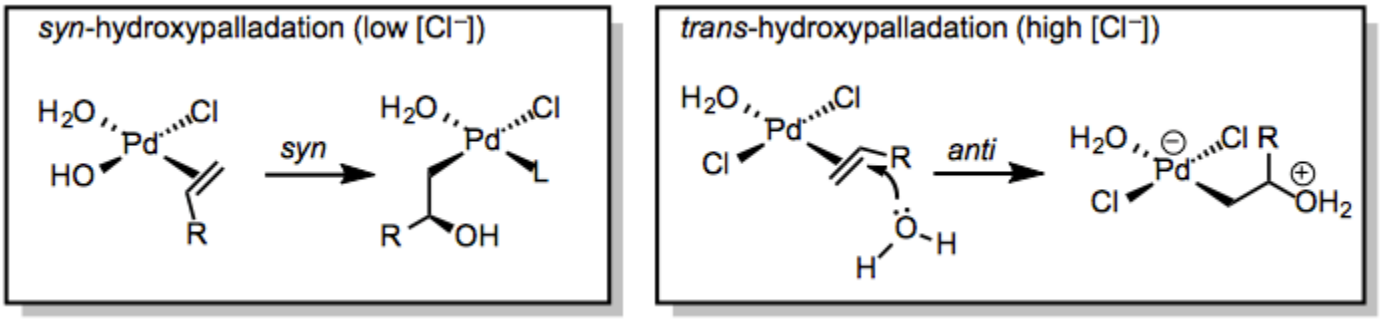
The mechanism of the Wacker oxidation has been studied both experimentally and theoretically (Eq. 2). The first step of the Wacker oxidation involves coordination of the the alkene to the palladium center to form π-complex **2**. Evidence for this step is provided by the relative sluggishness of electron-poor alkenes, which generally require higher catalyst loadings than unactivated alkenes. Hydroxypalladation then occurs to yield either zwitterionic complex **3** or neutral complex **4** depending on the mode of hydroxypalladation (see below). Studies employing deuterated substrates suggest that β-hydride elimination then occurs to afford enol complex **5**, which re-inserts into the Pd-H bond to afford complex **6**.[5] Computational studies support the involvement of chloride-assisted deprotonation in the subsequent step,[6] which affords the product and palladium(0). Oxidation of palladium(0)

by copper(II) then occurs, regenerating palladium(II) species **1**. The role of copper(II) in the mechanism is poorly understood at present.



Equation 14.3.4.2

The mode of hydroxypalladation is an important issue for the Wacker oxidation. Hydroxypalladation may occur either in a *syn* fashion through an inner-sphere mechanism or in an *anti* fashion via nucleophilic attack on the coordinated ***(2)*** alkene (Eq. 3). Although the stereocenter in **4** is ultimately destroyed upon elimination, the mode of hydroxypalladation can influence the site selectivity of the reaction. Markovnikov-type addition of water to the more substituted carbon of the alkene forms a methyl ketone, while attack of water at the less substituted position ultimately yields an aldehyde. The mode of hydroxypalladation has been shown to affect the distribution of ketone and aldehyde products, and is also important in stereoselective Wacker cyclization reactions.

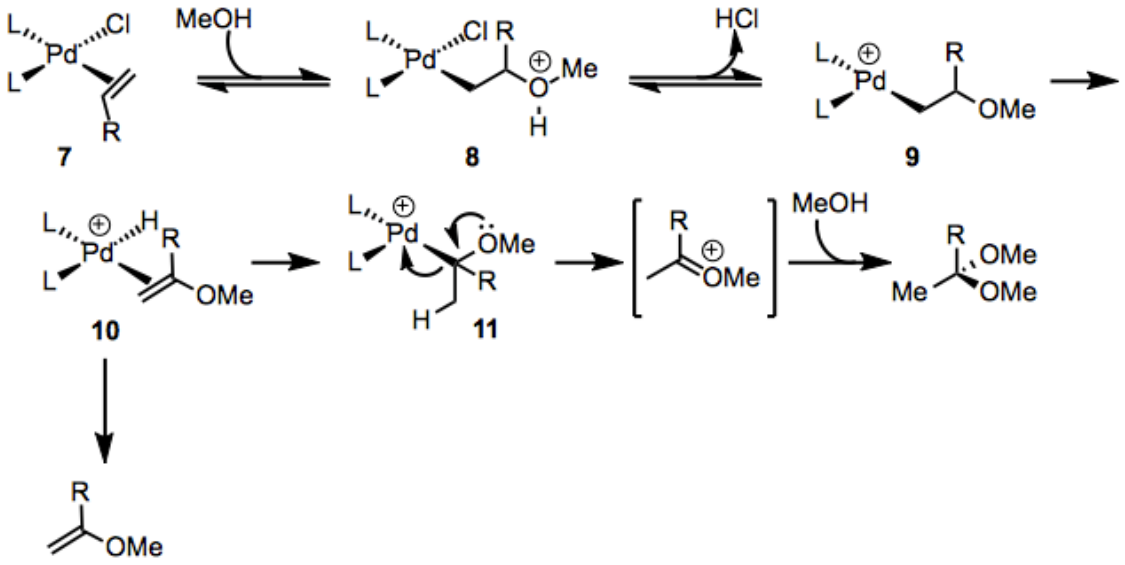


Equation 14.3.4.3

At low concentrations of chloride ion, *syn*-hydroxypalladation appears to be the norm.[7] Water coordinates to the metal and migratory insertion into the Pd-OH bond occurs to generate **4** directly. At high concentrations of chloride ***(3)*** ion, chloride competes with hydroxide for binding at palladium, and thus *anti*-hydroxypalladation may occur.[8]

Prevailing Mechanism: Alcohol Nucleophiles

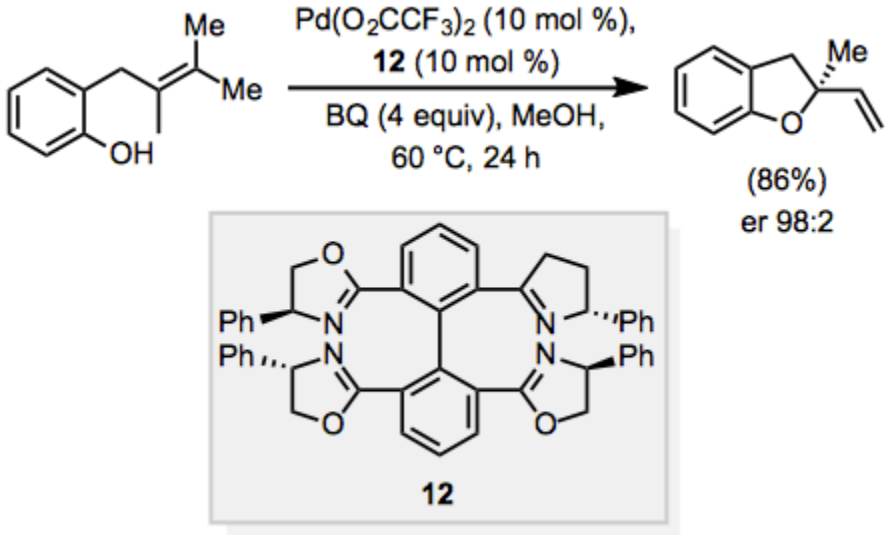
Alcohols may also be employed as nucleophiles in the Wacker process. The initial steps of the mechanism are similar to those for the Wacker oxidation with water, but the mechanisms diverge at alkoxy complex **11** (Eq. 4). Elimination of palladium occurs to generate an oxocarbenium ion, which may be captured by solvent to generate an acetal. Small amounts of vinyl ether products support the intermediacy of complex **10**.[9]



Equation 14.3.4.4

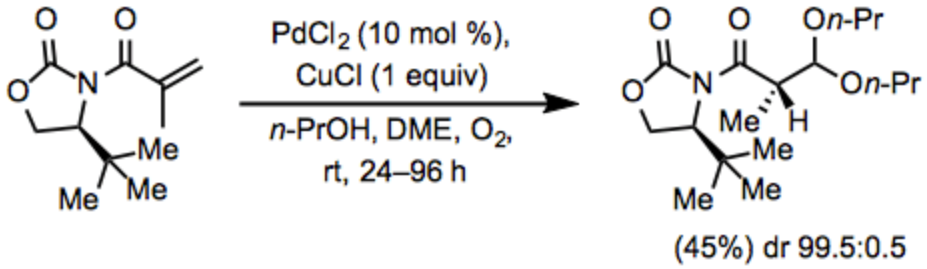
Enantioselective Variants

When the substrate contains a tethered nucleophile, such as a hydroxyl group or protected amine, the nucleophile may react to form a cyclic, allylic or vinylic ether or amine after β-hydride elimination. This process is known as the "Wacker cyclization," and when the product is allylic, a stereocenter may be established. Chiral ligands have been used to render the Wacker cyclization enantioselective. For example, use of tetra(dihydrooxazoline) ligand **12** and benzoquinone (BQ) as a co-oxidant resulted in formation of allylic ether product in an enantiomeric ratio of 98:2 (Eq. 5). [10]



Equation

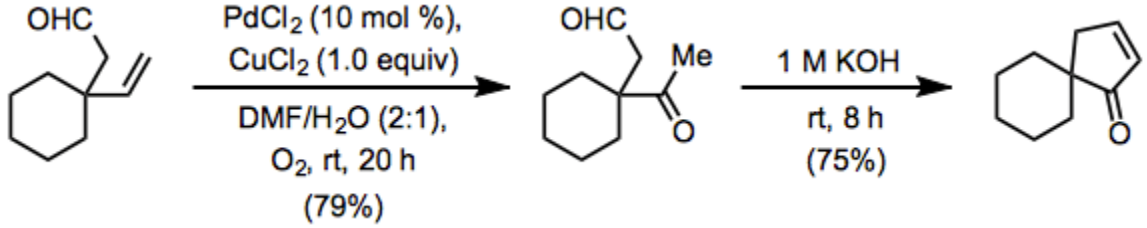
The Wacker process may also establish a stereocenter in 1,1-disubstituted alkenes via acetal formation. A chiral auxiliary in the alkene has been used successfully to generate chiral acetals with high diastereomeric ratio. The acetal forms at the more electron-deficient site of the alkene (Eq. 6).[11]



Equation 14.3.4.6

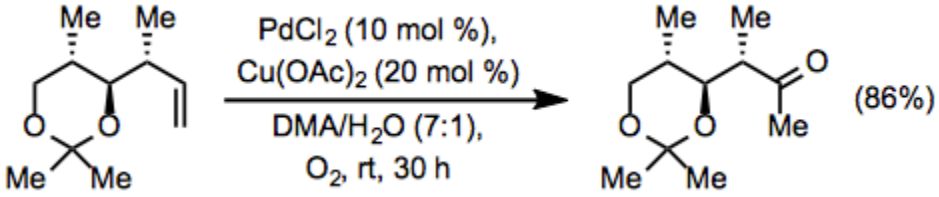
Scope and Limitations

Terminal alkenes are the most commonly employed substrates for the Wacker oxidation. Oxygen-containing functionality far from the reactive alkene is well tolerated by the reaction because palladium reacts selectively with the alkene in preference to lone pairs on oxygen. Wacker oxidation followed by intramolecular aldol condensation is a convenient method for the rapid synthesis of carbocycles (Eq. 7).[12]



Equation 14.3.4.7

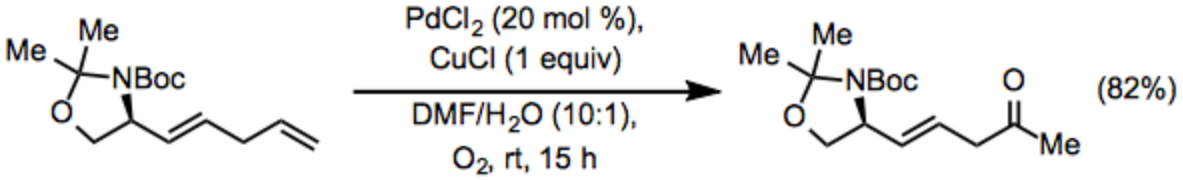
The original Wacker process and Tsuji-Wacker conditions can present problems for substrates containing acid-sensitive functionality, such as acetals and silyl ethers. Use of copper(II) chloride leads to the generation of strongly acidic hydrochloric acid. To mitigate this issue, a method employing copper(II) acetate has been developed. Some acid-sensitive groups are able to withstand the milder acetic acid generated by this method (Eq. 8).[13] Under similar conditions involving copper(I) chloride, a yield of only 56% was obtained.



Equation 14.3.4.8

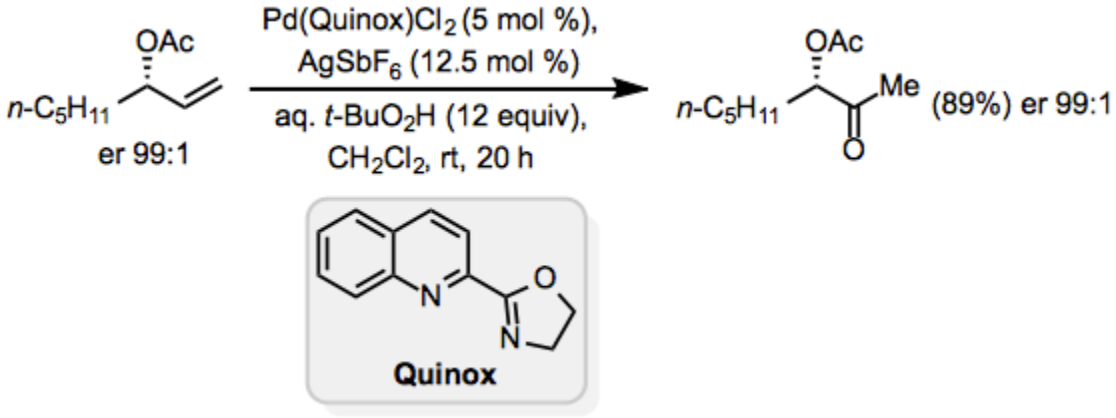
Unprotected amines coordinate strongly to palladium and thus cause problems for Wacker oxidations. Amines protected with electron-withdrawing substituents often do not interfere in Wacker oxidations,[14] although they may participate in aza-Wacker cyclizations if appropriately positioned in the substrate (see below).

Tri-substituted alkenes are completely inert to the conditions of the Wacker oxidation; only terminal and 1,1-disubstituted alkenes react. Terminal alkenes are usually oxidized selectively over internal alkenes, except under rather specialized circumstances.[15] Eq. 9 represents a typical case of selectivity for terminal alkenes.[14]



Equation 14.3.4.9

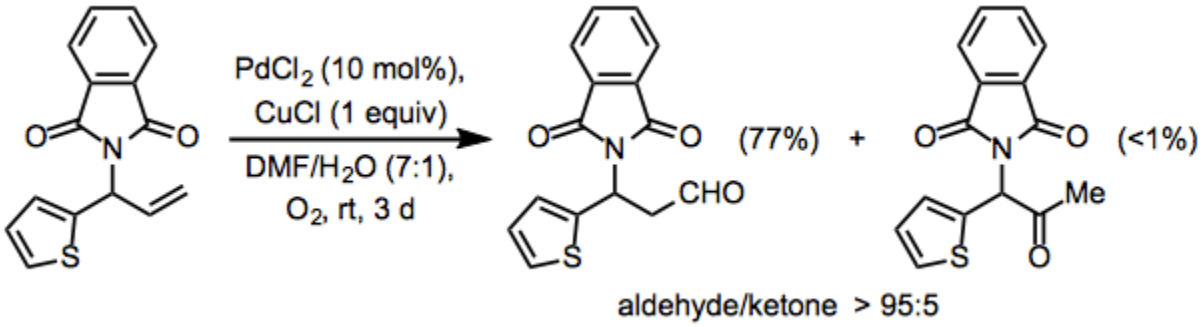
Lewis-basic functionality in the allylic or homoallylic position relative to the reactive alkene may cause unpredictable site selectivity in Wacker oxidations. Under standard Tsuji-Wacker conditions, unprotected allylic alcohols form mixtures of methyl ketone and aldehyde products.[16] The catalyst Pd(Quinox)Cl_2 was developed to address this problem; allylic alcohols react selectively in the presence of this catalyst to afford methyl ketones (Eq. 10).[17] *tert*-Butyl hydroperoxide (TBHP) is used as the oxygen source in this reaction.



Equation

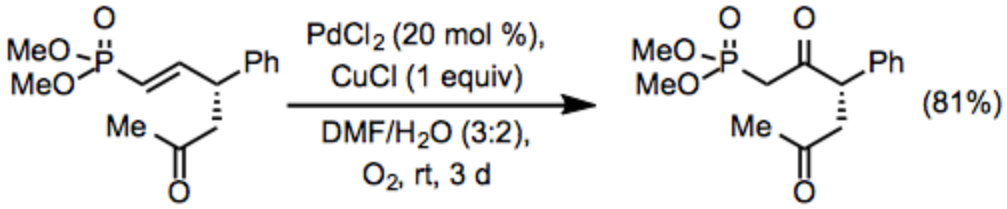
Protected, homoallylic alcohols generally form the methyl ketone selectively, but results are more unpredictable for unprotected homoallylic alcohols.[18]

Protected allylic amines generally give higher yields of aldehyde than comparable protected allylic alcohols; these results suggest that coordination of palladium to the Lewis base is responsible for the formation of aldehydes. Using a phthalimide group in the allylic position, the Wacker oxidation may be rendered completely selective for aldehydes (Eq. 11).[19]



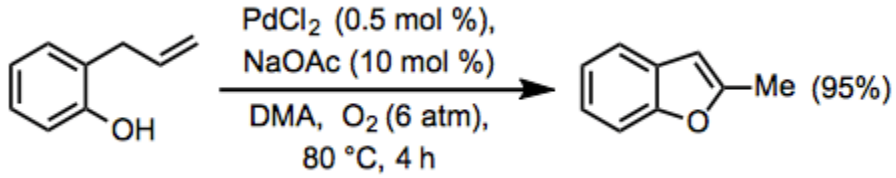
Equation

Site selectivity in reactions of internal alkenes is low unless an allylic or homoallylic Lewis base is present in the substrate. Electron-withdrawing groups can direct oxidation to the β position of the alkene (Eq. 12), but relatively high catalyst loadings are required.[20]



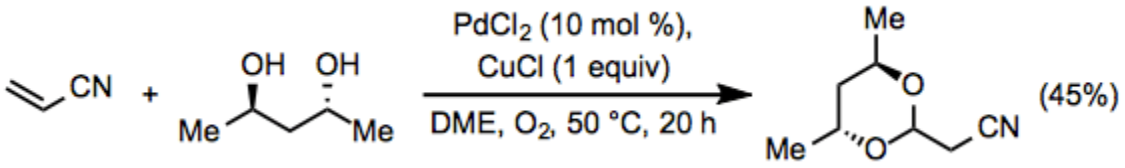
Equation

When an appropriately situated nucleophile is present in the substrate, Wacker cyclization may occur to yield an allylic or vinylic ether (Eq. 13).[21] The aza-Wacker cyclization involves protected amino nucleophiles such as sulfonamides.[22]



Equation

When an alcohol is used in stoichiometric or solvent quantities or a diol is present in the substrate, acetal formation may occur. Acetal formation, like ketone formation, generally occurs with Markovnikov selectivity. For example, a Michael acceptor forms an acetal at the β position in the presence of (*R*,*R*)-2,4-pentanediol (Eq. 14).[23]

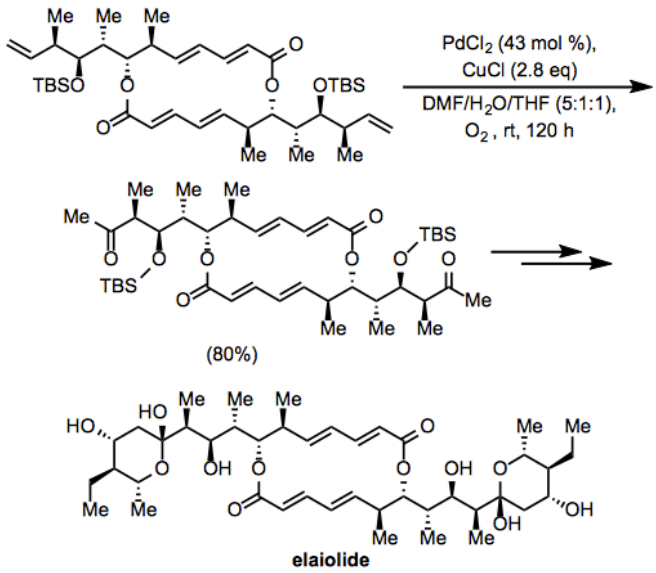


Equation

Synthetic Applications

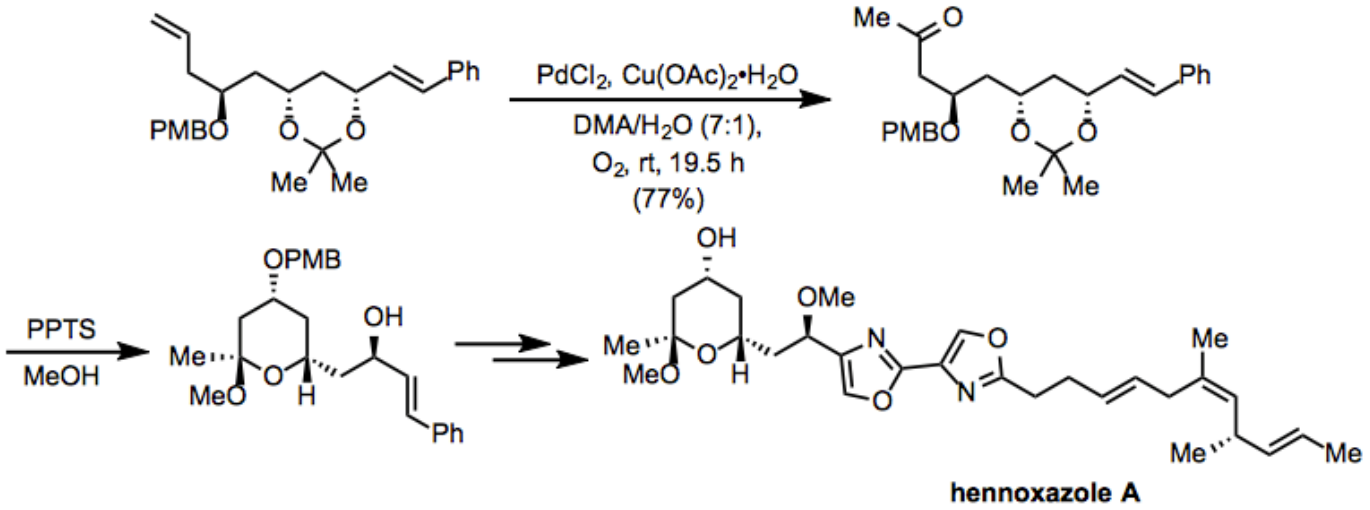
The Wacker oxidation has been used extensively in organic synthesis. A number of methods exist for the installation of terminal alkenes and the methyl ketone products of the reaction can be elaborated easily to more complex compounds. In addition, the reaction is aerobic and operationally simple.

The Wacker oxidation was employed in the course of synthesis of the macrolide elaiolide. Oxidation at two terminal alkenes in a C_2-symmetric intermediate afforded a diketone, which was subsequently elaborated to the symmetric natural product (Eq. 15).[24] Notably, the internal alkenes and esters in the intermediate appeared not to affect the oxidation.



Equation

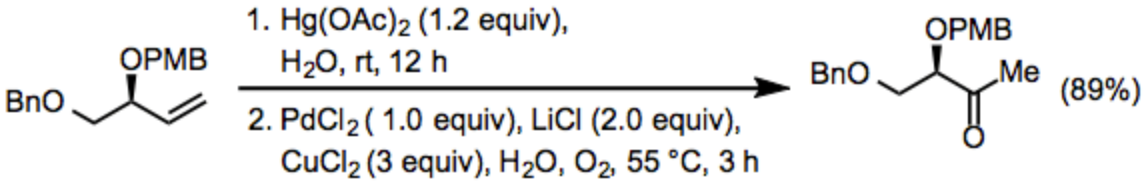
A modification of Tsuji-Wacker conditions employing copper(II) acetate was used in the course of a synthesis of hennoxazole A (Eq. 16).[25] After the oxidation, deprotection under acidic conditions led to the intramolecular formation of an acetal present in the target compound.



Equation

Comparison to Other Methods

Few true alternatives to the Wacker oxidation (that is, other hydration-oxidation reactions) are known. One rather harsh method involves oxymercuration followed by transmetalation to palladium (Eq. 17).[26]



Equation

Experimental Conditions and Procedure

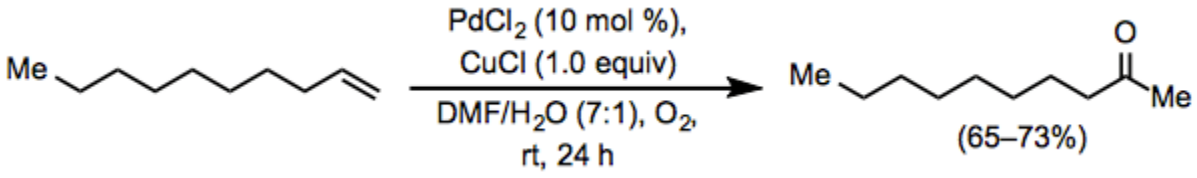
Typical Conditions

Tsuji-Wacker conditions represent a good starting point for experimental conditions for this reaction. Water is mixed with an organic co-solvent (often DMF) and 10 mol% $PdCl_2$, stoichiometric CuCl, and 1 atmosphere of oxygen gas. Copper(I) salts are generally superior to copper(II) salts because the former minimize the concentration of chloride in solution, encouraging *syn*-hydroxypalladation. Copper(I) is rapidly oxidized to copper(II) by dissolved oxygen; a period of 30 minutes prior to the introduction of the substrate is used to ensure that this oxidation is complete. For situations in which Tsuji-Wacker conditions fail, a wide variety of modifications of the reaction conditions may be employed.

Using high oxygen pressure and a judicious choice of solvent, Wacker oxidations can be carried out without the need for a co-oxidant. Certain ligands also promote direct O_2-coupled oxidations.[27]

Peroxides may also be used as the oxygen source in Wacker oxidations; these reactions do not require a co-oxidant. In the Pd(Quinox)/TBHP system, silver hexafluoroantimonate serves as a scavenger of chloride ions.

Experimental Procedure[4]



Equation

A 100-mL, 3-necked, round-bottomed flask was fitted with a magnetic stirring bar and a pressure-equalizing dropping funnel containing 1-decene (4.2 g, 30 mmol, 1.0 equiv). The flask was charged with a mixture of $PdCl_2$ (0.53 g, 3 mmol, 0.1 equiv), CuCl (2.97 g, 30 mmol, 1.0 equiv) and aqueous DMF (DMF/H_2O = 7:1, 24 mL). With the other outlets securely stoppered and wired down, an oxygen-filled balloon was placed over one neck, and the mixture was stirred at rt to allow oxygen uptake. After 1 h, the 1-decene (4.2 g, 30 mmol) was added over 10 min, and the solution was stirred vigorously at rt under an oxygen balloon. The color of the solution turned from green to black within 15 min and returned gradually to green. After 24 h, the mixture was poured into cold 3 N HCl (100 mL) and extracted with five, 50 mL portions of ether. The extracts were combined and washed successively with 50 mL of saturated aqueous $NaHCO_3$ solution, 50 mL of brine, and then dried over anhydrous magnesium sulfate. The solvent was removed by evaporation and the residue was distilled using a 15 cm Vigreux column to give 2-decanone as a colorless oil (3.0–3.4 g, 65–73%): bp 43.5 °C (1 mm Hg); IR (neat) 1722 cm^{-1}; ^1H NMR (CCl_4) δ 2.37 (t, J = 7 Hz, 2H), 2.02 (s, 3H), 0.7–1.8 (m, 15H).

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14.3.5: Hydrogenation by Wilkinson's Catalyst

Organometallic Compounds as Hydrogenation Catalysts

Migratory insertions play an important role in catalysis.

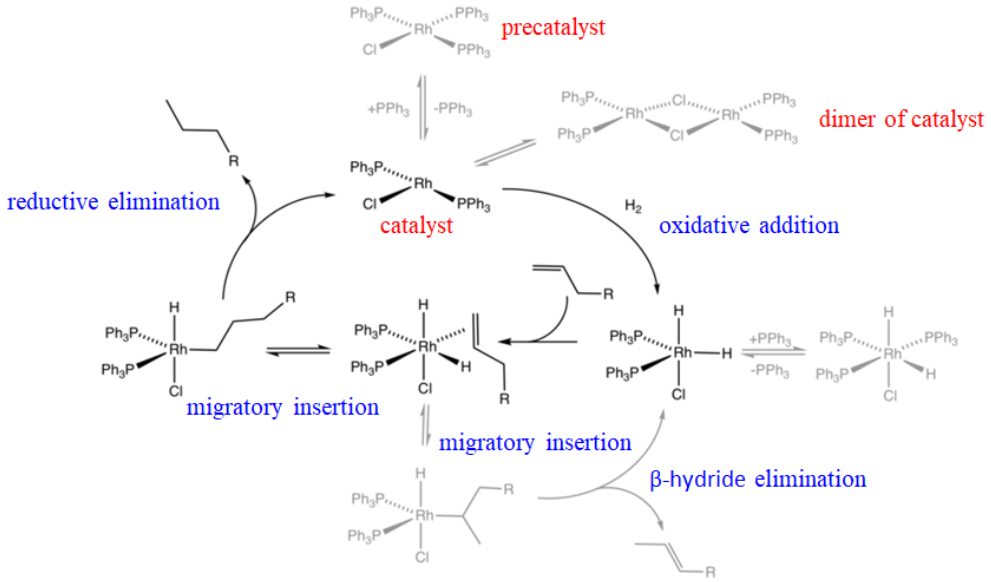


Figure 14.3.5.1: Mechanism of the Wilkinson hydrogenation catalyst (Attribution: Smokefoot / CC BY-SA (https://creativecommons.org/licenses/by-sa/4.0) https://commons.wikimedia.org/wiki/F...cleJMBrown.png)

For example a Rh-catalyst called the Wilkinson catalyst is an effective hydrogenation catalyst for olefins. The mechanism of the hydrogenation involves a combination of oxidative additions, olefin migratory insertions, and reductive eliminations (Fig. 14.3.5.1). Wilkinson's catalyst is the square planar chloro tris(triphenylphosphine) rhodium(I) complex. This molecule is actually a precatalyst that becomes the actual catalyst when it statistically loses a triphenylphosphine ligand producing chloro bis(triphenylphosphine) rhodium(I). The loss of this ligand is a reversible reaction, and thus the catalyst is in chemical equilibrium with the precatalyst. The actually catalyst is in a second chemical equilibrium with its dimer. The chloro bis(triphenylphosphine) rhodium(I) catalyst can undergo an oxidative addition in the presence of hydrogen to form a trigonal bipyramidal chlorodihydrido bis(triphenylphosphine) (III) rhodium complex. This species is in chemical equilibrium with an octahedral chlorodihydrido tris(triphenyl phosphine) rhodium(III) species that can form due to the presence of free triphenylphosphine ligands in the system. The trigonal bipyramidal species can then add an olefin that binds side-on to the Rh. Because the olefin is in cis-position to the hydride ligand it can undergo an olefin insertion. The Rh-C bond can either form with the first or the second carbon in the carbon chain of the olefin, giving a linear and a branched alkyl complex, respectively. The branched complex can undergo a β-hydride elimination thereby reforming the trigonal bipyramidal Rh-complex, and an olefin. This reaction is a side-reaction because the branched alkyl complex is sterically more crowded than the linear complex. The linear alkyl Rh complex can undergo a reductive elimination to form the linear alkane and the $RhCl(PPh_3)_2$ catalyst. This completes the catalytic cycle, and a new cycle can start.

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14.3.6: Olefin Metathesis

Olefin Metathesis

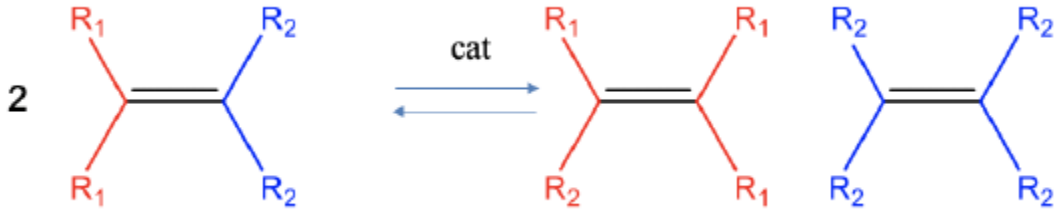


Figure 14.3.6.1: Olefin metathesis

Olefin metathesis is a reaction which allows to cut and rearrange C=C double bonds in olefins to make new olefins (Fig. 14.3.6.1). Formally, the carbon-carbon bond of the reactant is cleaved homoleptically and the two carbene fragments are combined in a different way. This reaction is typically an equilibrium reaction, and neither the reactants nor the products are clearly favored. This reaction is catalyzed by molybdenum arylamido carbene complexes or ruthenium carbene complexes.

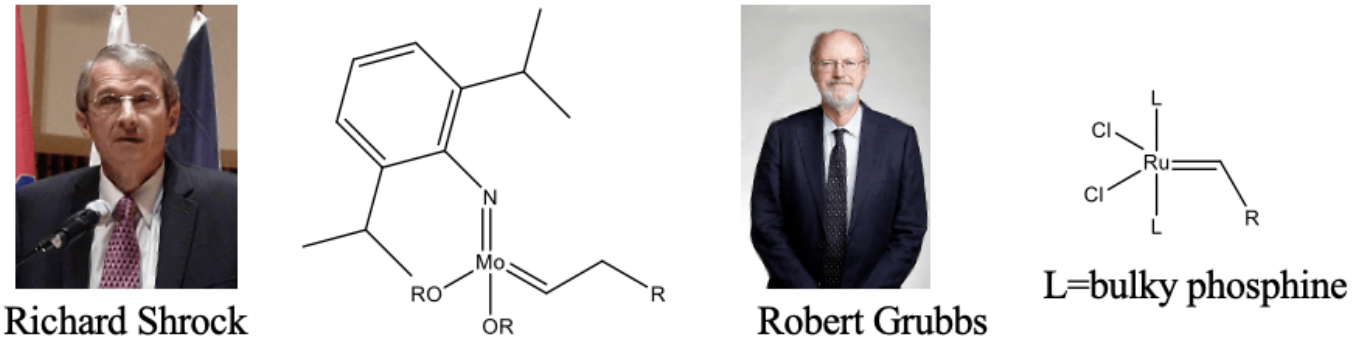


Figure 14.3.6.2: Shrock catalyst (Attribution: R._Schrock_-_IChO_2012_Opening_Ceremony.JPG: A.mela93derivative work: Materialscientist / CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0) https://commons.wikimedia.org/wiki/F...hrock_2012.jpg) and (Attribution: The Royal Society / CC BY-SA (https://creativecommons.org/licenses/by-sa/3.0) https://commons.wikimedia.org/wiki/F...al_Society.jpg)

The former are called Shrock catalysts, and the latter Grubbs catalysts named after their discoverers Richard Shrock and Robert Grubbs who received the Nobel prize for Chemistry in 2005 (Fig. 14.3.6.2). The Schrock catalysts are more active, but also very sensitive to air and water. The Grubbs catalysts, while less active, are less sensitive to air and water.

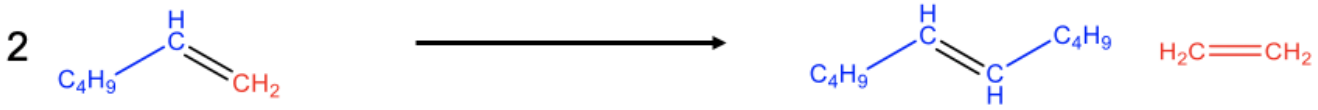


Figure 14.3.6.3: Regular metathesis

Olefin metathesis often allows for simpler preparation of olefins compared to other methods. Olefin metathesis is particularly powerful when one olefin product is gaseous because then it can be quite easily removed from the chemical equilibrium by purging. This drives the chemical equilibrium to the right side. An example is the preparation of 5-decene from 1-hexene. Cleavage of the C=C double bond in the hexene leads to C_5 and C_1 carbene fragments (Fig. 14.3.6.3). The two C_1 fragments can combine to form ethylene and the two C_5 fragments combine to 5-decene. The ethylene is volatile and can be purged from the reaction system thereby driving the chemical reaction to the right side.

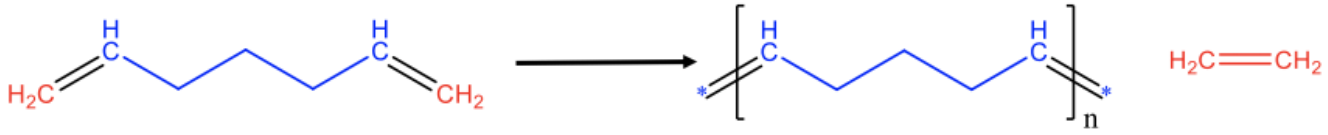


Figure 14.3.6.4: Acylic diene metathesis (ADMET)

The same principles can also be applied to produce polymers from dienes with two terminal C=C double bonds at the chain ends. This is called acylic diene metathesis (ADMET), Fig. 14.3.6.4. For instance the cleavage of the two terminal double bonds in a diene with seven C atoms leads to C_1 and C_5 fragments. The C_1 fragments can combine to form ethylene, and the C_5 fragments can combine to make an unsaturated polymer of the type $[CH(CH_2)_3CH]_n$. Again, the reaction can be driven to the right side by removing the gaseous ethylene from the reaction mixture through purging.

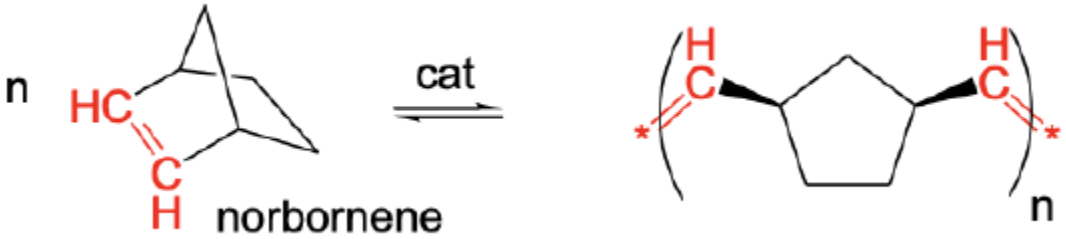


Figure 14.3.6.5: Ring-opening metathesis polymerization (ROMP)

Another variation of olefin metathesis is ring-opening metathesis polymerization (ROMP). It allows to make polymers from strained cycloolefins, for example norbornene. The reaction driving force is the relief of the strain. Because the strain is removed in the polymer, the chemical equilibrium lies far on the right side. The reaction product in norbornene is a polymer with 5-membered rings that are interconnected by ethylene -CH=CH- units (Fig. 14.3.6.5).

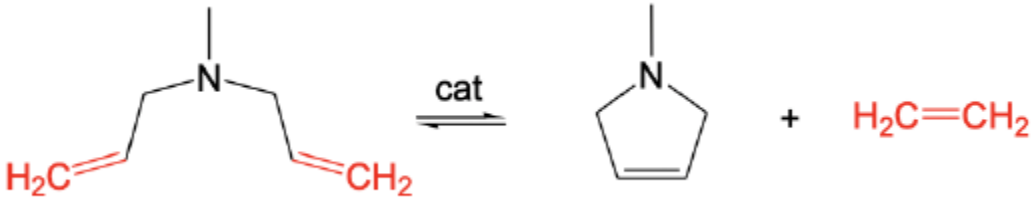


Figure 14.3.6.6: Ring-closing metathesis (RCM)

The opposite of ROMP is ring-closure metathesis (RCM). RCM allows for the preparation of unstrained rings with C=C double bonds from dienes with C=C double bonds that are five or six carbon atoms apart. This distance is suitable to produce unstrained rings. In the shown example a five-membered ring with a C=C double bond is formed from a diene with terminal C=C double bonds that are five atoms apart.

The Mechanism of Olefin Metathesis

What is the mechanism of olefin metathesis?

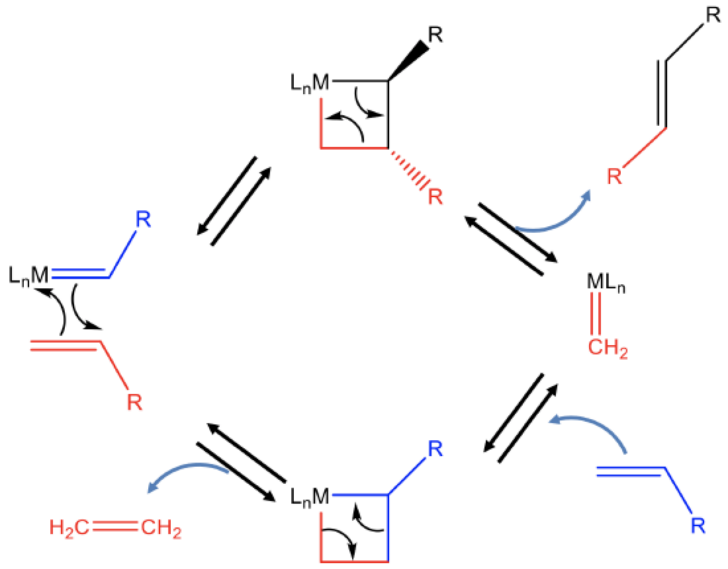


Figure 14.3.6.7: The mechanism of olefin metathesis

In the first step, the alkene adds to the the carbene fragment of the catalyst in a 2+2 cycloaddition reaction to produce an unstable intermediate with a highly strained four-membered ring (Fig. 14.3.6.7). This four membered ring can open to produce the first new alkene product R-CH=CH-R and a metal carbene species. This metal carbene can react with another reactant olefin to form another highly stained 4-ring intermediate via a 2+2 cycloaddition reaction. This ring can then reopen again to produce the second alkene metathesis product, in this case ethylene, and the original catalyst. The regenerated catalyst can then start a new catalytic cycle.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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14.4: Heterogeneous Catalysts

Heterogeneous Catalysis

In **heterogeneous catalysis**, the catalyst is in a different phase from the reactants. At least one of the reactants interacts with the solid surface in a physical process called adsorption in such a way that a chemical bond in the reactant becomes weak and then breaks. Poisons are substances that bind irreversibly to catalysts, preventing reactants from adsorbing and thus reducing or destroying the catalyst's efficiency.

An example of heterogeneous catalysis is the interaction of hydrogen gas with the surface of a metal, such as Ni, Pd, or Pt. As shown in part (a) in Figure 14.4.2, the hydrogen–hydrogen bonds break and produce individual adsorbed hydrogen atoms on the surface of the metal. Because the adsorbed atoms can move around on the surface, two hydrogen atoms can collide and form a molecule of hydrogen gas that can then leave the surface in the reverse process, called desorption. Adsorbed H atoms on a metal surface are substantially more reactive than a hydrogen molecule. Because the relatively strong H–H bond (dissociation energy = 432 kJ/mol) has already been broken, the energy barrier for most reactions of H_2 is substantially lower on the catalyst surface.

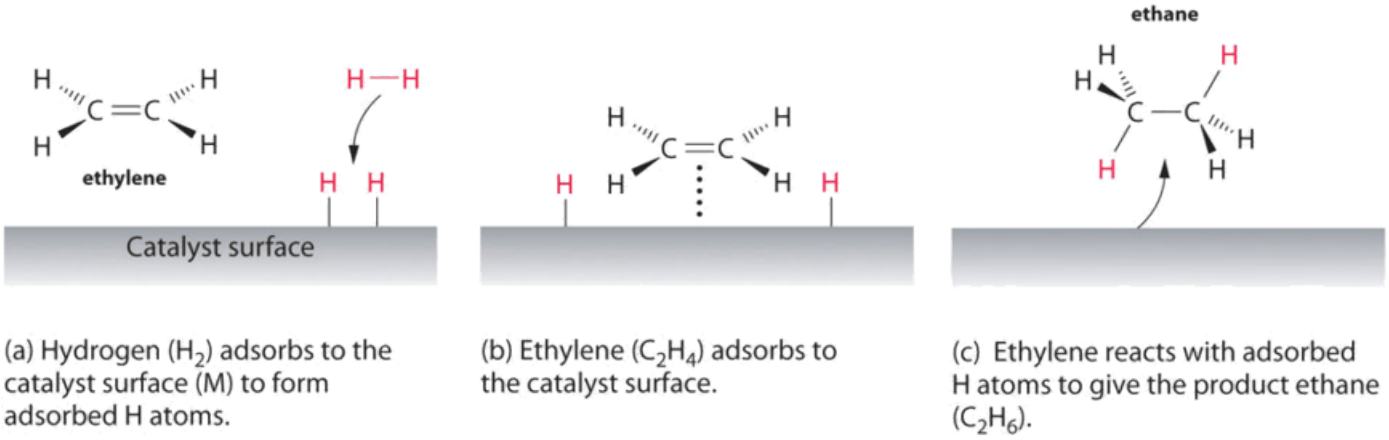


Figure 14.4.1: Hydrogenation of Ethylene on a Heterogeneous Catalyst. When a molecule of hydrogen adsorbs to the catalyst surface, the H–H bond breaks, and new M–H bonds are formed. The individual H atoms are more reactive than gaseous H_2. When a molecule of ethylene interacts with the catalyst surface, it reacts with the H atoms in a stepwise process to eventually produce ethane, which is released. (CC BY-NC-SA; anonymous)

Figure 14.4.1 shows a process called *hydrogenation*, in which hydrogen atoms are added to the double bond of an alkene, such as ethylene, to give a product that contains C–C single bonds, in this case ethane. Hydrogenation is used in the food industry to convert vegetable oils, which consist of long chains of alkenes, to more commercially valuable solid derivatives that contain alkyl chains. Hydrogenation of some of the double bonds in polyunsaturated vegetable oils, for example, produces margarine, a product with a melting point, texture, and other physical properties similar to those of butter.

Several important examples of industrial heterogeneous catalytic reactions are in Table 14.4.1. Although the mechanisms of these reactions are considerably more complex than the simple hydrogenation reaction described here, they all involve adsorption of the reactants onto a solid catalytic surface, chemical reaction of the adsorbed species (sometimes via a number of intermediate species), and finally desorption of the products from the surface.

Table 14.4.1: Some Commercially Important Reactions that Employ Heterogeneous Catalysts

Commercial Process	Catalyst	Initial Reaction	Final Commercial Product
contact process	V_2O_5 or Pt	$2SO_2 + O_2 \rightarrow 2SO_3$	H_2SO_4
Haber process	Fe, K_2O, Al_2O_3	$N_2 + 3H_2 \rightarrow 2NH_3$	NH_3
Ostwald process	Pt and Rh	$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$	HNO_3

Commercial Process	Catalyst	Initial Reaction	Final Commercial Product
water–gas shift reaction	Fe, Cr_2O_3, or Cu	$CO + H_2O \rightarrow CO_2 + H_2$	H_2 for NH_3, CH_3OH, and other fuels
steam reforming	Ni	$CH_4 + H_2O \rightarrow CO + 3H_2$	H_2
methanol synthesis	ZnO and Cr_2O_3	$CO + 2H_2 \rightarrow CH_3OH$	CH_3OH
Sohio process	bismuth phosphomolybdate	$CH_2{=}CHCH_3 + NH_3 + \frac{3}{2}O_2 \rightarrow CH_2{=}CHCN + 3H_2O$	$CH_2{=}CHCN$ acrylonitrile
catalytic hydrogenation	Ni, Pd, or Pt	RCH=CHR′ + H2 → RCH_2—CH_2R'	partially hydrogenated oils for margarine, and so forth

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14.4.1: Ziegler-Natta Polymerizations

Another example of an organometallic catalytic reaction is the Ziegler-Natta olefin polymerization. This reaction is of high industrial importance for the production of olefins like polyethylene. There are both heterogeneous and homogeneous Ziegler-Natta catalysts. The mechanism for the homogeneous catalysts is generally well understood. Homogeneous catalysts are typically metallocene catalysts.

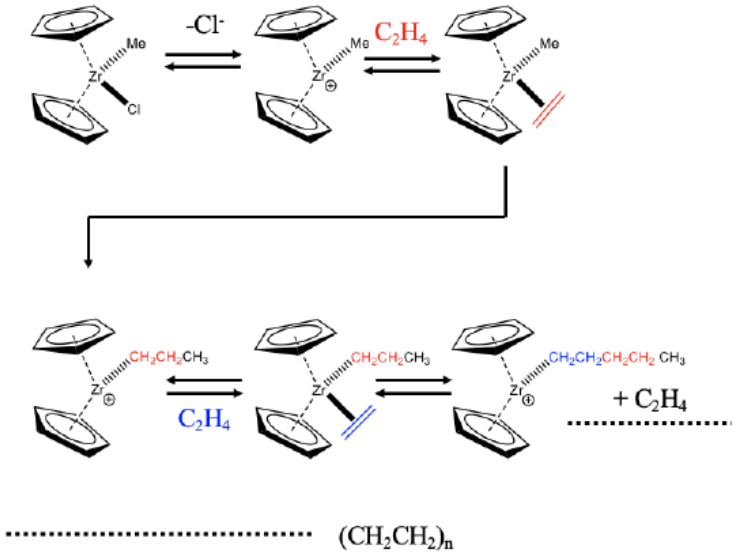


Figure 14.4.1.1: Zirconium-based Ziegler-Natta catalyst (Attribution: A. Vedernikov, U Maryland (modified).)

An example of a zirconium-based catalyst is shown (Fig. 14.4.1.1). The catalyst is a coordinatively unsaturated complex cation with two cyclopentadienyl rings and a methyl group. The catalyst is formed from its precatalyst, a neutral molecule with an additional chloro ligand. The catalyst oxidatively adds an olefin like an ethylene molecule to the coordinatively unsaturated site. This step is followed an olefin insertion step that produces a propyl group. The migratory insertion leads to the formation of a vacant site, that can be re-oocupied by another ethylene molecule. This molecule can insert into the propyl chain thereby prolonging the propyl chain to a pentyl chain. The olefin insertion step generates another vacant site that can be reoccupied by a new ethylene molecule. Repeating the catalytic cycle many times eventually leads to polyethylene.

The Ziegler-Natta (ZN) catalyst, named after two chemists: Karl Ziegler and Giulio Natta, is a powerful tool to polymerize α-olefins with high linearity and stereoselectivity (Figure 1). A typical ZN catalyst system usually contains two parts: a transition metal (Group IV metals, like Ti, Zr, Hf) compound and an organoaluminum compound (co-catalyst). The common examples of ZN catalyst systems include $TiCl_4$ + Et_3Al and $TiCl_3$ + $AlEt_2Cl$.

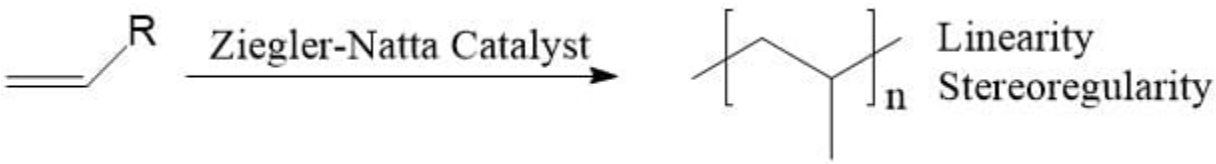


Figure 14.4.1.2: The generic reaction equation for polymerization of -olefins.

In 1953, German chemist Karl Ziegler discovered a catalytic system able to polymerize ethylene into linear, high molecular weight polyethylene which conventional polymerization techniques could not make.[1] The system contained a transition metal halide with a main group element alkyl compound (Figure 14.4.1.3).

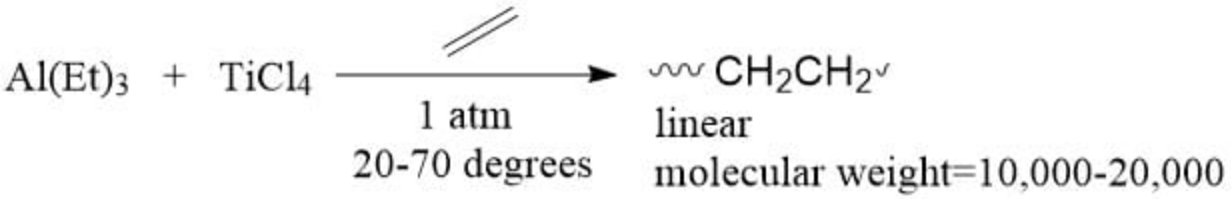


Figure 14.4.1.3: Linear polyethylene obtained by Ziegler's catalytic system (20-70).

Following the catalytic design, Italian chemist Giulio Natta found that polymerization of α-olefins resulted in stereoregular structures,[2] either syndiotactic or isotactic, depending on the catalyst used (Figure 14.4.1.4). Because of these important discoveries, Karl Ziegler and Giulio Natta shared the Nobel Prize in Chemistry in 1963.

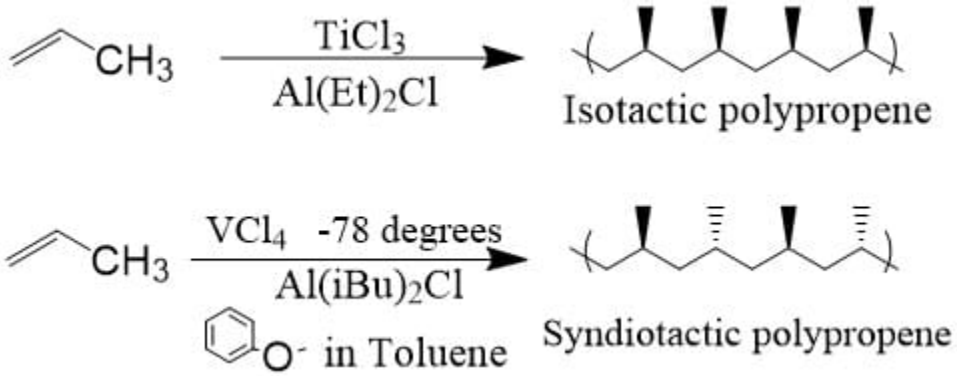


Figure 14.4.1.4: The ZN catalytic polymerization of linear polypropene with two different stereoregular structures.

Advantages over traditional polymerization method

Traditionally, polymerization of α-olefins was done by radical polymerization (Figure 14.4.1.5). Problem with this technique was that the formation of undesired allylic radicals leaded to branched polymers.[3] For example, radical polymerization of propene gived branched polymers with large molecular weight distribution. Also, radical polymerization had no control over stereochemistry. Linear unbranched polyethylene and stereoregulated polypropylene could not be fabricated by free radical polymerization. This technique largely limited the potential applications of these polymeric materials.

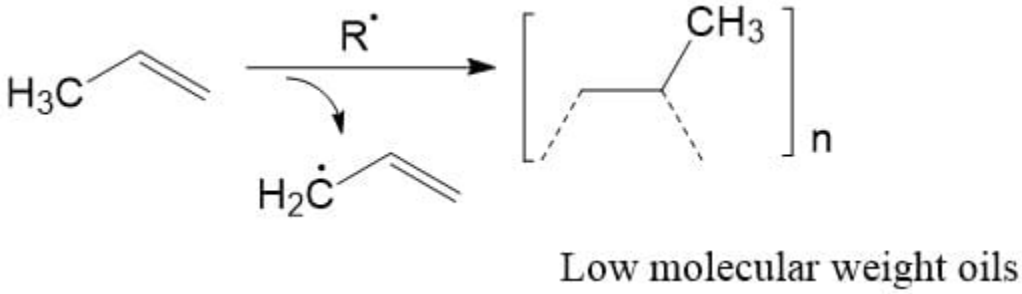


Figure 14.4.1.5: The radical polymerization of propylene using traditional method.

The invention of ZN catalyst successfully addressed these two problems. The catalyst can give linear α-olefin polymers with high and controllable molecular weights. Moreover, it makes the fabrication of polymers with specific tacticity possible. By controlling the stereochemistry of products, either syndiotactic or isotactic polymers can be achieved.

Mechanism of Ziegler-Natta catalytic polymerization

Activation of Ziegler-Natta catalyst

It is necessary to understand the catalyst's structure before understanding how this catalyst system works. Herein, $TiCl_4$+$AlEt_3$

catalyst system is taken as an example. The titanium chloride compound has a crystal structure in which each Ti atom is coordinated to 6 chlorine atoms. On the crystal surface, a Ti atom is surrounded by 5 chlorine atoms with one empty orbital to be filled. When Et_3Al comes in, it donates an ethyl group to Ti atom and the Al atom is coordinated to one of the chlorine atoms. Meanwhile, one chlorine atom from titanium is kicked out during this process. Thus, the catalyst system still has an empty orbital (Figure 14.4.1.6). The catalyst is activated by the coordination of $AlEt_3$ to Ti atom.

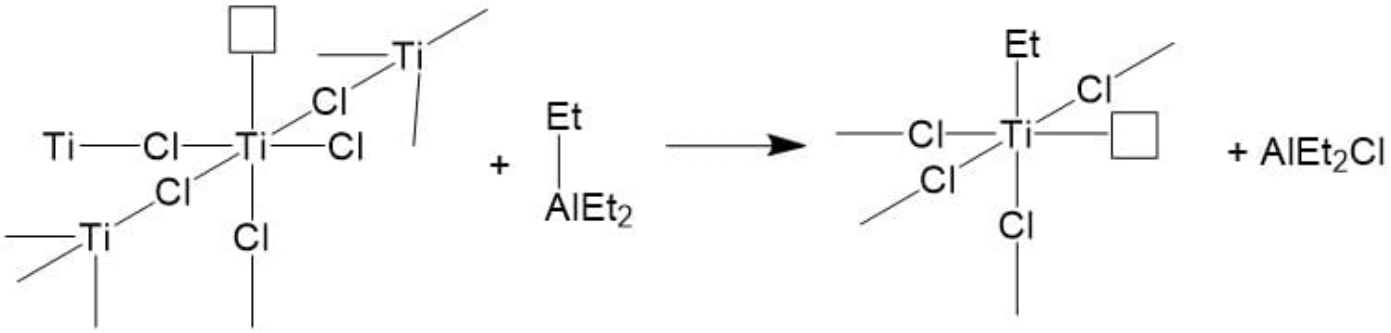


Figure 14.4.1.6: The activation of ZN catalyst system by coordination of $AlEt_3$ to Ti atom.

Initiation step

The polymerization reaction is initiated by forming alkene-metal complex. When a vinyl monomer like propylene comes to the active metal center, it can be coordinated to Ti atom by overlapping their orbitals. As shown in Figure 14.4.1.7, there is an empty dxy orbital and a filled dx^2-y^2 orbital in Ti's outermost shell (the other four orbitals are not shown here). The carbon-carbon double bond of alkene has a pi bond, which consists of a filled pi-bonding orbital and an empty pi-antibonding orbital. So, the alkene's pi-bonding orbital and the Ti's dxy orbital come together and share a pair of electrons. Once they're together, that Ti's dx^2-y^2 orbital comes mighty close to the pi-antibonding orbital, sharing another pair of electrons.

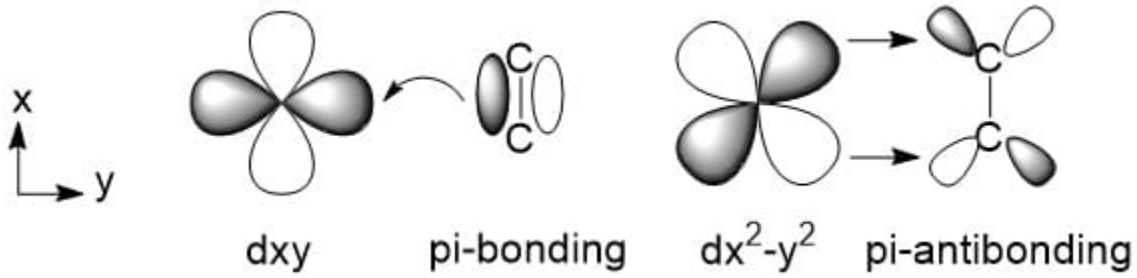


Figure 14.4.1.7: Molecular orbitals representation of monomer coordinating to metal center.

The formed alkene-metal complex (1) then goes through electron shuffling, with several pairs of electrons shifting their positions: The pair of electrons from the carbon-carbon pi-bond shifts to form Ti-carbon bond, while the pair of electrons from the bond between Ti and AlEt3' ethyl group shifts to form a bond between the ethyl group and the methyl-substituted carbon of propylene (Figure 14.4.1.8). After electron shuffling, Ti is back with an empty orbital again, needing electrons to fill it (2).

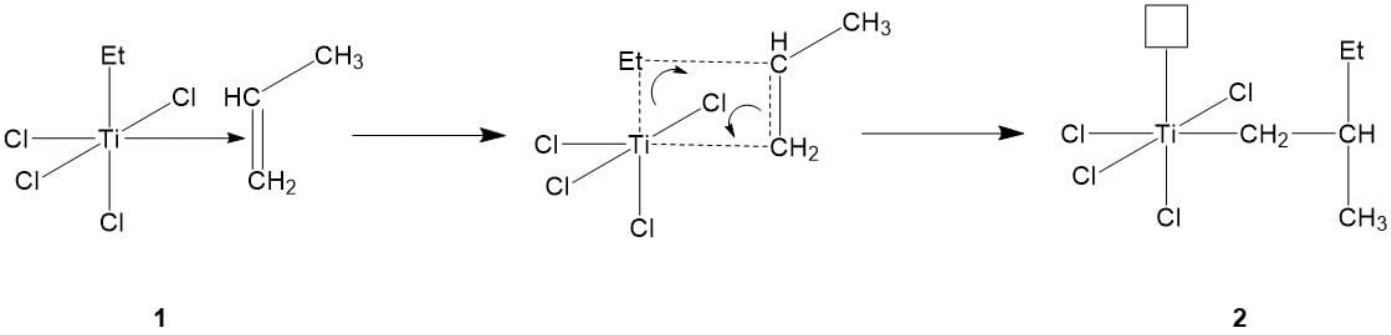


Figure 14.4.1.8: The formation process of alkene-metal complex.

Propagation step

When other propylene molecules come in, this process starts over and over, giving linear polypropylene (Figure 14.4.1.9).

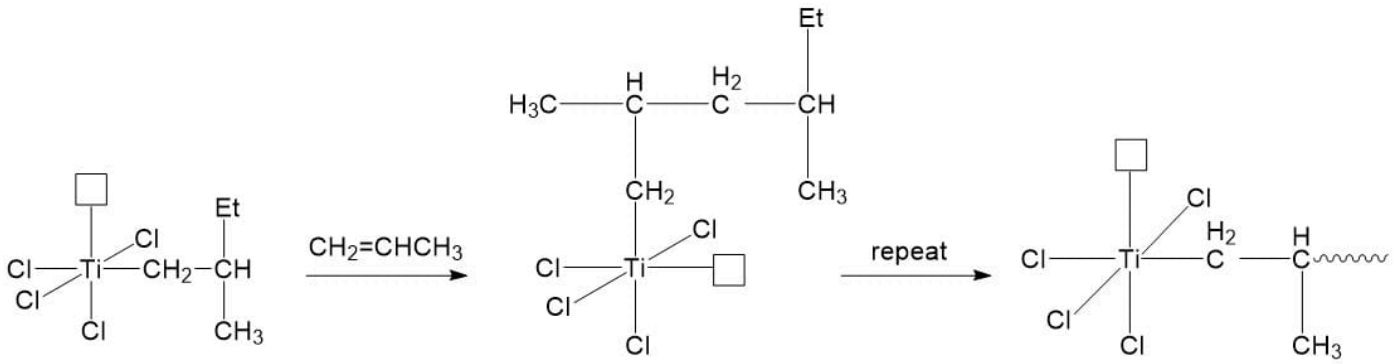


Figure 14.4.1.9: Propagation towards polymeric chains.

Termination step

Termination is the final step of a chain-growth polymerization, forming “dead” polymers (desired products). Figure 14.4.1.10 illustrates several termination approaches developed with the aid of co-catalyst $AlEt_3$.[4]

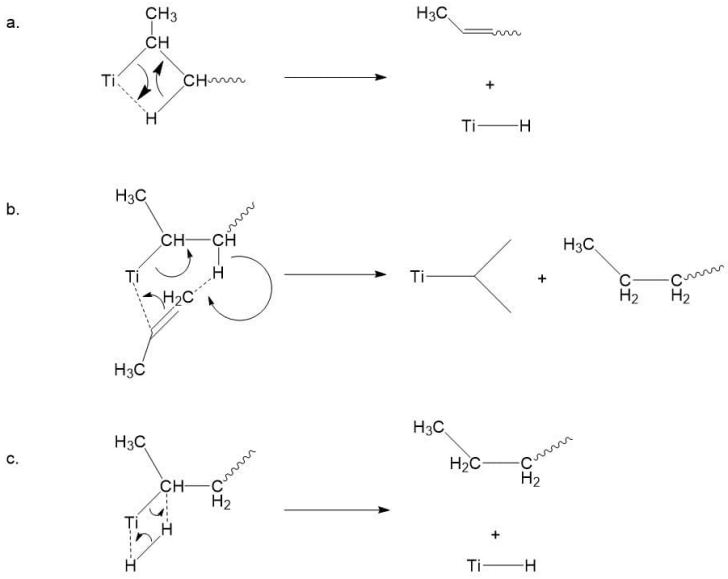


Figure 14.4.1.10: Three termination approaches: (a) β-elimination from the polymer chain, forming metal hydride; (b) β-elimination with hydrogen transfer to monomer; (c)hydrogenation.

Mechanistic study: kinetic isotope effect experiments

Unlike the mechanism discussed above, there is also a competing mechanism proposed by Ivin and coworkers.[5] They proposed that a 1,2-hydrogen shift occurs prior to monomer association, giving a carbene intermediate (Figure 14.4.1.11).

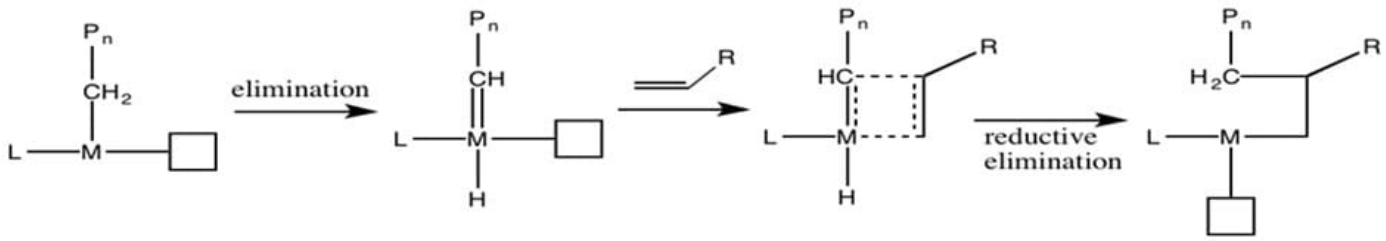


Figure 14.4.1.11: Alternative propagation mechanism: hydride shift prior to monomer association.

To determine the actual mechanism, Grubbs[6] conducted kinetic isotope effect (KIE) experiments. Due to their different weights, carbon-deuterium bond reacts slower than carbon-hydrogen bond (Figure 14.4.1.12). If such bonds are involved in the rate-determining step, the isotopic species should proceed in lower rate.

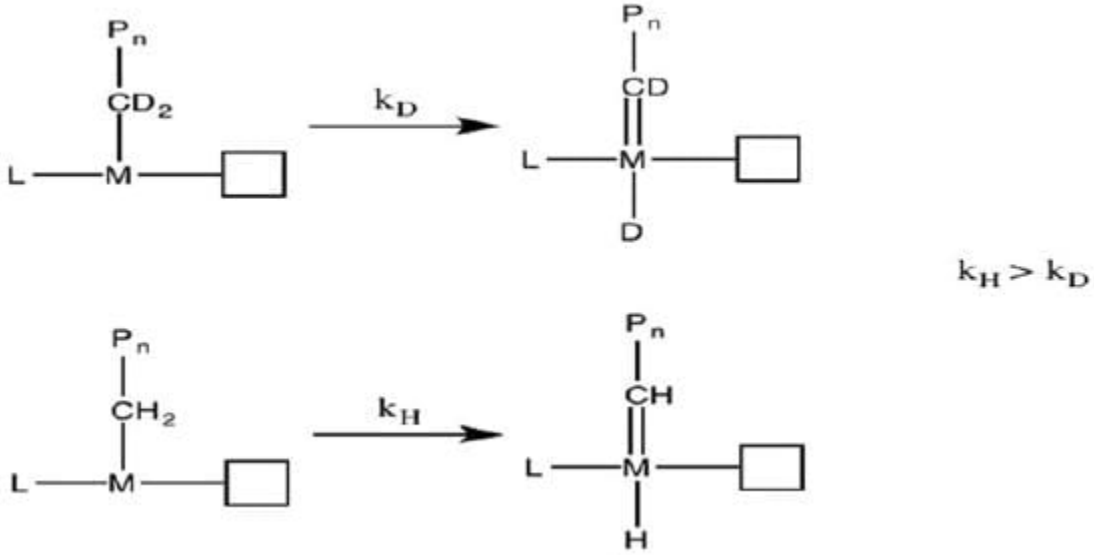


Figure 14.4.1.12: Carbon-deuterium bonds react slower than carbon-hydrogen bonds.

In Grubbs's experiment, deuterated ethylene and normal ethylene were catalyzed by Ziegler-Natta catalyst with 1:1 ratio (Figure 14.4.1.13). The result showed that H/D ratio in the resulting polymers was still 1:1.6 This indicated that no carbon-hydrogen bond cleavage or formation is involved in the rate determining step. Therefore, the mechanism proposed by Ivin was excluded.

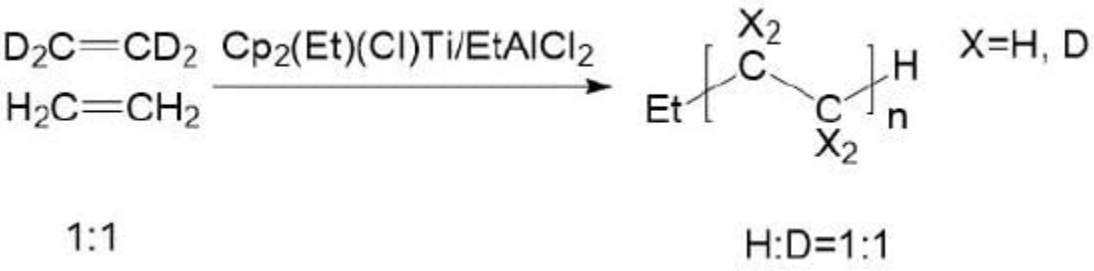


Figure 14.4.1.13: KIE experiment excludes Ivin's mechanism.

Regio- and stero-selectivity

Regio-selectivity

For propene polymerization, most ZN catalysts are highly regioselective, favoring 1,2-primary insertion [M-R + CH2=CH(Me)=M-CH2-CH(Me)(R)] (Figure 14.4.1.14), due to electronic and steric effects.[7]

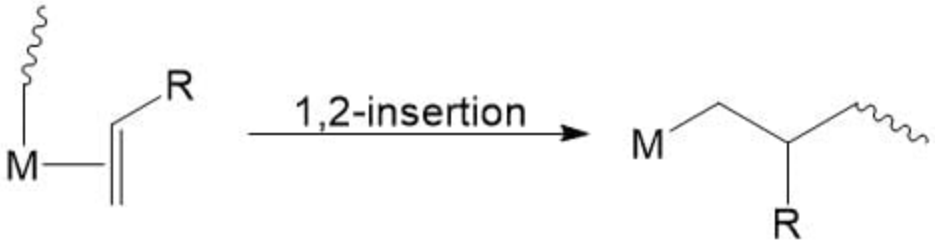


Figure 14.4.1.14: Primary insertion occurs in ZN-catalytic system to give regioselective products.

Stereo-selectivity

Stereochemistry of polymers made from ZN-catalyst can be well regulated by rational design of ligands. By using different ligand system, either syndiotactic or isotactic polymers can be obtained (Figure 14.4.1.15).

The relative stereochemistry of adjacent chiral centers within a macromolecule is defined as tacticity. Three kinds of stereochemistry are possible: isotactic, syndiotactic and atactic. In isotactic polymers, substituents are located on the same side of the polymer backbone, while substituents on syodiotactic polymers have alternative positions. In atactic polymers, substituents are placed randomly along the chain.

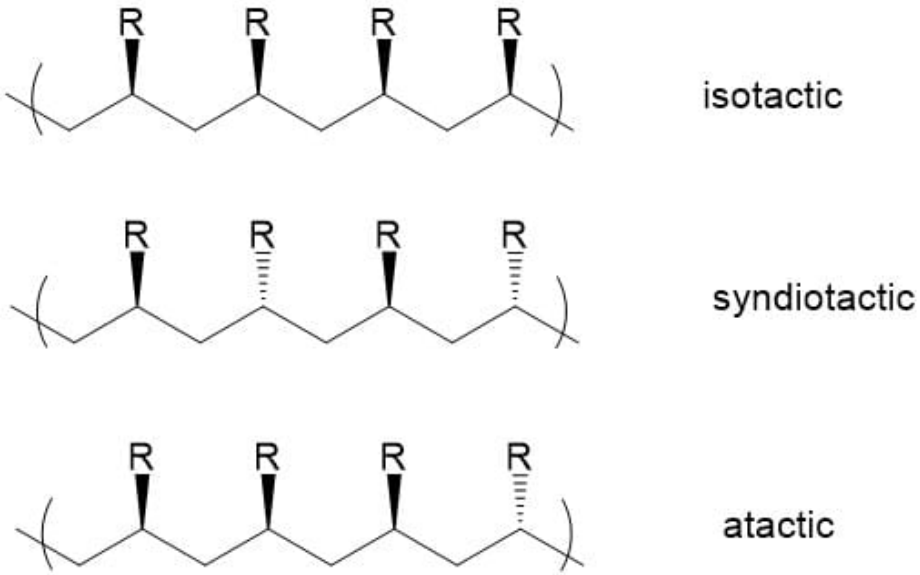


Figure 14.4.1.15: Tacticity of macromolecules

Choice of ZN catalyst regulates the stereochemistry. We use propylene polymerization as an example here. Recall the mechanism section, a monomer approaches the metal center and forms a four-membered ring intermediate. The binding of a monomer to the reactive metal-carbon bond should occur in from the least hindered site.[8] As shown in Figure 14.4.1.16, the trans-complex in which methyl on the growing chain is trans to the methyl group on the incoming monomer, should be energetically favored than the cis-complex, as the trans-complex experience less steric effect.

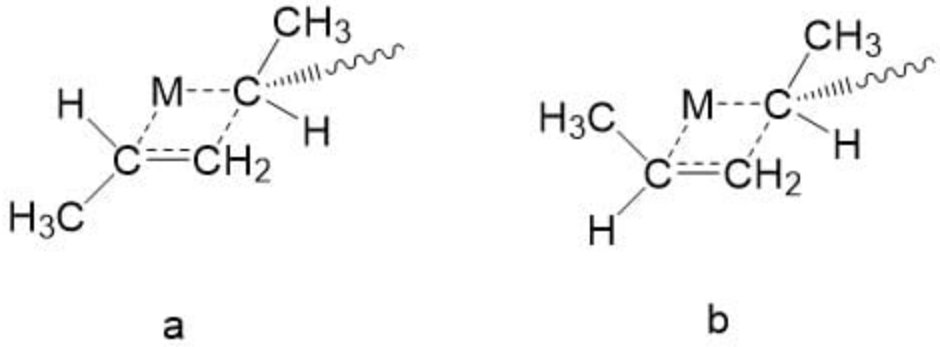


Figure 14.4.1.16: The active state a (trans) is more stable than b (cis) due to less steric effects of methyl groups.

Following the trans- complex, the methyl group on the newly added monomer is trans to that on the previous monomer. The step repeats so that a syndiotactic polypropylene is obtained (Figure 14.4.1.17a). However, if the metal center is coordinated with bulky ligands (e.g. –iBu, -Et2 groups), as denoted by Y in Figure 14.4.1.17b, the incoming monomer will adopt a cis-conformation to avoid serious steric effect with the bulky ligand. Thus, at the presence of bulky ligand, the propylene monomer is cis to the growing chain. This results in a isotactic product.

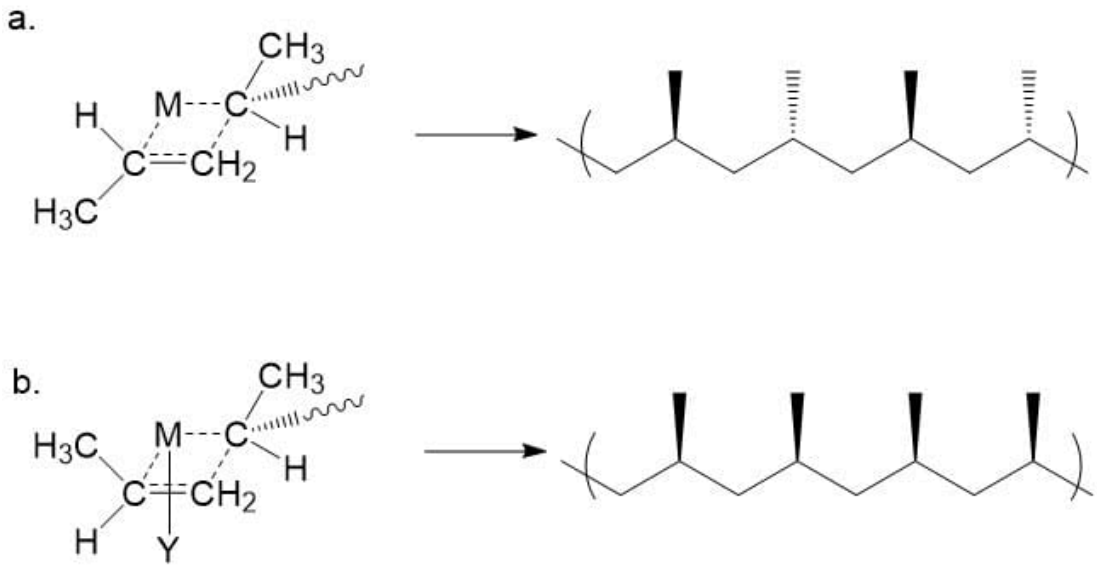


Figure 14.4.1.17: a. Trans-intermediate avoids 1,3-strain of methyl groups, producing syndiotactic polypropylene; b. at the presence of bulky ligand Y, a cis-intermediate is adopted, generating isotactic polypropylene.

Applications

ZN catalysts have provided a worldwide profitable industry with production of more than 160 billion pounds and creation of numerous positions.[9] These products have been extensively applied in different areas, largely improving the quality of people's life. They can catalyze α-olefins to produce various commercial polymers, like polyethylene, polypropylene and Polybutene-1. Polyethylene and polypropylene is reported to be the top two widely used synthetic plastic in the word.[10]

Among the polyethylene fabricated by ZN catalysts, there are three major classes: high density polyethylene (HDPE), linear low density polyethylene (LLDPE), and ultra-high molecular weight polyethylene (UHMWPE). HDPE, a linear homopolymer, is widely applied in garbage containers, detergent bottles and water pipes because of its high tensile strength. Compared with HDPE whose branching degree is quite low, LLDPE has many short branches. Its better toughness, flexibility and stress-cracking resistance makes it suitable for materials like cable coverings, bubble wrap and so on. UHMWPE is polyethylene with a molecular weight between 3.5 and 7.5 million. This material is extremely tough and chemically resistant. Therefore, it is often used to make gears and artificial joints.

Compared to polyethylene, polypropylene has enhanced mechanical properties and thermal resistance because of the additional methyl group. Moreover, isotactic polypropylene is stiffer and more resistant to creep than atactic polypropylene. Polypropylene has a wide range of applications in clothing, medical plastics, food packing, and building construction.

Substrate scope and limitations

ZN catalysts are effective for polymerization of α-Olefins (ethylene, propylene) and some dienes (butadiene, isoprene). However, they don't work for some other monomers, such as 1.2 disubstituted double bonds. Vinyl chloride cannot be polymerized by ZN catalyst either, because free radical vinyl polymerization is initiated during the reaction. Another situation that ZN catalysts don't work is when the substrate is acrylate. The reason is that ZN catalysts often initiate anionic vinyl polymerization in those monomers.[11]

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Contributors and Attributions

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14.4.2: Water-Gas Shift Reaction

The **water-gas shift reaction** (WGSR) describes the reaction of carbon monoxide and water vapor (steam) at very high temperatures to form carbon dioxide and hydrogen:

$$\mathrm{CO + H_2O \rightleftharpoons CO_2 + H_2} \tag{14.4.2.1}$$

The WGSR is a highly valuable industrial reaction that is used in the manufacture of ammonia, hydrocarbons, methanol, and hydrogen. Its most important application is in the conversion of carbon monoxide or other hydrocarbons to produce hydrogen gas, an important source of fuel for a modern hydrogen economy. If hydrogen could be produced at low cost and using a renewable resource, it could significantly advance the movement to sustainable energy.

Most of the catalysts that are used for this process are heterogeneous catalysts. Unfortunately, the process using heterogeneous catalysts occurs only at extremely high temperatures and pressures. The high energy cost of performing the reaction limits its industrial utility, and there are efforts to produce homogeneous catalysts that catalyze the reaction at more mild conditions. Another limitation is that the reaction requires sufficient quantities of CO, which are primarily obtained from non-renewable coal or petroleum sources. However, there are processes that can convert methane gas, which is an abundant greenhouse gas, to .

The WGSR has been extensively studied for over a hundred years. The kinetically relevant mechanism depends on the catalyst composition and the temperature. Two mechanisms have been proposed: an associative Langmuir–Hinshelwood mechanism and a redox mechanism. The redox mechanism is generally regarded as kinetically relevant during the high-temperature WGSR (> 350 °C) over the industrial Fe-Cr catalyst. Historically, there has been much more controversy surrounding the mechanism at low temperatures. Recent experimental studies confirm that the associative carboxyl mechanism is the predominant low temperature pathway on metal-oxide-supported transition metal catalysts.

Associative mechanism

In 1920 Armstrong and Hilditch first proposed the associative mechanism. In this mechanism CO and H_2O are adsorbed onto the surface of the catalyst, followed by formation of an intermediate and the desorption of H_2 and CO_2. In general, H_2O dissociates onto the catalyst to yield adsorbed OH and H. The dissociated water reacts with CO to form a carboxyl or formate intermediate. The intermediate subsequently dehydrogenates to yield CO_2 and adsorbed H. Two adsorbed H atoms recombine to form H_2.

There has been significant controversy surrounding the kinetically relevant intermediate during the associative mechanism. Experimental studies indicate that both intermediates contribute to the reaction rate over metal oxide supported transition metal catalysts. However, the carboxyl pathway accounts for about 90% of the total rate owing to the thermodynamic stability of adsorbed formate on the oxide support. The active site for carboxyl formation consists of a metal atom adjacent to an adsorbed hydroxyl. This ensemble is readily formed at the metal-oxide interface and explains the much higher activity of oxide-supported transition metals relative to extended metal surfaces. The turn-over-frequency for the WGSR is proportional to the equilibrium constant of hydroxyl formation, which rationalizes why reducible oxide supports (e.g. CeO_2) are more active than irreducible supports (e.g. SiO_2) and extended metal surfaces (e.g. Pt). In contrast to the active site for carboxyl formation, formate formation occurs on extended metal surfaces. The formate intermediate can be eliminated during the WGSR by using oxide-supported atomically dispersed transition metal catalysts, further confirming the kinetic dominance of the carboxyl pathway.

Redox mechanism

The redox mechanism involves a change in the oxidation state of the catalytic material. In this mechanism, CO is oxidized by an O-atom intrinsically belonging to the catalytic material to form CO_2. A water molecule undergoes dissociative adsorption at the newly formed O-vacancy to yield two hydroxyls. The hydroxyls disproportionate to yield H_2 and return the catalytic surface back to its pre-reaction state.

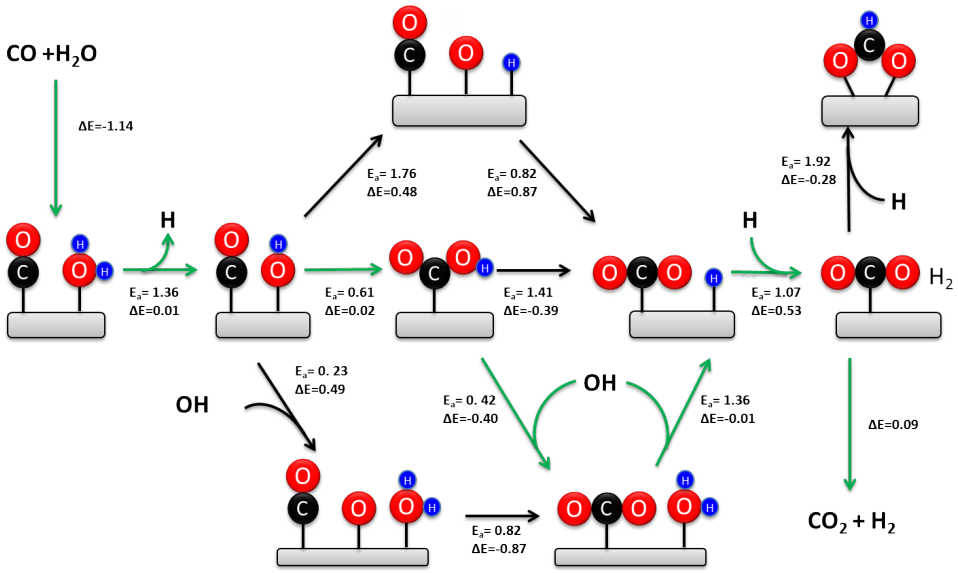


Figure 14.4.2.1: Proposed associative and redox mechanisms of the water gas shift reaction. (Zwickipedia, WGS mechanism, CC BY-SA 3.0)

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14.5: Problems

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14.5.1: Concept Review Questions Chapter 12

Concept Review Questions

Section 1

1) What is an oxidative addition?

2) What is a reductive elimination?

3) What is a cis and a trans addition, respectively?

4) Does the coordination number in oxidative additions always increase? Explain.

5) What is the reverse reaction of an oxidative addition?

6) What is a migratory insertion?

7) Are migratory insertions reversible reactions?

Section 2

1) Why are transition metal alkyl complexes that have alkyl groups longer than 1 carbon atom often unstable?

2) What is meant by beta-hydride elimination?

3) What is alpha-abstraction?

4) What is a nucleophilic displacement reaction?

5) What is meant by an oxidative addition of an intact ligand?

6) Write the catalytic cyclic for the deuteration of benzene with Cp_2TaH_3 as a catalyst. Name each reaction step.

7) What is Collman's reagent and how is it being used?

8) What is Wilkinson's catalyst, and what reactions can it be used for. Write the catalytic cycle.

9) Write done the reaction mechanism for the Ziegler-Natta olefin polymerization.

10) What is carbene migratory insertion?

11) Write down the catalytic cycle for the hydroformylation of olefins.

12) Name three hydrocarbonylation reactions. What are the reactants?

13) Write down the mechanism for the Monsanto acetic acid process.

14) What is olefin metathesis?

15) What is ring-opening olefin polymerization (ROMP)?

16) What is acyclic diene metathesis?

17) Why are olefins with terminal C=C double bonds particularly useful in olefin metathesis?

18) What is ring-closing metathesis?

19) What are the characteristics of Schrock and Grubbs catalysts, respectively?

20) Write down the catalytic cycle for olefin metathesis.

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14.5.2: Homework Problems Chapter 12

Homework Problems

Section 1

Exercise 1

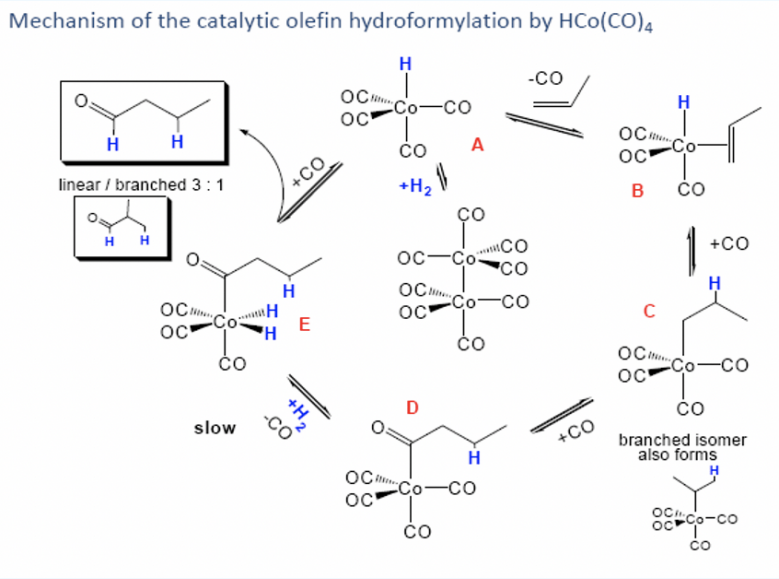
The coordination compound $CH_3Co(CO)_4$ undegoes a migratory insertion. What is the reaction product?

Answer available at the end of this section.

Section 2

Exercise 1

Identify all oxidative additions in the catalytic cycle of olefin hydroformylation:



Answer available at the end of this section.

Exercise 2

1. What are the reaction products of the following olefin metathesis reactions?

a) 2 CH_2=CH-Ph -->

b) n CH_2=CH-CH=CH_2 -->

Answer available at the end of this section.

Exercise 3

What reaction product would you expect would you expect from the following reaction:

$Fe(CO)_4^{2-}$ + CH_3CH_2I -->

Name the reaction.

Answer available at the end of this section.

Exercise 4

Which of the following phosphines would you expect to be most suitable to stabilize metals in low oxidation states:

a) $P(CF_3)_3$

b) $P(CH_3)_3$

c) PH_3

Answer available at the end of this section.

Exercise 5

What reaction product would you expect from the following reaction?

$Pt(PPh_3)_4$ + 4 NPh_3 -->

Answer available at the end of this section.

Exercise 6

Which of the following complexes would likely be unstable:

a) $[PtCl_3(C_2H_5)]^{2-}$

b) $[PtCl_3(CH_3)]^{2-}$

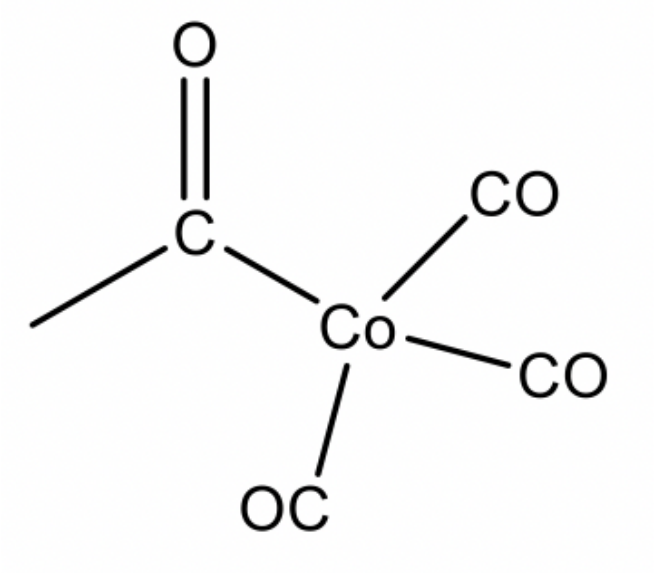
c) $PtCl_4^{2-}$

Answer available at the end of this section.

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Answers

Exercise 1



Exercise 1

Step D --> E is an oxidative addition

Formation of $HCo(CO)_4$ from $Co_2(CO)_8$ is also an oxidative addition.

Exercise 2

a) $CH_2{=}CH_2$ and Ph-CH=CH-Ph

b) $CH_2{=}CH_2$ and $(CH{=}CH)_n$

Exercise 3

$Fe(CO)_4CH_2CH_3^-$ + I^- Nucleophilic displacement

Exercise 4

a) $P(CF_3)_3$

Exercise 5

There would be no reaction.

Exercise 6

a) $[PtCl_3(C_2H_5)]^{2-}$

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15: PARALLELS BETWEEN MAIN GROUP AND ORGANOMETALLIC CHEMISTRY

15.1: Parallels between Main Group and Binary Carbonyl Complexes

15.2: The Isolobal Analogy

15.2.1: Extensions of the Analogy

15.2.2: Some Applications of the Isolobal Analogy

15.3: Metal-Metal Bonds

15.3.1: Metal-Metal Multiple Bonds

15.4: Cluster Compounds

15.4.1: Boranes

15.4.2: Heteroboranes

15.4.3: Metallaboranes and Metallacarboranes

15.4.4: Carbonyl Clusters

15.4.5: Carbon-Centered Clusters

15.4.6: Additional Comments on Clusters

15.5: Problems

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15.1: Parallels between Main Group and Binary Carbonyl Complexes

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15.2: The Isolobal Analogy

The **isolobal analogy** (aka isolobal principle) is a strategy used in organometallic chemistry to relate the structure of organic and inorganic molecular fragments in order to predict bonding properties of organometallic compounds. Roald Hoffmann described molecular fragments as isolobal: "*if the number, symmetry properties, approximate energy and shape of the frontier orbitals and the number of electrons in them are similar – not identical, but similar*." One can predict the bonding and reactivity of a species from that of a better-understood species **if the two molecular fragments have similar frontier orbitals**; **the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).** Isolobal compounds are analogues to *isoelectronic compounds* that share the same number of valence electrons and structure.

Isolobal species are indicated with an isolobal arrow symbol; a double-headed arrow with half an orbital (Figure 15.2.1).

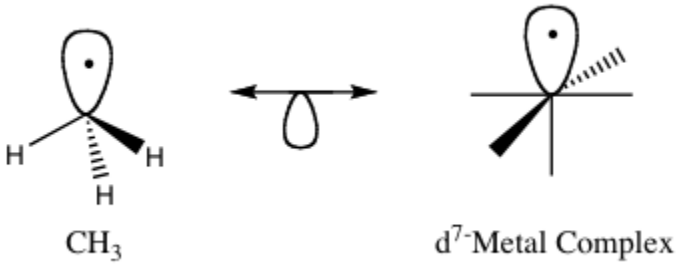


Figure 15.2.1: A methyl radical related to a d^7 metal complex by the isolobal analogy. A double headed arrow with a half orbital indicates that the two structures are related by the isolobal analogy. (public domain)

The concept of isolobality was developed by Roald Hoffmann (Figure 15.2.2), who won the Nobel prize in chemistry in 1981. It comes from the greek words “isos” meaning “similar” and “lobos” meaning lobe. Hence, “isolobal” means “similar lobes”. In his Nobel speech he defined isolobality as follows: “Molecular fragments are isolobal if the number, symmetry properties, approximate energy and shape of the frontier orbitals and the number of electrons in them are similar - not identical, but similar. “ When molecular fragments are isolobal then they can likely be combined to form a stable molecule. Thus, isolobal fragments are compatible building blocks for the construction of stable molecules. We can also say that the concept of isolobality helps us to predict when a stable bond forms. Whenever two molecular fragments are isolobal, then they will likely form stable bonds between them.

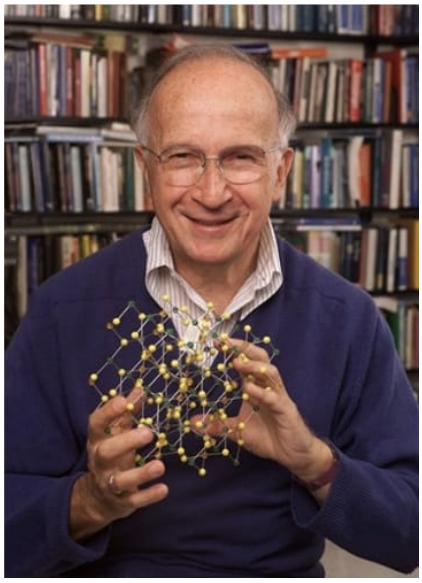


Figure 15.2.2: Roald Hoffman (Attribution: .The original uploader was Xtreambar at English Wikipedia. / Public domain https://commons.wikimedia.org/wiki/F...d_Hoffmann.jpg)

Isolobal Fragments of main group elements

There is a simple means to determine if fragments are isolobal. In main group chemistry the octet rule is a very helpful guide, especially for the period 2 elements (B,C,N,O,F) for which the octet rule holds fairly strictly. The difference between the number "8" and the number of valence electrons (VE) of the molecular fragment is equal to the number of frontier orbitals and the number of electrons in it.

# of frontier orbitals = # of electrons in frontier orbitals = 8 – VE

Thus, **when two fragments (of main group elements) have the same number of valence electrons, they can be considered isolobal.** For example, the CH_3 fragment created by homolytic cleavage of a $C-H$ bond from CH_4 is shown in Figure 15.2.1. This CH_3 fragment has 7 VE on the carbon, and therefore it has one frontier orbital with one electron it (Figure 15.2.1). The same is true for the NH_2 (7 VE) and OH (7 VE) fragments shown in XXX. All of these fragments have 7 VE and one frontier orbital (Figure 15.2.3).

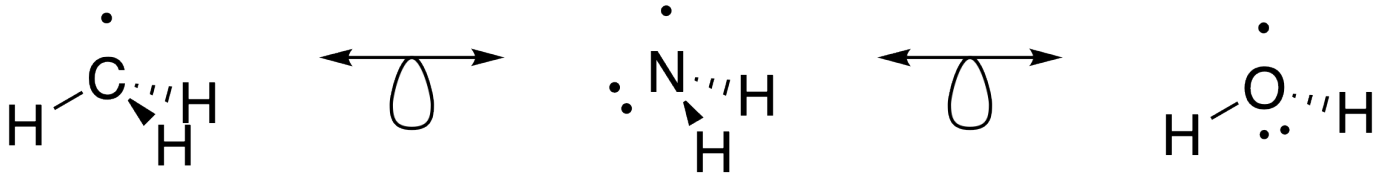


Figure 15.2.3: Examples of fragments that are isolobal. These fragments are comprised of main group elements, and all have 7 valence electrons around the central atom, thus they each have one frontier orbital. (CC-BY-SA; Kathryn Haas)

According to the isolobal analogy, it should be possible to combine isolobal fragments to form stable molecules. Let's test this on the fragments shown in Figure 15.2.3. All the posible combinations are shown in Figure 15.2.4. Two CH_3 fragments can be combined to form an ethane molecule which is known to be stable. The combination of CH_3 andNH_2 gives methylamine which is stable, and the combination of CH_3 and OH gives methanol, which is also stable. TwoNH_2 fragments give hydrazine, H_2N-NH_2 which exists, the combination of$NH_2$and OH gives the known hydroxylamine molecule NH_2OH. The combination of two OH fragments gives hydrogen peroxide H_2O_2.

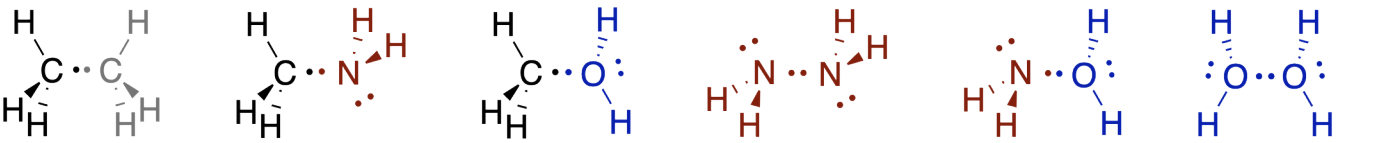


Figure 15.2.4: Combinations of isolobal fragments lead to stable molecules (stable enough to exist). (CC-BY-SA; Kathryn Haas)

As another example, a CH_2 fragment is a 6 VE fragment, thus there are 8-6=2 frontier orbitals with overall two electrons in them (Figure 15.2.5). An NH-fragment and an O-atom also have 6 VE, and are therefore isolobal to CH_2. In NH there are 5+1=6 valence electrons, and an oxygen atom has 6 valence electrons. We can combine two CH_2 fragments to form ethene $H_2C{=}CH_2$. Combining CH_2 with NH and O, respectively gives methanimine H_2CNH, and formaldehyde $H_2C{=}O$, respectively. Methylene imine is stable in the gas phase, and oligomerizes in higher concentrations to form a hexamer, called urotropine. Other oligomers and polymers are also known. The combination of two NH fragments gives the known molecule diazene $HN{=}NH$, and the combination with an O atom gives $HN{=}O$, which is known as nitroxyl or azanone, and is stable in the gas phase. The combination of two oxygen atoms gives the well known O_2 molecule.

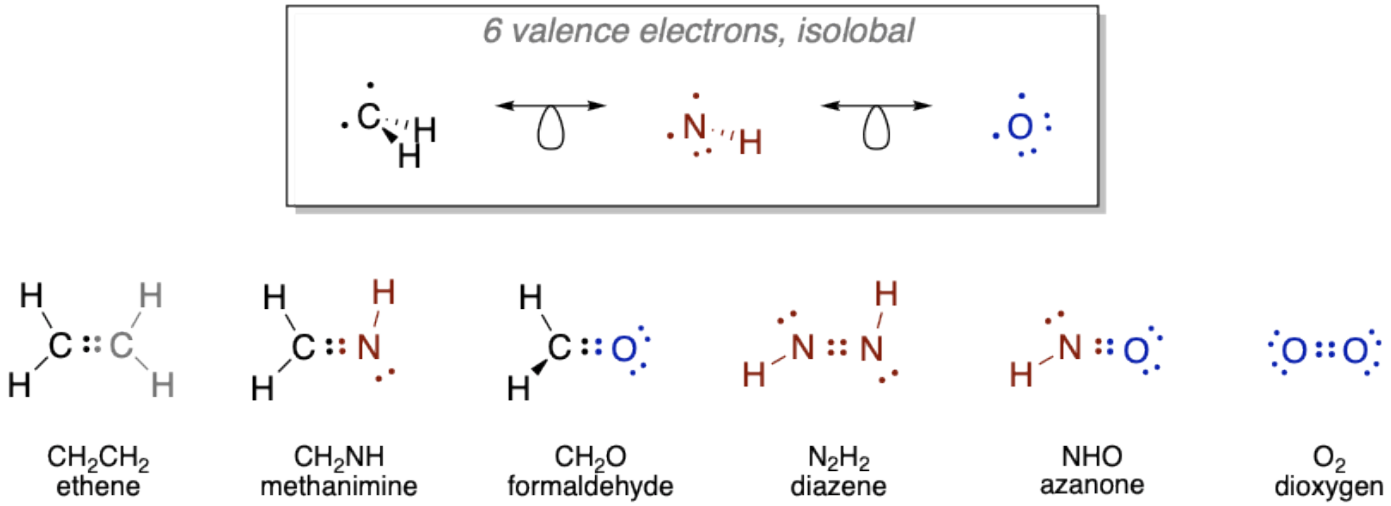


Figure 15.2.5: Examples of isolobal fragments of main group elements with 6 valence electrons, and combination of those fragments that result in stable compounds. (CC-BY-SA; Kathryn Haas)

The analogy could also be extended to 5 VE fragments (not shown). The CH fragment has 4+1=5 VE, and an N-atom has 5 VE as well, thus they can be considered isolobal. Two CH fragments give acetylene C_2H_2, and two N atoms give the dinitrogen molecule N_2. The combination of a CH fragment with an N fragment gives H-CN, well known as hydrogen cyanide.

Isolobal fragments of transition elements

In the way the octet rule can help to predict the number of frontier orbitals and the electrons in them for main group element fragments, **the 18 electron rule can be used to predict the number of frontier orbitals and electrons for organometallic fragments**, including carbonyl fragments. The number of frontier orbitals and the number of electrons in them is 18 minus the number of valence electrons the organometallic fragment has:

 # frontier orbitals = # of electrons in frontier orbitals = 18 – VE

For example, a metal complex with a count of 17 electrons, such as $\mathrm{Mn(CO)_5}$, there is one frontier orbital with one electron. This implies that a 17 VE carbonyl fragment is isolobal to a 7 VE organic fragment such as $\mathrm{CH_3}$. For a 16 VE fragment such as $\mathrm{Fe(CO)_4}$ there are two frontier orbitals with one electron in each of them, and for a 15 VE fragment such as $\mathrm{(CO)_3Co}$ there are three frontier orbitals with overall three valence electrons (Figure 15.2.6). Similarly, a 16 VE metal carbonyl fragment is isolobal to a 6 VE fragment such as $\mathrm{CH_2}$, and a 15 VE fragment is isolobal to a 5 VE fragment such as CH (Figure 15.2.6).

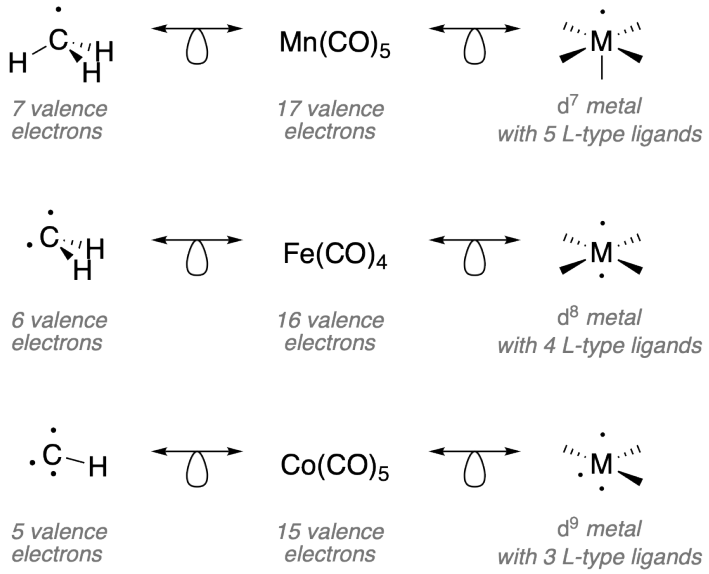


Figure 15.2.6: Examples for isolobal metal carbonyl and organic fragments (CC-BY-SA; Kathryn Haas)

It should be possible to combine the isolobal fragments from Figure 15.2.6 to form stable molecules. Let us check how well this works (Figure 15.2.7). It should be possible to combine the two 17 VE electron fragments such as $\mathrm{Mn(CO)_5}$ to form $\mathrm{(CO)_5Mn{-}Mn(CO)_5}$. This is a known molecule. Remember we encountered it previously when we discussed the homoleptic carbonyls of metals with an odd number of electrons. Combining this fragment with a 7 VE $\mathrm{CH_3}$ fragment leads to $\mathrm{(CO)_5Mn{-}CH_3}$ which is also stable.

Can we also combine two 16 VE electron fragments to form $\mathrm{(CO)_4Fe{=}Fe(CO)_4}$ with an Fe=Fe double bond? The answer is no. Metal-metal double bonds, and also metal-metal triple bonds in carbonyl complexes are not formed. Instead clusters with single bonds are realized. The number of single bonds a metal makes is equal to the number of its frontier orbitals. In the case of 16 VE fragments trimeric clusters with single bonds are formed. In this cluster the two frontier orbitals of each fragment make two single bonds to two other fragments. In contrast, a 16 VE carbonyl fragment such as $\mathrm{(CO)_4Fe}$ can be combined with a 6 VE fragment to form a compound with a Fe=C double bond. A compound with a metal-carbon double bond is called a carbene complex. Similarly, the combination of 15 VE fragments of the type $\mathrm{Co(CO)_3}$ does not lead to a stable $\mathrm{(CO)_3Co{\equiv}Co(CO)_3}$ molecule with a $\mathrm{Co{\equiv}Co}$ triple bond. Instead, nature realizes a tetrameric tetrahedral cluster in which the three frontier orbitals of each 15 VE fragment make three single bonds to the other three 15 VE fragments. In clusters the CO ligands may not only be terminal, they can also be bridging. In the tetrameric Co-cluster, there are are nine terminal and three bridging CO-ligands. The three bridging CO ligands are connecting the three Co atoms at the base triangular face of the tetrahedron. What about the combination of a 15 VE fragment with an organic 5 VE fragment? The combination of a 15 VE fragment such as $Co(CO)_3$ with a 5 VE organic fragment such as CH to does yield stable complexes such as the $\mathrm{(CO)_3Co{\equiv}CH}$ complex with a $\mathrm{Co{\equiv}C}$ triple bond. Complexes with metal-carbon triple bonds are called carbine complexes.

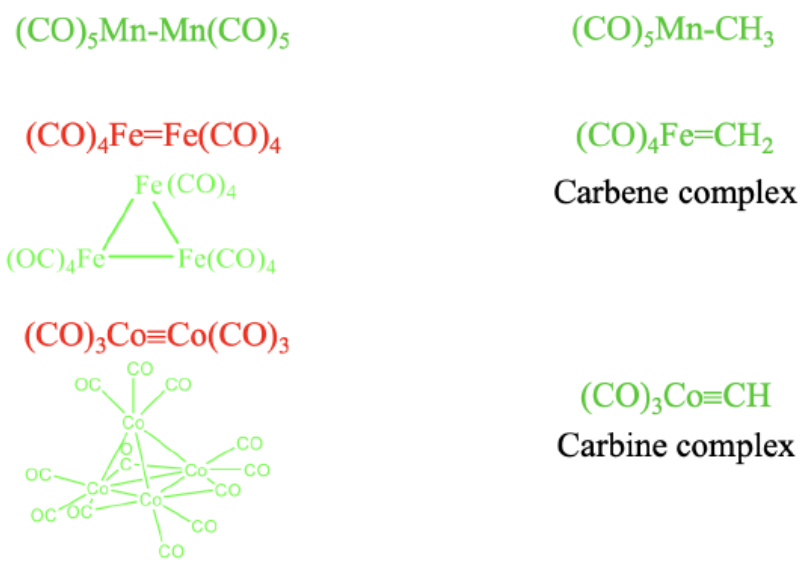


Figure 15.2.7: Stable molecules formed from isolobal fragments are shown in green. Species that have not been isolated (they are unstable) are shown in red (Attribution: W. Petz).

Synthesis of Terameric Cluster Carbonyls

How can we make a carbonyl cluster like $((Co(CO)_3)_4$?



Figure 15.2.8: Thermal reaction of $Co_2(CO)_8$ leading to $Co_4(CO)_{12}$ (Attribution: W. Petz)

It can be prepared by heating the $Co_2(CO)_8$ to a temperature above 54°C. Above this temperature the reactant loses four CO ligands and rearranges to form the cluster (Fig. 15.2.8). Interestingly, the higher homologues of the Co-cluster, the $Rh_4(CO)_{12}$ and the $Ir_4(CO)_{12}$ form spontaneously from the elements. Remember, that we previously determined that the $Rh_2(CO)_8$ and the $Ir_2(CO)_8$ are not stable. Rh and Ir favor the tetrameric clusters with 12 COs over the dimer with 8 CO ligands.

Structures of $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$ and $Ir_4(CO)_{12}$

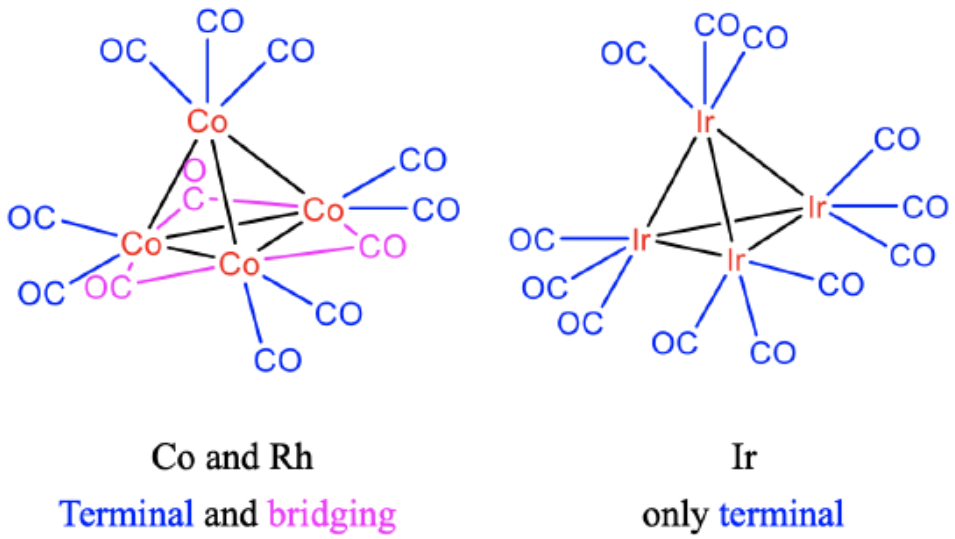


Figure 15.2.9: Structures of tetrameric group 9 carbonyl clusters (Attribution: W. Petz)

Like in the Co-cluster, there are 9 terminal and three bridging CO ligands in the $Rh_4(CO)_{12}$ cluster. By contrast, there are only terminal CO ligands in the iridium cluster (Fig.15.2.9) . This may be explained by the larger Ir-Ir bond length in comparison to the Co-Co and Rh-Rh bond lengths. The observation reflects the general rule that only 3d and 4d elements have bridging CO ligands, while only terminal ligands are observed in metals with 5d electrons.

Isoelectronic Charged Carbonyl Clusters

The previously discussed clusters were charge-neutral. Can we construct charged isoelectronic ones with different metals, and what is their stability? Let us start with the tetrameric Co-cluster made of four 15 VE fragments. The element left to the Co is the Fe. It has one electron less, therefore $Fe(CO)_3^-$ is the 15 VE electron fragment which is isoelectronic to the neutral $Co(CO)_3$ fragment. Its tetramer would be a $Fe_4(CO)_{12}^{4-}$ cluster. This cluster is not known. The cluster already carries a 4- charge which is too high to support stable Fe-Fe bonds. Each Fe carries formally a 1- negative charge and there is too much electrostatic repulsion between the Fe atoms. Another possibility to realize a 15 VE fragment with Fe is a $(CO)_4Fe^+$ fragment. Here an additional ligand is added contributing two electrons, and one electron is removed resulting in a fragment with a 1+ charge. The fragment could be combined to form an $Fe_4(CO)_{16}^{4+}$ cluster. However, such a cluster is also not stable. This is because the coordination number would be 7, which is too high for a carbonyl. In addition, there is the destabilizing effect of the positive charge on the Fe-C bond. Similarly, tetramers of the 15 VE fragments $Mn(CO)_4$, $Cr(CO)_4^-$ and $(CO)_5Cr^+$ are also not known. Also in these cases, the coordination numbers would be too high. The $Mn(CO)_4$ and the $Cr(CO)_4^-$ would lead to a coordination number of 7, in the case of the $Cr(CO)_5^+$ fragment the coordination number would be even 8. We see here the limitations of the concept of isolobality. The presence of isolobality is not always sufficient to make a stable molecule, also other factors like coordination numbers and charge needs to be considered.What about charged isoelectronic clusters made from 16 VE? We saw previously that the neutral 16 VE $Fe(CO)_4$ fragment gave a $Fe_3(CO)_{12}$ trimer. If we go from the Fe to the Mn, the isoelectronic 16 VE fragment would be a $Mn(CO)_4^-$ fragment because Mn has one electron less than Fe. This fragment can indeed be trimerized to give a stable $Mn_3(CO)_{12}^{3-}$ cluster with a 3- charge. This charge is not too high yet to destabilize the Mn-Mn bond and the coordination number of 6 is ideal for the stability of carbonyls. We could add a ligand and remove two electrons to produce a 15 VE $Mn(CO)_5^+$ fragment. However, in this case the coordination number would become 7 upon trimerization, which is too high to produce a stable cluster. In addition, the positive charge destabilizes the Mn-C bond. Replacing Mn by Cr in $Mn(CO)_5^+$ would give a neutral 16 VE $Cr(CO)_5$ fragment, but its trimer is not stable because also in this case the coordination number becomes too high. Replacing Fe in $Fe(CO)_4$ by Co would require a 1+ charge giving a $Co(CO)_4^+$ 16 VE fragment. Its trimer would have the coordination number 6, but it would carry a 4+ charge which is too high. A $Co(CO)_3^-$ fragment would also have 16 VE, but its trimer is also not known, possibly because the

relatively small coordination number of 5, which is less favorable than a coordination number of 6. Overall we can say as a rule for the stability for carbonyl clusters that there should not be positive charges, and no high negative charges. There should not be high coordination numbers.

Clusters with 16 VE and 6 VE Fragments

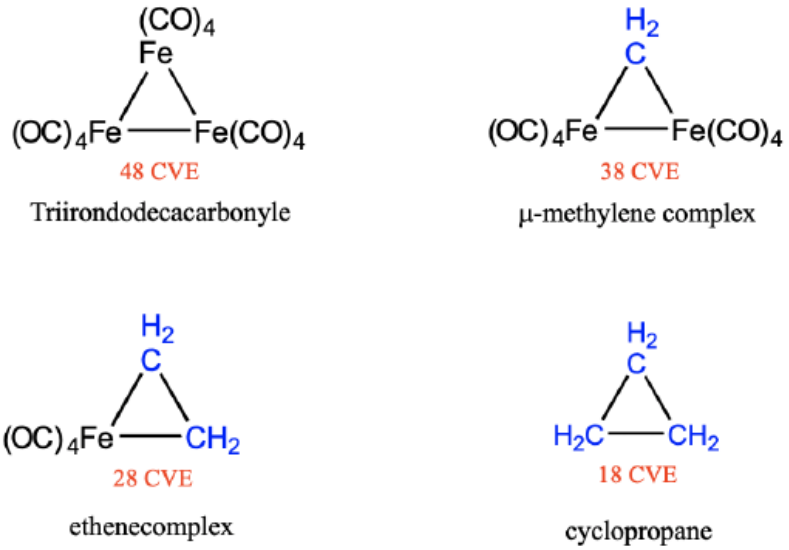


Figure 15.2.10: Clusters with 16 VE and 6 VE fragments (Attribution: W. Petz)

The cluster chemistry of carbonyls is even more versatile due to the possibility to substitute 16 and 15 VE fragments by 6 and 5 VE fragments, respectively. For instance, we can replace one 16 VE $Fe(CO)_4$ fragment by a 6 VE CH_2 fragment in the trimeric triiron dodecacarbonyl $Fe_3(CO)_{12}$ cluster (Fig. 15.2.10). In the resulting cluster a methylene group bridges two Fe atoms, therefore the complex can be regarded a μ-methylene complex. The substitution reduces the number of cluster valence electrons (CVE) from 48 to 38. A second substitution of another 16 VE tetracarbonyl iron fragment by another 6 VE methylene fragment gives a cluster with two Fe-C bonds and one carbon-carbon bond having 28 cluster valence electrons. This complex can be regarded as a ethene complex in which an ethene molecule binds side-on to a 15 VE $Fe(CO)_4$ fragment. Upon binding, the two Fe-C bonds are formed at the expense of the C-C π-bond and the bond order in the C-C bond is reduced from 2 to 1. If we substitute the last tetracarbonyl iron fragment by a third CH_2 unit, then a completely organic molecule, cyclopropane, results. All the molecules are known to be stable molecules, and their stability can be nicely understood by using the concept of isolobality.

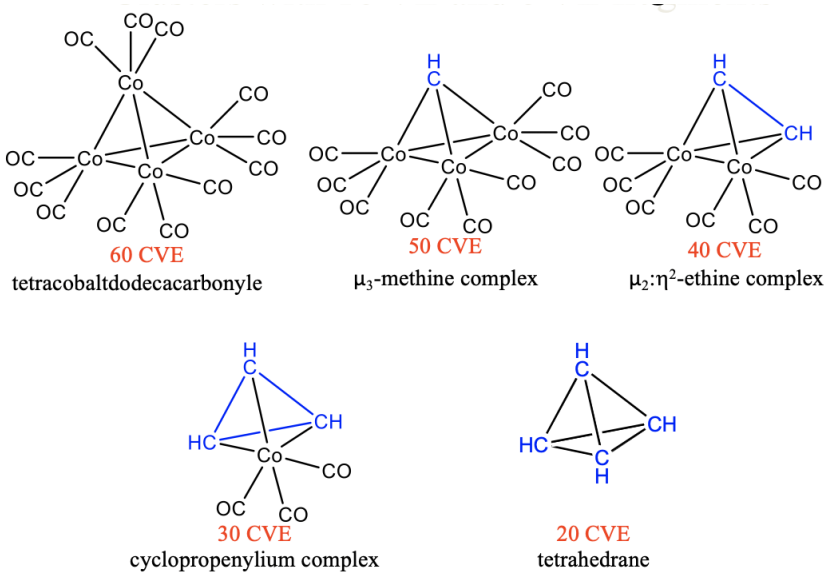


Figure 15.2.11: Clusters with 15 VE and 5 VE fragments (Attribution: W. Petz)

Similarly, we can substitute 15 VE tricarbonyl cobalt units by 5 VE CH fragments in tetracobaltdodecacarbonyl $Co_4(CO)_{12}$. A first substitution gives a 50 VE cluster with one CH fragment that makes three bonds to three $Co(CO)_4$ fragments (Fig. 15.2.11). Because the CH group bridges three metal atoms it is regarded a μ_3-methine complex. A second substitution produces a 40 VE cluster with an organic CH-CH unit that makes four bonds to two Co atoms of two 15 VE $Co(CO)_3$ fragments. The CH-CH fragment can be considered an ethine molecule binding side-on to a dicobalthexacarbonyl fragment, whereby the two π-bonds in ethine are expended to form four Co-C single bonds. The cluster can be considered a μ_2:η_2-ethine complex because the ethine bridges two Co atoms and both carbons are involved in the bonding with Co. A third substitution leads to a 30 CVE cluster with three CH units binding to one $Co(CO)_3$ fragment. There are three C-C single bonds and three Co-C bonds in the cluster. The three CH units form a cyclopropenylium complex that binds side-on to a $Co(CO)_4$ fragment. A free cyclopropenylium molecule is a 3-ring with three π-electrons that are delocalized in the ring. Therefore, the bond order in a free cyclopropenylium molecule is 1.5. In the complex the three π-electrons are being used to make the three single bonds with the cobalt atoms. The bond order in cyclopropenylium is thereby reduced from 1.5 to 1. Finally, the fourth substitution of a tricarbonyl cobalt fragment by a methine fragment yields the completely organic tetrahedrane molecule. This molecule and the others discussed before are stable. The isolobality concept lets us rationalize these complex structures easily and understand their stability.

Synthesis of Cluster Complexes From Alkynes

The view that the 40 VE clusters are alkyne clusters is not just a formal view. They can be synthesized from alkynes. For instance alkyne-dicobalt clusters are accessible from dicobalt octacarbonyl and alkynes (Fig. 15.2.12).

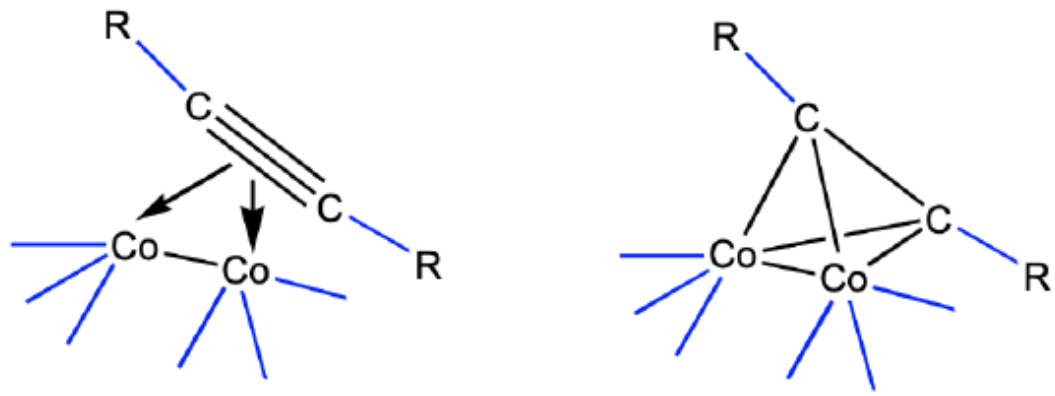
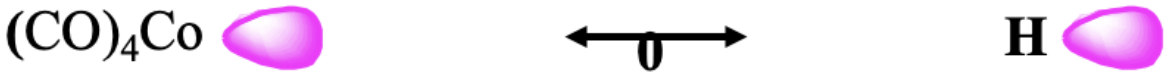


Figure 15.2.12: Synthesis of cluster complexes from alkynes (Attribution: W. Petz)

The cluster forms via the donation of the four π electrons of the alkynes into the metal d-orbitals of the dimeric cobalt carbonyl. This leads to a loss of of two CO ligands, and the formation of four Co-C bonds. Under harsher conditions the C-C triple bond can also cleave and this can give access to methine complexes.

Carbonyl Hydrides

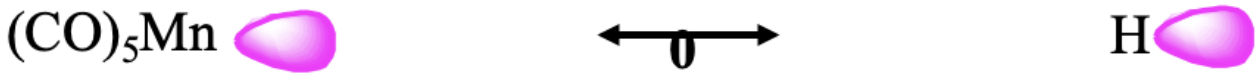
Now let us leave the carbonyl cluster compounds and talk about another interesting class of carbonyls: carbonyl hydrides. They can be rationalized by the concept of isolobality as well. A hydrogen atom can be conceived as a species with one frontier orbital containing one electron. In this case the frontier orbital is simply the 1s orbital of the hydrogen. Thus, it should be possible to combine an H atom with a 17 VE carbonyl fragment like tetracarbonyl cobalt.



$$Co_2(CO)_8 + H_2 \rightarrow 2\,HCo(CO)_4$$

Figure 15.2.13: Example for the formation of a cobalt carbonyl hydride (Attribution: W. Petz)

Indeed, one can combine such fragments to form stable carbonyl hydrides such as tetracarbonylhydrido cobalt (0). This molecule can be synthesized by reduction of bis(tetracarbonyl cobalt) (0) with dihydrogen (Fig. 15.2.13). Counter-intuitively, this molecule is a strong acid, it has an acidity similar to sulfuric acid. One would think that the Co-H bond would be polarized toward H based on electronegativity arguments. However, this is not the case. The carbonyl fragment has a frontier orbital which is energetically higher than that of H, and thus the bond is polarized toward H. In another view we can explain the high acidity be the fact that the loss of the proton leads to the very stable 18 VE tetrahedral $Co(CO)_4^-$ anion. Thus, loss of the proton occurs easily.



$$Mn_2(CO)_{10} + H_2 \xrightarrow{200\ \text{bar},\ 150^\circ\ \text{C}} 2\,(CO)_5MnH$$

Figure 15.2.14: Example for the formation of a manganese carbonyl hydride (Attribution: W. Petz)

Another 17 VE electron fragment is the $Mn(CO)_5$ fragment. Also this fragment can be combined with an isolobal H fragment to form a stable molecule, which has the composition $HMn(CO)_5$ (Fig. 15.2.14). It can be prepared from bis(pentacarbonyl manganese) and dihydrogen at 200 bar and 150°C. This carbonyl hydride is a weak acid, it has a similar acidity as H_2S. We could argue that this lower acidity may be because the loss of the proton reduces its coordination number from 6 to 5. The coordination number of 6 is the preferred coordination number for carbonyls and thus the tendency to lose the proton is relatively small. The different metal and the number of carbonyl ligands will likely lead to a different energy of the frontier orbital compared to the previous example, which leads to a different polarity.

Overall, one can tune the properties in carbonyl hydrides from highly acidic to hydridic by choice of the metal the coordination number, and also by the choice of additional ligands L other than carbonyl. The electronic and steric properties of the ligands have an influence on the energy of the HOMO of the fragment, and thus on the polarity of the metal-hydrogen bond, and the acidity.

Sources: https://en.Wikipedia.org/wiki/Isolobal_principle

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- 10.3: The Concept of Isolobality, Carbonyl Clusters, and Ligands Related to CO by Kai Landskron is licensed CC BY 4.0.

15.2.1: Extensions of the Analogy

The isolobal analogy has applications beyond simple octahedral complexes. It can be used with a variety of ligands, charged species and non-octahedral complexes.

The isolobal analogy can also be used with i**soelectronic fragments** having the same coordination number, which allows **charged species** to be considered. For example, $\mathrm{Re(CO)_5}$ is isolobal with $\mathrm{CH_3}$ and therefore, $\mathrm{[Ru(CO)_5]^+}$ and $\mathrm{[Mo(CO)_5]^-}$are also isolobal with $\mathrm{CH_3}$. Any 17-electron metal complex would be isolobal in this example.

In a similar sense, the **addition or removal of electrons from two isolobal fragments** results in two new isolobal fragments. Since $\mathrm{Re(CO)_5}$ is isolobal with $\mathrm{CH_3}$, $\mathrm{[Re(CO)_5]^+}$ is isolobal with $\mathrm{CH_3{}^+}$.

The analogy applies to other shapes besides tetrahedral and octahedral geometries. The derivations used in octahedral geometry are valid for most other geometries. The exception is square-planar because square-planar complexes typically abide by the 16-electron rule. Assuming ligands act as two-electron donors the metal center in square-planar molecules is d^8. To relate an octahedral fragment, ML_n, where M has a d^x electron configuration to a square planar analogous fragment, the formula ML_{n-2} where M has a d^{x+2} electron configuration should be followed.

Octahedral ML_n	Square Planar ML_n
$d^6:$ $\mathrm{Mo(CO)_5}$	$d^8:$ $\mathrm{[PdCl_3]^-}$
$d^8:$ $\mathrm{Os(CO)_4}$	$d^10:$ $\mathrm{Ni(PR_3)_2}$

Further examples of the isolobal analogy in various shapes and forms are shown

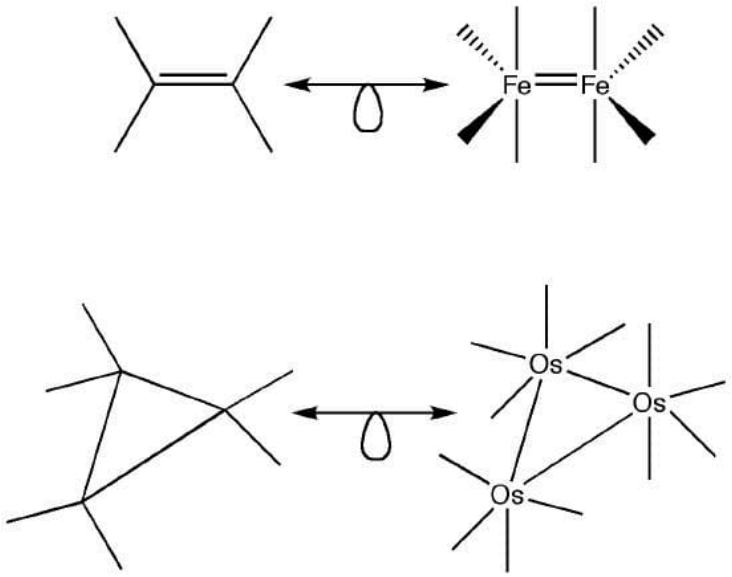


Figure 15.2.1.1: Examples of extensions of the isolobal analogy. (Public Domain; Chem507f10grp5via Wikipedia)

Sources: https://en.Wikipedia.org/wiki/Isolobal_principle

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15.2.2: Some Applications of the Isolobal Analogy

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15.3: Metal-Metal Bonds

Molecular orbital considerations in Dinuclear Metal Complexes with Multiple M-M Bonds

Let us begin a new chapter and think about dinuclear transition metal complexes with multiple metal-metal bonds. What is the maximum bond order that we could expect? The transition metals have five d-orbitals available, and in order to determine the maximum possible bond order we need to see how they overlap to form molecular orbitals (Fig. 11.1.1).

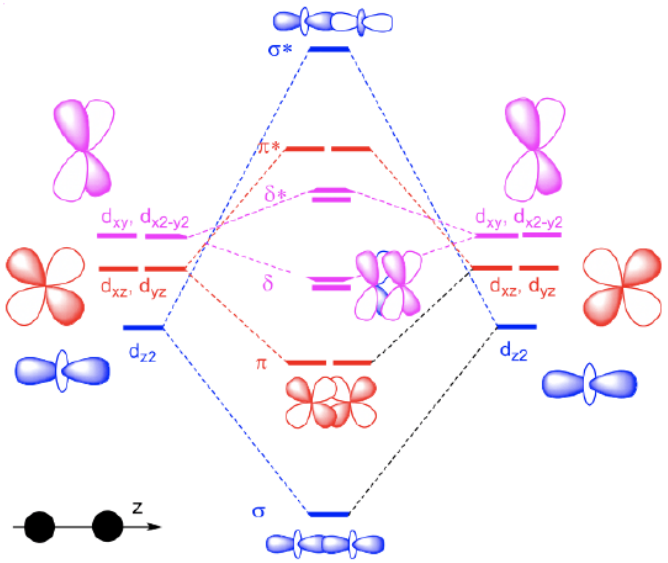


Figure 11.1.1 Molecular orbital overlap of metal d-orbitals forming M-M bonds

If we define the M-M bond axis as the z-axis, then two d_z^2-orbitals can overlap in σ-fashion to form a bonding and an anti-bonding σ-molecular orbital. A d_{xz}, and a d_{yz} can overlap with another d_{xz} and another d_{yz} in π-fashion to form two degenerated bonding π and two degenerated anti-bonding π*-orbitals. π-overlap is smaller than σ-overlap, therefore the split in energy between the bonding and the anti-bonding π-orbitals is smaller than the split between the bonding and the anti-bonding σ-orbitals. The d_{xy} orbital can overlap with another d_{xy} orbital in δ-fashion, and so can the $d_{x^2-y^2}$ with another $d_{x^2-y^2}$. This gives two bonding δ-orbitals and two anti-bonding δ-orbitals. The δ-overlap is even smaller than the π-overlap, therefore the energy split between the bonding and the anti-bonding δ-orbitals is even smaller than those for the π and π*-orbitals. So what would be the maximum bond order that could be achieved? The maximum bond order would be achieved when all bonding MOs were full, and all anti-bonding MOs were empty. We have overall five bonding MOs that we could fill with ten electrons from two metal atoms with d^5-electron configuration. The maximum bond order BO would therefore be BO=5. However, in practice only bond orders up to 4 are well known. This is because the $d_{x^2-y^2}$ orbital is usually too involved in the bonding with the ligands thereby becoming unavailable for metal-metal interactions. The $d_{x^2-y^2}$ orbital makes the strongest interactions with the ligands because most ligands approach on or near the x and the y-axes.

Electron Configurations and Multiple M-M Bonds

We can easily predict now which electron configuration leads to which metal-metal bond order. The bond order increases from 1 to 4 with the electron configuration changing from d^1 to d^4. At d^4 all bonding MOs are full with eight electrons.

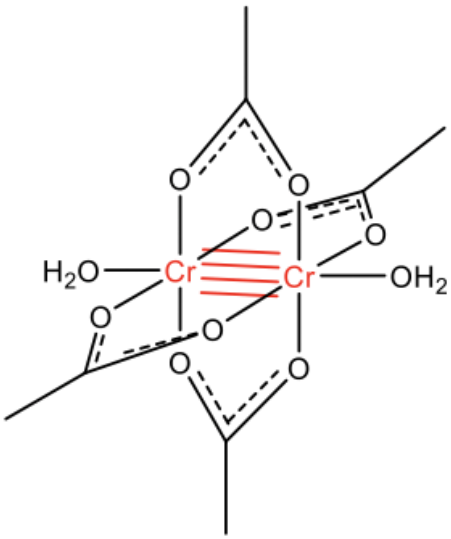


Figure 11.1.2 Tetraacetatodiaquadichromium complex

An example of a complex with a bond order of 4 is the tetraacetatodiaquadichromium complex shown (Fig. 11.1.2). Cr is in the oxidation state +2, which makes the chromium a d^4 species. We can quickly show this by counting the valence electrons. A neutral Cr atom has 6 VE, and an electron configuration $3d^5 4s^1$. There are four acetate ligands having a 1- charge each which gives four negative charges overall. The complex is overall neutral which means that each Cr must have formally a 2+ charge, and the electron configuration is $3d^4$.

d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8
1	2	3	4	3	2	1	0

Figure 11.1.3 Relationship between metal-metal bond order and electron configuration

With even more electrons in the metal d-orbitals the bond order begins to decrease again as anti-bonding MOs need to be filled (Fig. 11.1.3). The combination of two metals with d^5 electron configuration leads to a triple bond, two d^6-metals give a double bond, and two d^7 metals give a single bond. A metal-metal bond should not exist for two d^8-metals because then the bond order is zero.

Evidence for M-M Multiple Bonds

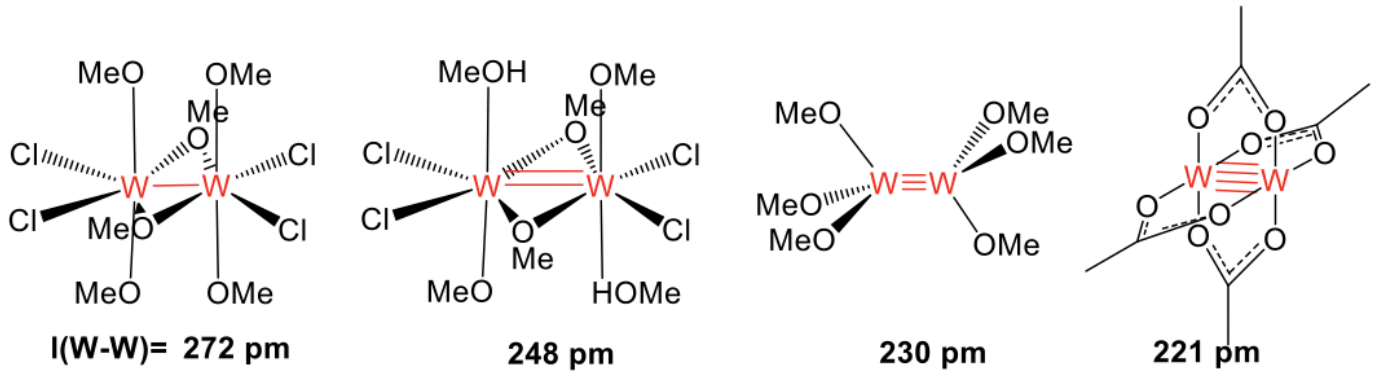


Figure 11.1.4 M-M bond length in four tungsten complexes

What experimental evidence can support the existence of a particular bond order (Fig. 11.1.4)? One argument is the bond length which can be obtained through the crystal structure determination of the complex. The shorter the bond, the higher the bond order. For instance, in the four tungsten complexes shown the bond lengths decrease from 272 pm, to 248 pm, to 230 pm to 221 pm corresponding to a single, double, triple, and quadruple bond, respectively.

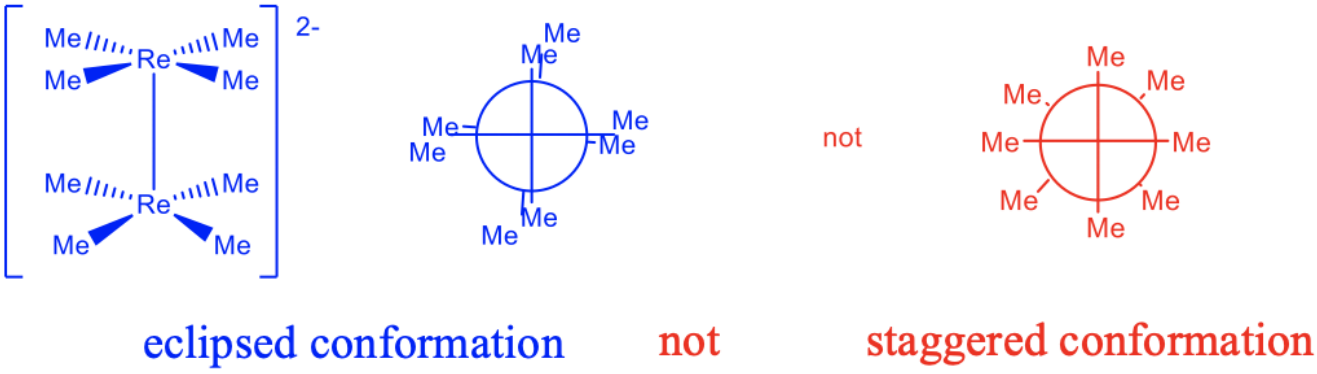


Figure 11.1.5 $ReMe_4$ confirmations

Another hint can be the conformation of a molecule (Fig. 11.1.5). For instance, the two square-planar units of the $Re_2Me_8^{2-}$ complex anion show eclipsed conformation. Steric repulsion arguments would favor the staggered conformation, so there must be a reason why the two $ReMe_4$ units are eclipsed. The rhenium is in the oxidation state +3, thus it is a d^4 species, and we would argue that there may be a Re-Re quadruple bond. This quadruple bond can only form when the d_{xy} orbitals are in eclipsed conformation, and this is only possible when the two $ReMe_4$ fragments are in eclipsed conformation. The very short bond length of 218 pm further supports the existence of the quadruple bond.

Dr. Kai Landskron (Lehigh University). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: Click Here to Donate.

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15.3.1: Metal-Metal Multiple Bonds

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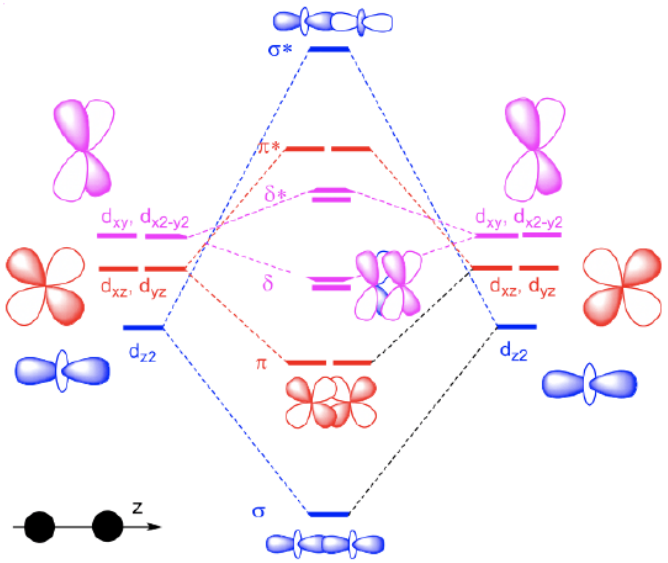


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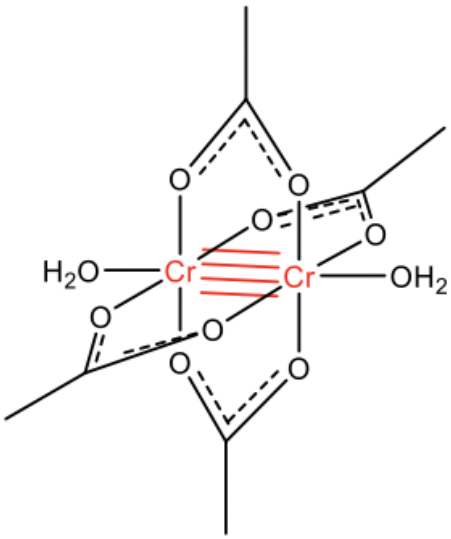


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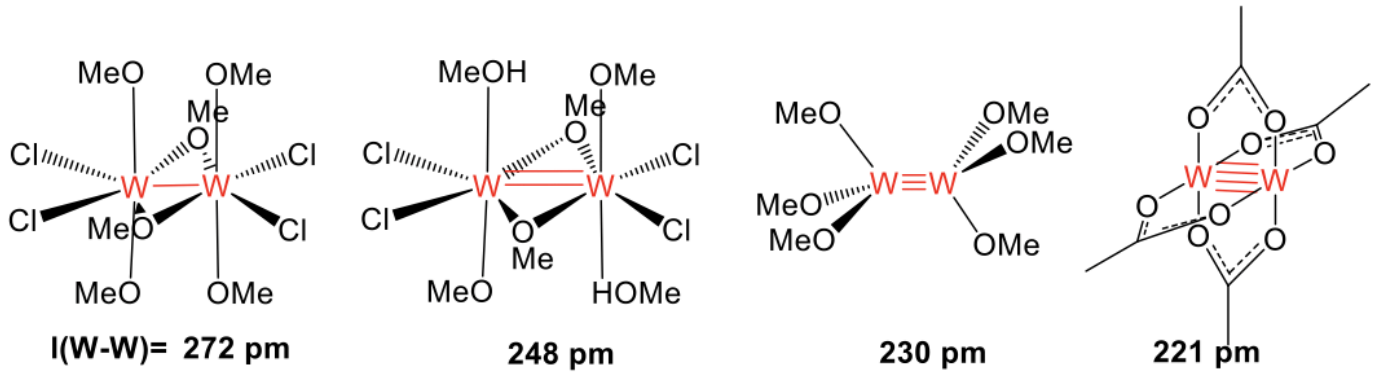


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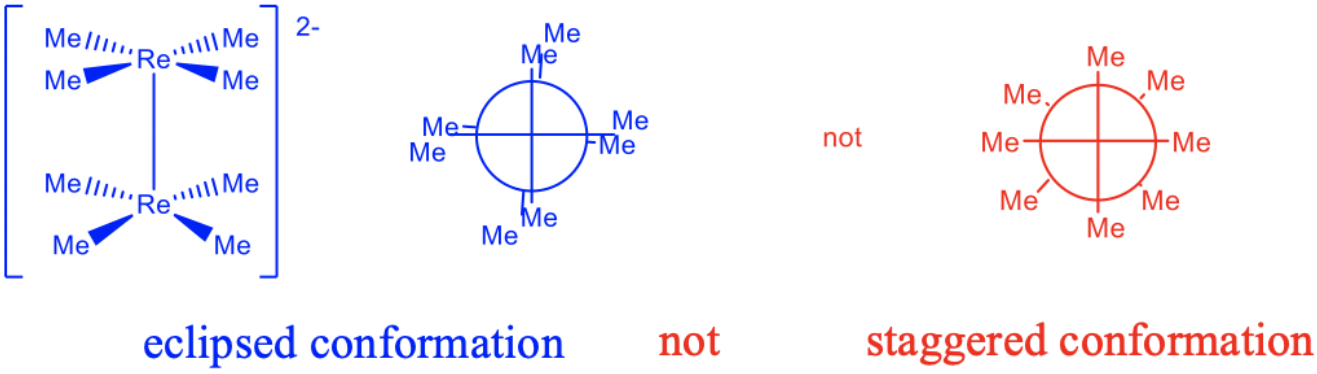


Figure 11.1.5 $ReMe_4$ confirmations

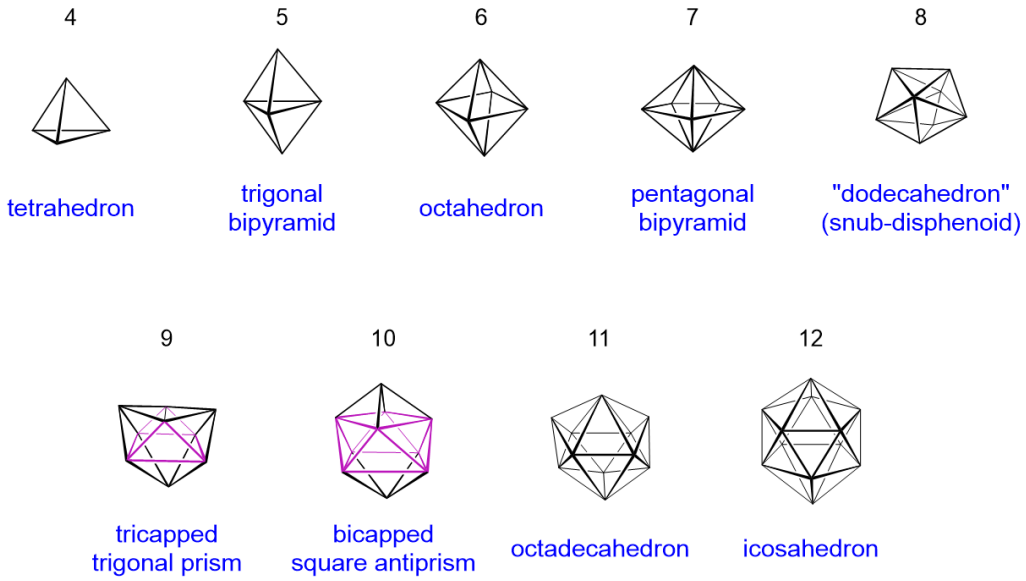
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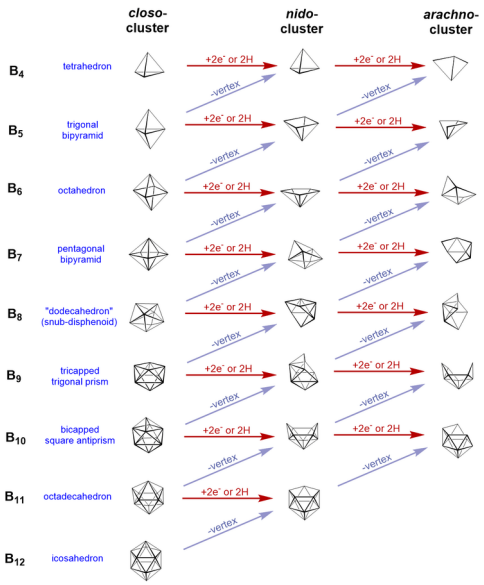
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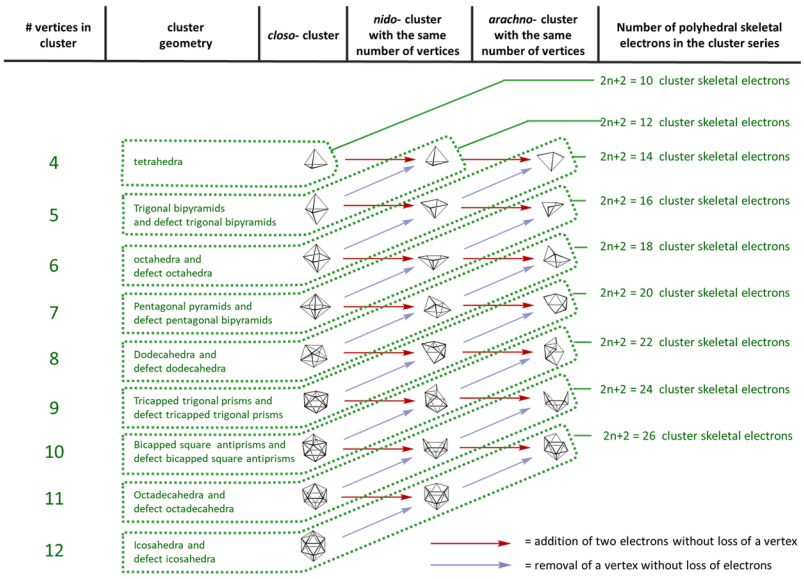
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15.4: Cluster Compounds







Notes and References

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15.4.1: Boranes

Boranes and the Bonding in boranes

Boranes were introduced in Chapter 8 (Section 8.6.1). Boranes are compounds consisting of boron and hydrogen.The most basic example is diborane (B_2H_6), all boranes are electron-deficient compounds. For B_2H_6 usually 14 electrons are needed to form 2c,2e-bonds, but only 12 valence electrons are present. Because of this there are two B-H-B bonds, which have three centers, but only two electrons (3c, 2e bond). This can be interpreted as a molecular orbital that is formed by combining the contributed atomic orbitals of the three atoms. In more complicated boranes not only B-H-B bonds but also B-B-B 3c, 2e-bonds occur. In such a bond the three B-atoms lie at the corners of an equilateral triangle with their sp^3 hybrid orbitals overlapping at its center. One of the common properties of boranes is, that they are flammable or react spontaneously with air. They burn with a characteristic green flame. And they are colorless, diamagnetic substances.

Nomenclature

In neutral boranes the number of boron atoms is given by a prefix and the number of Hydrogen-atoms is given in parentheses behind the name. example: B_5H_{11} -> pentaborane(11), B_4H_{10} -> tetraborane(10) For ions primarily the number of hydrogen-atoms and than the number of boron-atoms is given, behind the name the charge is given in parentheses. example: $[B_6H_6]^{2-}$ -> hexahydrohexaborat(2-)

Wades rule, Structures of boranes

Wades rule helps to predict the general shape of a borane from its formula. Ken Wade developed a method for the prediction of shapes of borane clusters; however, it may be used for a wide range of substituted boranes (such as carboranes) as well as other classes of cluster compounds. Wade's rules are used to rationalize the shape of borane clusters by calculating the total number of skeletal electron pairs (SEP) available for cluster bonding. In using Wade's rules it is key to understand structural relationship of various boranes.

Wade's rules:

The general methodology to be followed when applying Wade's rules is as follows:

I. First, find the number of skeletal electron pairs

1. Determine the total number of valence electrons from the chemical formula, i.e., 3 electrons per B, and 1 electron per H.
2. Subtract 2 electrons for each vertex unit (B-H, C-H in a carborane, etc.).
3. Divide the number of remaining electrons by 2 to get the number of skeletal electron pairs (SEP).

II. Then determine the number of vertices in the parent deltahedron, *n*, from the number of SEP.

n = vertices in the parent deltahedron = SEP -1

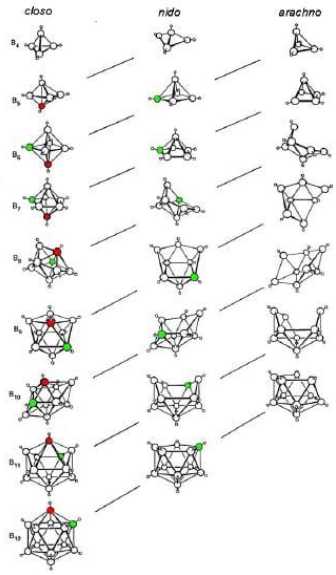
III. Finally, determine whether the cluster is *closo*-, *nido*-, *arachno*-, *hypho*-, *klado*-, or otherwise by comparing the number of vertex atoms with those in the parent deltahedron.

1. When *n* vertex atoms are present (i.e., *n* boron atoms) the cluster has a *closo*- structure, specifically that of the parent deltahedron.
2. When *n*-1 vertex atoms are present (i.e., *n* boron atoms) the cluster has a *nido* structure.
3. When *n*-2 vertex atoms are present (i.e., *n* boron atoms) the cluster has a *arachno* structure.
4. When *n*-3 vertex atoms are present (i.e., *n* boron atoms) the cluster has a *hypho* structure.
5. When *n*-4 vertex atoms are present (i.e., *n* boron atoms) the cluster has a *klado* structure.

6. If there are more vertex atoms than are vertices present in the parent deltahedron then the extra boron occupies a capping position on a triangular face.

Formula Skeletal	Skeletal electron pairs	type
$[\mathrm{B}_n\ \mathrm{H}_n]^{2-}$	n+1	closo
$\mathrm{B}_n\ \mathrm{H}_{n+4}$	n+2	nido
$\mathrm{B}_n\ \mathrm{H}_{n+6}$	n+3	arachno
$\mathrm{B}_n\ \mathrm{H}_{n+8}$	n+4	hype

The polyhedra are always made up of triangular faces, so they are called **deltahedra**. Usually there are three possible structure types:



*Structural relationship between closo, nido, and arachno boranes (and hetero-substituted boranes). The diagonal lines connect species that have the same number of skeletal electron pairs (SEP). Hydrogen atoms except those of the B-H framework are omitted. The red atom is omitted first, the green atom removed second. Adapted from R. W. Rudolph, Acc. Chem. Res., 1976, **9**, 446.*

Closo-boranes

- closed deltahedra without B-H-B 3c,2e-bonds
- thermally stable and moderately reactive.
- example: $[\mathrm{B}_5\mathrm{H}_5]^{2-}$: the ion builds up a trigonal, bipyramidal polyhedron

Nido-boranes

- closo borane with one corner less and addition of two hydrogen-atoms instead
- B-H-B-bonds and B-B-bonds are possible.
- thermally stability lies between closo- and arachno-boranes.
- example: $\mathrm{B}_5\mathrm{H}_9$ its structure can be assumed as the octahedral deltahedron of $[\mathrm{B}_6\mathrm{H}_6]^{2-}$ without one corner tetragonal pyramid

Arachno-boranes

- closo borane deltahedron but with two BH-units removed and two H-atoms added.

- it has to have B-H-B 3c, 2e-bonds.
- thermally unstable at room temperature and highly reactive.
- example: \{\ce{B4H10}\} the structure can be derived from $[B_6H_6]^{2-}$ -> deltahedron with two corners less.

There exist also other structures like the hypho-boranes, but they are less important.

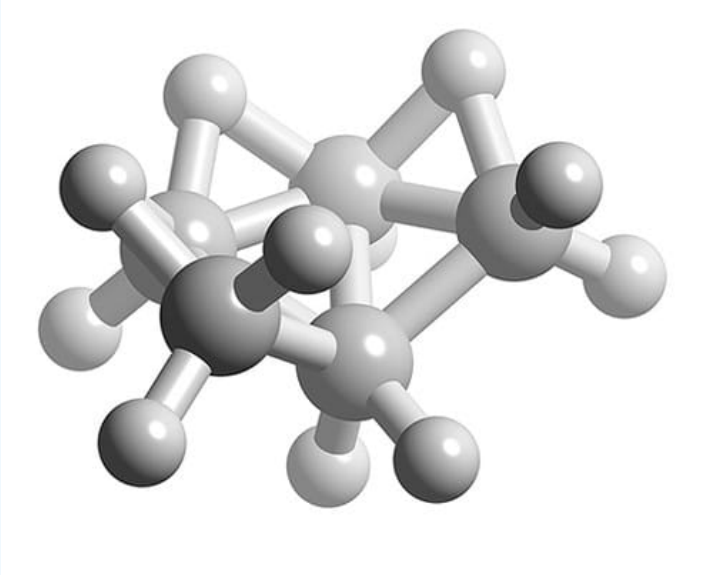
Wade's Rules

Example 15.4.1.1: B_5H_{11}

What is the structure of B_5H_{11}?

Solution

1. Total number of valence electrons = (5 x B) + (11 x H) = (5 x 3) + (11 x 1) = 26
2. Number of electrons for each B-H unit = (5 x 2) = 10
3. Number of skeletal electrons = 26 – 10 = 16
4. Number SEP = 16/2 = 8
5. If *n*+1 = 8 and *n*-2 = 5 boron atoms, then *n* = 7
6. Structure of *n* = 7 is pentagonal bipyramid, therefore B_5H_{11} is an *arachno* based upon a pentagonal bipyramid with two apexes missing.



Ball and stick representation of the structure of B_5H_{11}.

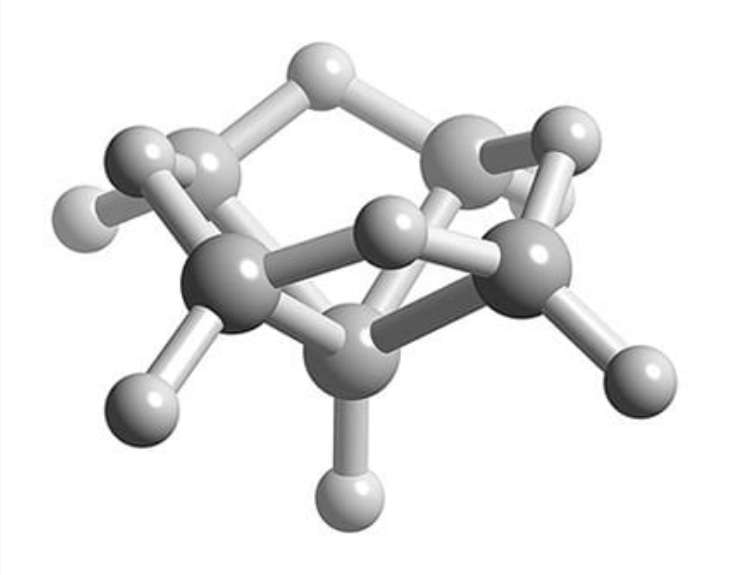
Example 15.4.1.2: B_5H_9?

What is the structure of B_5H_9?

Solution

1. Total number of valence electrons = (5 x B) + (9 x H) = (5 x 3) + (9 x 1) = 24
2. Number of electrons for each B-H unit = (5 x 2) = 10
3. Number of skeletal electrons = 24 – 10 = 14
4. Number SEP = 14/2 = 7
5. If *n*+1 = 7 and *n*-1 = 5 boron atoms, then *n* = 6

6. Structure of n = 6 is octahedral, therefore B_5H_9 is a *nido* structure based upon an octahedral structure with one apex missing.

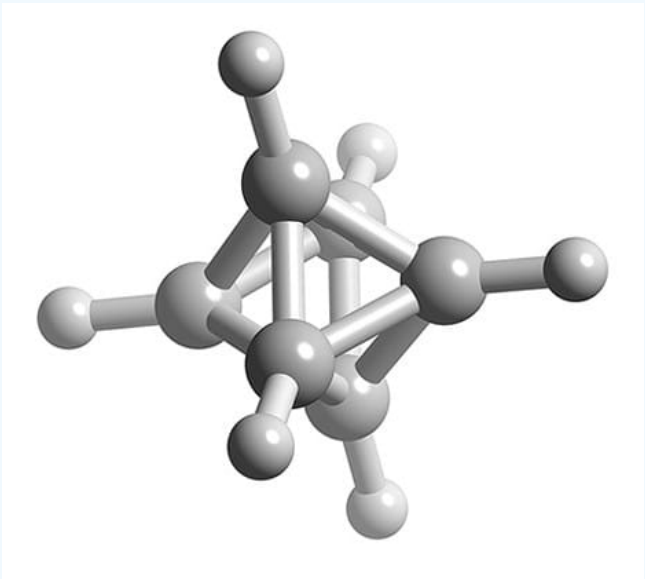


Ball and stick representation of the structure of B_5H_9.

Example 15.4.1.3: $B_6H_6^{2-}$

What is the structure of $B_6H_6^{2-}$?

1. Total number of valence electrons = (6 x B) + (3 x H) = (6 x 3) + (6 x 1) + 2 = 26
2. Number of electrons for each B-H unit = (6 x 2) = 12
3. Number of skeletal electrons = 26 – 12 = 14
4. Number SEP = 14/2 = 7
5. If n+1 = 7 and n boron atoms, then n = 6
6. Structure of n = 6 is octahedral, therefore $B_6H_6^{2-}$ is a *closo* structure based upon an octahedral structure.

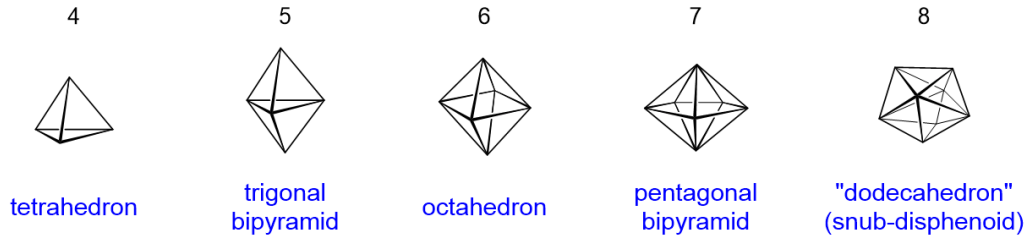


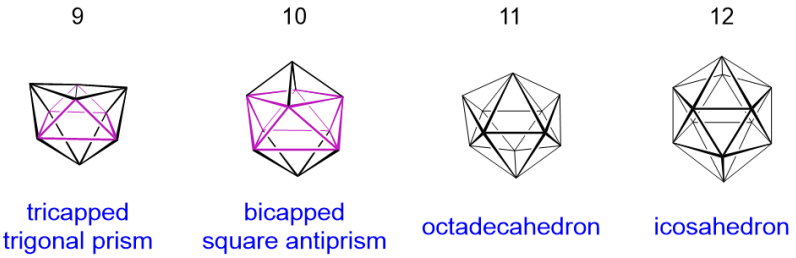
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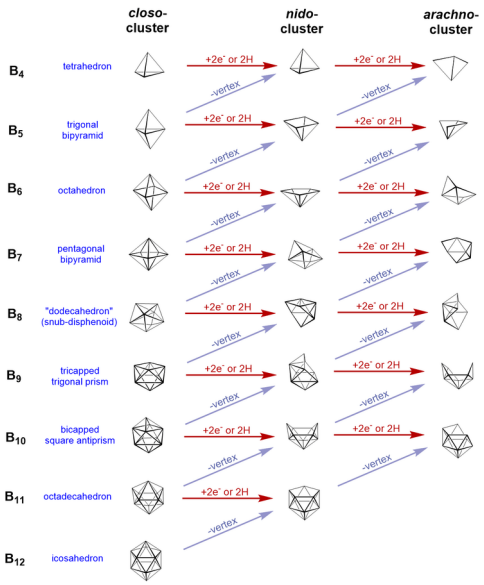
Table 15.4.1.1 provides a summary of borane cluster with the general formula $B_nH_n^{x-}$ and their structures as defined by Wade's rules.

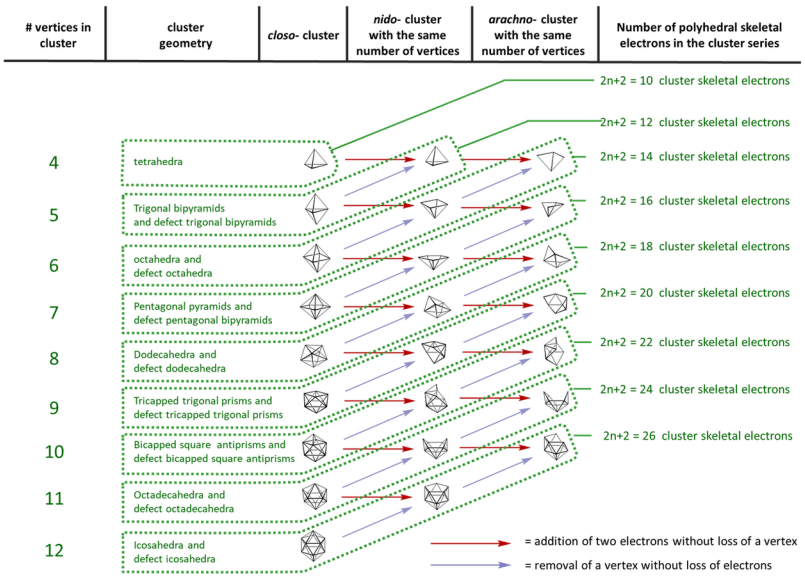
Table 15.4.1.1: Wade's rules for boranes.

Type	Basic formula	Example	# of verticies	# of vacancies	# of e- in B + charge	# of bonding MOs
Closo	$B_nH_n^{2-}$	$B_6H_6^{2-}$	n	0	3n + 2	n + 1
Nido	$B_nH_n^{4-}$	B_5H_9	n + 1	1	3n + 4	n + 2
Arachno	$B_nH_n^{6-}$	B_4H_{10}	n + 2	2	3n + 6	n + 3
Hypho	$B_nH_n^{8-}$	$B_5H_{11}^{2-}$	n + 3	3	3n + 8	n + 4









Notes and References

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K. Wade, *Adv. Inorg. Chem. Radiochem.*, 1976, **18**, 1.

D. F. Shriver, P. W. Atkins, Inorganic Chemistry Third edition, Oxford University Press, 2001

Patrick O' Malley from the University of Manchester via Wolearn.org (https://www.wolearn.org/pluginfile.php/1492/mod_resource/content/1/Wades_Rules.pdf)

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17.3B: Hemocyanin

Hemocyanin is used for oxygen transport in many arthropods (spiders, crabs, lobsters, and centipedes) and in mollusks (shellfish, octopi, and squid); it is responsible for the bluish-green color of their blood. The protein is a polymer of subunits that each contain two copper atoms (rather than iron), with an aggregate molecular mass of greater than 1,000,000 amu. Deoxyhemocyanin contains two Cu^{+} ions per subunit and is colorless, whereas oxyhemocyanin contains two Cu^{2+} ions and is bright blue. As with hemerythrin, the binding and release of O_2 correspond to a two-electron reaction:

$$2\,Cu^{+} + O_2 \rightleftharpoons Cu^{2+}{-}{O_2}^{2-}{-}Cu^{2+} \tag{17.3B.1}$$

Although hemocyanin and hemerythrin perform the same basic function as hemoglobin, these proteins are not interchangeable. In fact, hemocyanin is so foreign to humans that it is one of the major factors responsible for the common allergies to shellfish.

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17.3C: Hemerythrin

Hemerythrin is used to transport O_2 in a variety of marine invertebrates. It is an octamer (eight subunits), with each subunit containing two iron atoms and binding one molecule of O_2. Deoxyhemerythrin contains two Fe^{2+} ions per subunit and is colorless, whereas oxyhemerythrin contains two Fe^{3+} ions and is bright reddish violet. These invertebrates also contain a monomeric form of hemerythrin that is located in the tissues, analogous to myoglobin. The binding of oxygen to hemerythrin and its release can be described by the following reaction, where the HO_2^- ligand is the hydroperoxide anion derived by the deprotonation of hydrogen peroxide (H_2O_2):

$$2\,Fe^{2+} + O_2 + H^+ \rightleftharpoons 2\,Fe^{3+}{-}O_2H \tag{17.3C.1}$$

Thus O_2 binding is accompanied by the transfer of two electrons (one from each Fe^{2+}) and a proton to O_2.

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