CHEM 325: INORGANIC CHEMISTRY



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Chem 325: Inorganic Chemistry

Joya Cooley

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Detailed Licensing

Licensing

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CHAPTER OVERVIEW

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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.

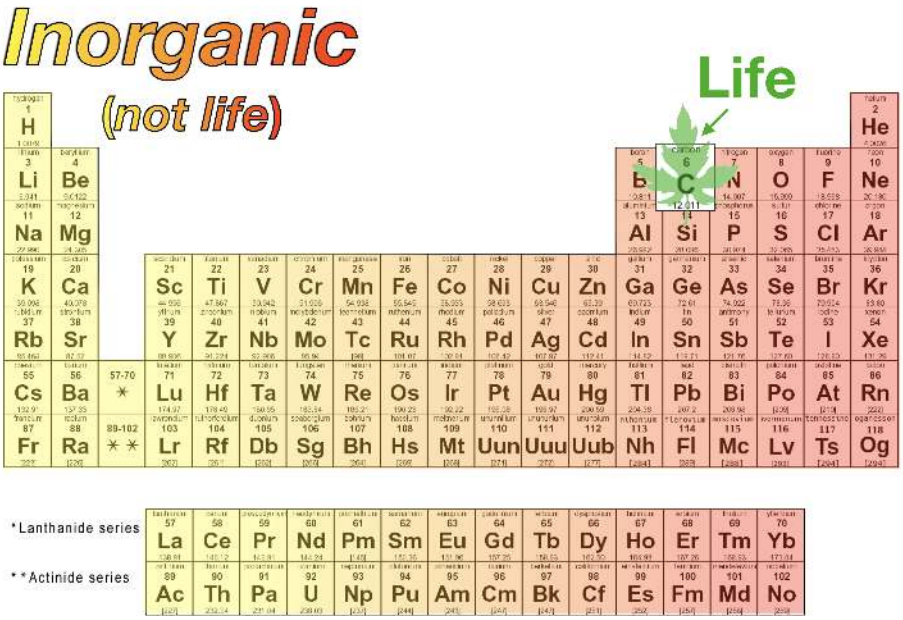


Figure 1.1.1. An illustration of the historic meaning of "organic" and "inorganic". The modern understanding of organic and inorganic chemistry is not consistent with these historical meanings.

External links:

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

Practice

What are the Sub-Fields of Inorganic Chemistry?

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

Answer

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

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1.2: The Nuclear Atom

Learning Objectives

- To become familiar with the components and structure of the atom.

Dissecting the Atom

Once scientists concluded that all matter contains negatively charged electrons, it became clear that atoms, which are electrically neutral, must also contain positive charges to balance the negative ones. Thomson proposed that the electrons were embedded in a uniform sphere that contained both the positive charge and most of the mass of the atom, much like raisins in plum pudding or chocolate chips in a cookie (Figure 2.3.1).

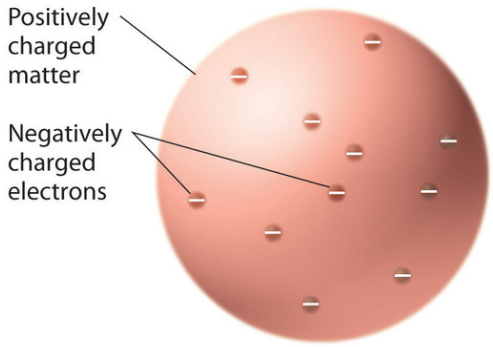


Figure 2.3.1: Thomson's Plum Pudding or Chocolate Chip Cookie Model of the Atom. In this model, the electrons are embedded in a uniform sphere of positive charge.

In a single famous experiment, however, Rutherford showed unambiguously that Thomson's model of the atom was incorrect. Rutherford aimed a stream of α particles at a very thin gold foil target (part (a) in Figure 2.3.2) and examined how the α particles were scattered by the foil. Gold was chosen because it could be easily hammered into extremely thin sheets, minimizing the number of atoms in the target. If Thomson's model of the atom were correct, the positively-charged α particles should crash through the uniformly distributed mass of the gold target like cannonballs through the side of a wooden house. They might be moving a little slower when they emerged, but they should pass essentially straight through the target (part (b) in Figure 2.3.2). To Rutherford's amazement, a small fraction of the α particles were deflected at large angles, and some were reflected directly back at the source (part (c) in Figure 2.3.2). According to Rutherford, "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."

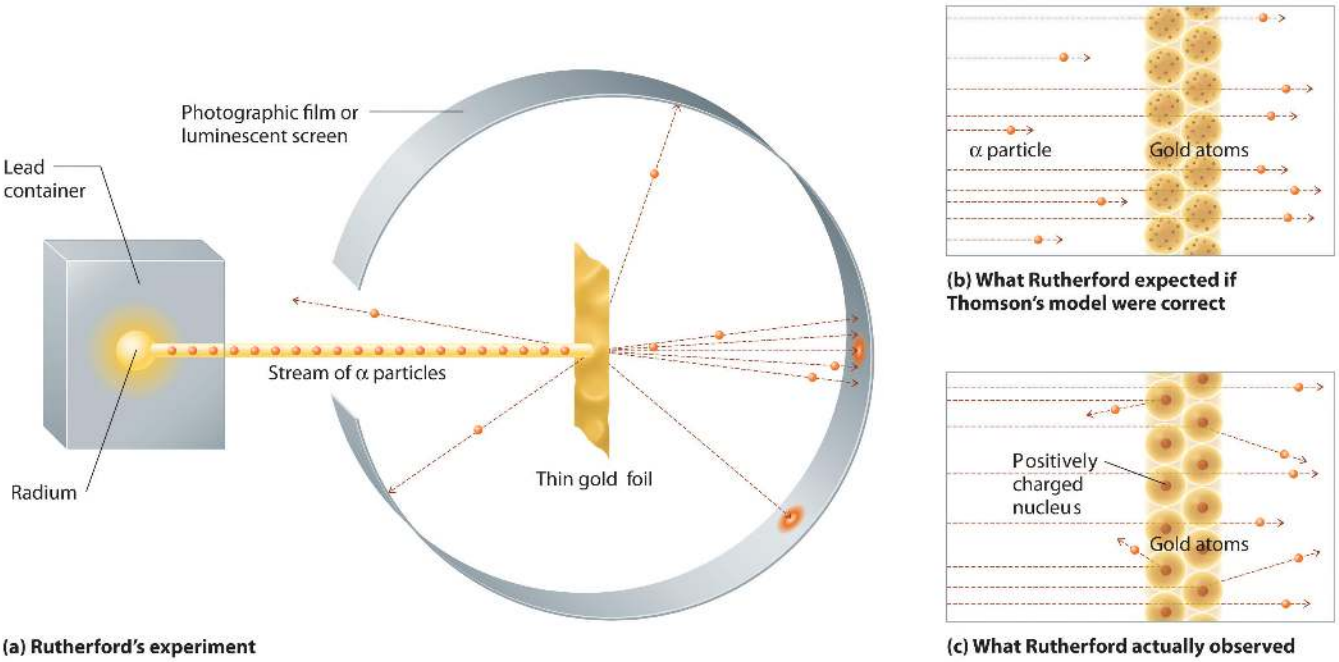


Figure 2.3.2: A Summary of Rutherford's Experiments. (a) A representation of the apparatus Rutherford used to detect deflections in a stream of α particles aimed at a thin gold foil target. The particles were produced by a sample of radium. (b) If Thomson's model of the atom were correct, the α particles should have passed straight through the gold foil. (c) However, a small number of α particles were deflected in various directions, including right back at the source. This could be true only if the positive charge were much more massive than the α particle. It suggested that the mass of the gold atom is concentrated in a very small region of space, which he called the nucleus.

Rutherford's results were not consistent with a model in which the mass and positive charge are distributed uniformly throughout the volume of an atom. Instead, they strongly suggested that both the mass and positive charge are concentrated in a tiny fraction of the volume of an atom, which Rutherford called the nucleus. It made sense that a small fraction of the α particles collided with the dense, positively charged nuclei in either a glancing fashion, resulting in large deflections, or almost head-on, causing them to be reflected straight back at the source.

Although Rutherford could not explain why repulsions between the positive charges in nuclei that contained more than one positive charge did not cause the nucleus to disintegrate, he reasoned that repulsions between negatively charged electrons would cause the electrons to be uniformly distributed throughout the atom's volume.Today it is known that strong nuclear forces, which are much stronger than electrostatic interactions, hold the protons and the neutrons together in the nucleus. For this and other insights, Rutherford was awarded the Nobel Prize in Chemistry in 1908. Unfortunately, Rutherford would have preferred to receive the Nobel Prize in Physics because he considered physics superior to chemistry. In his opinion, "All science is either physics or stamp collecting."

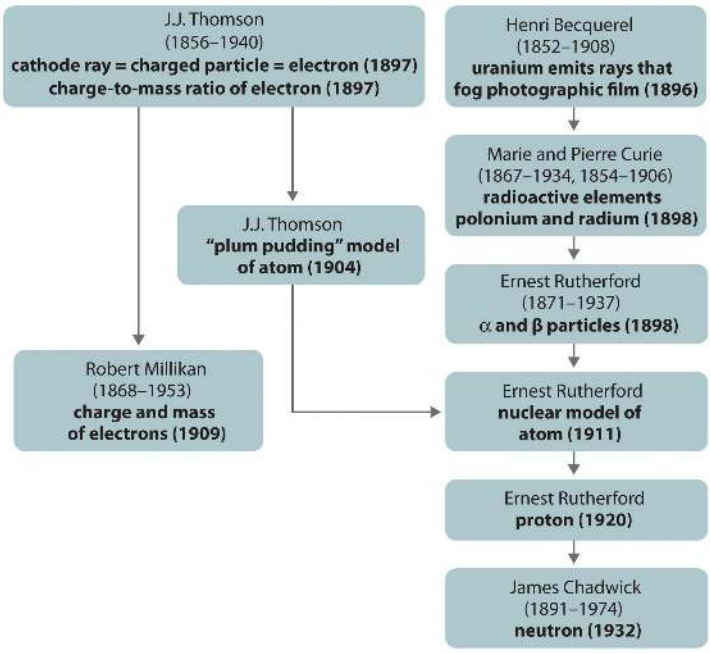


Figure 2.3.3: A Summary of the Historical Development of Models of the Components and Structure of the Atom. The dates in parentheses are the years in which the key experiments were performed.

The historical development of the different models of the atom's structure is summarized in Figure 2.3.3. Rutherford established that the nucleus of the hydrogen atom was a positively charged particle, for which he coined the name proton in 1920. He also suggested that the nuclei of elements other than hydrogen must contain electrically neutral particles with approximately the same mass as the proton. The neutron, however, was not discovered until 1932, when James Chadwick (1891–1974, a student of Rutherford; Nobel Prize in Physics, 1935) discovered it. As a result of Rutherford's work, it became clear that an α particle contains two protons and neutrons, and is therefore the nucleus of a helium atom.

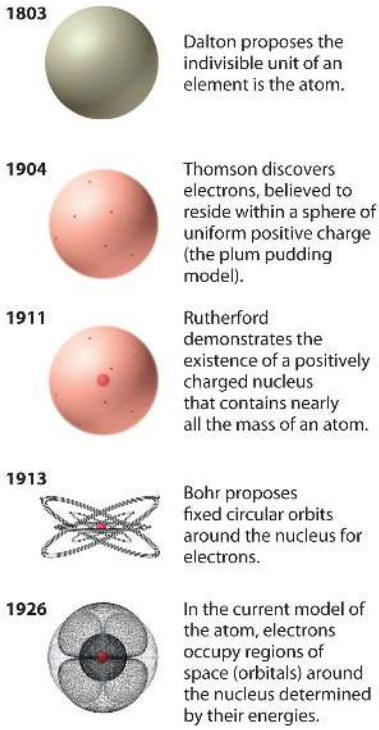


Figure 2.3.4: The Evolution of Atomic Theory, as Illustrated by Models of the Oxygen Atom. Bohr's model and the current model are described in Chapter 6, "The Structure of Atoms."

Rutherford's model of the atom is essentially the same as the modern model, except that it is now known that electrons are not uniformly distributed throughout an atom's volume. Instead, they are distributed according to a set of principles described by Quantum Mechanics. Figure 2.3.4 shows how the model of the atom has evolved over time from the indivisible unit of Dalton to the modern view taught today.

The Nuclear Atom

The precise physical nature of atoms finally emerged from a series of elegant experiments carried out between 1895 and 1915. The most notable of these achievements was Ernest Rutherford's famous 1911 alpha-ray scattering experiment, which established that

- Almost all of the *mass* of an atom is contained within a tiny (and therefore extremely dense) *nucleus* which carries a positive electric charge whose value identifies each element and is known as the *atomic number* of the element.
- Almost all of the *volume* of an atom consists of empty space in which electrons, the fundamental carriers of negative electric charge, reside. The extremely small mass of the electron (1/1840 the mass of the hydrogen nucleus) causes it to behave as a quantum particle, which means that its location at any moment cannot be specified; the best we can do is describe its behavior in terms of the probability of its manifesting itself at any point in space. It is common (but somewhat misleading) to describe the volume of space in which the electrons of an atom have a significant probability of being found as the *electron cloud*. The latter has no definite outer boundary, so neither does the atom. The radius of an atom must be defined arbitrarily, such as the boundary in which the electron can be found with 95% probability. Atomic radii are typically 30-300 pm.

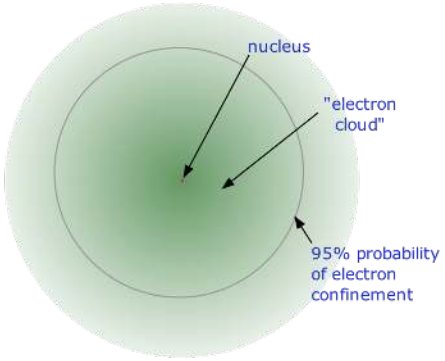


Figure 2.3.5: The structure of the nuclear atom with a central nucleus and surrounding electrons.

The nucleus is itself composed of two kinds of particles. *Protons* are the carriers of positive electric charge in the nucleus; the proton charge is exactly the same as the electron charge, but of opposite sign. This means that in any [electrically neutral] atom, the number of protons in the nucleus (often referred to as the *nuclear charge*) is balanced by the *same* number of electrons outside the nucleus.

The other nuclear particle is the *neutron*. As its name implies, this particle carries no electrical charge. Its mass is almost the same as that of the proton. Most nuclei contain roughly equal numbers of neutrons and protons, so we can say that these two particles together account for almost all the mass of the atom.

Note

Because the electrons of an atom are in contact with the outside world, it is possible for one or more electrons to be lost, or some new ones to be added. The resulting electrically-charged atom is called an *ion*.

Atoms consist of electrons, protons, and neutrons. This is an oversimplification that ignores the other subatomic particles that have been discovered, but it is sufficient for discussion of chemical principles. Some properties of these subatomic particles are summarized in Table 2.3.1 which illustrates three important points:

1. Electrons and protons have electrical charges that are identical in magnitude but opposite in sign. Relative charges of −1 and +1 are assigned to the electron and proton, respectively.
2. Neutrons have approximately the same mass as protons but no charge. They are electrically neutral.
3. The mass of a proton or a neutron is about 1836 times greater than the mass of an electron. Protons and neutrons constitute the bulk of the mass of atoms.

The discovery of the electron and the proton was crucial to the development of the modern model of the atom and provides an excellent case study in the application of the scientific method. In fact, the elucidation of the atom's structure is one of the greatest detective stories in the history of science.

Table 2.3.1: Properties of Subatomic Particles*

Particle	Mass (g)	Atomic Mass (amu)	Electrical Charge (coulombs)	Relative Charge
electron	9.109×10^{-28}	0.0005486	−1.602 × 10−19	−1
neutron	1.675×10^{-24}	1.008665	0	0
proton	1.673×10^{-24}	1.007276	+1.602 × 10−19	+1

* For a review of using scientific notation and units of measurement, see Essential Skills 1 (Section 1.9 "Essential Skills 1").

Summary

- The atom consists of discrete particles that govern its chemical and physical behavior.

Atoms, the smallest particles of an element that exhibit the properties of that element, consist of negatively charged electrons around a central nucleus composed of more massive positively charged protons and electrically neutral neutrons. Radioactivity is the emission of energetic particles and rays (radiation) by some substances. Three important kinds of radiation are α particles (helium nuclei), β particles (electrons traveling at high speed), and γ rays (similar to x-rays but higher in energy).

Conceptual Problems

1. Describe the experiment that provided evidence that the proton is positively charged.
2. What observation led Rutherford to propose the existence of the neutron?
3. What is the difference between Rutherford's model of the atom and the model chemists use today?
4. If cathode rays are not deflected when they pass through a region of space, what does this imply about the presence or absence of a magnetic field perpendicular to the path of the rays in that region?
5. Describe the outcome that would be expected from Rutherford's experiment if the charge on α particles had remained the same but the nucleus were negatively charged. If the nucleus were neutral, what would have been the outcome?
6. Describe the differences between an α particle, a β particle, and a γ ray. Which has the greatest ability to penetrate matter?

Problems

Please be sure you are familiar with the topics discussed in Essential Skills 1 (Section 1.9 "Essential Skills 1") before proceeding to the Numerical Problems.

1. Using the data in Table 1.3 "Properties of Subatomic Particles*" and the periodic table (see Chapter 32 "Appendix H: Periodic Table of Elements"), calculate the percentage of the mass of a silicon atom that is due to

    a. electrons.

    b. protons.

2. Using the data in Table 1.3 "Properties of Subatomic Particles*" and the periodic table (see Chapter 32 "Appendix H: Periodic Table of Elements"), calculate the percentage of the mass of a helium atom that is due to

    a. electrons.

    b. protons.

3. The radius of an atom is approximately 10^4 times larger than the radius of its nucleus. If the radius of the nucleus were 1.0 cm, what would be the radius of the atom in centimeters? in miles?
4. The total charge on an oil drop was found to be 3.84×10^{-18} coulombs. What is the total number of electrons contained in the drop?

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1.3: Chemical Elements

Learning Objectives

- To know the meaning of isotopes and atomic masses.

To date, about 115 different elements have been discovered; by definition, each is chemically unique. To understand why they are unique, you need to understand the structure of the atom (the fundamental, individual particle of an element) and the characteristics of its components. In most cases, the symbols for the elements are derived directly from each element's name, such as C for carbon, U for uranium, Ca for calcium, and Po for polonium. Elements have also been named for their properties [such as radium (Ra) for its radioactivity], for the native country of the scientist(s) who discovered them [polonium (Po) for Poland], for eminent scientists [curium (Cm) for the Curies], for gods and goddesses [selenium (Se) for the Greek goddess of the moon, Selene], and for other poetic or historical reasons. Some of the symbols used for elements that have been known since antiquity are derived from historical names that are no longer in use; only the symbols remain to indicate their origin. Examples are Fe for iron, from the Latin *ferrum*; Na for sodium, from the Latin *natrium*; and W for tungsten, from the German *wolfram*. Examples are in Table **1.3.1**.

Table **1.3.1**: Element Symbols Based on Names No Longer in Use

Element	Symbol	Derivation	Meaning
antimony	Sb	stibium	Latin for "mark"
copper	Cu	cuprum	from Cyprium, Latin name for the island of Cyprus, the major source of copper ore in the Roman Empire
gold	Au	aurum	Latin for "gold"
iron	Fe	ferrum	Latin for "iron"
lead	Pb	plumbum	Latin for "heavy"
mercury	Hg	hydrargyrum	Latin for "liquid silver"
potassium	K	kalium	from the Arabic al-qili, "alkali"
silver	Ag	argentum	Latin for "silver"
sodium	Na	natrium	Latin for "sodium"
tin	Sn	stannum	Latin for "tin"
tungsten	W	wolfram	German for "wolf stone" because it interfered with the smelting of tin and was thought to devour the tin

Atomic Number (Z)

What single parameter uniquely characterizes the atom of a given element? It is not the atom's relative mass, as we will see in the section on isotopes below. It is, rather, the number of protons in the nucleus, which we call the *atomic number* and denote by the symbol *Z*. Each proton carries an electric charge of +1, so the atomic number also specifies the electric charge of the nucleus. In the neutral atom, the *Z protons* within the nucleus are balanced by *Z electrons* outside it.

Henry Moseley

Atomic numbers were first worked out in 1913 by Henry Moseley, a young member of Rutherford's research group in Manchester. Moseley searched for a measurable property of each element that increases linearly with atomic number. He found this in a class of X-rays emitted by an element when it is bombarded with electrons. The frequencies of these X-rays are unique to each element, and they increase uniformly in successive elements. Moseley found that the square roots of these frequencies give a straight line when plotted against Z; this enabled him to sort the elements in order of increasing atomic number.



You can think of the atomic number as a kind of serial number of an element, commencing at 1 for hydrogen and increasing by one for each successive element. The chemical name of the element and its symbol are uniquely tied to the atomic number; thus the symbol "Sr" stands for strontium, whose atoms all have $Z = 38$.

Mass number (A)

This is just the sum of the numbers of protons and neutrons in the nucleus. It is sometimes represented by the symbol *A*, so

$$A = Z + N \tag{1.3.1}$$

in which *Z* is the atomic number and *N* is the *neutron number*.

Nuclides and their Symbols

The term *nuclide* simply refers to any particular kind of nucleus. For example, a nucleus of atomic number 7 is a nuclide of nitrogen. Any nuclide is characterized by the pair of numbers (*Z* ,*A*). The element symbol depends on *Z* alone, so the symbol ^{26}Mg is used to specify the mass-26 nuclide of manganese, whose name implies *Z*=12. A more explicit way of denoting a particular kind of nucleus is to add the atomic number as a subscript. Of course, this is somewhat redundant, since the symbol Mg **always** implies *Z*=12, but it is sometimes a convenience when discussing several nuclides.

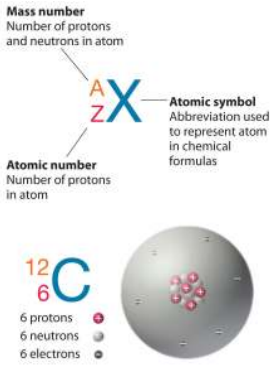


Figure **1.3.2**: Formalism used for identifying specific nuclide (any particular kind of nucleus)

The element carbon (C) has an atomic number of 6, which means that all neutral carbon atoms contain 6 protons and 6 electrons. In a typical sample of carbon-containing material, 98.89% of the carbon atoms also contain 6 neutrons, so each has a mass number of 12. An isotope of any element can be uniquely represented as $^{A}_{Z}X$, where X is the atomic symbol of the element. The isotope of carbon that has 6 neutrons is therefore $^{12}_{6}C$. The subscript indicating the atomic number is actually **redundant** because the atomic symbol already uniquely specifies Z. Consequently, $^{12}_{6}C$ is more often written as ^{12}C, which is read as “carbon-12.” Nevertheless, the value of Z is commonly included in the notation for nuclear reactions because these reactions involve changes in Z.

Isotopes

Recall that the nuclei of most atoms contain neutrons as well as protons. Unlike protons, the number of neutrons is not absolutely fixed for most elements. Atoms that have the same number of protons, and hence the same atomic number, but different numbers of neutrons are called isotopes. All isotopes of an element have the same number of protons and electrons, which means they exhibit the same chemistry. The isotopes of an element differ only in their atomic mass, which is given by the mass number (A), the sum of the numbers of protons and neutrons.

Two nuclides having the **same** atomic number but different mass numbers are known as *isotopes*. Most elements occur in nature as mixtures of isotopes, but twenty-three of them (including beryllium and fluorine, shown in the table) are monoisotopic. For example, there are three *natural isotopes* of magnesium: ^{24}Mg (79% of all Mg atoms), ^{25}Mg (10%), and ^{26}Mg (11%); all three are present in all compounds of magnesium in about these same proportions.

	Z	mass numbers
H	1	1 2 3
He	2	3 4
Li	3	6 7
Be	4	9
B	5	10 11
C	6	12 13 14
N	7	14 15
O	8	16 17 18
F	9	19
Ne	10	20 21 22

Approximately 290 isotopes occur in nature. The two heavy isotopes of hydrogen are especially important— so much so that they have names and symbols of their own:

$$\underset{\text{protium}}{{}^{1}_{1}\mathrm{H}} \tag{1.3.2}$$

$$\underset{\text{deuterium}}{{}^{2}_{1}\mathrm{H} \equiv \mathrm{D}} \tag{1.3.3}$$

$$\underset{\text{tritium}}{{}^{2}_{1}\mathrm{H} \equiv \mathrm{T}} \tag{1.3.4}$$

Deuterium accounts for only about 15 out of every one million atoms of hydrogen. Tritium, which is radioactive, is even less abundant. All the tritium on the earth is a by-product of the decay of other radioactive elements.

For carbon, in addition to ^{12}C, a typical sample of carbon contains 1.11% $^{13}_{6}C$ (^{13}C), with 7 neutrons and 6 protons, and a trace of $^{14}_{6}C$ (^{14}C), with 8 neutrons and 6 protons. The nucleus of ^{14}C is not stable, however, but undergoes a slow radioactive decay that is the basis of the carbon-14 dating technique used in archeology. Many elements other than carbon have more than one stable isotope; tin, for example, has 10 isotopes. The properties of some common isotopes are in Table **1.3.2**.

Table **1.3.2**: Properties of Selected Isotopes

Element	Symbol	Atomic Mass (amu)	Isotope Mass Number	Isotope Masses (amu)	Percent Abundances (%)
hydrogen	H	1.0079	1	1.007825	99.9855
			2	2.014102	0.0115
boron	B	10.81	10	10.012937	19.91
			11	11.009305	80.09
carbon	C	12.011	12	12 (defined)	99.89
			13	13.003355	1.11
oxygen	O	15.9994	16	15.994915	99.757
			17	16.999132	0.0378
			18	17.999161	0.205
iron	Fe	55.845	54	53.939611	5.82
			56	55.934938	91.66
			57	56.935394	2.19
			58	57.933276	0.33
uranium	U	238.03	234	234.040952	0.0054
			235	235.043930	0.7204
			238	238.050788	99.274

Sources of isotope data: G. Audi et al., Nuclear Physics A 729 (2003): 337–676; J. C. Kotz and K. F. Purcell, Chemistry and Chemical Reactivity, 2nd ed., 1991.



How Elements Are Represented on the Periodic Table: https://youtu.be/ik6ZsaSyISo

Example 1.3.1

An element with three stable isotopes has 82 protons. The separate isotopes contain 124, 125, and 126 neutrons. Identify the element and write symbols for the isotopes.

Given: number of protons and neutrons

Asked for: element and atomic symbol

Strategy:

A. Refer to the periodic table and use the number of protons to identify the element.
B. Calculate the mass number of each isotope by adding together the numbers of protons and neutrons.
C. Give the symbol of each isotope with the mass number as the superscript and the number of protons as the subscript, both written to the left of the symbol of the element.

Solution:

A The element with 82 protons (atomic number of 82) is lead: Pb.

B For the first isotope, A = 82 protons + 124 neutrons = 206. Similarly, A = 82 + 125 = 207 and A = 82 + 126 = 208 for the second and third isotopes, respectively. The symbols for these isotopes are $^{206}_{82}Pb$, $^{207}_{82}Pb$, and $^{208}_{82}Pb$, which are usually abbreviated as ^{206}Pb, ^{207}Pb, and ^{208}Pb.

? Exercise 1.3.1

Identify the element with 35 protons and write the symbols for its isotopes with 44 and 46 neutrons.

Answer: $^{79}_{35}\mathbf{Br}$ and $^{81}_{35}\mathbf{Br}$ or, more commonly, $^{79}\mathbf{Br}$ and $^{81}\mathbf{Br}$.

Summary

- The atom consists of discrete particles that govern its chemical and physical behavior.Contributors

Each atom of an element contains the same number of protons, which is the **atomic number** (*Z*). Neutral atoms have the same number of electrons and protons. Atoms of an element that contain different numbers of neutrons are called **isotopes**. Each isotope of a given element has the same atomic number but a different **mass number** (*A*), which is the sum of the numbers of protons and neutrons. The relative masses of atoms are reported using the **atomic mass unit** (**amu**), which is defined as one-twelfth of the mass of one atom of carbon-12, with 6 protons, 6 neutrons, and 6 electrons.

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1.4: 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 **1.4.1**). 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.

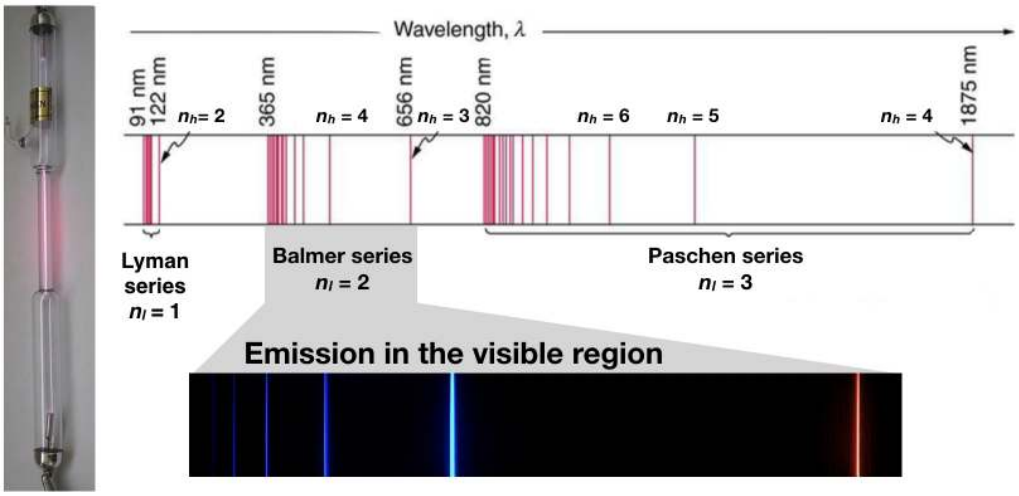


Figure **1.4.1**: The emission of light by hydrogen atoms. (left) A sample of excited hydrogen atoms emits a characteristic red light. (bottom) When the light emitted by a sample of excited hydrogen atoms is split into its component wavelengths by a prism, four characteristic violet, blue, green, and 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:

$$u = constant\left(\frac{1}{2^2} - \frac{1}{n^2}\right) \tag{1.4.1}$$

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*:

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_l^2} - \frac{1}{n_h^2}\right) \tag{1.4.2}$$

,

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

Other Series

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

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

$$\frac{1}{\lambda} = R_H \left(\frac{1}{1^2} - \frac{1}{n^2} \right) \tag{1.4.3}$$

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

Table 1.4.1: 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 1.4.1: The Lyman Series

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

Given: lowest-energy orbit in the Lyman series

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

Strategy:

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

Solution:

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

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

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

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

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

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

and

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

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

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

? Exercise 1.4.1: The Pfund Series

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

Answer

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

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

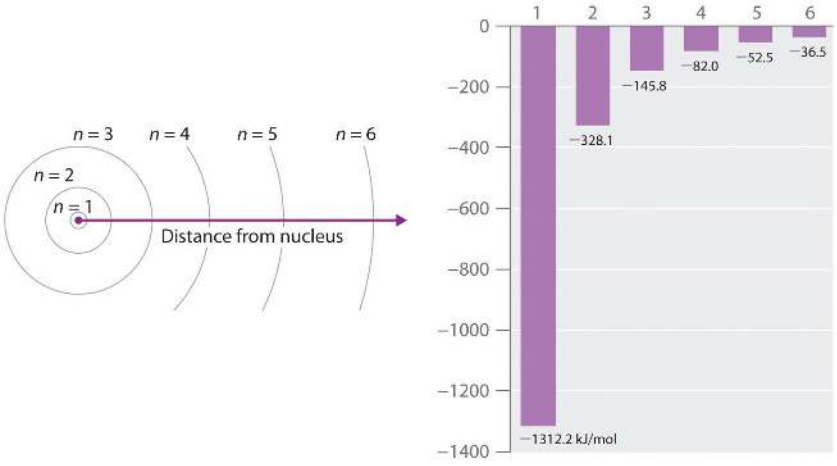
The Bohr Model

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

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

$$E_n = \frac{-R_H hc}{n^2} \tag{1.4.4}$$

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

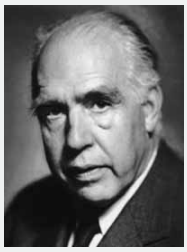


(a) Hydrogen orbits (Bohr model). Orbits are not drawn to scale. **(b) Hydrogen orbit energy (kJ/mol) vs. *n***

Figure **1.4.2**: *The Bohr Model of the hydrogen atom (a) The distance of the orbit from the nucleus increases with increasing n. (b) The energy of the orbit becomes increasingly less negative with increasing n.*

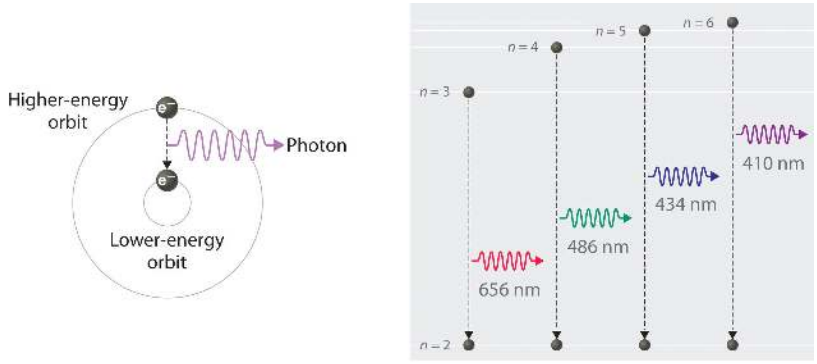
Niels Bohr (1885–1962)

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



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

As n decreases, the energy holding the electron and the nucleus together becomes increasingly negative; the radius of the orbit shrinks and more energy is needed to ionize the atom. The orbit with n = 1 is the lowest lying and most tightly bound. The negative sign in Equation ??? 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 **1.4.2*a***). A hydrogen atom with an electron in an orbit with n > 1 is therefore in an **excited state**, defined as any arrangement of electrons that is higher in energy than the ground state. When an atom in an excited state undergoes a transition to the ground state in a process called decay, it loses energy by emitting a photon whose energy corresponds to the *difference* in energy between the two states (Figure **1.4.1**).



(a) Electronic emission transition (b) Balmer series transitions

Figure **1.4.3**: *The emission of light by a hydrogen atom in an excited state. (a) Light is emitted when the electron undergoes a transition from an orbit with a higher value of n (at a higher energy) to an orbit with a lower value of n (at lower energy). (b) The Balmer series of emission lines is due to transitions from orbits with n ≥ 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

$$\Delta E = E_{final} - E_{initial} = -\frac{R_H hc}{n_h^2} - \left(-\frac{R_H hc}{n_l^2}\right) = -R_H hc\left(\frac{1}{n_h^2} - \frac{1}{n_l^2}\right) \tag{1.4.5}$$

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 **1.4.3**. Substituting hc/λ for Δ*E* gives

$$\Delta E = \frac{hc}{\lambda} = -R_H hc\left(\frac{1}{n_h^2} - \frac{1}{n_l^2}\right) \tag{1.4.6}$$

Canceling *hc* on both sides gives

$$\frac{1}{\lambda} = -R_H\left(\frac{1}{n_h^2} - \frac{1}{n_l^2}\right) \tag{1.4.7}$$

Except for the negative sign, this is the same equation that Rydberg obtained experimentally. The negative sign in Equations 1.4.6 and 1.4.7 indicates that energy is released as the electron moves from orbit n_h to orbit n_l because orbit n_h is at a higher energy than orbit n_l. Bohr calculated the value of R_H from fundamental constants such as the charge and mass of the electron and Planck's constant and obtained a value of $1.0974 \times 10^7\ m^{-1}$, the same number Rydberg had obtained by analyzing the emission spectra.

We can now understand the physical basis for the Balmer series of lines in the emission spectrum of hydrogen (**1.4.3***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 **1.4.3***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 **1.4.1***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 **1.4.4** :

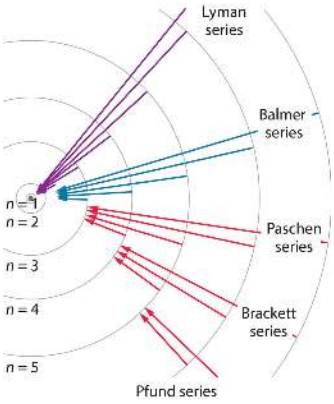


Figure **1.4.4**: Electron transitions responsible for the various series of lines observed in the emission spectrum of hydrogen. The Lyman series of lines is due to transitions from higher-energy orbits to the lowest-energy orbit (n = 1); these transitions release a great deal of energy, corresponding to radiation in the ultraviolet portion of the electromagnetic spectrum. The Paschen, Brackett, and Pfund series of lines are due to transitions from higher-energy orbits to orbits with n = 3, 4, and 5, respectively; these transitions release substantially less energy, corresponding to infrared radiation. (Orbits are not drawn to scale.)

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 1.4.1: The Lyman Series

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

Given: lowest-energy orbit in the Lyman series

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

Strategy:

A. Substitute the appropriate values into Equation 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 1.4.1: The Pfund Series

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

Answer

4.65 × 10^3 nm; infrared

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

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

Unfortunately, Bohr could not explain *why* the electron should be restricted to particular orbits. Also, despite a great deal of 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 **1.4.5**). In fact, Bohr's model worked only for species that contained just one electron: H, He^+, Li^{2+}, and so forth. Scientists needed a fundamental change in their way of thinking about the electronic structure of atoms to advance beyond the Bohr model.

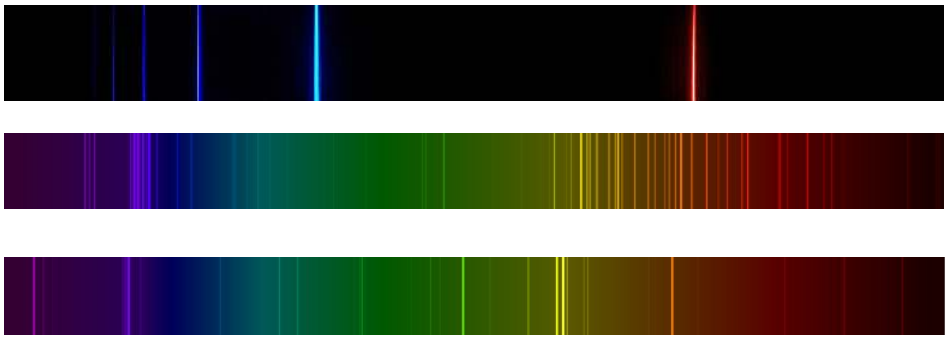


Figure 1.4.5: The emission spectra of elements compared to hydrogen. **Top:** hydrogen gas (atomized to hydrogen atoms in the discharge tube). **Middle:** neon. **Bottom:** mercury. The strongest lines in the hydrogen spectrum are in the far UV Lyman series starting at 124 nm and below. The strongest 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.

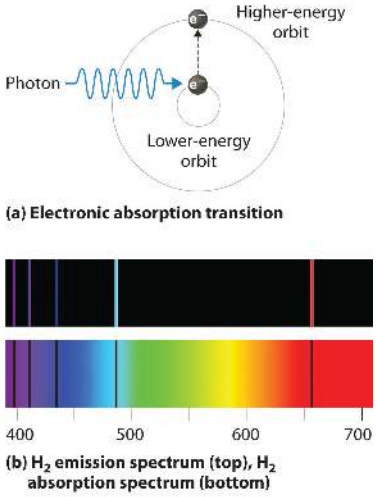


Figure 1.4.6: Absorption and emission spectra. Absorption of light by a hydrogen atom. (a) When a hydrogen atom absorbs a photon of light, an electron is excited to an orbit that has a higher energy and larger value of n. (b) Images of the emission and absorption spectra of hydrogen are shown here.

Emission and absorption spectra form the basis of *spectroscopy*, which uses spectra to provide information about the structure and the composition of a substance or an object. In particular, astronomers use emission and absorption spectra to determine the composition of stars and interstellar matter. As an example, consider the spectrum of sunlight shown in Figure 1.4.7. 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.

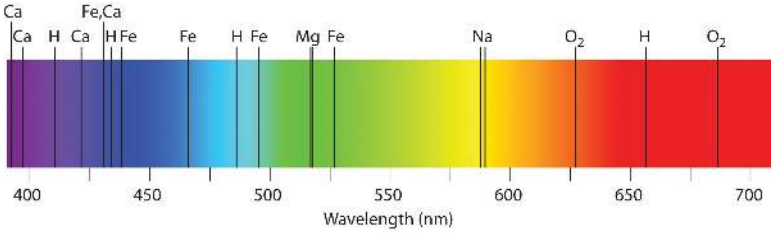


Figure **1.4.7**: *The visible spectrum of sunlight. The characteristic dark lines are mostly due to the absorption of light by elements that are present in the cooler outer part of the sun's atmosphere; specific elements are indicated by the labels. The lines at 628 and 687 nm, however, are due to the absorption of light by oxygen molecules in Earth's atmosphere.*

The familiar red color of neon signs used in advertising is due to the emission spectrum of neon shown in part (b) in Figure **1.4.5**. Similarly, the blue and yellow colors of certain street lights are caused, respectively, by mercury and sodium discharges. In all these cases, an electrical discharge excites neutral atoms to a higher energy state, and light is emitted when the atoms decay to the ground state. In the case of mercury, most of the emission lines are below 450 nm, which produces a blue light (part (c) in Figure **1.4.5**). In the case of sodium, the most intense emission lines are at 589 nm, which produces an intense yellow light.

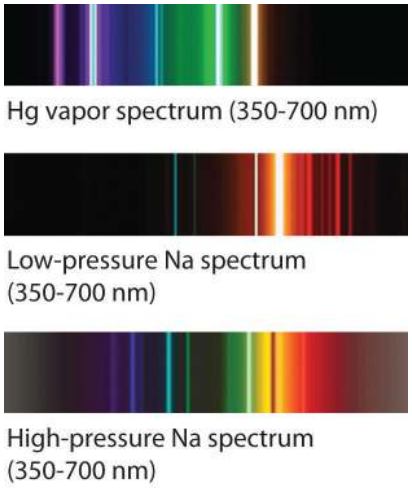


Figure **1.4.8**: *The emission spectra of sodium and mercury. Many street lights use bulbs that contain sodium or mercury vapor. Due to the very different emission spectra of these elements, they emit light of different colors. The lines in the sodium lamp are broadened by collisions. The dark line 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

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1.5: 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: posessing 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:

$$\hat{H}\psi = E\psi \tag{1.5.1}$$

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:

$$\hat{H} = \frac{-h^2}{8\pi^2 m_e}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) - \frac{Ze^2}{4\pi\epsilon_0 r} \tag{1.5.2}$$

Where h is Planc'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 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 or $V(x,y,z)$.

$$V(x,y,x) = \frac{-Ze^2}{4\pi\epsilon_0 r} = \frac{-Ze^2}{4\pi\epsilon_0\sqrt{x^2+y^2+z^2}} \tag{1.5.3}$$

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 x, y, and z axes of the atom's Cartesian coordinates (nucleus is at the origin). The general form of the (ψ) for an electron in a hydrogen atom can be written as follows:

$$\psi_{n,l,m_l} = R_{n,l}(r) + Y_{l,m_l}(\theta,\phi) \tag{1.5.4}$$

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	principle	$1, 2, 3$...(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. 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 total probability of finding the electron anywhere in space is 1. (Show integral)
4. Any two orbitals must not occupy the same space. (Show integral)
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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1.6: 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 **1.6.1**. 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

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** ($Y_{l,m_l}(\theta,\phi)$).

$$\psi_{(n,l,m_l)} = R_{n,l}(r) \times Y_{l,m_l}(\theta,\phi) \tag{1.6.1}$$

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 1.6.2 from 1.6.1 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 1.6.2.

$$E_n = -\frac{hcRZ^2}{n^2} = -(13.607\,eV)\left(\frac{Z}{n}\right)^2 \tag{1.6.2}$$

,

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 1.6.1

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 1.6.2 and the Rydberg equation.

a. Using Equation 1.6.2 for allowed energies of electrons in a hydrogen atom, derive the energy of the ground state electron in H. Then repeat this process for a He^+ ion. What do the values indicate about the relative attraction between an electron and the nuclei of these two hydrogenic atoms?
b. Show that the IE of H's 1s electron can also be predicted by the Rydberg formula (equation 2.1.2.2).

Answer (a)

Use Equation 1.6.2 . For a hydrogen atom with one proton, $Z = 1$, and the ground state energy level is the lowest energy level, $n = 1$. Therefore, the energy of an electron in the ground state of a H atom is:

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

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

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

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

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

Answer (b)

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

Step 1.

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

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

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

Step 2.

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

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

? Exercise 1.6.2

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

Answer

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

Radial and Angular contributions to the wavefunction:

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

The radial part of the wavefunction, $R_{n,l}(r)$ gives the radial variation of ψ. In other words, $R_{n,l}(r)$ defines how the wavefunction depends on the distance of the electron from the nucleus (the radius). The $R_{n,l}(r)$ parts of the wavefunction for a hydrogenic atom are listed in Table **1.6.2**, and they are plotted in Figure **1.6.1**. 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.

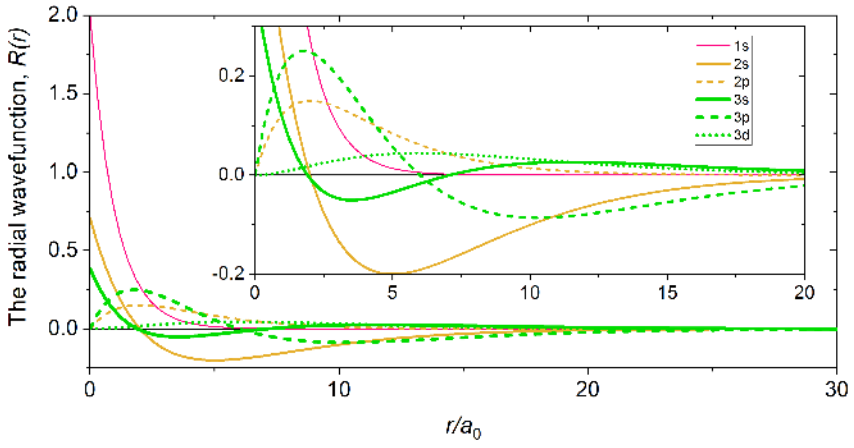


Figure **1.6.1**. Plots of the radial wavefunction, $R_{n,l}(r)$, for the first three shells. The wavefunctions are plotted relative to $\frac{r}{a_0}$, where $a_0 = 52.9pm = 0.529\text{Å}$ is the Bohr Radius (the radius of a hydrogen 1s orbital). The expressions for these radial wavefunctions ($R_{n,l}(r)$) are shown in Table **1.6.2**. (Kathryn Haas; CC-NC-BY-SA)

Table 1.6.2. 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 1.6.1.

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

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

Just like in the particle-in-a-box model, the square of the wavefunction is proportional to the probability of finding a particle (electron) at some point in space. The square of the radial part of the wavefunction is called the radial distribution function $4\pi r^2(R_{n,l}(r))^2$, and it describes the probability of locating the electron at some distance r away from the nucleus. When we normalize the probability functions by dividing the function by its integral over all space, we get the plots shown in Figure 1.6.2. The normalized probability functions are compared to the original radial part of the wavefunctions in Figure 1.6.3. 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 $\frac{r}{a_0}$.

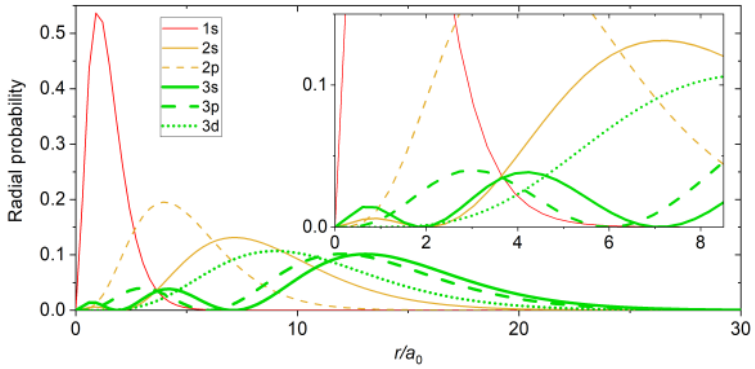


Figure 1.6.2: Plots of the normalized radial probability functions for the first three shells. The radial wavefunctions ($R_{n,l}(r)$) are shown in Table 1.6.2. (Kathryn Haas; CC-NC-BY-SA)

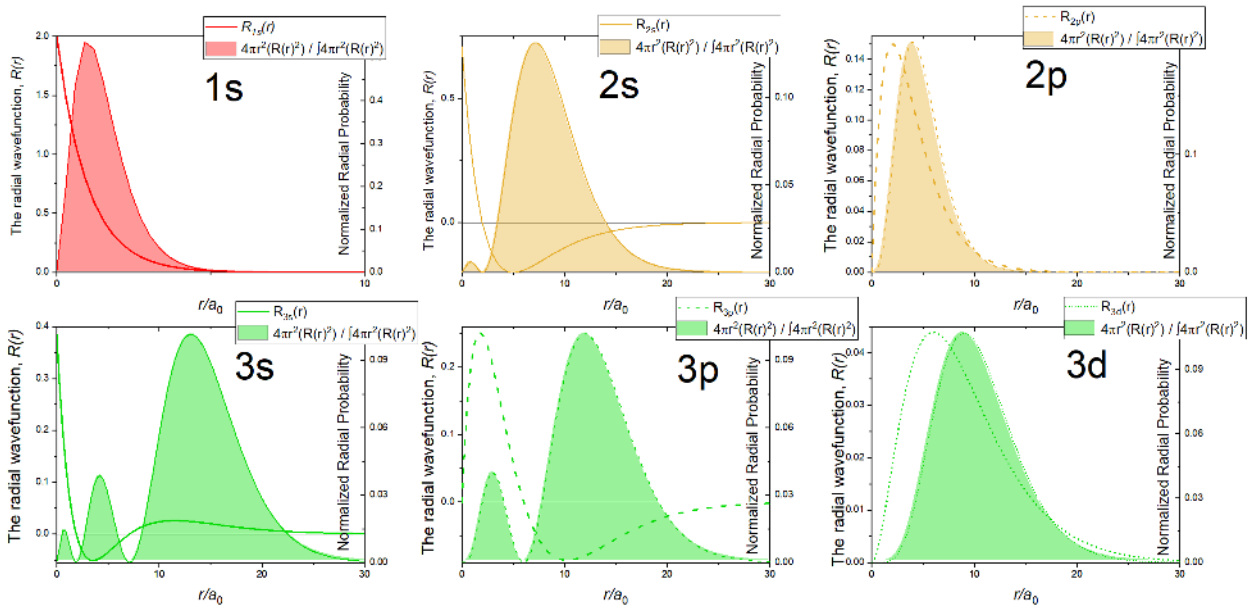


Figure **1.6.2**. Plots of the normalized radial probability function for each orbital in the first three shells (shaded curves). The radial wavefunctions are also shown (Table **1.6.2**). The y-axis on the left of each plot corresponds to the radial wavefunction (line); the y-axis on the right of each plot corresponds to the radial probability function (shaded). (Kathryn Haas; CC-NC-BY-SA)

Radial nodes

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

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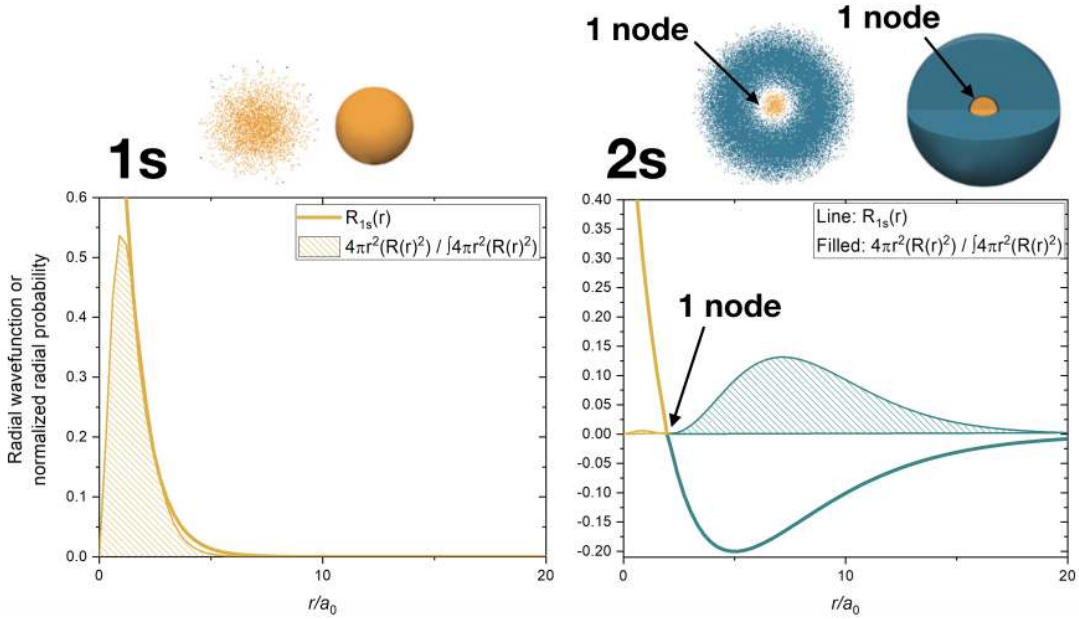


Figure **1.6.3**: Visualization of the 1s and 2s atomic orbitals. Each orbital is shown as both an electron probability density plot and a contour plot above its wavefunction and probability density function. The 1s orbital has zero radial nodes. The 2s orbital has one radial node where its wavefunction 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 1.6.1

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

Answer

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

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

s-orbitals:

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

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

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

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

p-orbitals

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

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

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

d-orbitals

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

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

f-orbital

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

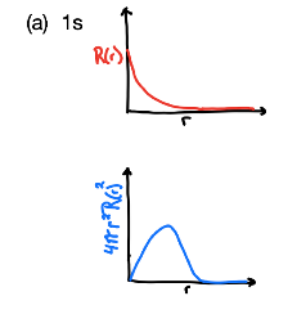
? Exercise 1.6.1

Draw a rough plot of the following:

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

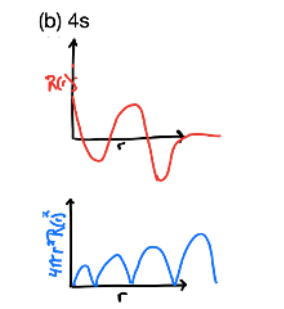
Answer, 1s

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



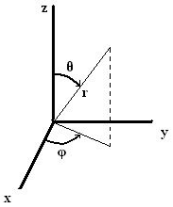
Answer, 4s

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



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

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



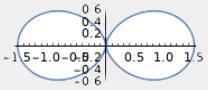
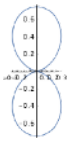
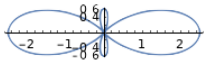
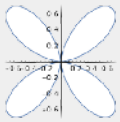
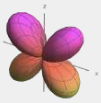
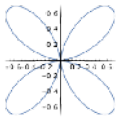
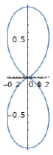
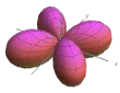
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$$Y_{l,m_l}(\theta,\phi) = \left(\frac{1}{4\pi}\right)^{1/2} y(\theta,\phi)$$

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

The values of θ, ϕ, and $y(\theta,\phi)$ for orbitals in the hydrogen atom are listed in Table 1.6.3. 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 1.6.3. Components of the angular wavefunction and the resulting orbital shapes. The plots in the two right hand columns were created using Desmos and Mathematica: specifically "Spherical Harmonics" from the Wolfram Demonstrations Project, http://demonstrations.wolfram.com/SphericalHarmonics/ and "Visualizing Atomic Orbitals" demonstrations.wolfram.com/Vi...tomicOrbitals/.

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

Angular nodes

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

orbitals ($l = 2$) have two angular nodes, and so on. Planar nodes can be flat planes (like the nodes in all p orbitals) or they can have a conical shape, like the two angular nodes in the d_{z^2} orbital. Angular nodes in some p and d orbitals are shown in Figure **1.6.4**.

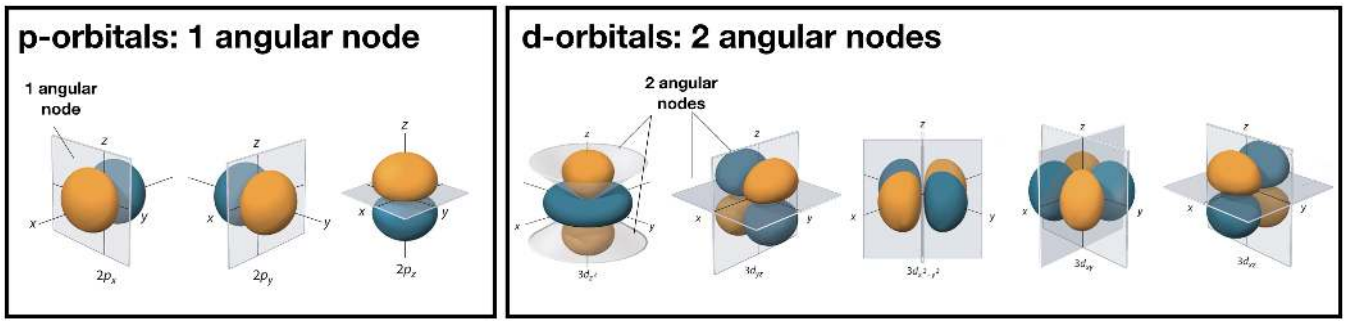
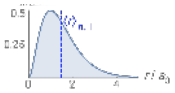
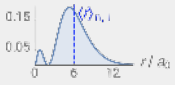
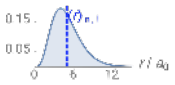
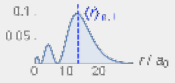
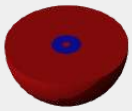
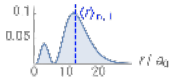
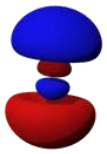
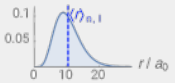
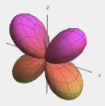


Figure **1.6.4**: The angular nodes in p-orbitals and d-orbitals are shown. Every p orbital has one angular node, and every d orbital has two angular nodes. The number of angular nodes in any orbital is equal to the value of the quantum number, l. (CC BY-NC-SA; anonymous by request)

Atomic Orbitals

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

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

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

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1.7: 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*)

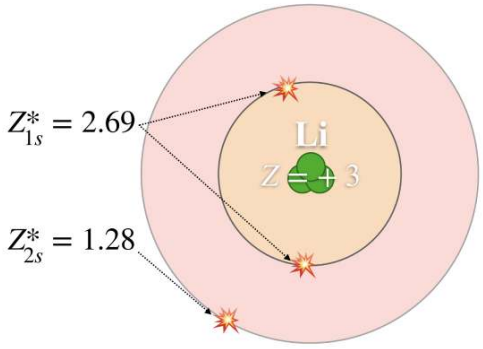


Figure 1.7.1. In a lithium atom, the nuclear charge (Z) is +3. 1s electrons experience an effective nuclear charge (Z*) of +2.69, and 2s electrons experience an Z* of +1.28. (CC-BY-NC-SA; Kathryn Haas)

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 1.7.1). 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 **1.7.2** 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 **1.7.4** for values).

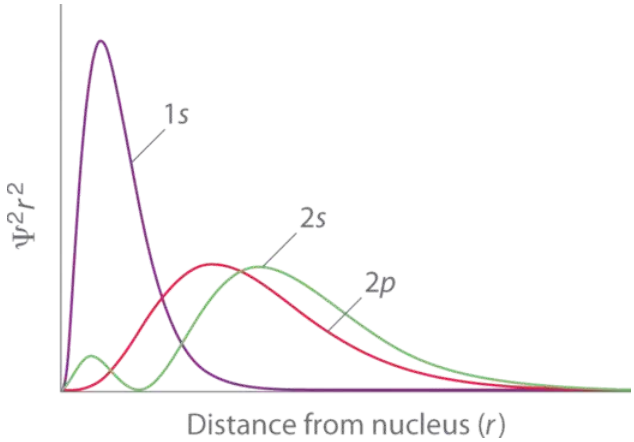


Figure **1.7.2**. Orbital Penetration. A comparison of the radial probability distribution of the 2s and 2p orbitals for various states of the hydrogen atom shows that the 2s orbital penetrates inside the 1s orbital more than the 2p orbital does. Consequently, when an electron is in the small inner lobe of the 2s orbital, it experiences a relatively large value of Z*, which causes the energy of the 2s orbital to be lower than the energy of the 2p orbital.

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

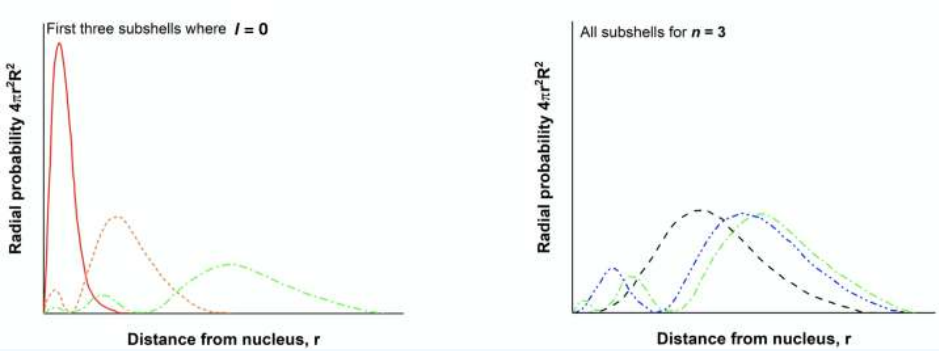
Within the same shell value (n), the penetrating power of an electron follows this trend in subshells (m_l):

s>p>d>f

Exercises

Exercises

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



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

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

Answer 1

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

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

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

Answer 2

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

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

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

Answer 3

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

Answer 4

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

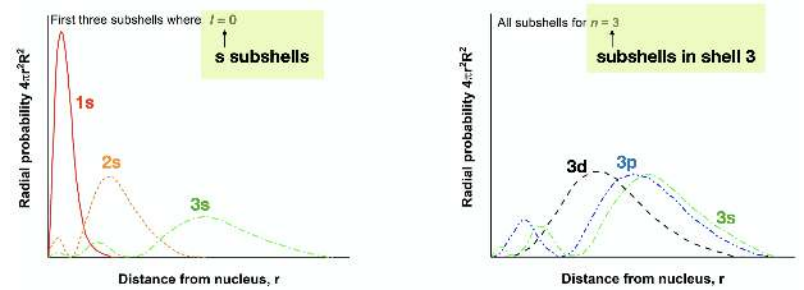
Answer 5

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

Answer 6

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

Answer 7



Answer 8

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

Answer 9

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

Slater's rules for estimating Z*

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

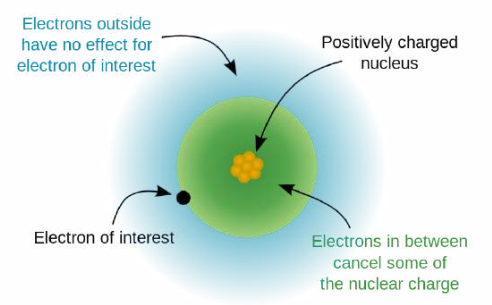


Figure **1.7.3**. Diagram illustrating effective nuclear charge according to Slater's rules.

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

$$Z* = Z - S$$

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

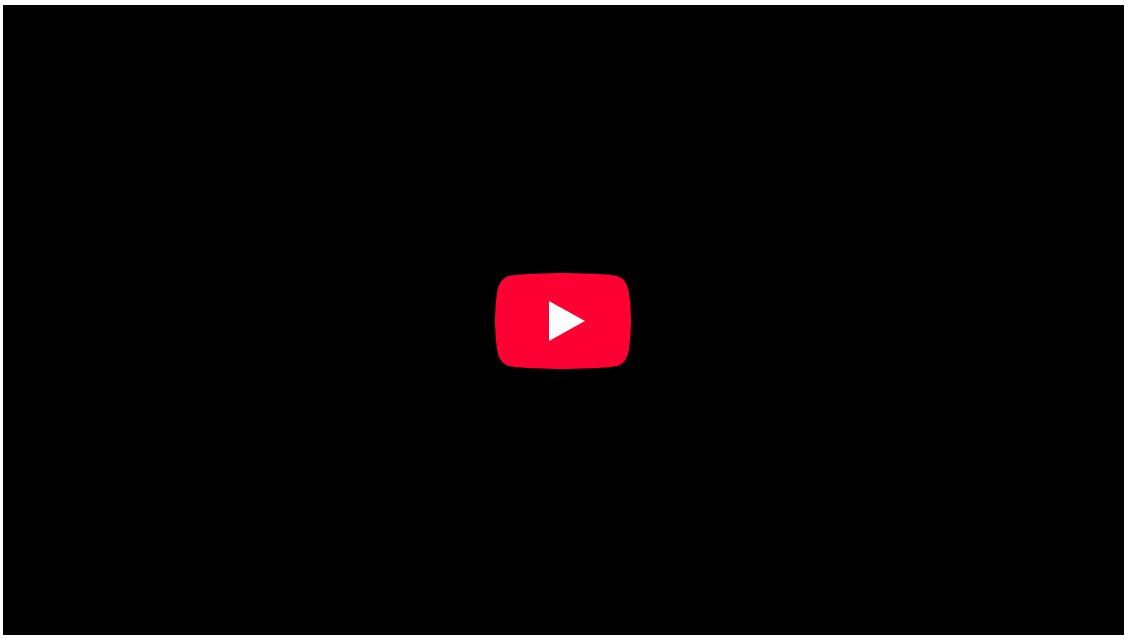
In the calculation of S, it is assumed that electrons closer to the nucleus than our electron-of-interest cancel some of the nuclear charge; those farther from the nucleus have no effect. To calculate S, all the relevant orbitals in an atom are written out in order of increasing energy, separating them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

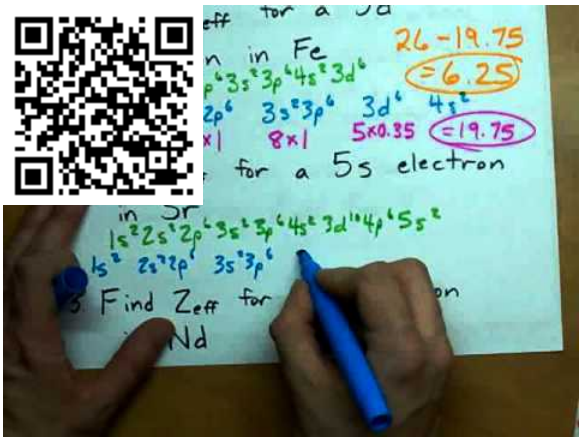
(1s)(2s,2p)(3s,3p)(3d)(4s,4p)(4d)(4f)(5s,5p) etc.

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

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

A video explaining how to use Slater's Rules





Example 1.7.1: 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 1.7.1

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

Answer

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

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

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

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

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

"Best" values for Z*

Slater's rules are a set of simple rules for predicting S and Z* based on empirical evidence from quantum mechanical calculations. In other words, the Z* calculated from Slater's rules are approximate values. The values considered to be the most accurate are derived from quantum mechanical calculations directly. You can find these values in a nice chart on the Wikipedia article of Effective Nuclear Charge. The chart is recreated here in Figure 1.7.3 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 1.7.4. 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 **1.7.3** and analysis of Slater's rules indicate that there are some predictable trends in Z*. The data from Figure **1.7.3** is plotted below in Figure **1.7.4** to provide a visual aid to the discussion below.

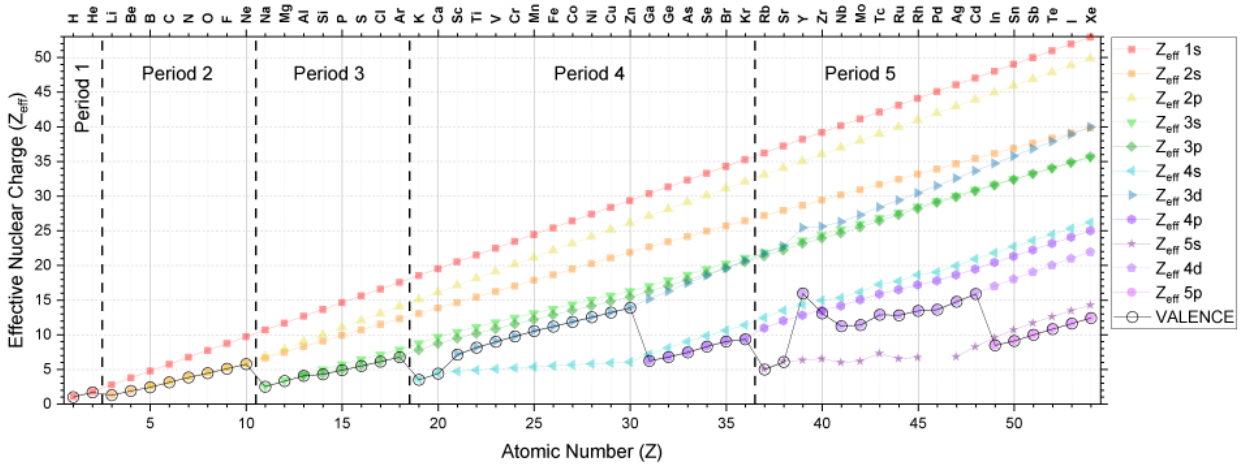


Figure **1.7.5**: The Z* values for electrons in each subshell of the first 54 elements (H to Xe). Each subshell is plotted as a different series (see legend) and the valence shell is highlighted by a solid black line with open circles. (Kathryn Haas; CC-NC-BY-SA)

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 **1.7.4**. (CC-BY-NC-SA; Kathryn Haas)

Do you notice any exceptions to this general trend?

Inspection of Figure **1.7.4** 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 **1.7.4** 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 **1.7.3**.

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 **1.7.4**, 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 1.7.2

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

Answer

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

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

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1.8: Aufbau Principle

Introduction

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

The Ground State of Hydrogenic Atoms/Ions

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

The Ground State of Multi-electron Atoms/Ions

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

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

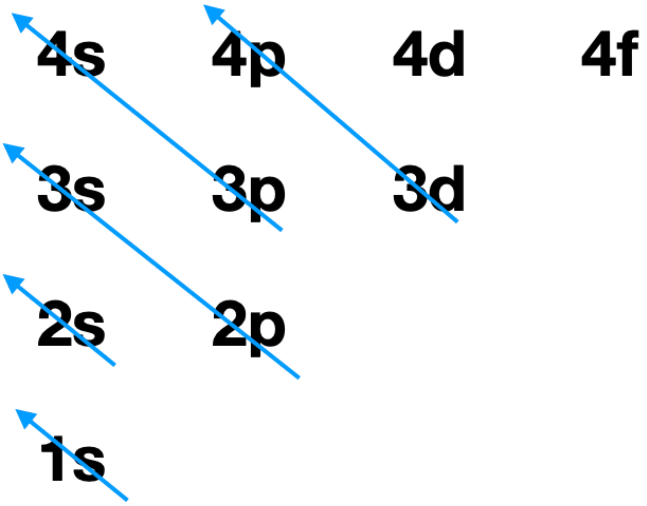


Figure 1.8.1. The order of filling of ground state electron orbitals is 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, etc... (CC-BY-NC-SA; Kathryn Haas)

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

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

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

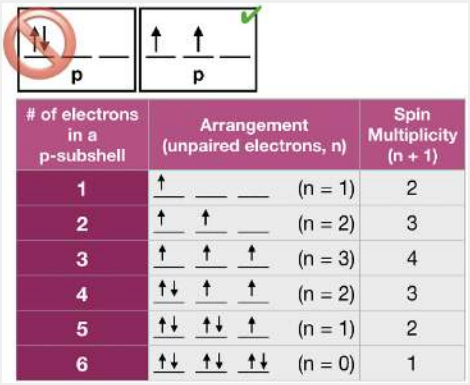


Figure 1.8.2. Hund's rule is that spin multiplicity must be maximized in the ground state.

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

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

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

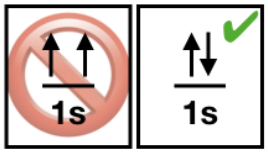


Figure 1.8.3. Pauli's principle tells us that paired electrons must have opposite spin. (Kathryn Haas; CC-NC-BY-SA)

(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.

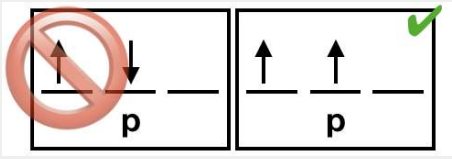


Figure 1.8.4. Unpaired electrons should have identical spins due to the exchange interaction. (Kathryn Haas; CC-NC-BY-SA)

Trends in Expected Electron Configuration

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

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

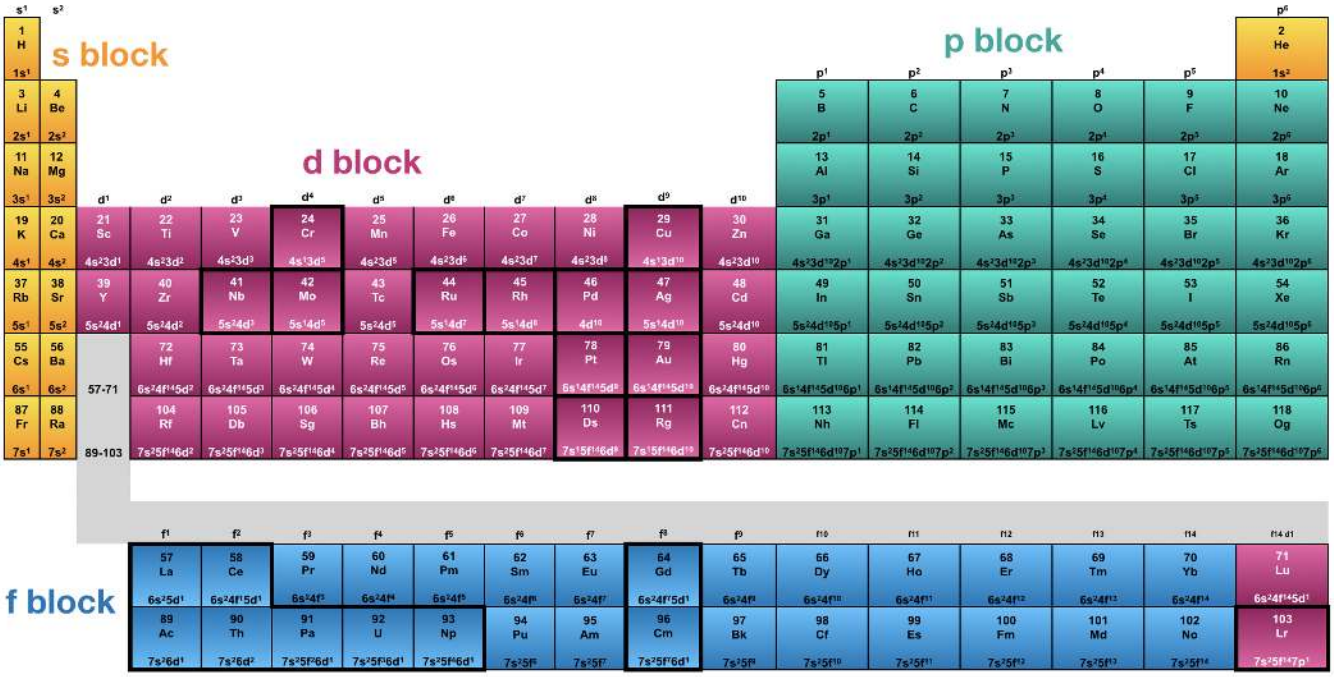


Figure 1.8.5. This is a depiction of the periodic table that highlights the s-, p-, d-, and f- blocks in different colors. Violations of the expected trend in electron configurations are outlined in a heavy black line. Several elements of the d block and f block violate the general trends in electron 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 1.8.5. All of the exceptions are within the d- and f- blocks, and the violations are caused by an unexpected order of the orbital energy levels.

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

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SECTION OVERVIEW

1.9: 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.

1.9.1: Ionization energy

1.9.2: Electron Affinity

1.9.3: Covalent and Ionic Radii

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1.9.1: 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 1.9.1.1 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.

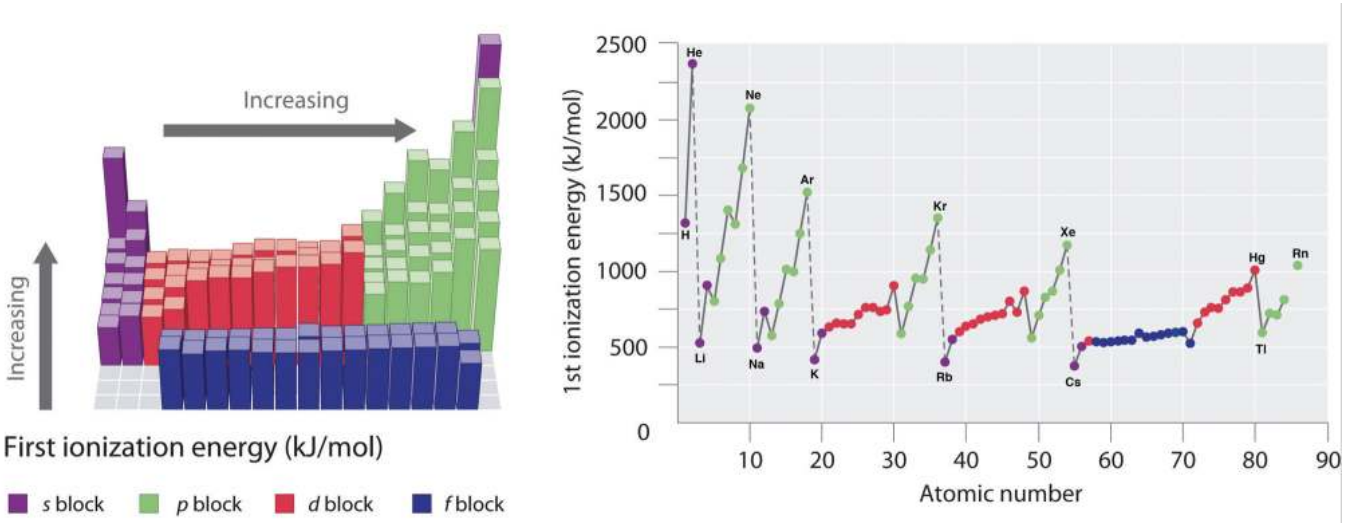


Figure 1.9.1.1: Graph showing the First Ionization Energy of the Elements. Left: ionization energies are mapped onto the periodic table, where the magnitude of ionization energy is depicted as a bar graph. Right: the first ionization energy is plotted against atomic number. In both panels the elements 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 1.9.1.2. 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!

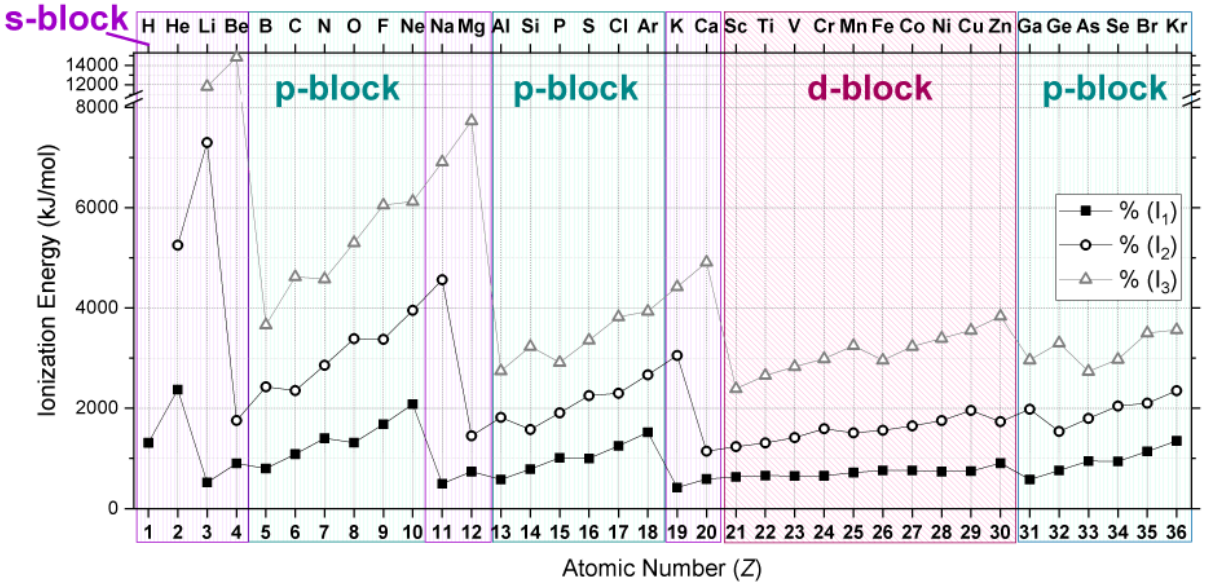


Figure 1.9.1.2. The first (I_1), second (I_2), and third (I_3) ionization energies plotted for elements with Z = 1 to 36 (H to Kr). The position of each element in its atomic form is indicated as s- p- or d-block. (CC-BY-NC-SA; Kathryn Haas)

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1.9.2: 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 1.9.2.1 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.

$$A^-_{(g)} \longrightarrow A_{(g)} + e^- \qquad EA = \Delta U \tag{1.9.2.1}$$

The reaction shown in Equation 1.9.2.1 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 1.9.2.1. 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 1.9.2.2. The reaction as shown in equation 1.9.2.2 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.

$$A_{(g)} + e^- \longrightarrow A^-_{(g)} \qquad EA = \Delta U \tag{1.9.2.2}$$

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 1.9.2.1., where the shifts in the peaks and valleys within each zig-zag trend are indicated.

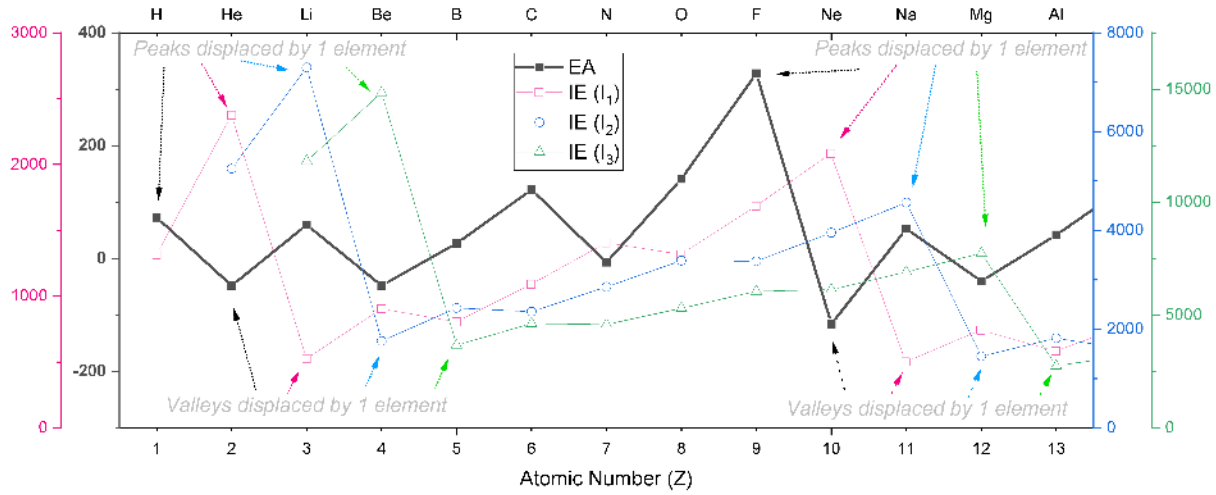


Figure **1.9.2.1**. A plot of electron affinity (the zeroth ionization energy) is overlaid on plots of the first (I_1), second (I_2), and third (I_3) ionization energies. Each plot is shown using separate y-axes. Trends in EA are similar to those in ionization energies, except that the peaks and valleys 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

1. IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). Online version (2019-) created by S. J. Chalk. ISBN 0-9678550-9-8. doi.org/10.1351/goldbook.
2. Electron Affinity (data page), Wikipedia. en.Wikipedia.org/wiki/Electron_affinity_(data_page) Accessed 12/3/19.

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1.9.3: 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 **1.9.3.1** 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.

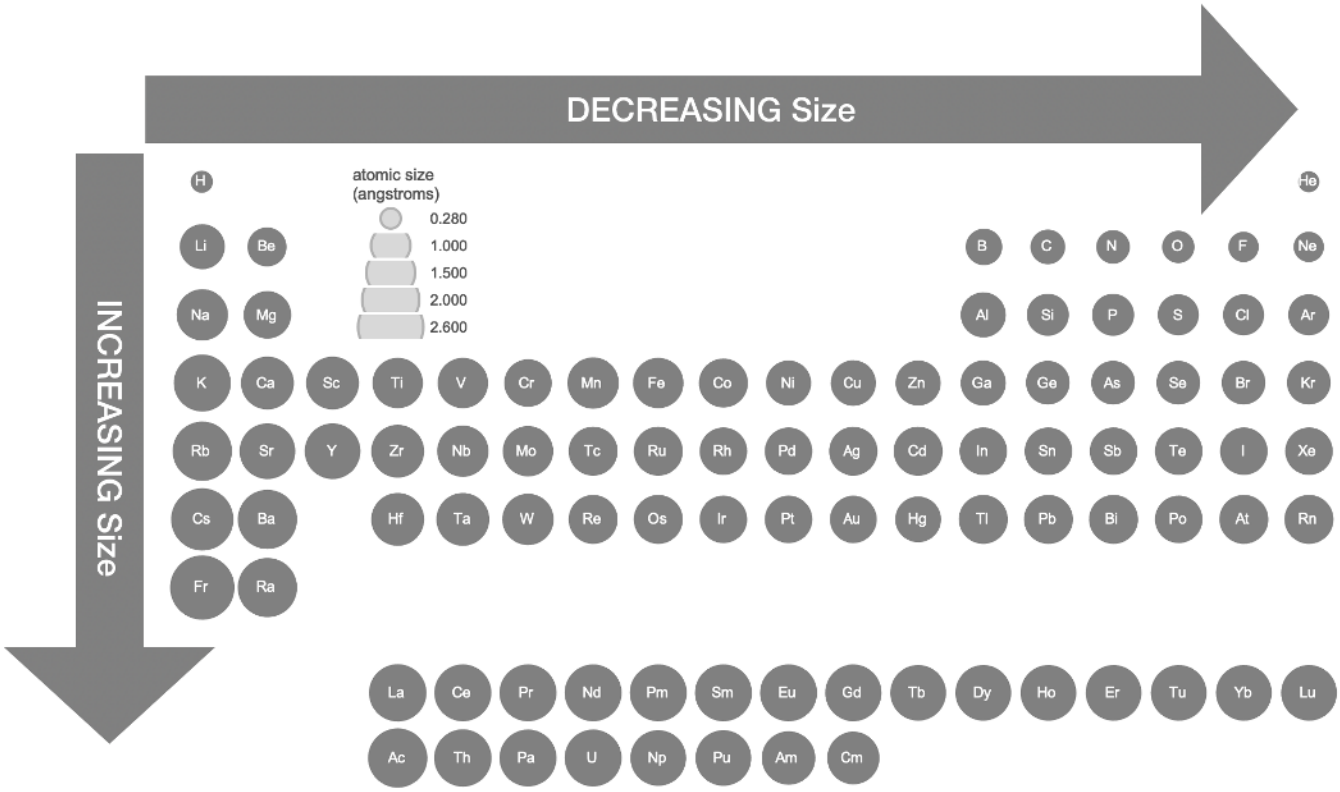


Figure **1.9.3.1**. *Atomic Radii Calculated from Crystalographic Data. Data from Cordero, Beatriz, Veronica Gomez, Ana E. Platero-Prats, Marc Reves, Jorge Echeverria, Eduard Cremades, Flavia Barragan, and Santiago Alvarez. "Covalent Radii Revisited." Dalton Transactions, no. 21 (2008): 2832–38. doi:10.1039/b801115j.* (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 **1.9.3.2** visually illustrates the relative size of atoms and some cations of the first four periods; the data is available in tabular format in Figure **1.9.3.3**.

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 **1.9.3.2** 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 **1.9.3.3**.

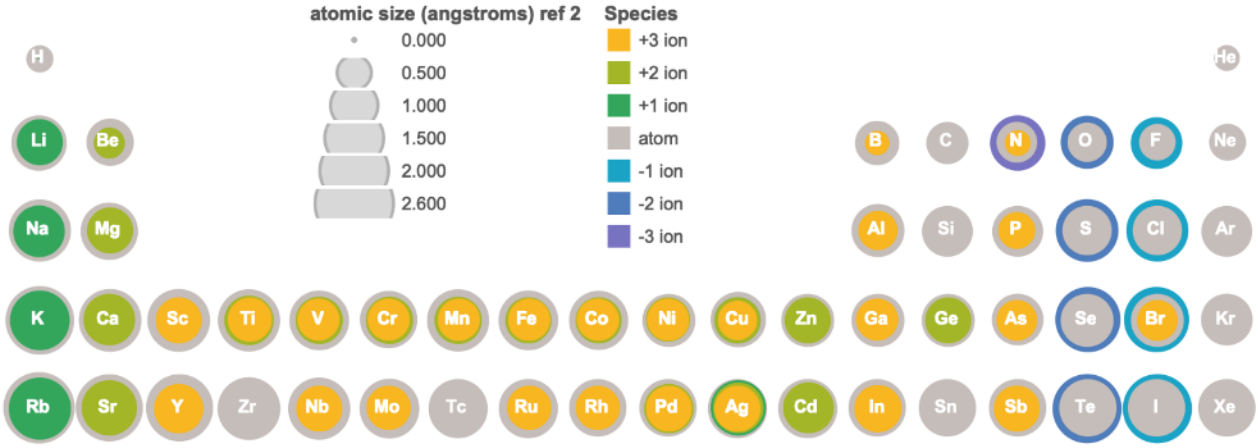


Figure **1.9.3.2**. This figure illustrates relative size of atoms and ions of the first four periods of the periodic table. Atomic radius is indicated by grey circles. Radius of cations is shown in green (+1), lime (+2), and yellow (+3) circles. Radius of anions are shown as aqua (-1), blue (-2), and purple (-3) circles. Data from sources 1-3. (Kathryn Haas; CC-NC-BY-SA)

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

Figure 1.9.3.3.

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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CHAPTER OVERVIEW

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2.2: Lewis Electron-Dot Diagrams

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

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2.5.1: Lone Pair Repulsion

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2.5.4: Ligand Close Packing

2.6: Molecular Orbital Theory

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2.1: Lewis Theory - An Overview

Learning Objectives

- To use Lewis electron dot symbols to predict the number of bonds an element will form.

Why are some substances chemically bonded molecules and others are an association of ions? The answer to this question depends upon the electronic structures of the atoms and nature of the chemical forces within the compounds. Although there are no sharply defined boundaries, chemical bonds are typically classified into three main types: ionic bonds, covalent bonds, and metallic bonds. In this chapter, each type of bond wil be discussed and the general properties found in typical substances in which the bond type occurs

1. Ionic bonds results from ***electrostatic forces that exist between ions of opposite charge***. These bonds typically involves a metal with a nonmetal
2. Covalent bonds ***result from the sharing of electrons between two atoms***. The bonds typically involves one nonmetallic element with another
3. Metallic bonds These bonds are found in solid metals (copper, iron, aluminum) with each metal bonded to several neighboring groups and bonding electrons free to move throughout the 3-dimensional structure.

Each bond classification is discussed in detail in subsequent sections of the chapter. Let's look at the preferred arrangements of electrons in atoms when they form chemical compounds.

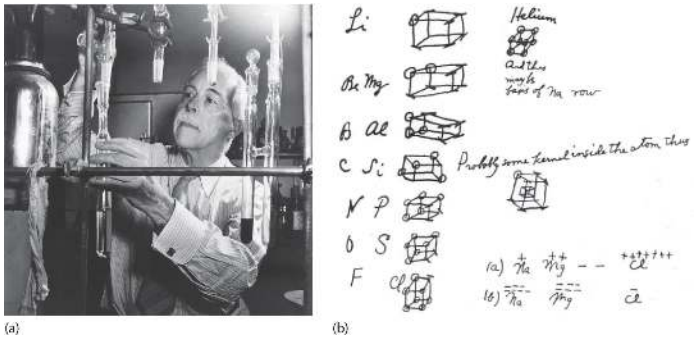


Figure **2.1.1**: G. N. Lewis and the Octet Rule. (a) Lewis is working in the laboratory. (b) In Lewis's original sketch for the octet rule, he initially placed the electrons at the corners of a cube rather than placing them as we do now.

Lewis Symbols

At the beginning of the 20th century, the American chemist G. N. Lewis (1875–1946) devised a system of symbols—now called *Lewis electron dot symbols* (often shortened to *Lewis dot symbols*) that can be used for predicting the number of bonds formed by most elements in their compounds. Each Lewis dot symbol consists of the chemical symbol for an element surrounded by dots that represent its valence electrons.

Note

Lewis Dot symbols:

- convenient representation of valence electrons
- allows you to keep track of valence electrons during bond formation
- consists of the chemical symbol for the element plus a dot for each valence electron

To write an element's Lewis dot symbol, we place dots representing its valence electrons, one at a time, around the element's chemical symbol. Up to four dots are placed above, below, to the left, and to the right of the symbol (in any order, as long as elements with four or fewer valence electrons have no more than one dot in each position). The next dots, for elements with more than four valence electrons, are again distributed one at a time, each paired with one of the first four. For example, the electron configuration for atomic sulfur is [Ne]$3s^2 3p^4$, thus there are ***six*** valence electrons. Its Lewis symbol would therefore be:



Fluorine, for example, with the electron configuration [He]$2s^2 2p^5$, has seven valence electrons, so its Lewis dot symbol is constructed as follows:

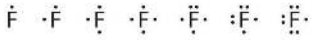


Figure **2.1.2**.

Lewis used the unpaired dots to predict the number of bonds that an element will form in a compound. Consider the symbol for nitrogen in Figure **2.1.2**. The Lewis dot symbol explains why nitrogen, with three unpaired valence electrons, tends to form compounds in which it shares the unpaired electrons to form three bonds. Boron, which also has three unpaired valence electrons in its Lewis dot symbol, also tends to form compounds with three bonds, whereas carbon, with four unpaired valence electrons in its Lewis dot symbol, tends to share all of its unpaired valence electrons by forming compounds in which it has four bonds.

Element	Electron config.	Electron dot symbol
Li	[He]$2s^1$	Li·
Be	[He]$2s^2$	·Be·
B	[He]$2s^2 2p^1$	·B·
C	[He]$2s^2 2p^2$	·C·
N	[He]$2s^2 2p^3$	·N:
O	[He]$2s^2 2p^4$	:O:
F	[He]$2s^2 2p^5$	:F:
Ne	[He]$2s^2 2p^6$	:Ne:

Figure **2.1.2**: Lewis Dot Symbols for the Elements in Period 2

The Octet Rule

In 1904, Richard Abegg formulated what is now known as *Abegg's rule*, which states that the difference between the maximum positive and negative valences of an element is frequently eight. This rule was used later in 1916 when Gilbert N. Lewis formulated the "octet rule" in his cubical atom theory.

The **octet rule** refers to the tendency of atoms to prefer to have eight electrons in the *valence shell*. When atoms have fewer than eight electrons, they tend to react and form more stable compounds. Atoms will react to get in the most stable state possible. A complete octet is very stable because all orbitals will be full. Atoms with greater stability have less energy, so a reaction that increases the stability of the atoms will release energy in the form of heat or light ;reactions that decrease stability must absorb energy, getting colder.

When discussing the octet rule, we do not consider *d* or *f* electrons. Only the s and p electrons are involved in the octet rule, making it a useful rule for the *main group elements* (elements not in the transition metal or inner-transition metal blocks); an octet in these atoms corresponds to an electron configurations ending with s^2p^6.

Octet Rule

A stable arrangement is attended when the atom is surrounded by eight electrons. This octet can be made up by own electrons and some electrons which are shared. Thus, an atom continues to form bonds until an octet of electrons is made. This is known as octet rule by Lewis.

1. Normally two electrons pairs up and forms a bond, e.g., H_2
2. For most atoms there will be a maximum of eight electrons in the valence shell (octet structure), e.g., CH_4

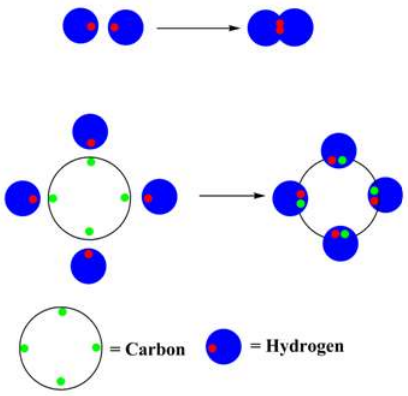


Figure 1: Bonding in H_2 and methane (CH_4)

The other tendency of atoms is to maintain a neutral charge. Only the noble gases (the elements on the right-most column of the periodic table) have zero charge with filled valence octets. All of the other elements have a charge when they have eight electrons all to themselves. The result of these two guiding principles is the explanation for much of the reactivity and bonding that is observed within atoms: atoms seek to share electrons in a way that minimizes charge while fulfilling an octet in the valence shell.

Note

The noble gases rarely form compounds. They have the most stable configuration (full octet, no charge), so they have no reason to react and change their configuration. All other elements attempt to gain, lose, or share electrons to achieve a noble gas configuration.

Example 1: Salt

The formula for table salt is NaCl. It is the result of Na^+ ions and Cl^- ions bonding together. If sodium metal and chlorine gas mix under the right conditions, they will form salt. The sodium loses an electron, and the chlorine gains that electron. In the process, a great amount of light and heat is released. The resulting salt is mostly unreactive — it is stable. It will not undergo any explosive reactions, unlike the sodium and chlorine that it is made of. Why?

Solution

Referring to the octet rule, atoms attempt to get a noble gas electron configuration, which is eight valence electrons. Sodium has one valence electron, so giving it up would result in the same electron configuration as neon. Chlorine has seven valence electrons, so if it takes one it will have eight (an octet). Chlorine has the electron configuration of argon when it gains an electron.

The octet rule could have been satisfied if chlorine gave up all seven of its valence electrons and sodium took them. In that case, both would have the electron configurations of noble gasses, with a full valence shell. However, their charges would be much higher. It would be Na^{7-} and Cl^{7+}, which is much less stable than Na^+ and Cl^-. Atoms are more stable when they have no charge, or a small charge.

Lewis dot symbols can also be used to represent the ions in ionic compounds. The reaction of cesium with fluorine, for example, to produce the ionic compound CsF can be written as follows:

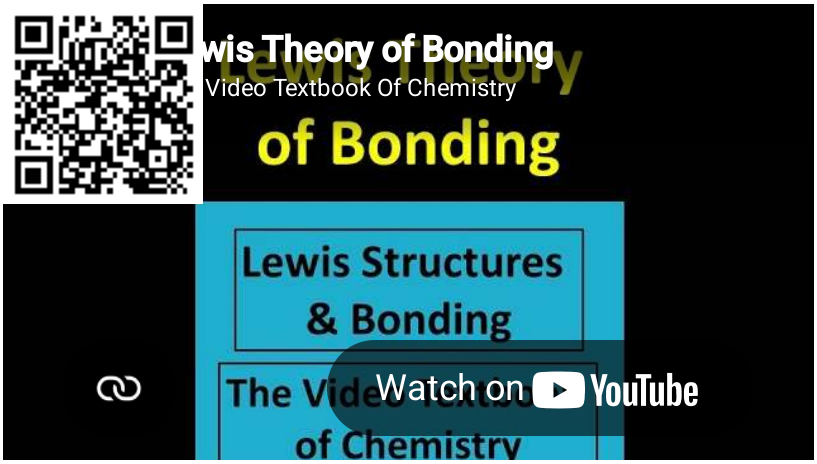


No dots are shown on Cs^+ in the product because cesium has lost its single valence electron to fluorine. The transfer of this electron produces the Cs^+ ion, which has the valence electron configuration of Xe, and the F^- ion, which has a total of eight valence electrons (an octet) and the Ne electron configuration. This description is consistent with the statement that among the main group elements, ions in simple binary ionic compounds generally have the electron configurations of the nearest noble gas. The charge of each ion is written in the product, and the anion and its electrons are enclosed in brackets. This notation emphasizes that the ions are associated electrostatically; no electrons are shared between the two elements.

Note

Atoms often gain, lose, or share electrons to achieve the same number of electrons as the noble gas closest to them in the periodic table.

As you might expect for such a qualitative approach to bonding, there are exceptions to the octet rule, which we describe elsewhere. These include molecules in which one or more atoms contain fewer or more than eight electrons.



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

Summary

- Lewis dot symbols can be used to predict the number of bonds formed by most elements in their compounds.

One convenient way to predict the number and basic arrangement of bonds in compounds is by using **Lewis electron dot symbols**, which consist of the chemical symbol for an element surrounded by dots that represent its valence electrons, grouped into pairs often placed above, below, and to the left and right of the symbol. The structures reflect the fact that the elements in period 2 and beyond tend to gain, lose, or share electrons to reach a total of eight valence electrons in their compounds, the so-called **octet rule**. Hydrogen, with only two valence electrons, does not obey the octet rule.

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Mike Blaber (Florida State University)

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2.2: 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.

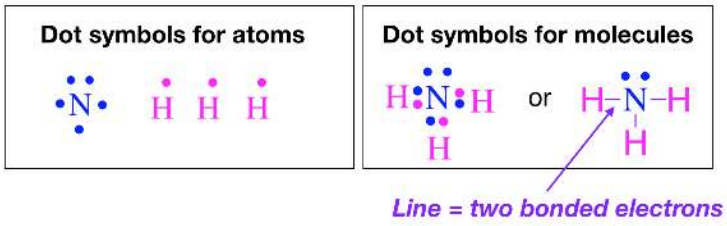


Figure **2.2.1**: Lewis dot structure of atoms comprising ammonia and the dot structure of the molecule. (Kathryn Haas; CC-NC-BY-SA)

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.

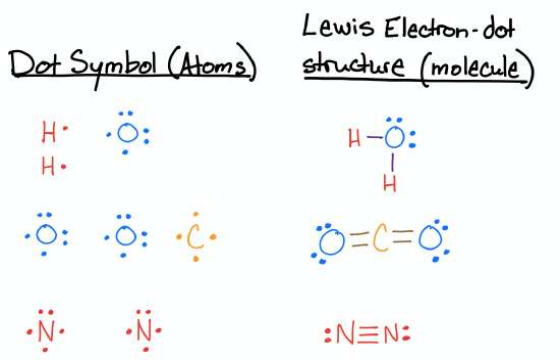
Electrons in valence (octet) = total unbonded electrons on the atom + total bonded electrons (2 electrons per bond)

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 2.2.1

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

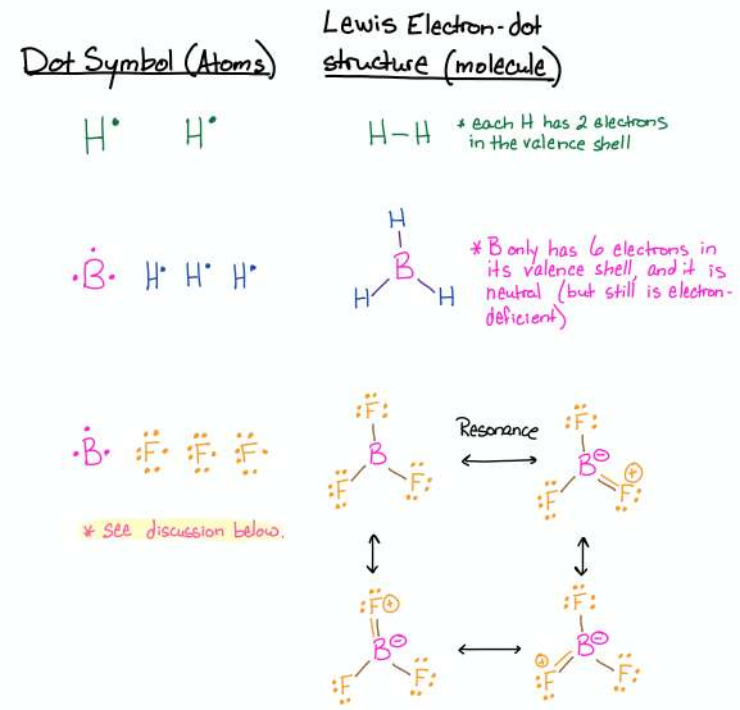
Answer



Exercise 2.2.2

Draw the Lewis structures for H_2, BH_3 and BF_3.

Answer



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

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

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

Outside Links

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

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2.2.1: Resonance

Learning Objectives

- To understand the concept of resonance.

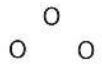
Resonance structures are a set of two or more Lewis Structures that collectively describe the electronic bonding of a single polyatomic species including fractional bonds and fractional charges. Resonance structures are capable of describing delocalized electrons that cannot be expressed by a single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

Sometimes one Lewis Structure is not Enough

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

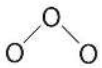
Ozone (O_3)

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



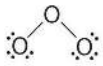
2. Each O atom has 6 valence electrons, for a total of 18 valence electrons.

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



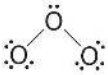
with 14 electrons left over.

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

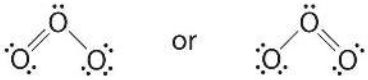


and have 2 electrons left over.

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

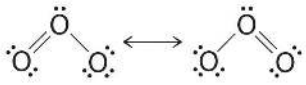


6. The central oxygen has only 6 electrons. We must convert one lone pair on a terminal oxygen atom to a bonding pair of electrons—but which one? Depending on which one we choose, we obtain either



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

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



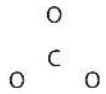
The double-headed arrow indicates that the actual electronic structure is an *average* of those shown, not that the molecule oscillates between the two structures.

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

The Carbonate (CO_3^{2-}) Ion

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

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



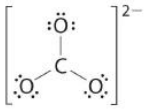
The three oxygens are drawn in the shape of a triangle with the carbon at the center of the triangle.

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

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



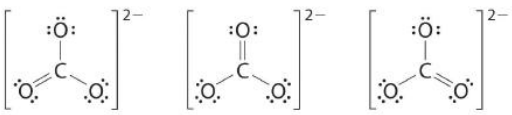
4. We divide the remaining 18 electrons equally among the three oxygen atoms by placing three lone pairs on each and indicating the −2 charge:



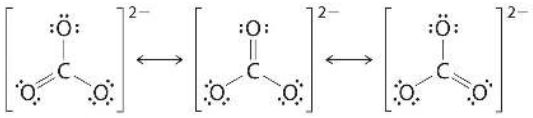
The Lewis dot structure has a central carbon that is bonded to 3 oxygens. Each oxygen has 3 lone pairs. The molecule is inside square brackets and has a charge of minus 2.

5. No electrons are left for the central atom.

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



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



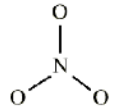
The resonance structure includes all three Lewis dot structures with double headed arrows between them.

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

The Nitrate (NO_3^-) ion

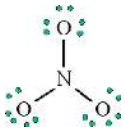
1. Count up the valence electrons: (1*5) + (3*6) + 1(ion) = **24** electrons

2. Draw the bond connectivities:

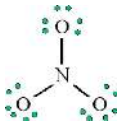


The three oxygens are drawn in the shape of a triangle with the nitrogen at the center of the triangle.

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

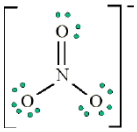


4. Place any leftover electrons (24-24 = **0**) on the center atom:



5. Does the central atom have an octet?

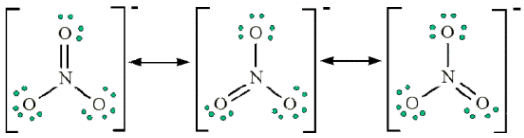
- **NO**, it has 6 electrons
- Add a multiple bond (first try a double bond) to see if the central atom can achieve an octet:



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

6. Does the central atom have an octet?

- YES
- Are there possible resonance structures? YES



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



Example 2.2.1.1: 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

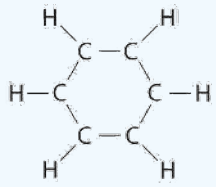
Asked for: resonance structures

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.

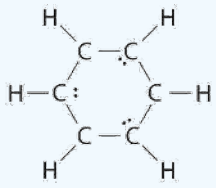
Solution:

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.

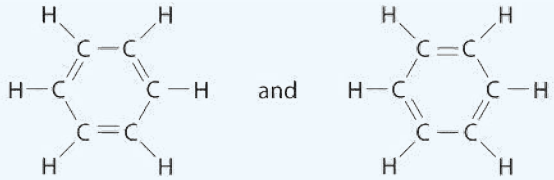
B If the 6 remaining electrons are uniformly distributed pairwise on alternate carbon atoms, we obtain the following:



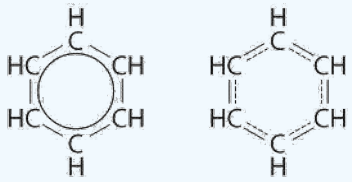
Three carbon atoms now have an octet configuration and a formal charge of −1, while three carbon atoms have only 6 electrons and a formal charge of +1. We can convert each lone pair to a bonding electron pair, which gives each atom an octet of

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:

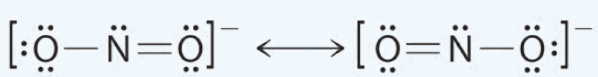


Benzene

? Exercise 2.2.1.1: Nitrite Ion

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

Answer



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

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

Warning

If several reasonable resonance forms for a molecule exists, the "actual electronic structure" of the molecule will probably be intermediate between all the forms that you can draw. The classic example is benzene in Example **2.2.1.1**. One would expect the double bonds to be shorter than the single bonds, but if one overlays the two structures, you see that one structure has a single bond where the other structure has a double bond. The best measurements that we can make of benzene do not show two bond lengths - instead, they show that the bond length is intermediate between the two resonance structures.

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

Summary

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

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

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

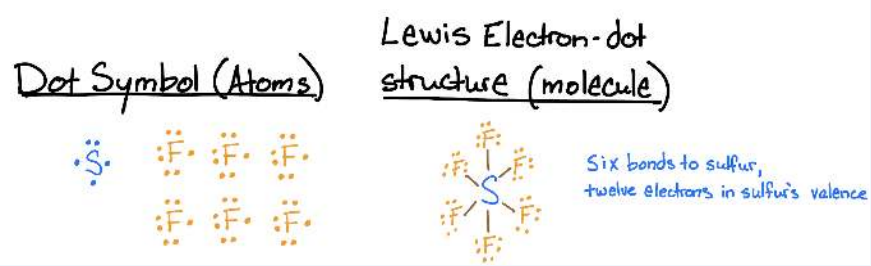
The octet rule applies well to atoms in the second row of the periodic table, where a full valence shell includes eight electrons with an electron configuration of s^2p^6. Even elements in the third and fourth row are known to follow this rule *sometimes*, but not always. In larger atoms, where $n \geq 3$ 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 2.2.2.1

Draw the Lewis structures for sulfur hexafluoride (SF_6).

Answer

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

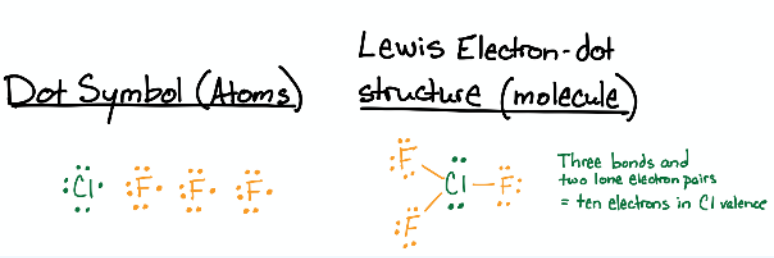


? Exercise 2.2.2.1

Draw the Lewis structure for chlorine trifluoride (ClF_3.

Answer

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



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

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

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

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

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

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2.2.3: Formal Charge

The formal charge of an atom in a molecule is the *hypothetical* charge the atom would have if we could redistribute the electrons in the bonds evenly between the atoms. Another way of saying this is that formal charge results when we take the number of valence electrons of a neutral atom, subtract the nonbonding electrons, and then subtract the number of bonds connected to that atom in the Lewis structure.

Calculating Formal Charges

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

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

We can double-check formal charge calculations by determining the sum of the formal charges for the whole structure. The sum of the formal charges of all atoms in a molecule must be zero; the sum of the formal charges in an ion should equal the charge of the ion.

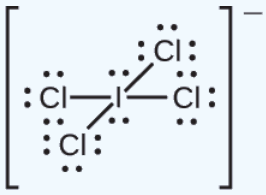
We must remember that the formal charge calculated for an atom is not the *actual* charge of the atom in the molecule. Formal charge is only a useful bookkeeping procedure; it does not indicate the presence of actual charges.

Calculating Formal Charge from Lewis Structures

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

Solution

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



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

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

- I: 7 – 8 = –1
- Cl: 7 – 7 = 0

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

Exercise 2.2.3.1

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



Answer

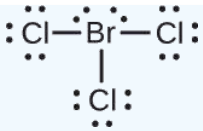
C −1, O +1

Example: Calculating Formal Charge from Lewis Structures

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

Solution

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



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

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

- Br: 7 – 7 = 0
- Cl: 7 – 7 = 0

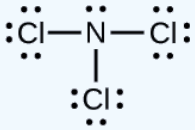
All atoms in $\mathbf{BrCl_3}$ have a formal charge of zero, and the sum of the formal charges totals zero, as it must in a neutral molecule.

? Exercise 2.2.3.2

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

Answer

N: 0; all three Cl atoms: 0



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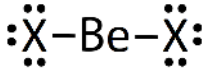
- **7.5: Formal Charges and Resonance** by OpenStax is licensed CC BY 4.0. Original source: https://openstax.org/details/books/chemistry-2e.

2.2.4: Lewis fails to predict unusual cases- Boron and Beryllium

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

Beryllium

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



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

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

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

BeF_2

At ambient temperature and pressure, BeF_2 is a solid that looks similar to quartz (Figure **2.2.4.1**) 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 **2.2.4.1**.

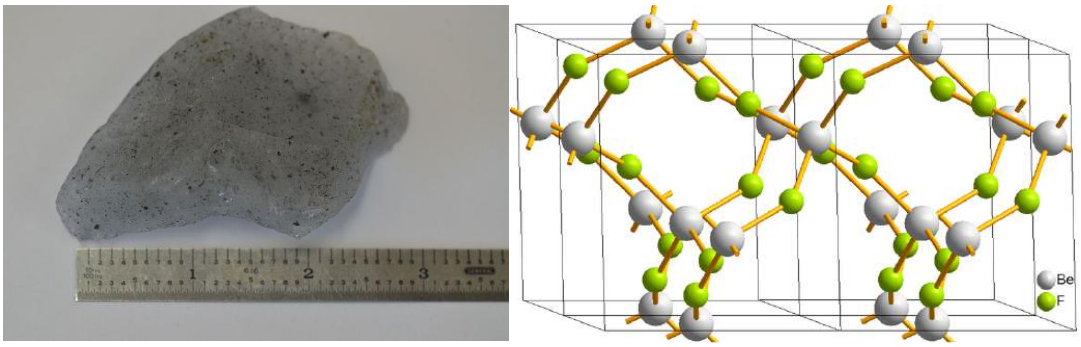


Figure **2.2.4.1**: (left) A nugget of beryllium fluoride obtained from Materion. Black spots are carbon (CC BY-SA 3.0; Bckelleher via Wikipedia). (right) BeF2 structure (CC BY-SA 3.0 Unported; Materialscientist via Wikipedia)

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

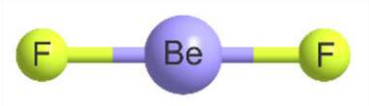


Figure **2.2.4.2**: Geometries of BeF_2. (CC BY; Ibon Alkorta and Anthony C. Legoe via Inorganics)

$BeCl_2$

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

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

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

Prediction based on Lewis structures:

Lewis structures of **BH_3** and **BF_3** were described in Exercise 3.1.2, and are drawn again below for convenience.

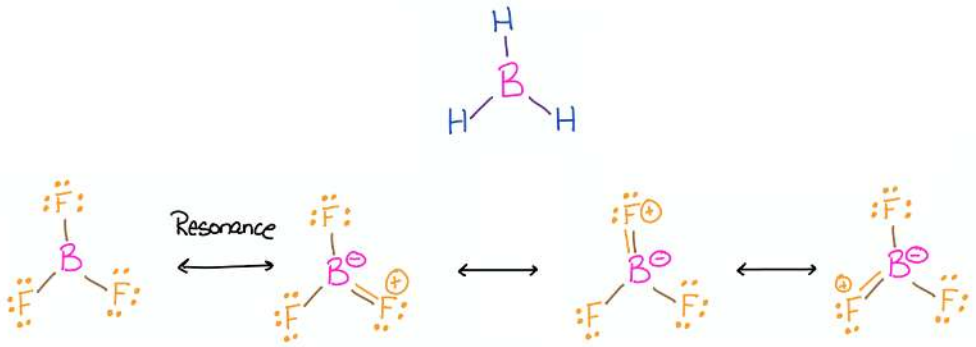


Figure **2.2.4.2**: Lewis structures of **BH_3** and **BF_3**. (Kathryn Haas; CC-NC-BY-SA)

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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2.3: Polar Covalent Bonds and Electrostatic Potential Maps

Learning Objectives

- To define electronegativity and bond polarity
- To calculate the percent ionic character of a covalent polar bond

The electron pairs shared between two atoms ***are not necessarily shared equally.*** For example, while the shared electron pairs is shared equally in the covalent bond in Cl_2, in $NaCl$ the 3s electron is stripped from the Na atom and is incorporated into the electronic structure of the Cl atom - and the compound is most accurately described as consisting of individual Na^+ and Cl^- ions (ionic bonding). For most covalent substances, their bond character falls **between** these two extremes. We demonstrated below, the **bond polarity** is a useful concept for describing the sharing of electrons between atoms within a covalent bond:

- A ***nonpolar covalent bond*** is one in which the electrons are shared *equally* between two atoms.
- A ***polar covalent bond*** is one in which ***one atom has a greater attraction for the electrons than the other atom***. If this relative attraction is great enough, then the bond is an ***ionic bond.***

Electronegativity

The elements with the highest ionization energies are generally those with the most negative electron affinities, which are located toward the upper right corner of the periodic table (compare Figure **2.3.2** and Figure **2.3.2**). Conversely, the elements with the lowest ionization energies are generally those with the least negative electron affinities and are located in the lower left corner of the periodic table.

Because the tendency of an element to gain or lose electrons is so important in determining its chemistry, various methods have been developed to quantitatively describe this tendency. The most important method uses a measurement called electronegativity (represented by the Greek letter *chi*, χ, pronounced “ky” as in “sky”), defined as the *relative* ability of an atom to attract electrons to itself *in a chemical compound*. Elements with high electronegativities tend to acquire electrons in chemical reactions and are found in the upper right corner of the periodic table. Elements with low electronegativities tend to lose electrons in chemical reactions and are found in the lower left corner of the periodic table.

Unlike ionization energy or electron affinity, the electronegativity of an atom is not a simple, fixed property that can be directly measured in a single experiment. In fact, an atom’s electronegativity should depend to some extent on its chemical environment because the properties of an atom are influenced by its neighbors in a chemical compound. Nevertheless, when different methods for measuring the electronegativity of an atom are compared, they all tend to assign similar relative values to a given element. For example, all scales predict that fluorine has the highest electronegativity and cesium the lowest of the stable elements, which suggests that all the methods are measuring the same fundamental property.

Note

Electronegativity is defined as the ability of an atom in a particular molecule to attract electrons to itself. The **greater** the value, the **greater** the attractiveness for electrons.

Electronegativity is a function of: (1) the atom's ***ionization energy*** (how strongly the atom holds on to its own electrons) and (2) the atom's ***electron affinity*** (how strongly the atom attracts other electrons). Both of these are properties of the *isolated* atom. An element that is will be *highly electronegative* has:

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

and will

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

The Pauling Electronegativity Scale

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

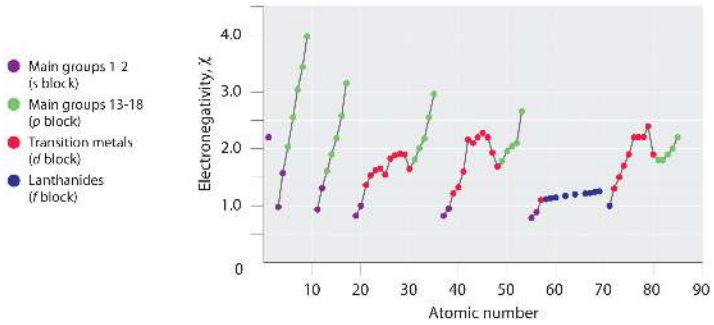


Figure 2.3.1: A Plot of Periodic Variation of Electronegativity with Atomic Number for the First Six Rows of the Periodic Table

Periodic variations in Pauling's electronegativity values are illustrated in Figure 2.3.1 and Figure 2.3.2. If we ignore the inert gases and elements for which no stable isotopes are known, we see that fluorine ($\chi = 3.98$) is the most electronegative element and cesium is the least electronegative nonradioactive element ($\chi = 0.79$). Because electronegativities generally increase diagonally from the lower left to the upper right of the periodic table, elements lying on diagonal lines running from upper left to lower right tend to have comparable values (e.g., O and Cl and N, S, and Br).

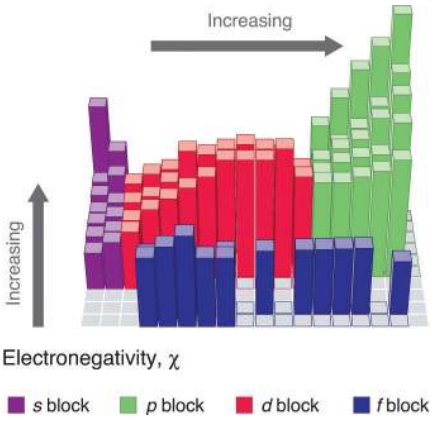
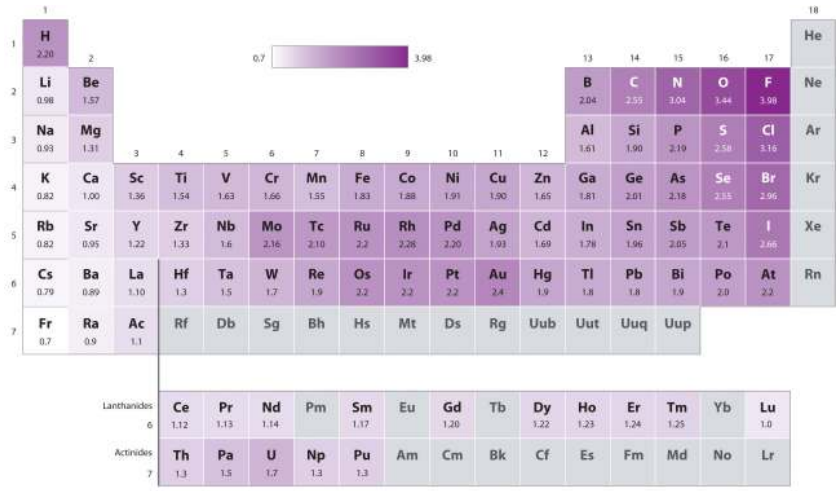


Figure 2.3.2: *Pauling Electronegativity Values of the s-, p-, d-, and f-Block Elements. Values for most of the actinides are approximate. Elements for which no data are available are shown in gray. Source: Data from L. Pauling, The Nature of the Chemical Bond, 3rd ed. (1960).*

Linus Pauling (1901-1994)

Pauling won two Nobel Prizes, one for chemistry in 1954 and one for peace in 1962. When he was nine, Pauling's father died, and his mother tried to convince him to quit school to support the family. He did not quit school but was denied a high school degree because of his refusal to take a civics class.



Pauling's method is limited by the fact that many elements do not form stable covalent compounds with other elements; hence their electronegativities cannot be measured by his method. Other definitions have since been developed that address this problem (e.g., the Mulliken electronegativity scale).

Electronegativity Differences between Metals and Nonmetals

An element's electronegativity provides us with a single value that we can use to characterize the chemistry of an element. Elements with a high electronegativity ($\chi \geq 2.2$) have very negative affinities and large ionization potentials, so they are generally nonmetals and electrical insulators that tend to gain electrons in chemical reactions (i.e., they are *oxidants*). In contrast, elements with a low electronegativity ($\chi \leq 1.8$) have electron affinities that have either positive or small negative values and small ionization potentials, so they are generally metals and good electrical conductors that tend to lose their valence electrons in chemical reactions (i.e., they are *reductants*). In between the metals and nonmetals, along the heavy diagonal line running from B to At is a group of elements with intermediate electronegativities ($\chi \sim 2.0$). These are the **semimetals** (or metalloids), elements that have some of the chemical properties of both nonmetals and metals. The distinction between metals and nonmetals is one of the most fundamental we can make in categorizing the elements and predicting their chemical behavior. Figure **2.3.3** shows the strong correlation between electronegativity values, metallic versus nonmetallic character, and location in the periodic table.

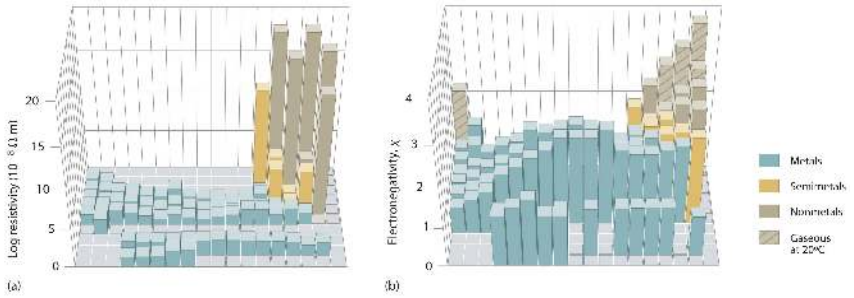


Figure **2.3.3**: Three-Dimensional Plots Demonstrating the Relationship between Electronegativity and the Metallic/Nonmetallic Character of the Elements. (a) A plot of electrical resistivity (measured resistivity to electron flow) at or near room temperature shows that substances with high resistivity (little to no measured electron flow) are electrical insulators, whereas substances with low resistivity (high measured electron flow) are metals. (b) A plot of Pauling electronegativities for a like set of elements shows that high electronegativity values (≥ about 2.2) correlate with high electrical resistivities (insulators). Low electronegativity values (≤ about 2.2) correlate with low resistivities (metals). Because electrical resistivity is typically measured only for solids and liquids, the gaseous elements do not appear in part (a).

Note

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

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

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

Example 2.3.1

On the basis of their positions in the periodic table, arrange Cl, Se, Si, and Sr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a semimetal.

Given: four elements

Asked for: order by increasing electronegativity and classification

<p">**Strategy:**

A. Locate the elements in the periodic table. From their diagonal positions from lower left to upper right, predict their relative electronegativities.
B. Arrange the elements in order of increasing electronegativity.
C. Classify each element as a metal, a nonmetal, or a semimetal according to its location about the diagonal belt of semimetals running from B to At.

Solution:

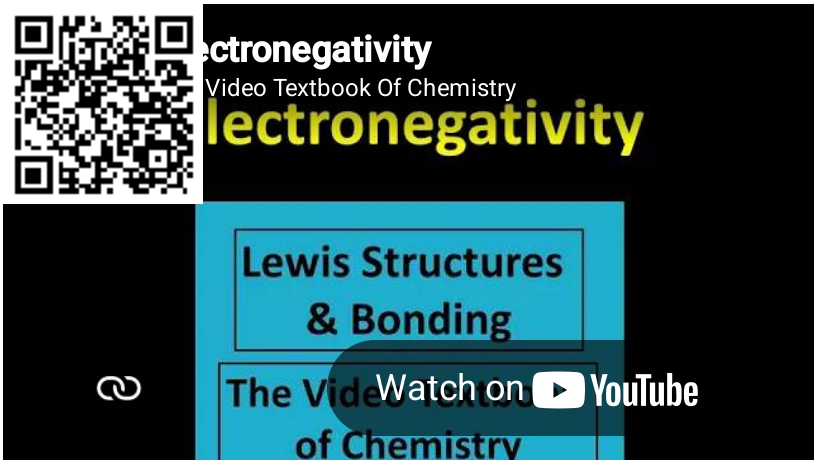
A Electronegativity increases from lower left to upper right in the periodic table (Figure 2.3.2). Because Sr lies far to the left of the other elements given, we can predict that it will have the lowest electronegativity. Because Cl lies above and to the right of Se, we can predict that $\chi_{Cl} > \chi_{Se}$. Because Si is located farther from the upper right corner than Se or Cl, its electronegativity should be lower than those of Se and Cl but greater than that of Sr. **B** The overall order is therefore $\chi_{Sr} < \chi_{Si} < \chi_{Se} < \chi_{Cl}$.

C To classify the elements, we note that Sr lies well to the left of the diagonal belt of semimetals running from B to At; while Se and Cl lie to the right and Si lies in the middle. We can predict that Sr is a metal, Si is a semimetal, and Se and Cl are nonmetals.

Exercise 2.3.1

On the basis of their positions in the periodic table, arrange Ge, N, O, Rb, and Zr in order of increasing electronegativity and classify each as a metal, a nonmetal, or a semimetal.

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



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

Percent Ionic Character of a Covalent polar bond

The two idealized extremes of chemical bonding: (1) ionic bonding—in which one or more electrons are transferred completely from one atom to another, and the resulting ions are held together by purely electrostatic forces—and (2) covalent bonding, in which electrons are shared equally between two atoms. Most compounds, however, have polar covalent bonds, which means that

electrons are shared unequally between the bonded atoms. Figure **2.3.4** compares the electron distribution in a polar covalent bond with those in an ideally covalent and an ideally ionic bond. Recall that a lowercase Greek delta (δ) is used to indicate that a bonded atom possesses a partial positive charge, indicated by δ^+, or a partial negative charge, indicated by δ^-, and a bond between two atoms that possess partial charges is a polar bond.

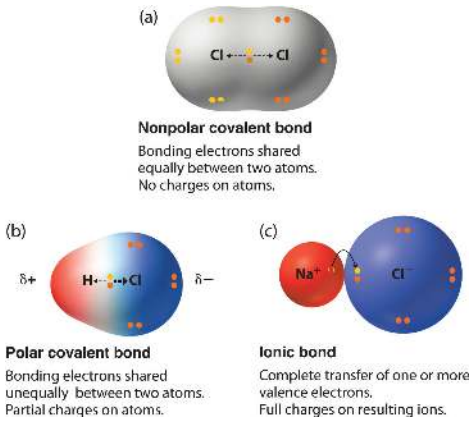


Figure **2.3.4**: The Electron Distribution in a Nonpolar Covalent Bond, a Polar Covalent Bond, and an Ionic Bond Using Lewis Electron Structures. In a purely covalent bond (a), the bonding electrons are shared equally between the atoms. In a purely ionic bond (c), an electron has been transferred completely from one atom to the other. A polar covalent bond (b) is intermediate between the two extremes: the bonding electrons are shared unequally between the two atoms, and the electron distribution is asymmetrical with the electron density being greater around the more electronegative atom. Electron-rich (negatively charged) regions are shown in blue; electron-poor (positively charged) regions are shown in red.

Bond Polarity

The polarity of a bond—the extent to which it is polar—is determined largely by the relative electronegativities of the bonded atoms. Electronegativity (χ) was defined as the ability of an atom in a molecule or an ion to attract electrons to itself. Thus there is a direct correlation between electronegativity and bond polarity. A bond is *nonpolar* if the bonded atoms have equal electronegativities. If the electronegativities of the bonded atoms are not equal, however, the bond is *polarized* toward the more electronegative atom. A bond in which the electronegativity of B (χ_B) is greater than the electronegativity of A (χ_A), for example, is indicated with the partial negative charge on the more electronegative atom:

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

One way of estimating the ionic character of a bond—that is, the magnitude of the charge separation in a polar covalent bond—is to calculate the difference in electronegativity between the two atoms: $\Delta\chi = \chi_B - \chi_A$.

To predict the polarity of the bonds in Cl_2, HCl, and NaCl, for example, we look at the electronegativities of the relevant atoms: $\chi_{Cl} = 3.16$, $\chi_H = 2.20$, and $\chi_{Na} = 0.93$ (see Figure **2.3.2**). Cl_2 must be nonpolar because the electronegativity difference ($\Delta\chi$) is zero; hence the two chlorine atoms share the bonding electrons equally. In NaCl, $\Delta\chi$ is 2.23. This high value is typical of an ionic compound ($\Delta\chi \geq \approx 1.5$) and means that the valence electron of sodium has been completely transferred to chlorine to form Na^+ and Cl^- ions. In HCl, however, $\Delta\chi$ is only 0.96. The bonding electrons are more strongly attracted to the more electronegative chlorine atom, and so the charge distribution is

$$\overset{\delta^+}{H} - \overset{\delta^-}{Cl}$$

Remember that electronegativities are difficult to measure precisely and different definitions produce slightly different numbers. In practice, the polarity of a bond is usually estimated rather than calculated.

Note

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

As with bond energies, the electronegativity of an atom depends to some extent on its chemical environment. It is therefore unlikely that the reported electronegativities of a chlorine atom in NaCl, Cl_2, ClF_5, and $HClO_4$ would be exactly the same.

Dipole Moments as a Measure of Bond Polarity

The asymmetrical charge distribution in a polar substance such as HCl produces a **dipole moment** where Qr in meters (m). is abbreviated by the Greek letter mu (μ). The dipole moment is defined as the product of the partial charge Q on the bonded atoms and the distance r between the partial charges:

$$\mu = Qr \tag{2.3.1}$$

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

$$1\ D = 3.3356 \times 10^{-30}\ C \cdot m \tag{2.3.2}$$

When a molecule with a dipole moment is placed in an electric field, it tends to orient itself with the electric field because of its asymmetrical charge distribution (Figure **2.3.2**).

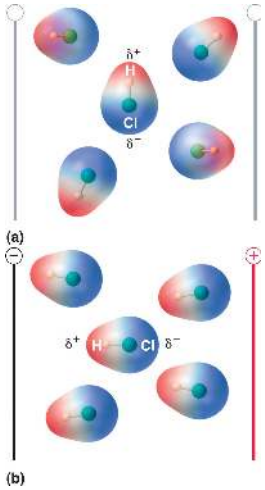


Figure **2.3.5**: Molecules That Possess a Dipole Moment Partially Align Themselves with an Applied Electric Field In the absence of a field (a), the HCl molecules are randomly oriented. When an electric field is applied (b), the molecules tend to align themselves with the field, such that the positive end of the molecular dipole points toward the negative terminal and vice versa.

We can measure the partial charges on the atoms in a molecule such as HCl using Equation 10.3.2 If the bonding in HCl were purely ionic, an electron would be transferred from H to Cl, so there would be a full +1 charge on the H atom and a full −1 charge on the Cl atom. The dipole moment of HCl is 1.109 D, as determined by measuring the extent of its alignment in an electric field, and the reported gas-phase H–Cl distance is 127.5 pm. Hence the charge on each atom is

$$Q = \frac{\mu}{r} = 1.109\ \cancel{D}\left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}}\right)\left(\frac{1}{127.8\ \cancel{pm}}\right)\left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}}\right) = 2.901 \times 10^{-20}\ C \tag{2.3.3}$$

By dividing this calculated value by the charge on a single electron (1.6022×10^{-19} C), we find that the electron distribution in HCl is asymmetric and that effectively it appears that there is a net negative charge on the Cl of about −0.18, effectively corresponding to about 0.18 e^-. This certainly does not mean that there is a fraction of an electron on the Cl atom, but that the distribution of electron probability favors the Cl atom side of the molecule by about this amount.

$$\frac{2.901 \times 10^{-20}\ \cancel{C}}{1.6022 \times 10^{-19}\ \cancel{C}} = 0.1811\ e^- \tag{2.3.4}$$

To form a neutral compound, the charge on the H atom must be equal but opposite. Thus the measured dipole moment of HCl indicates that the H–Cl bond has approximately 18% ionic character (0.1811 × 100), or 82% covalent character. Instead of writing HCl as

$$\overset{\delta+}{H} - \overset{\delta-}{Cl}$$

we can therefore indicate the charge separation quantitatively as

$$\overset{0.18\delta+}{H} - \overset{0.18\delta-}{Cl}$$

Our calculated results are in agreement with the electronegativity difference between hydrogen and chlorine $\chi_H = 2.20$; $\chi_{Cl} = 3.16$, $\chi_{Cl} - \chi_H = 0.96$), a value well within the range for polar covalent bonds. We indicate the dipole moment by writing an arrow above the molecule.Mathematically, dipole moments are vectors, and they possess both a magnitude and a direction. The dipole moment of a molecule is the vector sum of the dipoles of the individual bonds. In HCl, for example, the dipole moment is indicated as follows:



The arrow shows the direction of electron flow by pointing toward the more electronegative atom.

The charge on the atoms of many substances in the gas phase can be calculated using measured dipole moments and bond distances. Figure **2.3.6** shows a plot of the percent ionic character versus the difference in electronegativity of the bonded atoms for several substances. According to the graph, the bonding in species such as NaCl(g) and CsF(g) is substantially less than 100% ionic in character. As the gas condenses into a solid, however, dipole–dipole interactions between polarized species increase the charge separations. In the crystal, therefore, an electron is transferred from the metal to the nonmetal, and these substances behave like classic ionic compounds. The data in Figure **2.3.6** show that diatomic species with an electronegativity difference of less than 1.5 are less than 50% ionic in character, which is consistent with our earlier description of these species as containing polar covalent bonds. The use of dipole moments to determine the ionic character of a polar bond is illustrated in Example 11.

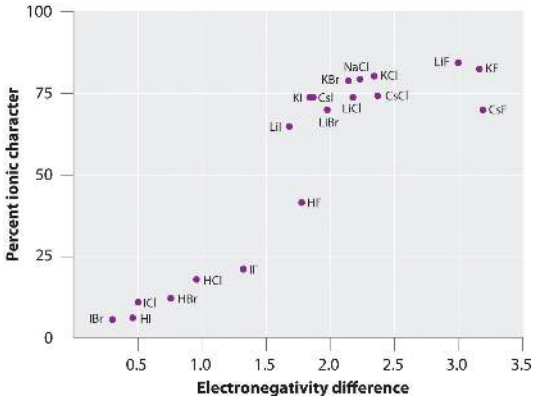


Figure **2.3.6**: A Plot of the Percent Ionic Character of a Bond as Determined from Measured Dipole Moments versus the Difference in Electronegativity of the Bonded Atoms.In the gas phase, even CsF, which has the largest possible difference in electronegativity between atoms, is not 100% ionic. Solid CsF, however, is best viewed as 100% ionic because of the additional electrostatic interactions in the lattice.

✔ Example **2.3.2**

In the gas phase, NaCl has a dipole moment of 9.001 D and an Na–Cl distance of 236.1 pm. Calculate the percent ionic character in NaCl.

Given: chemical species, dipole moment, and internuclear distance

Asked for: percent ionic character

Strategy:

A Compute the charge on each atom using the information given and Equation 10.3.2.

B Find the percent ionic character from the ratio of the actual charge to the charge of a single electron.

Solution:

A The charge on each atom is given by

$$Q = \frac{\mu}{r} = 9.001 \cancel{D} \left(\frac{3.3356 \times 10^{-30}\ C \cdot \cancel{m}}{1\ \cancel{D}} \right) \left(\frac{1}{236.1\ \cancel{pm}} \right) \left(\frac{1\ \cancel{pm}}{10^{-12}\ \cancel{m}} \right) = 1.272 \times 10^{-19}\ C \tag{2.3.5}$$

Thus NaCl behaves as if it had charges of 1.272×10^{-19} C on each atom separated by 236.1 pm.

B The percent ionic character is given by the ratio of the actual charge to the charge of a single electron (the charge expected for the complete transfer of one electron):

$$\%\ ionic\ character = \left(\frac{1.272 \times 10^{-19}\ \cancel{C}}{1.6022 \times 10^{-19}\ \cancel{C}} \right) (100) = 79.39\% \simeq 79\% \tag{2.3.6}$$

? Exercise 2.3.2

In the gas phase, silver chloride (AgCl) has a dipole moment of 6.08 D and an Ag–Cl distance of 228.1 pm. What is the percent ionic character in silver chloride?

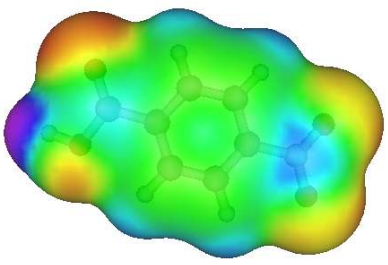
Answer: 55.5%



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

Electrostatic Potential Maps

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



Note: Constructing a Electrostatic Potential Map

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

The most important thing to consider when analyzing an electrostatic potential map is the charge distribution. The relative distributions of electrons will allow you to deduce everything you need to know from these maps. Recall the relationship between electrostatic potential and charge distribution. Areas of low potential, red, are characterized by an abundance of electrons. Areas of high potential, blue, are characterized by a relative absence of electrons. Oxygen has a higher electronegativity value than sulfur (Table A2), hence. oxygen atoms would have a higher electron density around them than sulfur atoms. Thus the spherical region that corresponds to an oxygen atom would have a red portion on it. Now note that there are two oxygen atoms in sulfur dioxide (Figure **2.3.7**). There are two sphere shaped objects that have red regions. These areas correspond to the location of the oxygen atoms. The blue tainted sphere at the top corresponds to the location of the sulfur atom.

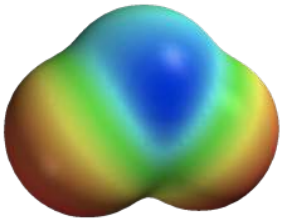


Figure **2.3.7**. The electrostatic diagram of Sulfur Dioxide (SO_2). Which parts of this diagram correlate to the respective atomic components? Red indicates the lowest electrostatic potential energy, and blue indicates the highest electrostatic potential energy. Intermediary colors represent intermediary electrostatic potentials.

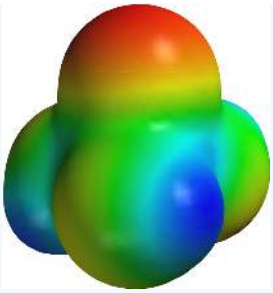
Note

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

Electrostatic potential maps can also be used to determine the nature of the molecules chemical bond. Consider SO_2 in Figure **2.3.7**, there is a great deal of intermediary potential energy, the non red or blue regions, in this diagram. This indicates that the electronegativity difference is not very great. In a molecule with a great electronegativity difference, charge is very polarized, and there are significant differences in electron density in different regions of the molecule. This great electronegativity difference leads to regions that are almost entirely red and almost entirely blue. Greater regions of intermediary potential, yellow and green, and smaller or no regions of extreme potential, red and blue, are key indicators of a smaller electronegativity difference. Note that the electronegativity difference is a key determinant in the nature of a chemical bond.

Example 2.3.3

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



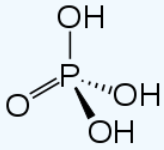
Solution

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

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

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

Here is the molecular diagram of phosphoric acid:



Summary

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

Dipole moment

Label '10.3.2' multiply defined

The **electronegativity (χ)** of an element is the relative ability of an atom to attract electrons to itself in a chemical compound and increases diagonally from the lower left of the periodic table to the upper right. The Pauling electronegativity scale is based on measurements of the strengths of covalent bonds between different atoms, whereas the Mulliken electronegativity of an element is the average of its first ionization energy and the absolute value of its electron affinity. Elements with a high electronegativity are generally nonmetals and electrical insulators and tend to behave as oxidants in chemical reactions. Conversely, elements with a low electronegativity are generally metals and good electrical conductors and tend to behave as reductants in chemical reactions.

Compounds with **polar covalent bonds** have electrons that are shared unequally between the bonded atoms. The polarity of such a bond is determined largely by the relative electronegativites of the bonded atoms. The asymmetrical charge distribution in a polar substance produces a **dipole moment**, which is the product of the partial charges on the bonded atoms and the distance between them.

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2.4: 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 2.4.1:

$$\vec{\mu} = \sum_i q_i \vec{r}_i \tag{2.4.1}$$

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 H_2O. Because of the lone pair on oxygen, the structure of H_2O is bent (via VSEPR theory), which means that the vectors representing the dipole moment of each bond do not cancel each other out. Hence, water is polar.

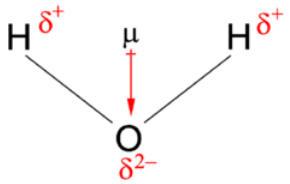


Figure 2.4.1: Dipole moment of water. The convention in chemistry is that the arrow representing the dipole moment goes from positive to negative. Physicist tend to use the opposite orientation.

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 2.4.2); 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 2.4.2).

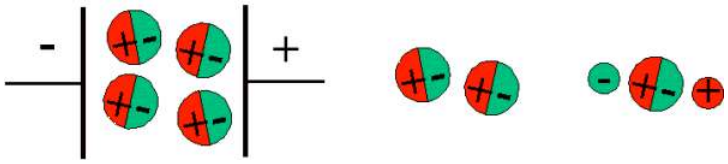


Figure 2.4.2: Polar molecules align themselves in an electric field (left), with respect to one another (middle), and with respect to ions (right)

Equation 2.4.1 can be simplified for a simple separated two-charge system like diatomic molecules or when considering a bond dipole within a molecule

$$\mu_{diatomic} = Q \times r \tag{2.4.2}$$

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 2.4.2):

$$\begin{aligned} \mu &= Qr \\ &= (1.60 \times 10^{-19}\, C)(1.00 \times 10^{-10}\, m) \\ &= 1.60 \times 10^{-29}\, C \cdot m \end{aligned}$$

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:

$$\mu = \frac{120}{100}(4.80\ D) = 5.76\, D \tag{2.4.3}$$

- If the proton and electron are separated by 150 pm:

$$\mu = \frac{150}{100}(4.80\ D) = 7.20\, D \tag{2.4.4}$$

- If the proton and electron are separated by 200 pm:

$$\mu = \frac{200}{100}(4.80\ D) = 9.60\, D \tag{2.4.5}$$

Example 2.4.1: Water

The water molecule in Figure 2.4.1 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.

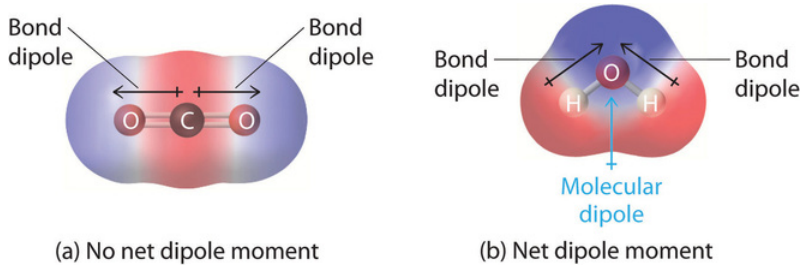


Figure 2.4.3: Charge distributions of CO_2 and H_2O\). Blue and red colored regions are negatively and positively signed regions, respectively. (CC BY-SA-NC 3.0; anonymous)

A good example of a nonpolar molecule that contains polar bonds is carbon dioxide (Figure 2.4.3*a*). This is a linear molecule and each C=O bond is, in fact, polar. The central carbon will have a net positive charge, and the two outer oxygen atoms a net negative charge. However, since the molecule is linear, these two bond dipoles cancel each other out (i.e. the vector addition of the dipoles equals zero) and the overall molecule has a zero dipole moment ($\mu = 0$).

> *Although a polar bond is a prerequisite for a molecule to have a dipole, not all molecules with polar bonds exhibit dipoles*

For AB_n molecules, where A is the central atom and B are all the same types of atoms, there are certain molecular geometries which are symmetric. Therefore, they will have no dipole even if the bonds are polar. These geometries include linear, trigonal planar, tetrahedral, octahedral and trigonal bipyramid.

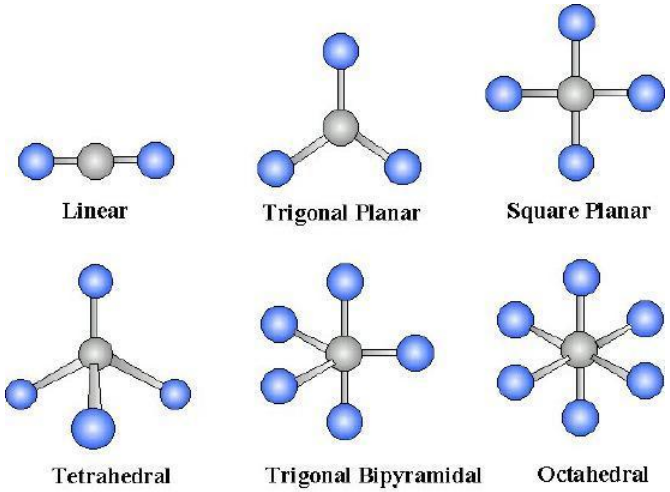
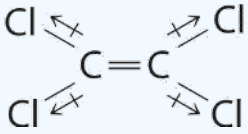


Figure 2.4.4: Molecular geometries with exact cancellation of polar bonding to generate a non-polar molecule ($\mu = 0$)

Example 2.4.3: C_2Cl_4

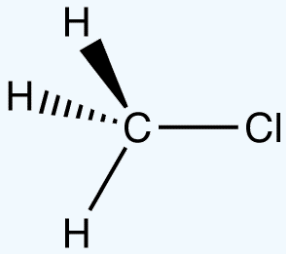
Although the C–Cl bonds are rather polar, the individual bond dipoles cancel one another in this symmetrical structure, and $Cl_2C{=}CCl_2$ does not have a net dipole moment.



Example 2.4.3: 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 **2.4.1**: 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

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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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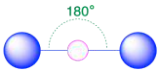
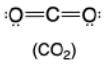
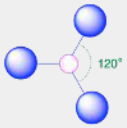
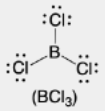
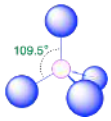
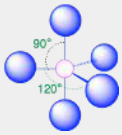
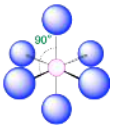
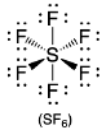
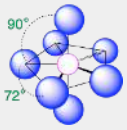
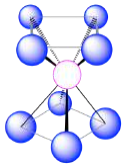
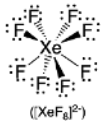
2.5: Valence Shell Electron-Pair Repulsion

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 AX_mE_n designation, where **A is the central atom**, **X is a bonded atom**, **E is a nonbonding** valence electron group (usually a lone pair of electrons), and m and n are integers. The number of groups is equal to the sum of m and n. Using this information, we can describe the molecular geometry around a central atom, that is, the arrangement of the *bonded atoms* in a molecule or polyatomic ion. The geometries that are predicted from VSEPR when a central atom has only bonded groups ($n = 0$) are listed below in Table **2.5.1**. The cases where lone pairs contribute to the total groups ($n \geq 1$) are discussed in the next section about lone pair repulsion.

Table **2.5.1**. Geometries predicted using VSEPR theory (bonded groups only).

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

Practice

VSEPR to predict Molecular Geometry

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

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

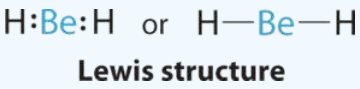
Use the procedure above to complete the exercises below

Exercise 2.5.1

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

Answer BeH_2

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



Lewis structure

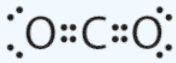
2. There are two groups around the central atom, and both groups are single bonds. Thus BeH_2 is designated as AX_2.

3. We see from Table **2.5.1** that the arrangement that minimizes repulsions places the groups 180° apart.

4. From Table **2.5.1** we see that with two bonding pairs, the molecular geometry that minimizes repulsions in BeH_2 is *linear.*

Answer CO_2

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



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

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

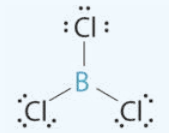
4. VSEPR only recognizes groups around the *central* atom (the carbon). Thus the lone pairs on the oxygen atoms do not influence the molecular geometry. With two bonded groups on the central atom and no lone pairs, the molecular geometry of CO_2 is linear (Table **2.5.1**). The structure of CO_2 is shown in Table **2.5.1**.

? Exercise 2.5.2

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

Answer BCl_3

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



Lewis structure

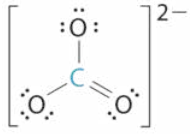
2. There are three groups around the central atom and all are single bonds. The structure is designated as AX_3.

3. To minimize repulsions, the groups are placed 120° apart (Table **2.5.1**).

4. From Table **2.5.1** 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

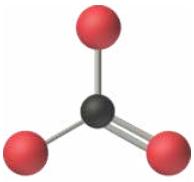


Lewis structure

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 **2.5.1**).

4. We see from Table **2.5.1** that the molecular geometry of CO_3^{2-} is trigonal planar with bond angles of 120°.



Molecular geometry
(trigonal planar)

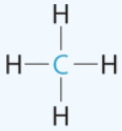
In our next example we encounter the effects of lone pairs and multiple bonds on molecular geometry for the first time.

? Exercise 2.5.3

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

Answer CH_4

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

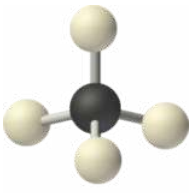


Lewis structure

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

3. As shown in Table **2.5.1**, repulsions are minimized by placing the groups in the corners of a tetrahedron with bond angles of 109.5°.

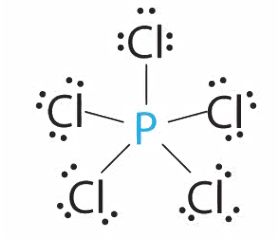
4. With four bonding pairs, the molecular geometry of methane is *tetrahedral* (Table **2.5.1**).



Molecular geometry
(tetrahedral)

Answer PCl_5

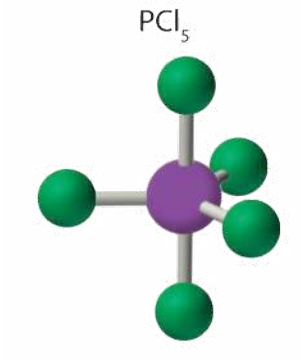
1. Phosphorus has five valence electrons and each chlorine has seven valence electrons, so the Lewis electron structure of PCl_5 is



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

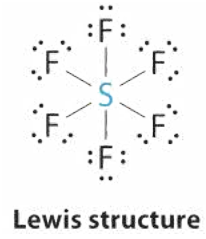
3. The structure that minimizes repulsions is a *trigonal bipyramid*, which consists of two trigonal pyramids that share a base (Table **2.5.1**).

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



Answer SF_6

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

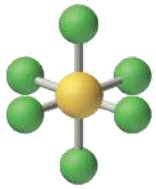


With an expanded valence, this species is an exception to the octet rule.

2. There are six electron groups around the central atom, each a bonding pair. We see from Figure **2.5.2** that the geometry that minimizes repulsions is *octahedral*.

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

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



Molecular geometry
(octahedral)

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2.5.1: Lone Pair Repulsion

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

Lone pairs have stronger repulsive forces than bonded groups.

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

Trend in bond angles:

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

Using empirical evidence as a guide, we can predict that lone pairs repel other electron groups more strongly than bonded pairs. The molecular geometry of molecules with lone pairs of electrons is better predicted when we consider that electronic repulsion created by lone pairs is stronger than the repulsion from bonded groups. It is difficult to predict the exact bond angle based on this principle, but we can predict approximate angles, as described and summarized below in Table **2.5.1.1**.

Table **2.5.1.1**: Predictions of molecular geometry and bond angles around atoms with a mixture of bonded (X) and unbonded (E) electron groups.

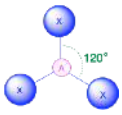
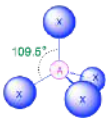
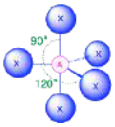
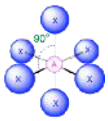
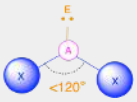
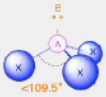
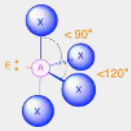
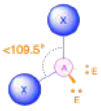
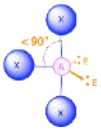
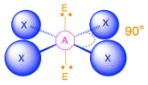
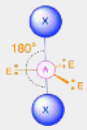
	Electron Groups (*m* + *n*)				
	2 (steric number = 2)	**3** (steric number = 3)	**4** (steric number = 4)	**5** (steric number = 5)	**6** (steric number = 6)
Parent Geometry (0 lone pairs) AX_m	 AX_2, linear 180°	 AX_3, trig. plane 120°	 $AX4$, tetrahedron 109.5°	 AX_5, trig. bipyramid 90°, 120°	 AX_6,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

Table **2.5.1.1** 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.

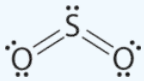
Three Electron Groups (m + n = 3)

(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 **2.5.1.1**).

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)

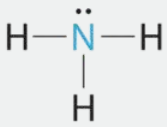
(Steric number = 4) In the case that there are four electron groups around a central atom, those groups will lie approximately 109.5° from one another in space. This results in an electronic geometry that is approximately **tetrahedral**. There are three different molecular geometries that are possible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

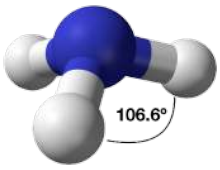
1. In ammonia, the central atom, nitrogen, has five valence electrons and each hydrogen donates one valence electron, producing the Lewis electron structure



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

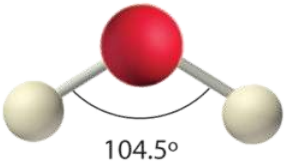
1. Oxygen has six valence electrons and each hydrogen has one valence electron, producing the Lewis electron structure



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)

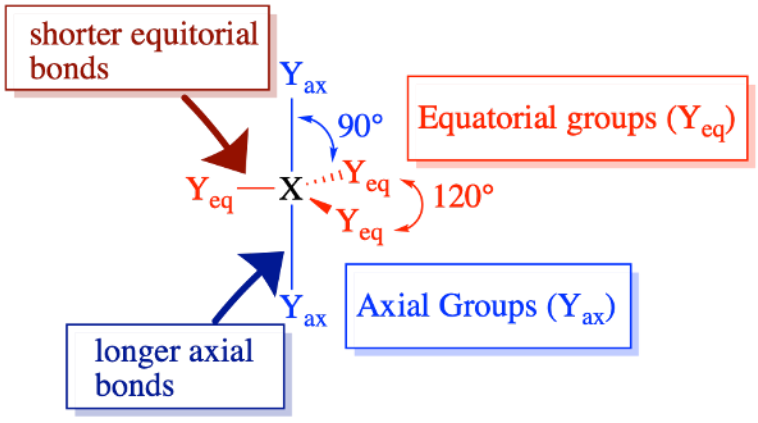


Figure: Trigonal pyramidal molecules (steric number 5) possess different bond angles and lengths for axial (ax) and equatorial (eq) pendant atoms. (CC-BY-NC-SA; Kathryn Haas).

(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.

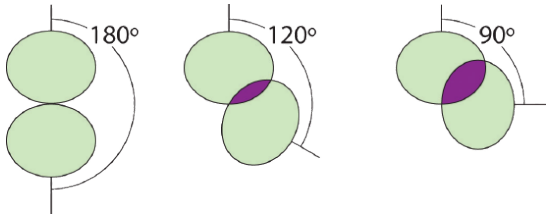
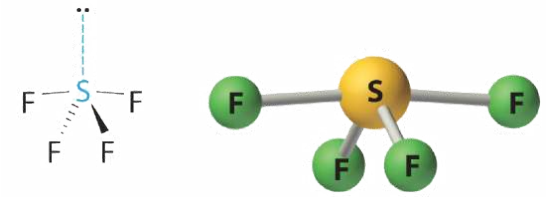


Illustration of the Area Shared by Two Electron Pairs versus the Angle between Them

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

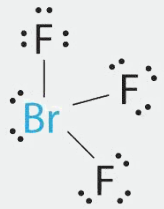
in the equatorial plane.



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	(a)	(b)	(c)
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.

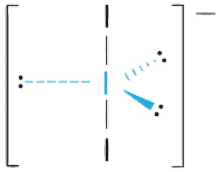
AX_2E_3 Molecules: I_3^-

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



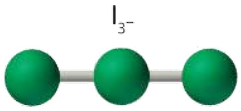
2. There are five electron groups about the central atom in I_3^-, two bonding pairs and three lone pairs. To minimize repulsions, the groups are directed to the corners of a trigonal bipyramid.

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.



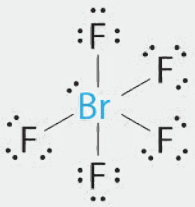
Six Electron Groups (m + n = 6)

(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

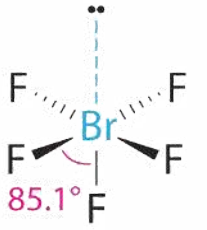
1. The central atom, bromine, has seven valence electrons, as does each fluorine, so the Lewis electron structure is



Lewis structure

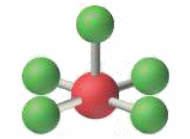
With its expanded valence, this species is an exception to the octet rule.

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.

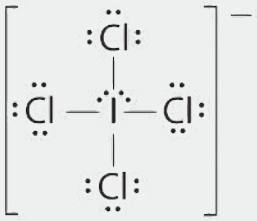
4. With five nuclei surrounding the central atom, the molecular structure is based on an octahedron with a vertex missing. This molecular structure is *square pyramidal*. The F_{axial}–B–$F_{equatorial}$ angles are 85.1°, less than 90° because of LP–BP repulsions.



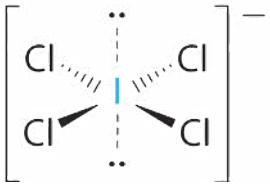
Molecular geometry
(square pyramidal)

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

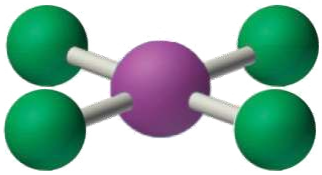


2. There are six electron groups around the central atom, four bonding pairs and two lone pairs. The structure that minimizes LP–LP, LP–BP, and BP–BP repulsions is



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 **2.5.1.1**.

Example Excercises

✔ Example 2.5.1.1

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

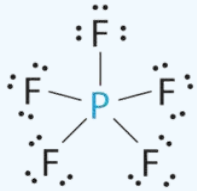
Asked for: molecular geometry

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



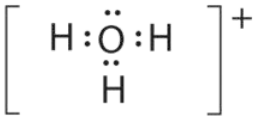
B There are five bonding groups about phosphorus. The structure that minimizes repulsions is a trigonal bipyramid.

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.



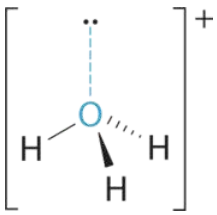
- **A** The central atom, O, has six valence electrons, and each H atom contributes one valence electron. Subtracting one electron for the positive charge gives a total of eight valence electrons, so the Lewis electron structure is



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 2.5.1.1

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

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

Answer a

trigonal pyramidal

Answer b

octahedral

Answer c

linear

Example 2.5.1.2

Predict the molecular geometry of each molecule.

1. XeF_2
2. $SnCl_2$

Given: two chemical compounds

Asked for: molecular geometry

Strategy:

Use the strategy given in Example 2.5.1.1.

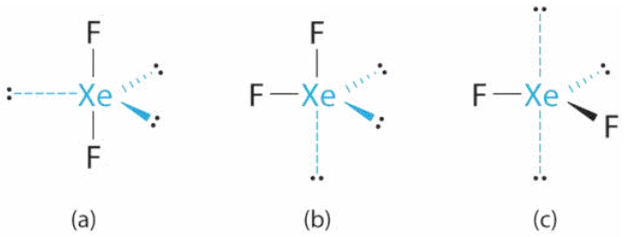
Solution:

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:

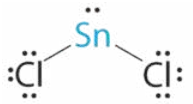


Interactions			
90 LP–LP	0	2	2

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 2.5.1.2

Predict the molecular geometry of each molecule.

a. SO_3
b. XeF_4

Answer a

trigonal planar

Answer b

square planar

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

2.5.2: 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.

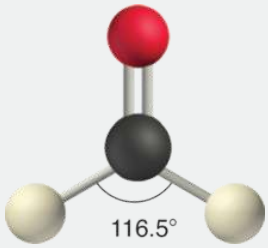
Double and triple bonds are more repulsive than single bonds

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 2.5.2.1

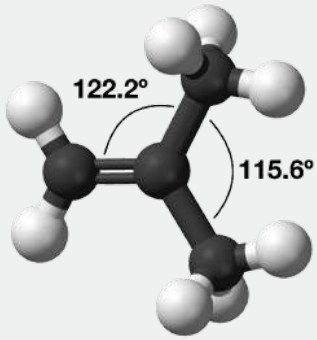
CH_2O

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

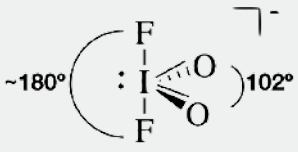
In general, we expect that a lone pair has slightly greater repulsive force than a multiple bond, and that a multiple bond has slightly greater repulsive force than a single bond. The **order of expected repulsive force** is:

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

Examples2.5.2.1

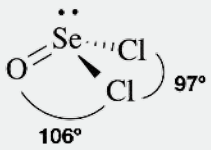
$IO_2F_2^-$

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

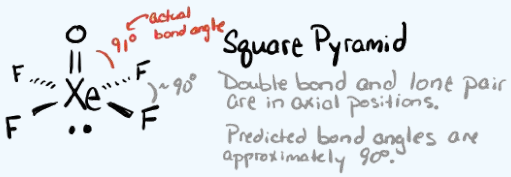
Exercise 2.5.2.1

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

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

Answer a

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



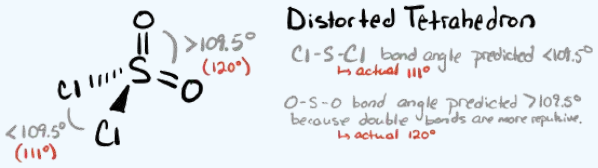
Answer b

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



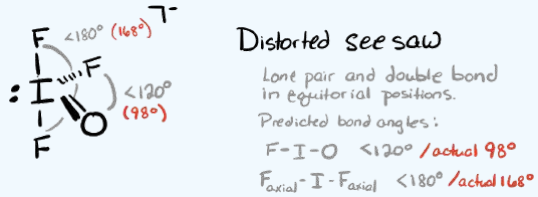
Answer c

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



Answer d

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



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2.5.3: 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 **2.5.3.1**: 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 **2.5.3.2** each have three identical "pendant groups" on the central atom (Figure **2.5.3.2**). *Pendant atoms* or *pendant groups* are the atoms, or groups of atoms, that are bonded directly to the central atom. The molecules shown here are arranged according to the size of the central and pendant atoms. Central atoms increase in size going down this figure, and pendant atoms increase in size going across from left to right. The bond angles and bond lengths are labeled in each case.

What trends can you identify?

Trends in Size

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

Size of the central atom

Examine the relationship between the size of the central atom and the bond angles in Figure **2.5.3.2** (go down any column in the figure). For example, compare NH_3, PH_3, AsH_3, and SbH_3, with bond angles 106.6°, 93.2°, 92.1°, and 91.6°, respectively. In this series, the size of the central atom increases from N to Sb while the size of the pendant atom (hydrogen) remains constant. *As the size of the central atom increases, the bond angles decrease; thus, we observe a negative relationship between size of the central atom and the bond angle in these molecules*. This relationship is explained by sterics. As the central atom increases in size, the

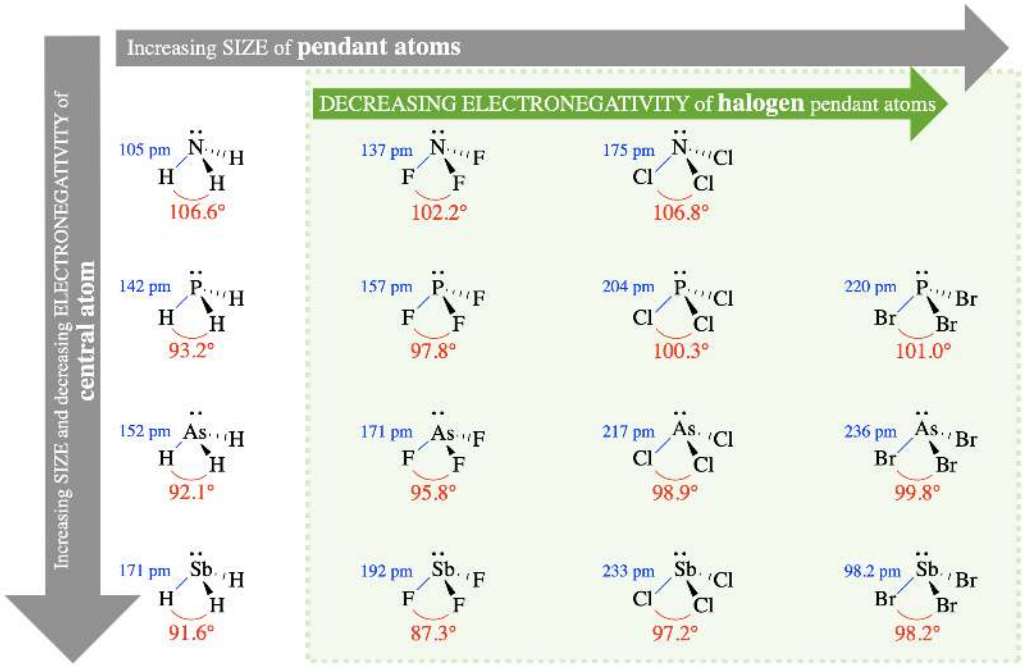


Figure **2.5.3.2**: Several molecules with trigonal pyramidal electronic geometry are shown arranged according to size of the central atom (increasing size of central atom from top to bottom) and pendant atom (increasing size of pendant atoms from left to right). Bond angles and bond lengths are indicated. (Kathryn Haas; CC-NC-BY-SA)

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

Size of the pendant atoms (or groups)

Examine the relationships between size of the halogen pendant atoms and bond angle in Figure **2.5.3.2** (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 **2.5.3.3**).

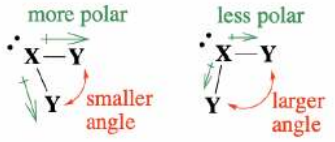


Figure **2.5.3.3**. When electron pairs are distributed away from the central atom, repulsions are decreased, allowing smaller bond angles. (Kathryn Haas; CC-NC-BY-SA)

Electronegativity is an alternative explanation to the trends we already examined above in Figure **2.5.3.2** . For example, when we compare the halogen pendant atoms (shaded region in Figure **2.5.3.2**) , 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 **2.5.3.2**).

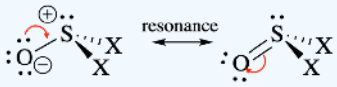
? Exercise 2.5.3.1

Predict the geometry and approximate bond angles. Then put the molecules in each series in order of smallest to largest bond angle. Defend your answer.

a. The X-S-X bond angle in OSF_2, $OSCl_2$, $OSBr_2$
b. H_2O, H_2S, H_2Se, H_2Te
c. H_2O, OF_2, OCl_2

Answer (a)

Geometry and predicted bond angles: These are molecules with steric number 4. They can be written as two different resonance structures, and the resonance hybrid would have double bond character between S and O.



We would expect a trigonal pyramidal geometry with all bond angles <109.5° because the lone pair is more repulsive than bonds. Because the double bond is more repulsive than single bonds, we should also expect the O-S-X bond angles to be greater than the X-S-X bond angles.

Trend: This is a series of molecules that varies in the identity of the pendant atoms; the variation is within the halogens. The size of the halogens increases, and the electronegativity decreases in the order F, Cl, Br. Both size and electronegativity would lead us to conclude that the X-S-X bond angles would increase in the order $OSF_2 < OSCl_2 < OSBr_2$

Explanation: (1) Increasing electonegativity of the pendant atom (F > Cl > Br) increases the polarity of the bond and reduces the electron density of the bonded pair on the central atom. This reduces the e-e repulsions of adjacent bonded electron pairs on S, allowing the halogens to become closer. The more electronegative pendant atoms can have smaller bond angles. (2) Increasing size of pendant atoms (F < Cl < Br) increases steric repulsions and increases bond angle. Both explanations lead to the same predicted trend.

The actual measured X-S-X bond angles are OSF_2 (92.3°) / $OSCl_2$ (96.2°) / $OSBr_2$ (98.2°). The trend in these bond angles is consistent with the prediction.

Answer (b)

Geometry and predicted bond angles: These are molecules with steric number 4, bent molecular geometry, with predicted bond angles <109.5° because the two lone pairs are each more repulsive than the bonds. There are two lone pairs and two single bonds to H around each central atom.

Trend: This is a series of molecules that varies in the identity of the central atom. The central atom increases in the order O < S < Se < Te, where Te is the largest element and O is the smallest. Arguments based on size would lead us to predict that the pendant groups of H_2Te would be less sterically crowded and thus have a smaller bond angle than the pendant groups of H_2O. The electronegativity decreases in the order O > S > Se > Te, where O is the most electronegative element and Te is the least. Thus, we expect the bonding electro pairs to be closer to the central atom on O than they would be on Te; we should expect H_2Te to have the least electron pair repulsions and thus smallest bond angle in this series, while H_2O would have the strongest electron pair repulsions and largest bond angles.

Both arguments lead to the same conclusion, that the order of increasing bond angle is $H_2Te < H_2Se < H_2S < H_2O$.

The actual measured bond angles are H_2Te (90.2°) / H_2Se (90.6°) / H_2S (92.1°) / H_2O (104.5). The trend in these bond angles is consistent with prediction.

Answer (c)

Geometry and predicted bond angles: These are molecules with steric number 4, bent molecular geometry, with predicted bond angles <109.5° because the two lone pairs are each more repulsive than the bonds. There are two lone pairs and two single bonds to H around each central atom. (This is similar to the case in (b)).

Trend: This is a series of molecules that varies in the identity of the pendant atoms; two of the molecules have halogens, and the other has hydrogen pendant atoms. This is a case where size and electronegativity will be conflicting factors because trends in electronegativity do not mirror the trend in size.

- *Size:* The size of pendant atoms increases in the order H < F < Cl where H is smallest and Cl is largest. Prediction of bond angles based on size alone would lead to the predicted order of increasing bond angle $H_2O < OF_2 < OCl_2$.
- *Electronegativity*: The electronegativity decreases in the order F > Cl > H where F has the greatest electronegativity and H has the least. Since we expect the most electronegative pendant atoms to have the smallest bond angles, prediction based on electronegativity alone would lead to the predicted order of increasing bond angle $OF_2 < OCl_2 < H_2O$.

The points above illustrate how the two different arguments would lead to different predictions about the trend in bond angle. This makes it difficult to predict the actual order of increasing bond angle. However, we saw above in the example of NH_3 vs NF_3 that electronegativity is more important than size; yet in the case of NH_3 vs NCl_3, the much larger size of the pendant atom is more important. If we apply this lesson to the current problem, we might predict the order $OF_2 < H_2O < OCl_2$, and in fact this more nuanced prediction, based on a similar case, matches the actual order for measured bond angles: OF_2 (103.3°) < H_2O (104.5°) < OCl_2 (110.9°).

Group Electronegativities

You probably heard the terms "electron donating group" and "electron withdrawing group" from your coursework in Organic Chemistry. For example, the acid trifluoroacetic acid (TFA) is more acidic than acetic acid due to the electron withdrawing effects of the CF_3 group compared to CH_3. CF_3 is an electron withdrawing group, while CH_3 is an electron donating group. In other words, CF_3 is more electronegative than CH_3.

The electron withdrawing ability (electronegativity) of groups can be estimated and compared, just as they are with atoms. Although there is no one scale that is used for group electronegativities, and published values even for the same groups vary widely, there are reliable trends within similar groups. The same size and electronegativity factors discussed above that affect bond angles for *pendant atoms*, also can be used to rationalize distorted bond angles for *pendant groups* around a central atom.

? Exercise 2.5.3.2

Consider the relative electronegativities and sizes of the pendant atoms/groups in the following examples. Is the trend in bond angles what you would expect from the relative group electronegativities and relative sizes? What, if any, is the more dominant factor in determining the trend?

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

Answer (a)

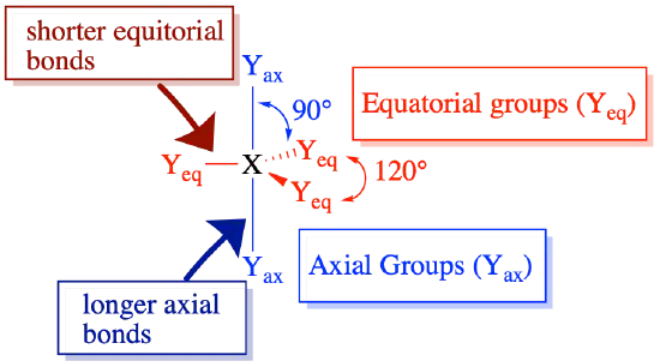
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Answer (b)

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Special case of electronegativity and size in steric number 5 (trigonal bypyramid)

Molecules with steric number 5 are interesting because they posses two different types of positions (equatorial and axial). These positions have unique bond angles and bond lengths. Pendant atoms/groups have different preferences for the axial and equatorial positions that depend somewhat on their electronegativity.



Molecules with steric number 5 possess different bond angles and lengths for axial (ax) and equatorial (eq) pendant atoms. (CC-BY-NC-SA; Kathryn Haas)

In a previous section, we discussed the preference of lone pairs and multiple bonds for the equatorial positions in trigonal bipyramidal molecules. VSEPR theory rationalizes this by assuming that lone pairs and multiple bonds are more repulsive than the electron pairs in single bonds. Equatorial positions are less crowded (with only two closest neighbors at 90°, and two farther neighbors at 120°) compared to axial positions (with three closest neighbors at 90°), thus the more repulsive groups prefer the less crowded equatorial positions.

Pendant groups that are more electronegative result in weaker electron pair repulsion around the central atom, while groups that are less electronegative result in stronger electron-pair repulsion around the central atom (as described above). The result for steric number 5: **bonding pairs to *less electronegative elements* are *more repulsive,* and *generally prefer equatorial* positions.** Still, lone pairs and multiple bonds are more repulsive than single bonds and would show a stronger preference for equatorial positions.

Examples and Nuances

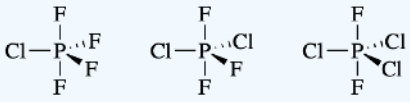
? Exercise 2.5.3.3

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

a. PF_4Cl, PF_3Cl_2, and PF_2Cl_3
b. $PF_4(CH_3)$ $PF_3(CH_3)_2$, and $PF_2(CH_3)_3$

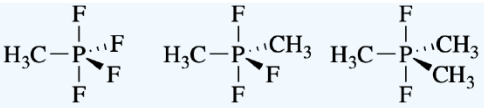
Answer (a)

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

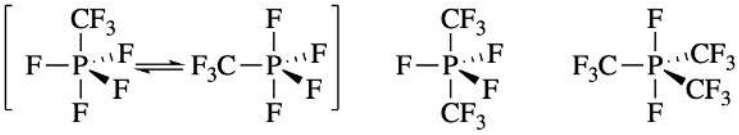


Answer (b)

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



In the exercise above, the structures can be explained by the electronegativity of the pendant groups; less electronegative groups prefer the equatorial positions. There are other similar molecules for which explanations (or predictions) are difficult. For example, the series of molecules below seems to have completely random placement of F and CF_3 groups. **These structures could not be predicted based on VSEPR theory.** It seems that in this case, the more symmetrical arrangements of pendant groups is preferred.



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2.5.4: Ligand Close Packing

Introduction

Ligand Close Packing (LCP) theory is complimentary to VSEPR, except that LCP focuses on repulsions between pendant *atoms* ("outer" atoms that are not directly bonded to one another), rather than focusing on the chemical environment around the central atom in a molecule. Both LCP and the VSEPR models were developed by Robert Gillespie.

The LCP model assumes that ligands (or pendant atoms) "pack" as closely as possible around a central atom. A given ligand will have a specific atomic radius when bound to a central atom. The distance between two ligands around the same central atom is simply the sum of the atomic radii of the pendant atoms. Therefore for a specific set of ligands around a specific central atom, the ligand-ligand distances are constant despite the coordination number or bond angles. In other words, for a series of similar molecules with the same central atom, while bond angles and bond distances of pendant atoms may change, the distances between two pendant atoms remain the same.

Ligand Close Packing Theory

According to LCP, distances between two pendant atoms are similar...

- even when steric number changes
- even when bond angles change
- Reason: pendant atoms "pack" around the central atom.

Ligand Close Packing and Bond Distances

If the distance between non-bonded atoms remains constant even while bond angles change, then the bond length between the pendant and central atom must change to accommodate. For example, $\mathbf{PF_4^+}$ and $\mathbf{PF_3O}$ have almost identical $\mathbf{F-F}$ distances of 238 and 237 pm, respectively. As expected from VSEPR, the $\mathbf{F-P-F}$ bond angle in $\mathbf{PF_4^+}$ is 109.5°. The $\mathbf{F-P-F}$ bond angle in $\mathbf{PF_3O}$ (101.1°) is smaller due to the increased repulsion of the oxygen double bond. Therefore the P-F bond lengths must be different. In fact, the P-F bond distances are 145.7 pm in $\mathbf{PF_4^+}$ and 154 pm in $\mathbf{PF_3O}$.

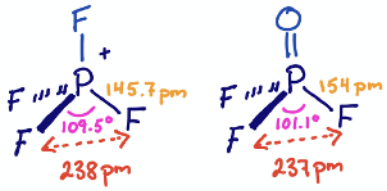


Figure **2.5.4.1**: The molecular structures of $\mathbf{PF_4^+}$ and $\mathbf{PF_3O}$. The distances between neighboring F atoms are similar in the two molecules, while bond lengths and angles differ. The $\mathbf{PF_4^+}$ ion has a $\mathbf{P-F}$ bond length of 145.7 pm, an $\mathbf{F-P-F}$ bond angle of 109.5°, and a distance of 238 pm between neighboring F atoms. The $\mathbf{PF_3O}$ molecule has a $\mathbf{P-F}$ bond length of 154 pm, an $\mathbf{F-P-F}$ bond angle of 101.1°, and a distance of 237 pm between neighboring F atoms. (CC-BY-NC-SA; Kathryn Haas)

The relationship between bond angles, bond lengths, and close-packing distance is described by right angle trigonometry (recall SOA-CAH-TOA). In a right triangle, the hypotenuse is the longest side, opposite to the right angle. For either of the other two angles in the triangle, the angle (θ) and lengths of the sides (*opposite* and *adjacent* to θ) are related by the trigometric functions shown in Figure **2.5.4.2** .



Figure **2.5.4.2**: 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 **2.5.4.2**. 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.

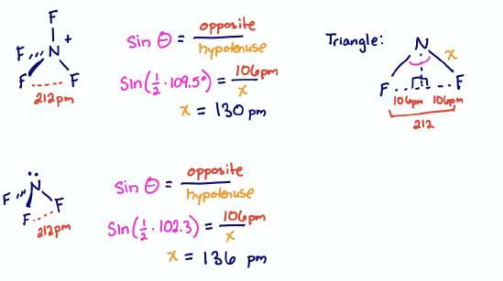


Figure 2.5.4.1: Illustration of how right angle trigonometry can be applied to determine bond angle, bond length, or distance between neighboring atoms: any bond angle can be divided into two right angles where the bond length is the hypotenuse, the distance between neighbors is twice the opposite side, and the bond angle is twice θ. (CC-BY-NC-SA; Kathryn Haas)

Exercise 2.5.4.1

The distance between F atoms is 212 pm in both NF_4^+ and NF_3. The bond angles are 109.5° and 102.3°, respectively. What are the expected $N-F$ bond lengths?

Answer



The actual measured bond lengths are 130 pm for NF_4^+ and 136.5 pm for NF_3.

Sources and Resources

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

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2.6: Molecular Orbital Theory

Learning Objectives

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

None of the approaches we have described so far can adequately explain why some compounds are colored and others are not, why some substances with unpaired electrons are stable, and why others are effective semiconductors. These approaches also cannot describe the nature of resonance. Such limitations led to the development of a new approach to bonding in which electrons are *not* viewed as being localized between the nuclei of bonded atoms but are instead delocalized throughout the entire molecule. Just as with the valence bond theory, the approach we are about to discuss is based on a quantum mechanical model.

Previously, we described the electrons in isolated atoms as having certain spatial distributions, called *orbitals*, each with a particular *orbital energy*. Just as the positions and energies of electrons in *atoms* can be described in terms of *atomic orbitals* (AOs), the positions and energies of electrons in *molecules* can be described in terms of molecular orbitals (MOs) A particular spatial distribution of electrons in a molecule that is associated with a particular orbital energy.—a spatial distribution of electrons *in a molecule* that is associated with a particular orbital energy. As the name suggests, molecular orbitals are not localized on a single atom but extend over the entire molecule. Consequently, the molecular orbital approach, called molecular orbital theory is a *delocalized* approach to bonding.

Although the molecular orbital theory is computationally demanding, the principles on which it is based are similar to those we used to determine electron configurations for atoms. The key difference is that in molecular orbitals, the electrons are allowed to interact with more than one atomic nucleus at a time. Just as with atomic orbitals, we create an energy-level diagram by listing the molecular orbitals in order of increasing energy. We then fill the orbitals with the required number of valence electrons according to the Pauli principle. This means that each molecular orbital can accommodate a maximum of two electrons with opposite spins.

Molecular Orbitals Involving Only *ns* Atomic Orbitals

We begin our discussion of molecular orbitals with the simplest molecule, H_2, formed from two isolated hydrogen atoms, each with a $1s^1$ electron configuration. As discussed previously, electrons can behave like waves. In the molecular orbital approach, the overlapping atomic orbitals are described by mathematical equations called *wave functions*. The 1*s* atomic orbitals on the two hydrogen atoms interact to form two new molecular orbitals, one produced by taking the *sum* of the two H 1*s* wave functions, and the other produced by taking their *difference*:

$$\begin{aligned} MO(1) &= AO(atom\ A) + AO(atom B) \\ MO(1) &= AO(atom\ A) - AO(atom B) \end{aligned} \tag{2.6.1}$$

The molecular orbitals created from Equation 2.6.1 are called linear combinations of atomic orbitals (LCAOs) Molecular orbitals created from the sum and the difference of two wave functions (atomic orbitals). A molecule must have as many molecular orbitals as there are atomic orbitals.

Adding two atomic orbitals corresponds to *constructive* interference between two waves, thus reinforcing their intensity; the internuclear electron probability density is *increased*. The molecular orbital corresponding to the sum of the two H 1*s* orbitals is called a σ_{1s} combination (pronounced “sigma one ess”) (part (a) and part (b) in Figure **2.6.1**). In a sigma (σ) orbital, A bonding molecular orbital in which the electron density along the internuclear axis and between the nuclei has cylindrical symmetry, the electron density along the internuclear axis and between the nuclei has cylindrical symmetry; that is, all cross-sections perpendicular to the internuclear axis are circles. The subscript 1*s* denotes the atomic orbitals from which the molecular orbital was derived: The ≈ sign is used rather than an = sign because we are ignoring certain constants that are not important to our argument.

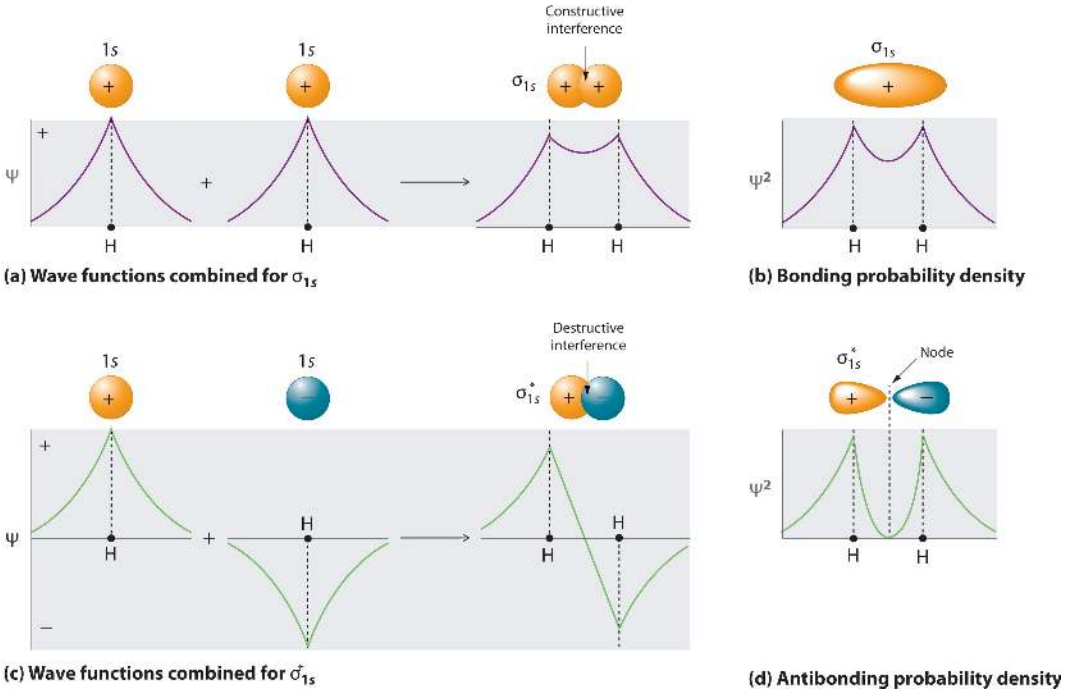


Figure **2.6.1**: Molecular Orbitals for the H_2 Molecule**.** (a) This diagram shows the formation of a bonding σ_{1s} molecular orbital for H_2 as the sum of the wave functions (Ψ) of two H 1s atomic orbitals. (b) This plot of the square of the wave function (Ψ^2) for the bonding σ_{1s} molecular orbital illustrates the increased electron probability density between the two hydrogen nuclei. (Recall that the probability density is proportional to the square of the wave function.) (c) This diagram shows the formation of an antibonding σ^*_{1s} molecular orbital for H_2 as the difference of the wave functions (Ψ) of two H 1s atomic orbitals. (d) This plot of the square of the wave function (Ψ^2) for the σ^*_{1s} antibonding molecular orbital illustrates the node corresponding to zero electron probability density between the two hydrogen nuclei.

$$\sigma_{1s} \approx 1s\,(A) + 1s\,(B) \tag{2.6.2}$$

Conversely, subtracting one atomic orbital from another corresponds to *destructive* interference between two waves, which reduces their intensity and causes a *decrease* in the internuclear electron probability density (part (c) and part (d) in Figure **2.6.1**). The resulting pattern contains a *node* where the electron density is zero. The molecular orbital corresponding to the difference is called σ^*_{1s} ("sigma one ess star"). In a sigma star (σ*) orbital An antibonding molecular orbital in which there is a region of zero electron probability (a nodal plane) perpendicular to the internuclear axis., there is a region of zero electron probability, a nodal plane, perpendicular to the internuclear axis:

$$\sigma^*_{1s} \approx 1s\,(A) - 1s\,(B) \tag{2.6.3}$$

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

The electron density in the σ_{1s} molecular orbital is greatest between the two positively charged nuclei, and the resulting electron–nucleus electrostatic attractions reduce repulsions between the nuclei. Thus the σ_{1s} orbital represents a bonding molecular orbital. A molecular orbital that forms when atomic orbitals or orbital lobes with the same sign interact to give increased electron probability between the nuclei due to constructive reinforcement of the wave functions. In contrast, electrons in the σ^*_{1s} orbital are generally found in the space outside the internuclear region. Because this allows the positively charged nuclei to repel one another, the σ^*_{1s} orbital is an antibonding molecular orbital (a molecular orbital that forms when atomic orbitals or orbital lobes of opposite sign interact to give decreased electron probability between the nuclei due to destructive reinforcement of the wave functions).

> *Antibonding orbitals contain a node perpendicular to the internuclear axis; bonding orbitals do not.*

Energy-Level Diagrams

Because electrons in the σ_{1s} orbital interact simultaneously with both nuclei, they have a lower energy than electrons that interact with only one nucleus. This means that the σ_{1s} molecular orbital has a *lower* energy than either of the hydrogen 1*s* atomic orbitals.

Conversely, electrons in the σ^*_{1s} orbital interact with only one hydrogen nucleus at a time. In addition, they are farther away from the nucleus than they were in the parent hydrogen 1*s* atomic orbitals. Consequently, the σ^*_{1s} molecular orbital has a *higher* energy than either of the hydrogen 1*s* atomic orbitals. The σ_{1s} (bonding) molecular orbital is *stabilized* relative to the 1*s* atomic orbitals, and the σ^*_{1s} (antibonding) molecular orbital is *destabilized*. The relative energy levels of these orbitals are shown in the energy-level diagram (a schematic drawing that compares the energies of the molecular orbitals (bonding, antibonding, and nonbonding) with the energies of the parent atomic orbitals) in Figure **2.6.2**

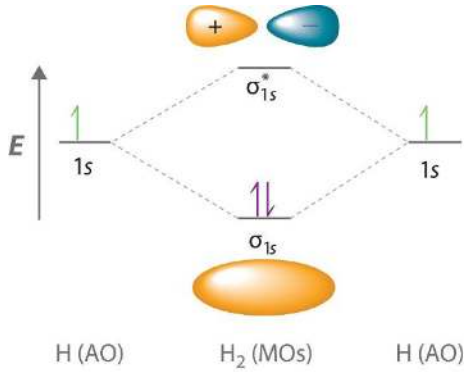


Figure **2.6.2**: Molecular Orbital Energy-Level Diagram for H_2. The two available electrons (one from each H atom) in this diagram fill the bonding σ_{1s} molecular orbital. Because the energy of the σ_{1s} molecular orbital is lower than that of the two H 1*s* atomic orbitals, the H_2 molecule is more stable (at a lower energy) than the two isolated H atoms.

> *A bonding molecular orbital is always lower in energy (more stable) than the component atomic orbitals, whereas an antibonding molecular orbital is always higher in energy (less stable).*

To describe the bonding in a homonuclear diatomic molecule (a molecule that consists of two atoms of the same element) such as H_2, we use molecular orbitals; that is, for a molecule in which two identical atoms interact, we insert the total number of valence electrons into the energy-level diagram (Figure **2.6.2**). We fill the orbitals according to the Pauli principle and Hund's rule: each orbital can accommodate a maximum of two electrons with opposite spins, and the orbitals are filled in order of increasing energy. Because each H atom contributes one valence electron, the resulting two electrons are exactly enough to fill the σ_{1s} bonding molecular orbital. The two electrons enter an orbital whose energy is lower than that of the parent atomic orbitals, so the H_2 molecule is more stable than the two isolated hydrogen atoms. Thus molecular orbital theory correctly predicts that H_2 is a stable molecule. Because bonds form when electrons are concentrated in the space between nuclei, this approach is also consistent with our earlier discussion of electron-pair bonds.

Bond Order in Molecular Orbital Theory

In the Lewis electron structures, the number of electron pairs holding two atoms together was called the *bond order*. In the molecular orbital approach, bond order One-half the net number of bonding electrons in a molecule. is defined as one-half the *net* number of bonding electrons:

$$\textit{bond order} = \frac{\textit{number of bonding electrons} - \textit{number of antibonding electrons}}{2} \tag{2.6.4}$$

To calculate the bond order of H_2, we see from Figure **2.6.2** that the σ_{1s} (bonding) molecular orbital contains two electrons, while the σ^*_{1s} (antibonding) molecular orbital is empty. The bond order of H_2 is therefore

$$\frac{2-0}{2} = 1 \tag{2.6.5}$$

This result corresponds to the single covalent bond predicted by Lewis dot symbols. Thus molecular orbital theory and the Lewis electron-pair approach agree that a single bond containing two electrons has a bond order of 1. Double and triple bonds contain four or six electrons, respectively, and correspond to bond orders of 2 and 3.

We can use energy-level diagrams such as the one in Figure **2.6.2** to describe the bonding in other pairs of atoms and ions where n = 1, such as the H_2^+ ion, the He_2^+ ion, and the He_2 molecule. Again, we fill the lowest-energy molecular orbitals first while being

sure not to violate the Pauli principle or Hund's rule.

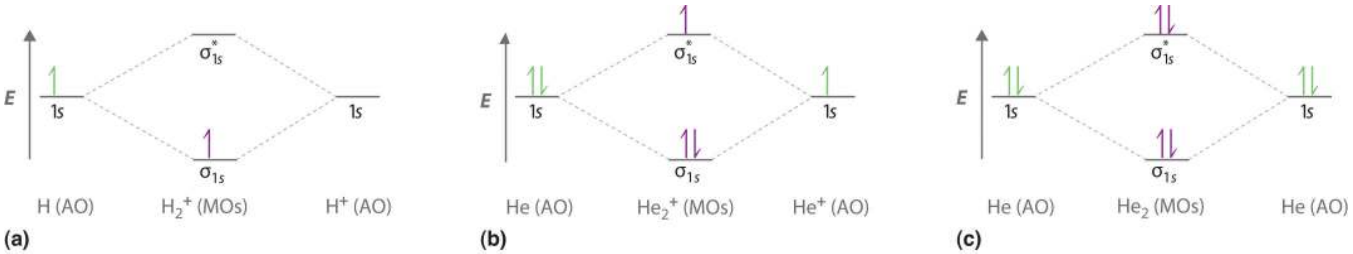


Figure **2.6.3**: Molecular Orbital Energy-Level Diagrams for Diatomic Molecules with Only 1*s* Atomic Orbitals. (a) The H_2^+ ion, (b) the He_2^+ ion, and (c) the He_2 molecule are shown here.

Part (a) in Figure **2.6.3** shows the energy-level diagram for the H_2^+ ion, which contains two protons and only one electron. The single electron occupies the σ_{1s} bonding molecular orbital, giving a $(\sigma_{1s})^1$ electron configuration. The number of electrons in an orbital is indicated by a superscript. In this case, the bond order is (1-0)/2=1/2 Because the bond order is greater than zero, the H_2^+ ion should be more stable than an isolated H atom and a proton. We can therefore use a molecular orbital energy-level diagram and the calculated bond order to predict the relative stability of species such as H_2^+. With a bond order of only 1/2 the bond in H_2^+ should be weaker than in the H_2 molecule, and the H–H bond should be longer. As shown in Table **2.6.1**, these predictions agree with the experimental data.

Part (b) in Figure **2.6.3** is the molecular orbital energy-level diagram for He_2^+. This ion has a total of three valence electrons. Because the first two electrons completely fill the σ_{1s} molecular orbital, the Pauli principle states that the third electron must be in the σ^*_{1s} antibonding orbital, giving a $(\sigma_{1s})^2(\sigma^*_{1s})^1$ electron configuration. This electron configuration gives a bond order of (2-1)/2=1/2. As with H_2^+, the He_2^+ ion should be stable, but the He–He bond should be weaker and longer than in H_2. In fact, the He_2^+ ion can be prepared, and its properties are consistent with our predictions (Table **2.6.1**).

Table **2.6.1**: Molecular Orbital Electron Configurations, Bond Orders, Bond Lengths, and Bond Energies for some Simple Homonuclear Diatomic Molecules and Ions

Molecule or Ion	Electron Configuration	Bond Order	Bond Length (pm)	Bond Energy (kJ/mol)
H_2^+	$(\sigma_{1s})^1$	1/2	106	269
H_2	$(\sigma_{1s})^2$	1	74	436
He_2^+	$(\sigma_{1s})^2(\sigma^*_{1s})^1$	1/2	108	251
He_2	$(\sigma_{1s})^2(\sigma^*_{1s})^2$	0	not observed	not observed

Finally, we examine the He_2 molecule, formed from two He atoms with $1s^2$ electron configurations. Part (c) in Figure **2.6.3** is the molecular orbital energy-level diagram for He_2. With a total of four valence electrons, both the σ_{1s} bonding and σ^*_{1s} antibonding orbitals must contain two electrons. This gives a $(\sigma_{1s})^2(\sigma^*_{1s})^1$ electron configuration, with a predicted bond order of $(2 - 2) \div 2 = 0$, which indicates that the He_2 molecule has no net bond and is not a stable species. Experiments show that the He_2 molecule is actually *less* stable than two isolated He atoms due to unfavorable electron–electron and nucleus–nucleus interactions.

In molecular orbital theory, *electrons in antibonding orbitals effectively cancel the stabilization resulting from electrons in bonding orbitals*. Consequently, any system that has equal numbers of bonding and antibonding electrons will have a bond order of 0, and it is predicted to be unstable and therefore not to exist in nature. In contrast to Lewis electron structures and the valence bond approach, molecular orbital theory is able to accommodate systems with an odd number of electrons, such as the H_2^+ ion.



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

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

Example 2.6.1

Use a molecular orbital energy-level diagram, such as those in Figure **2.6.3**, to predict the bond order in the He_2^{2+} ion. Is this a stable species?

Given: chemical species

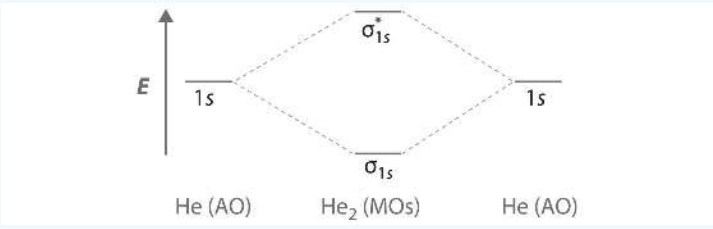
Asked for: molecular orbital energy-level diagram, bond order, and stability

Strategy:

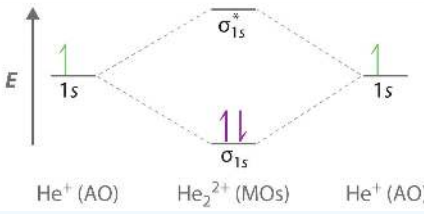
A. Combine the two He valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for the system.
B. Determine the total number of valence electrons in the He_2^{2+} ion. Fill the molecular orbitals in the energy-level diagram beginning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

Solution:

A Two He 1*s* atomic orbitals combine to give two molecular orbitals: a σ_{1s} bonding orbital at lower energy than the atomic orbitals and a σ^*_{1s} antibonding orbital at higher energy. The bonding in any diatomic molecule with two He atoms can be described using the following molecular orbital diagram:



B The He_2^{2+} ion has only two valence electrons (two from each He atom minus two for the +2 charge). We can also view He_2^{2+} as being formed from two He^+ ions, each of which has a single valence electron in the 1*s* atomic orbital. We can now fill the molecular orbital diagram:



The two electrons occupy the lowest-energy molecular orbital, which is the bonding (σ_{1s}) orbital, giving a $(\sigma_{1s})^2$ electron configuration. To avoid violating the Pauli principle, the electron spins must be paired. **C** So the bond order is

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

He_2^{2+} is therefore predicted to contain a single He–He bond. Thus it should be a stable species.

? Exercise 2.6.1

Use a molecular orbital energy-level diagram to predict the valence-electron configuration and bond order of the H_2^{2-} ion. Is this a stable species?

Answer

H_2^{2-} has a valence electron configuration of $(\sigma_{1s})^2(\sigma^*_{1s})^2$ with a bond order of 0. It is therefore predicted to be unstable.

So far, our discussion of molecular orbitals has been confined to the interaction of valence orbitals, which tend to lie farthest from the nucleus. When two atoms are close enough for their valence orbitals to overlap significantly, the filled inner electron shells are largely unperturbed; hence they do not need to be considered in a molecular orbital scheme. Also, when the inner orbitals are completely filled, they contain exactly enough electrons to completely fill both the bonding and antibonding molecular orbitals that arise from their interaction. Thus the interaction of filled shells always gives a bond order of 0, so filled shells are not a factor when predicting the stability of a species. This means that we can focus our attention on the molecular orbitals derived from valence atomic orbitals.

A molecular orbital diagram that can be applied to any **homonuclear diatomic molecule** with two identical alkali metal atoms (Li_2 and Cs_2, for example) is shown in part (a) in Figure **2.6.4**, where M represents the metal atom. Only two energy levels are important for describing the valence electron molecular orbitals of these species: a σ_{ns} bonding molecular orbital and a σ^*_{ns} antibonding molecular orbital. Because each alkali metal (M) has an ns^1 valence electron configuration, the M_2 molecule has two valence electrons that fill the σ_{ns} bonding orbital. As a result, a bond order of 1 is predicted for all homonuclear diatomic species formed from the alkali metals (Li_2, Na_2, K_2, Rb_2, and Cs_2). The general features of these M_2 diagrams are identical to the diagram for the H_2 molecule in Figure **2.6.2**. Experimentally, all are found to be stable in the gas phase, and some are even stable in solution.

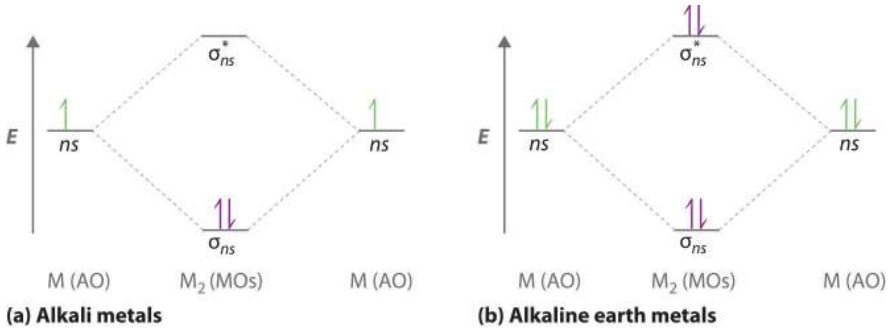


Figure **2.6.4**: Molecular Orbital Energy-Level Diagrams for Alkali Metal and Alkaline Earth Metal Diatomic (M_2) Molecules. *(a) For alkali metal diatomic molecules, the two valence electrons are enough to fill the σ_{ns} (bonding) level, giving a bond order of 1. (b) For alkaline earth metal diatomic molecules, the four valence electrons fill both the σ_{ns} (bonding) and the σ_{ns}* (nonbonding) levels, leading to a predicted bond order of 0.*

Similarly, the molecular orbital diagrams for homonuclear diatomic compounds of the alkaline earth metals (such as Be_2), in which each metal atom has an ns^2 valence electron configuration, resemble the diagram for the He_2 molecule in part (c) in Figure **2.6.3** As

shown in part (b) in Figure **2.6.4**, this is indeed the case. All the homonuclear alkaline earth diatomic molecules have four valence electrons, which fill both the σ_{ns} bonding orbital and the σ_{ns}* antibonding orbital and give a bond order of 0. Thus Be_2, Mg_2, Ca_2, Sr_2, and Ba_2 are all expected to be unstable, in agreement with experimental data.In the solid state, however, all the alkali metals and the alkaline earth metals exist as extended lattices held together by metallic bonding. At low temperatures, $\boldsymbol{Be_2}$ is stable.

Example 2.6.2

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Na_2^- ion.

Given: chemical species

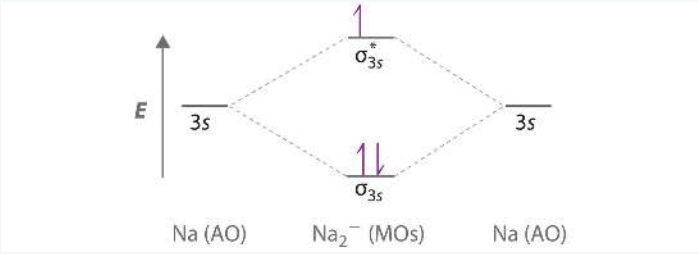
Asked for: molecular orbital energy-level diagram, valence electron configuration, bond order, and stability

Strategy:

A. Combine the two sodium valence atomic orbitals to produce bonding and antibonding molecular orbitals. Draw the molecular orbital energy-level diagram for this system.
B. Determine the total number of valence electrons in the Na_2^- ion. Fill the molecular orbitals in the energy-level diagram beginning with the orbital with the lowest energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
C. Calculate the bond order and predict whether the species is stable.

Solution:

A Because sodium has a [Ne]$3s^1$ electron configuration, the molecular orbital energy-level diagram is qualitatively identical to the diagram for the interaction of two 1*s* atomic orbitals. **B** The Na_2^- ion has a total of three valence electrons (one from each Na atom and one for the negative charge), resulting in a filled σ_{3s} molecular orbital, a half-filled σ_{3s*} and a $(\sigma_{3s})^2(\sigma^*_{3s})^1$ electron configuration.



C The bond order is (2-1)÷2=1/2 With a fractional bond order, we predict that the Na_2^- ion exists but is highly reactive.

Exercise 2.6.2

Use a qualitative molecular orbital energy-level diagram to predict the valence electron configuration, bond order, and likely existence of the Ca_2^+ ion.

Answer

Ca_2^+ has a $(\sigma_{4s})^2(\sigma^*_{4s})^1$ electron configurations and a bond order of 1/2 and should exist.

Molecular Orbitals Formed from *ns* and *np* Atomic Orbitals

Atomic orbitals other than *ns* orbitals can also interact to form molecular orbitals. Because individual *p*, *d*, and *f* orbitals are not spherically symmetrical, however, we need to define a coordinate system so we know which lobes are interacting in three-dimensional space. Recall that for each *np* subshell, for example, there are np_x, np_y, and np_z orbitals. All have the same energy and are therefore degenerate, but they have different spatial orientations.

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{2.6.6}$$

Just as with *ns* orbitals, we can form molecular orbitals from *np* orbitals by taking their mathematical sum and difference. When two positive lobes with the appropriate spatial orientation overlap, as illustrated for two np_z atomic orbitals in part (a) in Figure **2.6.5**, it is the mathematical *difference* of their wave functions that results in *constructive* interference, which in turn increases the electron probability density between the two atoms. The difference therefore corresponds to a molecular orbital called a σ_{np_z} *bonding molecular orbital* because, just as with the σ orbitals discussed previously, it is symmetrical about the internuclear axis (in this case, the *z*-axis):

$$\sigma_{np_z} = np_z(A) - np_z(B) \tag{2.6.7}$$

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

$$\sigma_{np_z} = np_z(A) + np_z(B) \tag{2.6.8}$$

In this combination, shown in part (b) in Figure **2.6.5**, the positive lobe of one np_z atomic orbital overlaps the negative lobe of the other, leading to *destructive* interference of the two waves and creating a node between the two atoms. Hence this is an antibonding molecular orbital. Because it, too, is symmetrical about the internuclear axis, this molecular orbital is called a $\sigma_{np_z} = np_z(A) - np_z(B)$ *antibonding molecular orbital*. Whenever orbitals combine, *the bonding combination is always lower in energy* (more stable) than the atomic orbitals from which it was derived, and *the antibonding combination is higher in energy* (less stable).

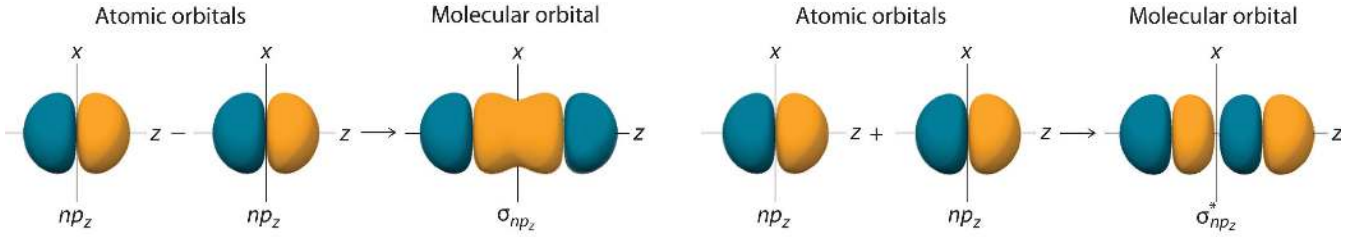


Figure **2.6.5**: Formation of Molecular Orbitals from np_z Atomic Orbitals on Adjacent Atoms.(a) By convention, in a linear molecule or ion, the *z*-axis always corresponds to the internuclear axis, with +*z* to the right. As a result, the signs of the lobes of the np_z atomic orbitals on the two atoms alternate − + − +, from left to right. In this case, the σ (bonding) molecular orbital corresponds to the mathematical *difference*, in which the overlap of lobes with the same sign results in increased probability density between the nuclei. (b) In contrast, the σ* (antibonding) molecular orbital corresponds to the mathematical *sum*, in which the overlap of lobes with opposite signs results in a nodal plane of zero probability density perpendicular to the internuclear axis.

> Overlap of atomic orbital lobes with the *same sign* produces a bonding molecular orbital, regardless of whether it corresponds to the sum or the difference of the atomic orbitals.

The remaining *p* orbitals on each of the two atoms, np_x and np_y, do not point directly toward each other. Instead, they are perpendicular to the internuclear axis. If we arbitrarily label the axes as shown in Figure **2.6.6**, we see that we have two pairs of *np* orbitals: the two np_x orbitals lying in the plane of the page, and two np_y orbitals perpendicular to the plane. Although these two pairs are equivalent in energy, the np_x orbital on one atom can interact with only the np_x orbital on the other, and the np_y orbital on one atom can interact with only the np_y on the other. These interactions are side-to-side rather than the head-to-head interactions characteristic of σ orbitals. Each pair of overlapping atomic orbitals again forms two molecular orbitals: one corresponds to the arithmetic sum of the two atomic orbitals and one to the difference. The sum of these side-to-side interactions increases the electron probability in the region above and below a line connecting the nuclei, so it is a bonding molecular orbital that is called a pi (π) orbital (a bonding molecular orbital formed from the side-to-side interactions of two or more parallel np atomic orbitals). The difference results in the overlap of orbital lobes with opposite signs, which produces a nodal plane perpendicular to the internuclear axis; hence it is an antibonding molecular orbital, called a pi star (π*) orbital An antibonding molecular orbital formed from the difference of the side-to-side interactions of two or more parallel *np* atomic orbitals, creating a nodal plane perpendicular to the internuclear axis..

$$\pi_{np_x} = np_x(A) + np_x(B) \tag{2.6.9}$$

$$\pi^*_{np_x} = np_x(A) - np_x(B) \tag{2.6.10}$$

The two np_y orbitals can also combine using side-to-side interactions to produce a bonding π_{np_y} molecular orbital and an antibonding $\pi^*_{np_y}$ molecular orbital. Because the np_x and np_y atomic orbitals interact in the same way (side-to-side) and have the same energy, the π_{np_z} and π_{np_y} molecular orbitals are a degenerate pair, as are the $\pi^*_{np_z}$ and $\pi^*_{np_y}$ molecular orbitals.

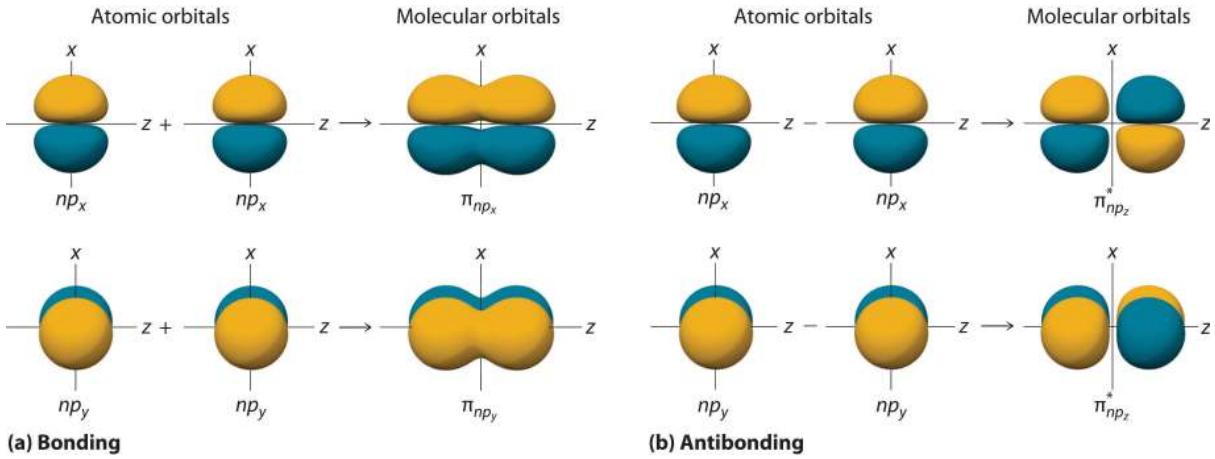


Figure **2.6.6**: Formation of π Molecular Orbitals from np_x and np_y Atomic Orbitals on Adjacent Atoms.(a) Because the signs of the lobes of both the np_x and the np_y atomic orbitals on adjacent atoms are the same, in both cases the mathematical sum corresponds to a π (bonding) molecular orbital. (b) In contrast, in both cases, the mathematical difference corresponds to a π* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

Figure **2.6.7** is an energy-level diagram that can be applied to two identical interacting atoms that have three *np* atomic orbitals each. There are six degenerate *p* atomic orbitals (three from each atom) that combine to form six molecular orbitals, three bonding and three antibonding. The bonding molecular orbitals are lower in energy than the atomic orbitals because of the increased stability associated with the formation of a bond. Conversely, the antibonding molecular orbitals are higher in energy, as shown. The energy difference between the σ and σ* molecular orbitals is significantly greater than the difference between the two π and π* sets. The reason for this is that the atomic orbital overlap and thus the strength of the interaction are greater for a σ bond than a π bond, which means that the σ molecular orbital is more stable (lower in energy) than the π molecular orbitals.

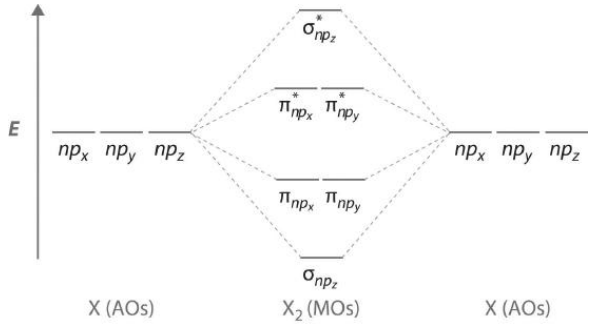


Figure **2.6.7**: The Relative Energies of the σ and π Molecular Orbitals Derived from np_x, np_y, and np_z Orbitals on Identical Adjacent Atoms. Because the two np_z orbitals point directly at each other, their orbital overlap is greater, so the difference in energy between the σ and σ* molecular orbitals is greater than the energy difference between the π and π* orbitals.

Although many combinations of atomic orbitals form molecular orbitals, we will discuss only one other interaction: an *ns* atomic orbital on one atom with an np_z atomic orbital on another. As shown in Figure **2.6.8**, the sum of the two atomic wave functions ($ns + np_z$) produces a σ bonding molecular orbital. Their difference ($ns - np_z$) produces a σ* antibonding molecular orbital, which has a nodal plane of zero probability density perpendicular to the internuclear axis.

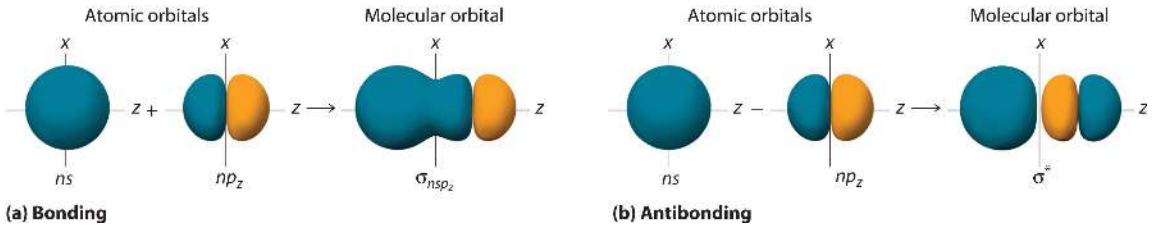


Figure **2.6.8**: Formation of Molecular Orbitals from an ns Atomic Orbital on One Atom and an np_z Atomic Orbital on an Adjacent Atom.(a) The mathematical sum results in a σ (bonding) molecular orbital, with increased probability density between the nuclei. (b) The mathematical difference results in a σ* (antibonding) molecular orbital, with a nodal plane of zero probability density perpendicular to the internuclear axis.

Second Row Diatomic Molecules

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

We now describe examples of systems involving period 2 homonuclear diatomic molecules, such as N_2, O_2, and F_2. When we draw a molecular orbital diagram for a molecule, there are four key points to remember:

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

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

We illustrate how to use these points by constructing a molecular orbital energy-level diagram for F_2. We use the diagram in part (a) in Figure **2.6.9**; the $n = 1$ orbitals (σ_{1s} and σ_{1s}*) are located well below those of the $n = 2$ level and are not shown. As illustrated in the diagram, the σ_{2s} and σ_{2s}* molecular orbitals are much lower in energy than the molecular orbitals derived from the 2*p* atomic orbitals because of the large difference in energy between the 2*s* and 2*p* atomic orbitals of fluorine. The lowest-energy molecular orbital derived from the three 2*p* orbitals on each F is σ_{2p_z} and the next most stable are the two degenerate orbitals, π_{2p_x} and π_{2p_y}. For each bonding orbital in the diagram, there is an antibonding orbital, and the antibonding orbital is destabilized by about as much as the corresponding bonding orbital is stabilized. As a result, the $\sigma^*_{2p_z}$ orbital is higher in energy than either of the degenerate $\pi^*_{2p_x}$ and $\pi^*_{2p_y}$ orbitals. We can now fill the orbitals, beginning with the one that is lowest in energy.

Each fluorine has 7 valence electrons, so there are a total of 14 valence electrons in the F_2 molecule. Starting at the lowest energy level, the electrons are placed in the orbitals according to the Pauli principle and Hund's rule. Two electrons each fill the σ_{2s} and σ_{2s}* orbitals, 2 fill the σ_{2p_z} orbital, 4 fill the two degenerate π orbitals, and 4 fill the two degenerate π^* orbitals, for a total of 14 electrons. To determine what type of bonding the molecular orbital approach predicts F_2 to have, we must calculate the bond order. According to our diagram, there are 8 bonding electrons and 6 antibonding electrons, giving a bond order of $(8 - 6) \div 2 = 1$. Thus F_2 is predicted to have a stable F–F single bond, in agreement with experimental data.

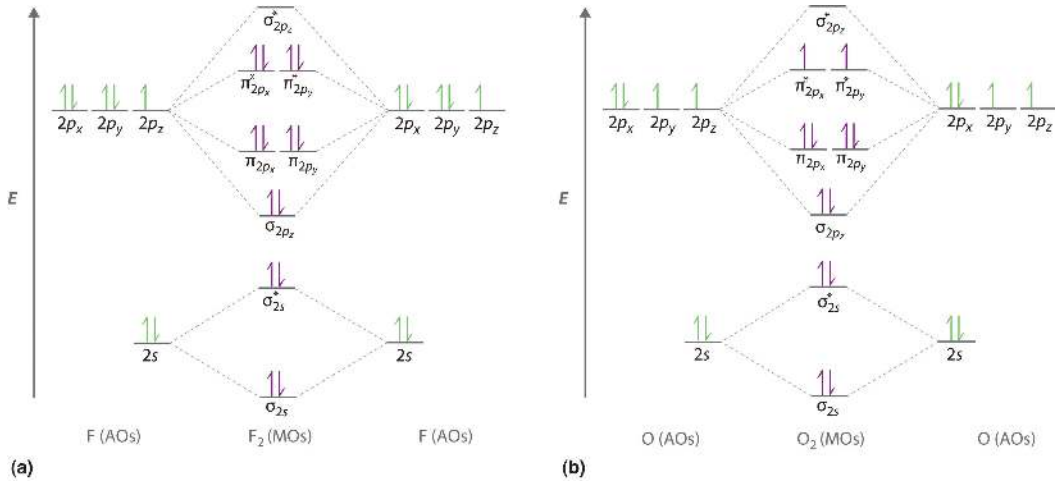


Figure **2.6.9**: Molecular Orbital Energy-Level Diagrams for Homonuclear Diatomic Molecules.(a) For F_2, with 14 valence electrons (7 from each F atom), all of the energy levels except the highest, $\sigma^*_{2p_z}$ are filled. This diagram shows 8 electrons in bonding orbitals and 6 in antibonding orbitals, resulting in a bond order of 1. (b) For O_2, with 12 valence electrons (6 from each O atom), there are only 2 electrons to place in the $\left(\pi^*_{np_z}, \pi^*_{np_y}\right)$ pair of orbitals. Hund's rule dictates that one electron occupies each orbital, and their spins are parallel, giving the O_2 molecule two unpaired electrons. This diagram shows 8 electrons in bonding orbitals and 4 in antibonding orbitals, resulting in a predicted bond order of 2.

We now turn to a molecular orbital description of the bonding in O_2. It so happens that the molecular orbital description of this molecule provided an explanation for a long-standing puzzle that could not be explained using other bonding models. To obtain the molecular orbital energy-level diagram for O_2, we need to place 12 valence electrons (6 from each O atom) in the energy-level diagram shown in part (b) in Figure **2.6.9**. We again fill the orbitals according to Hund's rule and the Pauli principle, beginning with the orbital that is lowest in energy. Two electrons each are needed to fill the σ_{2s} and σ_{2s}* orbitals, 2 more to fill the σ_{2p_z} orbital, and 4 to fill the degenerate $\pi^*_{2p_z}$ and $\pi^*_{2p_y}$ orbitals. According to Hund's rule, the last 2 electrons must be placed in separate π^* orbitals with their spins parallel, giving two unpaired electrons. This leads to a predicted bond order of $(8 - 4) \div 2 = 2$, which corresponds to a double bond, in agreement with experimental data (Table 4.5): the O–O bond length is 120.7 pm, and the bond energy is 498.4 kJ/mol at 298 K.

None of the other bonding models can predict the presence of two unpaired electrons in O_2. Chemists had long wondered why, unlike most other substances, liquid O_2 is attracted into a magnetic field. As shown in Figure **2.6.10**, it actually remains suspended between the poles of a magnet until the liquid boils away. The only way to explain this behavior was for O_2 to have unpaired electrons, making it paramagnetic, exactly as predicted by molecular orbital theory. This result was one of the earliest triumphs of molecular orbital theory over the other bonding approaches we have discussed.



Figure **2.6.10**: Liquid O_2 Suspended between the Poles of a Magnet.Because the O_2 molecule has two unpaired electrons, it is paramagnetic. Consequently, it is attracted into a magnetic field, which allows it to remain suspended between the poles of a powerful magnet until it evaporates. Full video can be found at https://www.youtube.com/watch?featur...&v=Lt4P6ctf06Q.

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

For period 2 diatomic molecules to the left of N_2 in the periodic table, a slightly different molecular orbital energy-level diagram is needed because the σ_{2p_z} molecular orbital is slightly *higher* in energy than the degenerate $\pi^*_{np_x}$ and $\pi^*_{np_y}$ orbitals. The difference in energy between the 2*s* and 2*p* atomic orbitals increases from Li_2 to F_2 due to increasing nuclear charge and poor screening of the 2*s* electrons by electrons in the 2*p* subshell. The bonding interaction between the 2*s* orbital on one atom and the 2*pz* orbital on the other is most important when the two orbitals have similar energies. This interaction decreases the energy of the σ_{2s} orbital and increases the energy of the σ_{2p_z} orbital. Thus for Li_2, Be_2, B_2, C_2, and N_2, the σ_{2p_z} orbital is higher in energy than the σ_{3p_z} orbitals, as shown in Figure **2.6.11** Experimentally, it is found that the energy gap between the *ns* and *np* atomic orbitals *increases* as the nuclear charge increases (Figure **2.6.11**). Thus for example, the σ_{2p_z} molecular orbital is at a lower energy than the $\pi_{2p_{x,y}}$ pair.

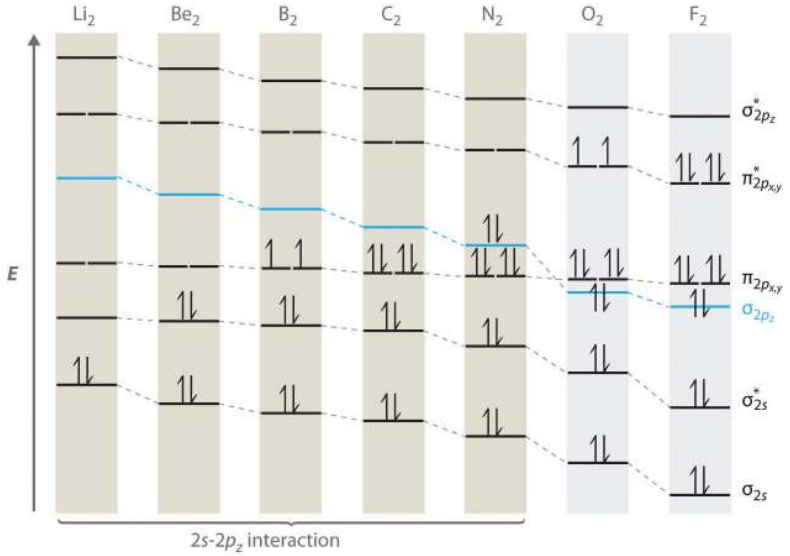


Figure **2.6.11**: Molecular Orbital Energy-Level Diagrams for the Diatomic Molecules of the Period 2 Elements. Unlike earlier diagrams, only the molecular orbital energy levels for the molecules are shown here. For simplicity, the atomic orbital energy levels for the component *atoms* have been omitted. For Li_2 through N_2, the σ_{2p_z} orbital is higher in energy than the $\pi_{2p_{x,y}}$ orbitals. In contrast, the σ_{2p_z} orbital is *lower* in energy than the $\pi_{2p_{x,y}}$ orbitals for O_2 and F_2 due to the increase in the energy difference between the 2*s* and 2*p* atomic orbitals as the nuclear charge increases across the row.

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

✔ Example **2.6.3**

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

Given: chemical species

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

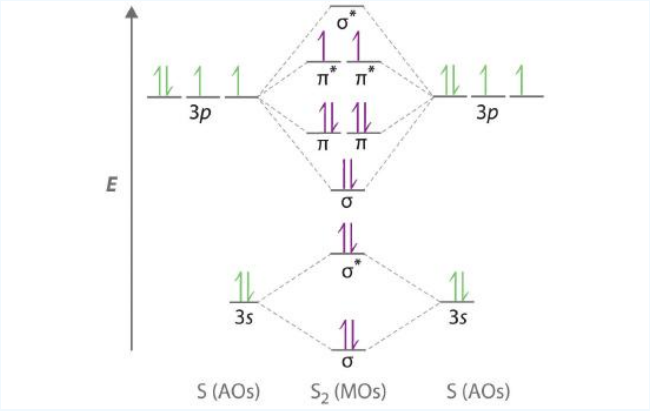
Strategy:

A. Write the valence electron configuration of sulfur and determine the type of molecular orbitals formed in S_2. Predict the relative energies of the molecular orbitals based on how close in energy the valence atomic orbitals are to one another.
B. Draw the molecular orbital energy-level diagram for this system and determine the total number of valence electrons in S_2.
C. Fill the molecular orbitals in order of increasing energy, being sure to obey the Pauli principle and Hund's rule.
D. Calculate the bond order and describe the bonding.

Solution:

A Sulfur has a [Ne]$3s^2 3p^4$ valence electron configuration. To create a molecular orbital energy-level diagram similar to those in Figure **2.6.9** and Figure **2.6.11**, we need to know how close in energy the 3*s* and 3*p* atomic orbitals are because their energy separation will determine whether the $\pi_{3p_{z,y}}$ or the σ_{3p_z}> molecular orbital is higher in energy. Because the *ns*–*np* energy gap *increases* as the nuclear charge increases (Figure **2.6.11**), the σ_{3p_z} molecular orbital will be lower in energy than the $\pi_{3p_{z,y}}$ pair.

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



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

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

? Exercise 2.6.3

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

Answer

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

bond order of 1;

no unpaired electrons

Molecular Orbitals for Heteronuclear Diatomic Molecules

Diatomic molecules with two different atoms are called heteronuclear diatomic molecules. When two nonidentical atoms interact to form a chemical bond, the interacting atomic orbitals do not have the same energy. If, for example, element B is more electronegative than element A ($\chi_B > \chi_A$), the net result is a "skewed" molecular orbital energy-level diagram, such as the one shown for a hypothetical A–B molecule in Figure **2.6.12**. The atomic orbitals of element B are uniformly lower in energy than the corresponding atomic orbitals of element A because of the enhanced stability of the electrons in element B. The molecular orbitals are no longer symmetrical, and the energies of the bonding molecular orbitals are more similar to those of the atomic orbitals of B.

Hence the electron density of bonding electrons is likely to be closer to the more electronegative atom. In this way, molecular orbital theory can describe a polar covalent bond.

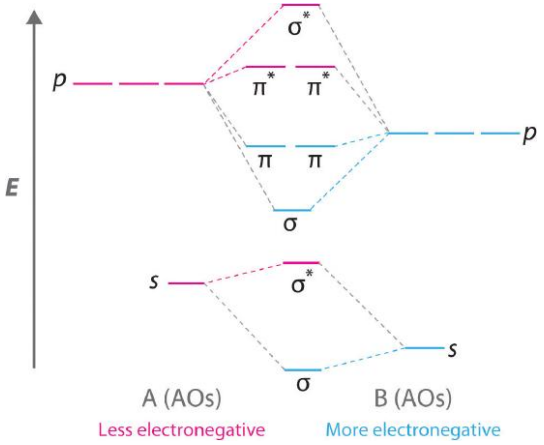


Figure **2.6.12**: Molecular Orbital Energy-Level Diagram for a Heteronuclear Diatomic Molecule AB, Where $\chi_B > \chi_A$. The bonding molecular orbitals are closer in energy to the atomic orbitals of the more electronegative B atom. Consequently, the electrons in the bonding orbitals are not shared equally between the two atoms. On average, they are closer to the B atom, resulting in a polar covalent bond.

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

An Odd Number of Valence Electrons: NO

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

Because NO has an odd number of valence electrons (5 from nitrogen and 6 from oxygen, for a total of 11), its bonding and properties cannot be successfully explained by either the Lewis electron-pair approach or valence bond theory. The molecular orbital energy-level diagram for NO (Figure **2.6.13**) shows that the general pattern is similar to that for the O_2 molecule (Figure **2.6.11**). Because 10 electrons are sufficient to fill all the bonding molecular orbitals derived from 2*p* atomic orbitals, the 11th electron must occupy one of the degenerate π^* orbitals. The predicted bond order for NO is therefore (8-3) ÷ 2 = 2 1/2 . Experimental data, showing an N–O bond length of 115 pm and N–O bond energy of 631 kJ/mol, are consistent with this description. These values lie between those of the N_2 and O_2 molecules, which have triple and double bonds, respectively. As we stated earlier, molecular orbital theory can therefore explain the bonding in molecules with an odd number of electrons, such as NO, whereas Lewis electron structures cannot.

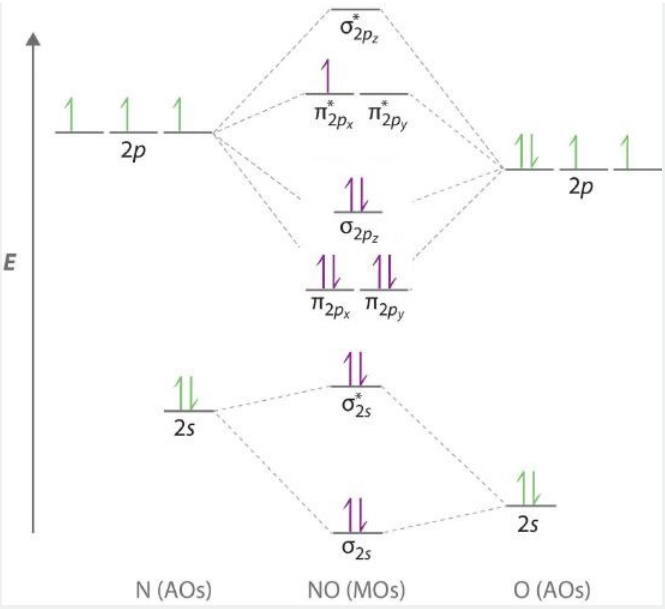


Figure **2.6.13**: Molecular Orbital Energy-Level Diagram for **NO**. Because **NO** has 11 valence electrons, it is paramagnetic, with a single electron occupying the $\left(\pi^{\star}_{2p_z}, \pi^{\star}_{2p_y}\right)$ pair of orbitals.

Note that electronic structure studies show the ground state configuration of **NO** to be $(\sigma_{2s})^2 (\sigma^{\star}_{2s})^2 \left(\pi_{2p_{z,y}}\right)^4 (\sigma_{2p_z})^2 \left(\pi_{2p^{\star}_{z,y}}\right)^2$ in order of increasing energy. Hence, the $\pi_{2p_{z,y}}$ orbitals are lower in energy than the σ_{2p_z} orbital. This is because the **NO** molecule is near the transition of flipping energies levels observed in homonuclear diatomics where the sigma bond drops below the pi bond (Figure **2.6.11**).

Molecular orbital theory can also tell us something about the *chemistry* of ***NO***. As indicated in the energy-level diagram in Figure **2.6.13**, NO has a single electron in a relatively high-energy molecular orbital. We might therefore expect it to have similar reactivity as alkali metals such as Li and Na with their single valence electrons. In fact, ***NO*** is easily oxidized to the NO^+ cation, which is isoelectronic with N_2 and has a bond order of 3, corresponding to an N≡O triple bond.



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

Nonbonding Molecular Orbitals

Molecular orbital theory is also able to explain the presence of lone pairs of electrons. Consider, for example, the HCl molecule, whose Lewis electron structure has three lone pairs of electrons on the chlorine atom. Using the molecular orbital approach to describe the bonding in HCl, we can see from Figure **2.6.14** that the 1*s* orbital of atomic hydrogen is closest in energy to the 3*p* orbitals of chlorine. Consequently, the filled Cl 3*s* atomic orbital is not involved in bonding to any appreciable extent, and the only important interactions are those between the H 1*s* and Cl 3*p* orbitals. Of the three *p* orbitals, only one, designated as $3p_z$, can interact with the H 1*s* orbital. The $3p_x$ and $3p_y$ atomic orbitals have no net overlap with the 1*s* orbital on hydrogen, so they are not

involved in bonding. Because the energies of the Cl 3*s*, 3p_x, and 3p_y orbitals do not change when HCl forms, they are called **nonbonding molecular orbitals**. A nonbonding molecular orbital occupied by a pair of electrons is the molecular orbital equivalent of a lone pair of electrons. By definition, electrons in nonbonding orbitals have no effect on bond order, so they are not counted in the calculation of bond order. Thus the predicted bond order of HCl is (2 − 0) ÷ 2 = 1. Because the σ bonding molecular orbital is closer in energy to the Cl 3p_z than to the H 1*s* atomic orbital, the electrons in the σ orbital are concentrated closer to the chlorine atom than to hydrogen. A molecular orbital approach to bonding can therefore be used to describe the polarization of the H–Cl bond to give $H^{\delta+}-\!-Cl^{\delta-}$.

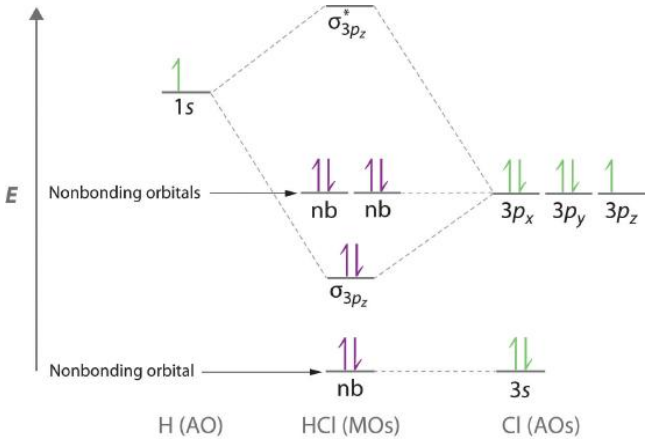


Figure **2.6.14**: Molecular Orbital Energy-Level Diagram for HCl. The hydrogen 1*s* atomic orbital interacts most strongly with the 3p_z orbital on chlorine, producing a bonding/antibonding pair of molecular orbitals. The other electrons on Cl are best viewed as nonbonding. As a result, only the bonding σ orbital is occupied by electrons, giving a bond order of 1.

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

Example 2.6.4

Use a "skewed" molecular orbital energy-level diagram like the one in Figure **2.6.12** to describe the bonding in the cyanide ion (CN^-). What is the bond order?

Given: chemical species

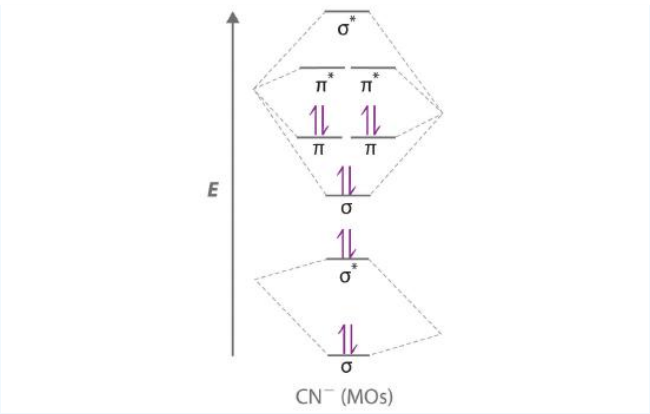
Asked for: "skewed" molecular orbital energy-level diagram, bonding description, and bond order

Strategy:

A. Calculate the total number of valence electrons in CN^-. Then place these electrons in a molecular orbital energy-level diagram like Figure **2.6.12** in order of increasing energy. Be sure to obey the Pauli principle and Hund's rule while doing so.
B. Calculate the bond order and describe the bonding in CN^-.

Solution:

A The CN^- ion has a total of 10 valence electrons: 4 from C, 5 from N, and 1 for the −1 charge. Placing these electrons in an energy-level diagram like Figure **2.6.12** fills the five lowest-energy orbitals, as shown here:



Because $\chi_N > \chi_C$, the atomic orbitals of N (on the right) are lower in energy than those of C. **B** The resulting valence electron configuration gives a predicted bond order of $(8 - 2) \div 2 = 3$, indicating that the CN^- ion has a triple bond, analogous to that in N_2.

? Exercise 2.6.4

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

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

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

Summary

- Molecular orbital theory, a delocalized approach to bonding, can often explain a compound's color, why a compound with unpaired electrons is stable, semiconductor behavior, and resonance, none of which can be explained using a localized approach.

A **molecular orbital (MO)** is an allowed spatial distribution of electrons in a molecule that is associated with a particular orbital energy. Unlike an atomic orbital (AO), which is centered on a single atom, a molecular orbital extends over all the atoms in a molecule or ion. Hence the **molecular orbital theory** of bonding is a *delocalized* approach. Molecular orbitals are constructed using **linear combinations of atomic orbitals (LCAOs)**, which are usually the mathematical sums and differences of wave functions that describe overlapping atomic orbitals. Atomic orbitals interact to form three types of molecular orbitals.

1. Orbitals or orbital lobes with the same sign interact to give increased electron probability along the plane of the internuclear axis because of *constructive* reinforcement of the wave functions. Consequently, electrons in such molecular orbitals help to hold the positively charged nuclei together. Such orbitals are **bonding molecular orbitals**, and they are always lower in energy than the parent atomic orbitals.
2. Orbitals or orbital lobes with opposite signs interact to give decreased electron probability density between the nuclei because of *destructive* interference of the wave functions. Consequently, electrons in such molecular orbitals are primarily located outside the internuclear region, leading to increased repulsions between the positively charged nuclei. These orbitals are called **antibonding molecular orbitals**, and they are always higher in energy than the parent atomic orbitals.
3. Some atomic orbitals interact only very weakly, and the resulting molecular orbitals give essentially no change in the electron probability density between the nuclei. Hence electrons in such orbitals have no effect on the bonding in a molecule or ion. These orbitals are **nonbonding molecular orbitals**, and they have approximately the same energy as the parent atomic orbitals.

A completely bonding molecular orbital contains no nodes (regions of zero electron probability) perpendicular to the internuclear axis, whereas a completely **antibonding molecular orbital** contains at least one node perpendicular to the internuclear axis. A **sigma (σ) orbital** (bonding) or a **sigma star (σ*) orbital** (antibonding) is symmetrical about the internuclear axis. Hence all cross-sections perpendicular to that axis are circular. Both a **pi (π) orbital** (bonding) and a **pi star (π*) orbital** (antibonding) possess a nodal plane that contains the nuclei, with electron density localized on both sides of the plane.

The energies of the molecular orbitals versus those of the parent atomic orbitals can be shown schematically in an **energy-level diagram**. The electron configuration of a molecule is shown by placing the correct number of electrons in the appropriate energy-level diagram, starting with the lowest-energy orbital and obeying the Pauli principle; that is, placing only two electrons with opposite spin in each orbital. From the completed energy-level diagram, we can calculate the **bond order**, defined as one-half the net number of bonding electrons. In bond orders, electrons in antibonding molecular orbitals cancel electrons in bonding molecular orbitals, while electrons in nonbonding orbitals have no effect and are not counted. Bond orders of 1, 2, and 3 correspond to single, double, and triple bonds, respectively. Molecules with predicted bond orders of 0 are generally less stable than the isolated atoms and do not normally exist.

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

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CHAPTER OVERVIEW

3: Molecular Symmetry

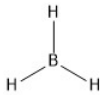
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3.1: Introduction

Symmetry is important in the study of chemistry. It can be studied on both the molecular level and the crystalline level, of which the former will be discussed in this book.

A molecule is symmetrical if it stays in an indistinguishable configuration after some movement. For example, the molecule BH_3 in **3.1** can be rotated about an axis perpendicular to the screen and passes through the boron atom. If the rotation angle is 120°, the new configuration is indistinguishable from the original form.



3.1

The study of symmetry has many applications, some of which will be introduced in this chapter. Also in this chapter, some of the terminology and definitions used in group theory, the mathematical representation of symmetry, will be introduced.

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3.2: 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 **3.2.1**). In this example, the symmetry operation is the rotation and the symmetry element is the axis of rotation.

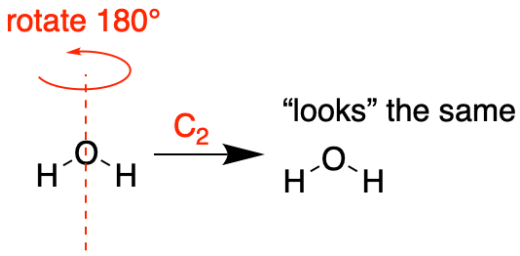


Figure **3.2.1**: An example of a symmetry operation is a 180° rotation where the resulting position is indistinguishable from the original. A 180° rotation is called a C_2 operation; the axis of rotation is the symmetry element. (Kathryn Haas; CC-NC-BY-SA)

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 **3.2.1**.

Table **3.2.1**: Table of elements and operations

Element	Operation	Symbol
Identity	identity	E
Proper axis	rotation by (360/n)°	C_n
Symmetry plane	reflection in the plane	σ
Inversion center	inversion of a point at (x,y,z) to (-x,-y,-z)	*i*
Improper axis	rotation by (360/n)°, followed by reflection in the plane perpendicular to the rotation axis	S_n

Symmetry Operations and Elements

Identity (E)

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

Proper Rotation and Proper Axis (C_n)

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

PRINCIPAL AXIS: The principal axis of a molecule is the highest order proper rotation axis. For example, if a molecule had C_2 and C_4 axes, the C_4 is the principal axis.

Reflection and Symmetry Planes (σ)

Symmetry planes are mirror planes within the molecule. A reflection operation occurs with respect to a plane of symmetry. There are three classes of symmetry elements:

1. σ_h (horizontal): horizontal planes are perpendicular to principal axis
2. σ_v (vertical): vertical planes are parallel to the principal axis
3. σ_d (dihedral): dihedral planes are parallel to the principal axis and bisecting two C_2' axes

Inversion and Inversion Center (i)

The inversion operation requires a point of symmetry (a center of symmetry within a molecule). In other words, a point at the center of the molecule that can transform (x,y,z) into (-x,-y,-z) coordinate. Structures of tetrahedrons, triangles, and pentagons lack an inversion center.

Improper rotation (S_n)

Improper rotation is a combination of a rotation with respect to an axis of rotation (C_n), followed by a reflection through a plane perpendicular to that C_n axis. In short, an S_n operation is equivalent to C_n followed by σ_h.

References

1. Introduction to Molecular Symmetry by J. S Ogden
2. Inorganic Chemistry by Catherine Housecroft And Alan G. Sharpe.

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3.3: Successive Operations

Sometimes, new symmetry operations form by carrying out two or more simpler operations successively to result in an indistinguishable configuration. For example, the improper rotation axis that was introduced in the last section results from rotation about an axis of rotation (C_n) followed by reflection about a plane perpendicular to that axis (σ_h).

$$S_n = C_n \times \sigma_h$$

Note also that C_n in this case need not be a symmetry element for the molecule. For example, staggered ethane has an S_6 symmetry element although it does not have a C_6. Another example of a symmetry element that results from a combination of two different elements is the inversion center (i), which results from a C_2 rotation followed by a reflection about a plane perpendicular to that axis (σ_h).

$$i = C_2 \times \sigma_h$$

Note that an inversion center is a special case of an improper rotation axis because it results when, in the first equation, $n = 2$. That is,

$$i = S_2$$

In fact, any symmetry operation can be carried out multiple time in a row. For example, when BH_3 is rotated twice by 120°, the two-step operation can be symboled by C_3^2. When the C_3 operation is performed a third time, the molecule returns to its original configuration; i.e,

$$C_3^3 = E$$

In general,

$$C_n^n = E$$

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3.4: 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.

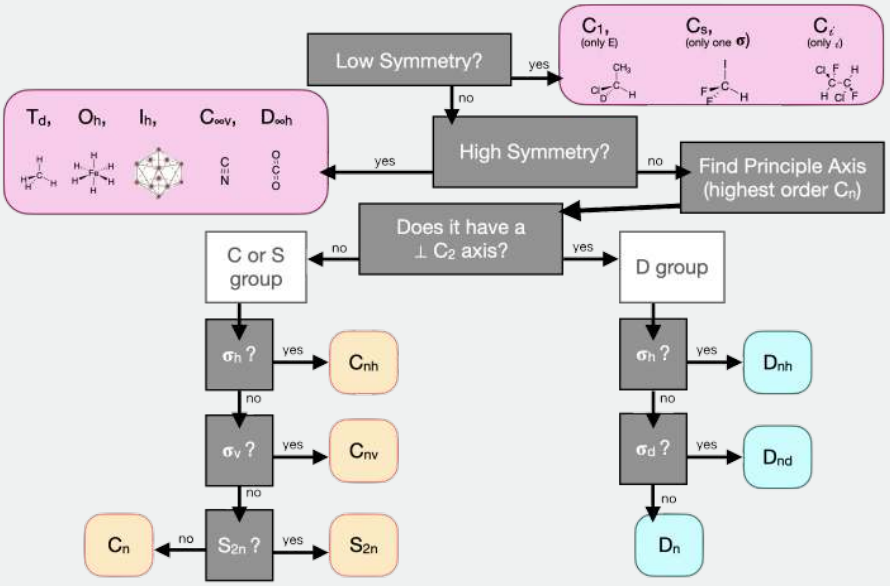


Figure **3.4.1**: Decision tree for determining a molecule's point group (CC-BY-NC-SA; Kathryn Haas)

Example 3.4.1

Find the point group of benzene (C_6H_6).

Answer

Solution

1. Benzene is neither high nor low symmetry
2. Highest order rotation axis: C_6
3. There are 6 C_2 axes perpendicular to the principal axis
4. There is a horizontal mirror plane (σ_h)

Benzene is in the D_{6h} point group.

See Also

Symmetry Gallery

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3.5: 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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3.6: 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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3.7: Character Tables

Introduction to Character Tables, using C_{2v} as example

A character table is the complete set of irreducible representations of a symmetry group. In the previous section, we derived three of the four irreducible representations for the C_{2v} point group. These three irreducible representations are labeled A_1, B_1, and B_2. The fourth irreducible representation, A_2, can be derived using the properties (or "rules") for irreducible representations listed below.

Properties of Characters of Irreducible Representations in Point Groups

1. There is always a totally symmetric representation in which all the characters are 1.
   e.g. In C_{2v}, A_1 is totally symmetric.
2. The order of the group (h) is the total number of symmetry operations in the group.
   e.g. In C_{2v}, $h = 4$
3. Similar operations are listed as classes (R) and appear as columns in the table.
   e.g. In C_{2v}, there are four classes of operations, E, C_2, $\sigma_{v(xz)}$, and $\sigma'_{v(yz)}$
4. The number of irreducible representations (rows) must equal the number of classes (columns). This results in all character tables being square.
   e.g. In C_{2v}, there are four classes and four irreducible representations.
5. The sum of squares of all characters under E is equal to the order of the group: $h = \sum [\chi_i]^2$
   e.g. In C_{2v}, $h = 1^2 + 1^2 + 1^2 + 1^2 = 4$
6. For any irreducible representation (i), the sum of squares of its characters multiplied by the number of operations in the class is the order of the group: $h = \sum [\chi_i(R)]^2$
   e.g. For A_2 in C_{2v}, $h = (1 \times 1)^2 + (1 \times 1)^2 + (-1 \times 1)^2 + (-1 \times 1)^2 = 4$
7. Irreducible representations are orthogonal. For any two representations (i and j): $\sum [\chi_i * (R) \chi_j(R)] = 0$
   e.g. For B_1 and B_2 of C_{2v}, $[1 \times 1] + [-1 \times -1] + [1 \times -1] + [-1 \times 1] = 0$

The complete character table for C_{2v} is given below.

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

The various sections of the table are as follows:

i. The first element in the table gives the name of the point group, usually in Schoenflies (C_{2v}) notation.
ii. Along the first row are the symmetry operations of the group, E, C_2, σ_v and σ_v'', followed by the order of the group, h.
iii. In the first column are the irreducible representations of the group, represented by Mulliken Labels. In C_{2v} the irreducible representations are A_1, A_2, B_1 and B_2. The Mulliken labels indicate the symmetry of each representation (explained further below).
iv. The characters (χ) of the irreducible representations under each symmetry operation are given in the bulk of the table.
v. The final column(s) of the table lists a number of functions that transform as the various irreducible representations of the group. These are the Cartesian axes (x, y, z), the Cartesian products ($z^2, x^2 + y^2, xy, xz, yz$), and the rotations ($R_x, R_y, R_z$) (explained further below).

Another example: C_{3v}

Th C_{3v} point group has three classes of operations: E, C_3, and $\sigma_{v(xz)}$. The derivation of transformation matrices for E and $\sigma_{v(xz)}$ is similar to the case for C_{2v}. However, the C_{3v} operation does not give simple 1 or -1 characters. If we carry out a rotation about z by an angle θ, our x and y axes are transformed onto new axes x' and y'. The new axes can each be written as a linear combination of our original x and y axes. The derivation of the rotation matrices will not be covered in this text, but is described elsewhere:

$$x' = x\cos\theta + y\sin\theta$$
$$y' = -x\sin\theta + y\cos\theta$$

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

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

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

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

The C_3 transformation matrix contains off-diagonal entries, and therefore it cannot be block diagonalized as 1x1 matrices. However, the first two lines can be diagonalized as a 2x2 and the last line as a 1x1 matrix (Figure **3.7.1**):

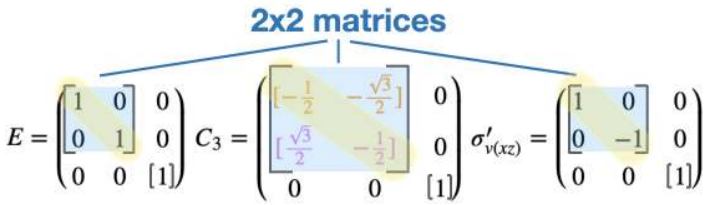


Figure **3.7.1**: The C_3 transformation matrix contains off-diagonal entries, and therefore it cannot be block diagonalized as 1x1 matrices. However, the first two lines can be diagonalized as a 2x2 and the last line as a 1x1 matrix. (CC-BY-NC-SA; Kathryn Haas)

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 **3.7.2**. Character tables for common point groups are given in the References section of LibreTexts Bookshelves.

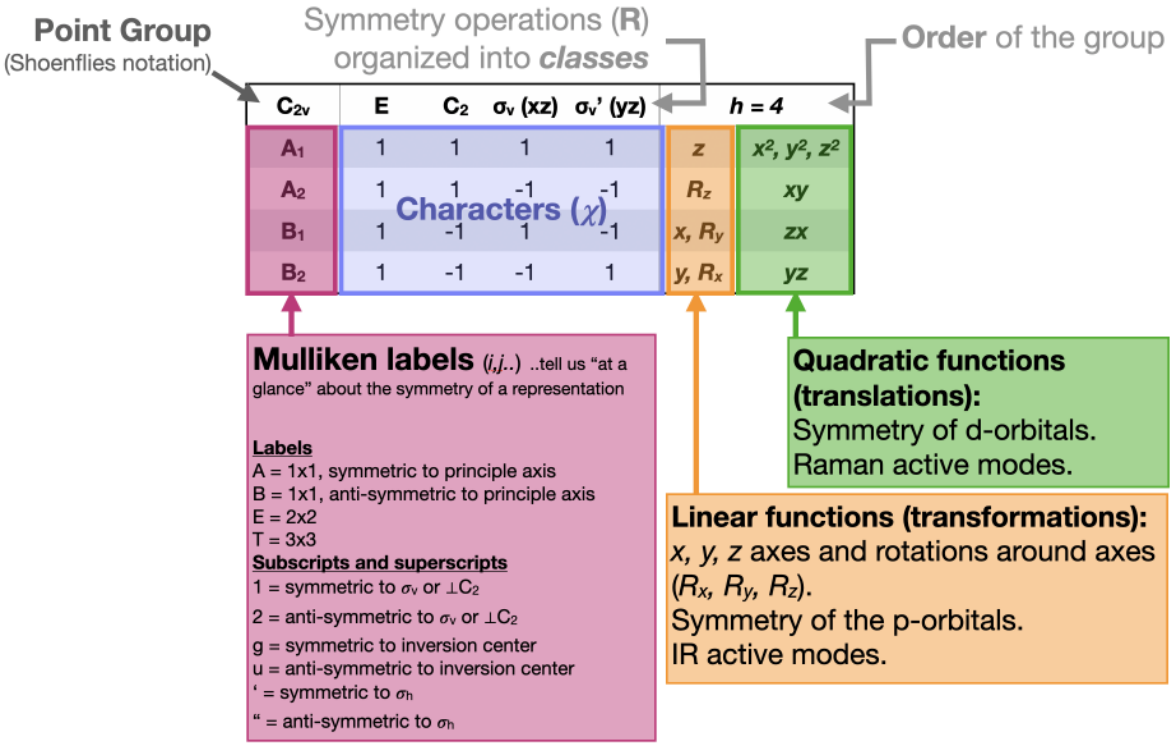


Figure **3.7.2**: Visual summary of the sections of a character table and their meaning. (CC-BY-NC-SA; Kathryn Haas)

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3.8: Molecular Vibrations

Symmetry and group theory can be applied to understand molecular vibrations. This is particularly useful in the context of predicting the number of peaks expected in the infrared (IR) and Raman spectra of a given compound.

We will use water as a case study to illustrate how group theory is used to predict the number of peaks in IR and Raman spectra.

How many IR and Raman peaks would we expect for H_2O?

To answer this question with group theory, a pre-requisite is that you **assign the molecule's point group and assign an axis system** to the entire molecule. By convention, the z axis is collinear with the principle axis, the x axis is in-plane with the molecule or the most number of atoms. It is a good idea to stick with this convention (see Figure 3.8.1).

What is the point group for H_2O? (click to see answer)

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

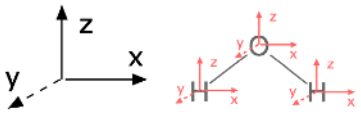


Figure 3.8.1: The first step to finding normal modes is to assign a consistent axis system to the entire molecule and to each atom. (CC-BY-SA; Kathryn Haas)

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 3.8.1).

Γ_{modes} is the sum of the characters (trace) of the transformation matrix for the entire molecule (in the case of water, there are 9 degrees of freedom and this is now a 9x9 matrix). Let's walk through this step-by-step. The transformation matrix of E and C_2 are shown below:

$$E = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_{oxygen} \\ y_{oxygen} \\ z_{oxygen} \\ x_{hydrogen-a} \\ y_{hydrogen-a} \\ z_{hydrogen-a} \\ x_{hydrogen-b} \\ y_{hydrogen-b} \\ z_{hydrogen-b} \end{pmatrix} = \begin{pmatrix} x'_{oxygen} \\ y'_{oxygen} \\ z'_{oxygen} \\ x'_{hydrogen-a} \\ y'_{hydrogen-a} \\ z'_{hydrogen-a} \\ x'_{hydrogen-b} \\ y'_{hydrogen-b} \\ z'_{hydrogen-b} \end{pmatrix}, \chi = 9$$

$$C_2 = \begin{pmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} x_{oxygen} \\ y_{oxygen} \\ z_{oxygen} \\ x_{hydrogen-a} \\ y_{hydrogen-a} \\ z_{hydrogen-a} \\ x_{hydrogen-b} \\ y_{hydrogen-b} \\ z_{hydrogen-b} \end{pmatrix} = \begin{pmatrix} x'_{oxygen} \\ y'_{oxygen} \\ z'_{oxygen} \\ x'_{hydrogen-a} \\ y'_{hydrogen-a} \\ z'_{hydrogen-a} \\ x'_{hydrogen-b} \\ y'_{hydrogen-b} \\ z'_{hydrogen-b} \end{pmatrix}, \chi = 1$$

It is unnecessary to find the transformation matrix for each operation since it is only the TRACE that gives us the character, and any off-diagonal entries do not contribute to Γ_{modes}. The values that contribute to the trace can be found simply by performing each operation in the point group and assigning a value to each individual atom to represent how it is changed by that operation. If the atom moves away from itself, that atom gets a character of zero (this is because any non-zero characters of the transformation matrix are off of the diagonal). If the atom remains in place, each of its three dimensions is assigned a value of $\cos\theta$. For the example of H_2O under the C_{2v} point group, the axes that remain unchanged ($\theta = 0°$) are assigned a value of $\cos(0°) = 1$, while those that are moved into the negative of themselves (rotated or reflected to $\theta = 180°$) are assigned $\cos(180°) = -1$. The character for Γ is the sum of the values for each transformation.

Let's walk through the steps to assign characters of Γ_{modes} for H_2O to illustrate how this works:

For the operation E, performed on H_2O, all three atoms remain in place. The three axes x, y, z on each atom remain unchanged. Thus, each of the three axes on each of three atom (nine axes) is assigned the value $\cos(0°) = 1$, resulting in a sum of $\chi = 9$ for the Γ_{modes}.

For the operation C_2, the two hydrogen atoms are moved away from their original position, and so the hydrogens are assigned a value of zero. The oxygen remains in place; the z-axis on oxygen is unchanged ($\cos(0°) = 1$), while the x and y axes are inverted ($\cos(180°)$). The sum of these characters gives $\chi = -1$ in the Γ_{modes}.

Now you try! Find the characters of $\sigma_{v(xz)}$ and $\sigma_{v(yz)}$ under the C_{2v} point group. Compare what you find to the Γ_{modes} for all normal modes given below.

C_{2v}	E	C_2	σ_v	σ'_v
Γ_{modes}	9	−1	3	1

(3.8.1)

STEP 2: Break Γ_{modes} into its component irreducible representations.

Now that we've found the Γ_{modes} (3.8.1), we need to break it down into the individual irreducible representations (i, j, k...) for the point group. We can do this systematically using the following formula:

Misplaced '#'

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

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

$$\Gamma_{modes} = 3A_1 + 1A_2 + 3B_1 + 2B_2 \tag{3.8.2}$$

.

Notice there are 9 irreducible representations in Equation 3.8.2. These irreducible representations represent the symmetries of all 9 motions of the molecule: vibrations, rotations, and translations.

? Exercise 3.8.1: Derive the irreducible representation in equation 3.8.2.

Derive the nine irreducible representations of Γ_{modes} for H_2O, expression 3.8.2.

Hint

To find the number of each kind of irreducible representation that combine to form the Γ_{modes}, we need the characters of Γ_{modes} that we found above (3.8.1), the C_{2v} character table (below), and equation ???.

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

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

Answer

The number of $A_1 = \frac{1}{4}[(1\times 9\times 1) + (1\times(-1)\times 1) + (1\times 3\times 1) + (1\times 1\times 1)] = 3A_1$

The number of $A_2 = \frac{1}{4}[(1\times 9\times 1) + (1\times(-1)\times 1) + ((-1)\times 3\times 1) + ((-1)\times 1\times 1)] = 1A_2$

The number of $B_1 = \frac{1}{4}[(1\times 9\times 1) + ((-1)\times(-1)\times 1) + (1\times 3\times 1) + ((-1)\times 1\times 1)] = 3B_1$

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

STEP 3: Subtract rotations and translations to find vibrational modes.

Because we are interested in molecular vibrations, we need to subtract the rotations and translations from the total degrees of freedom.

$$\text{Vibrations} = \Gamma_{modes} - \text{Rotations} - \text{Translations}$$

In the example of H_2O, the total degrees of freedom are given above in equation 3.8.2, and therefore the vibrational degrees of freedom can be found by:

$$H_2O \text{ vibrations} = (3A_1 + 1A_2 + 3B_1 + 2B_2) - \text{Rotations} - \text{Translations} \tag{3.8.3}$$

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

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

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

In C_{2v}, translations correspond to B_1, B_2, and A_1 (respectively for x, yz), and rotations correspond to B_2, B_1, and A_1 (respectively for R_x, R_y, R_z). Subtracting these six irreducible representations from Γ_{modes} will leave us with the irreducible representations for vibrations.

$$\begin{aligned} H_2O \text{ vibrations} &= \Gamma_{modes} - \text{Rotations} - \text{Translations} \\ &= (3A_1 + 1A_2 + 3B_1 + 2B_2) - (A_1 + B_1 + B_2) - (A_2 + B_1 + B_2) \\ &= 2A_1 + 1B_1 \end{aligned}$$

The three vibrational modes for H_2O are $2A_1 + 1B_1$. Note that we have the correct number of vibrational modes based on the expectation of $3N - 6$ vibrations for a non-linear molecule.

STEP 4: Determine which of the vibrational modes are IR-active and Raman-active.

The next step is to determine which of the vibrational modes is IR-active and Raman-active. To do this, we apply the IR and Raman Selection Rules below:

IR and Raman Selection Rules

Infrared selection rules:

If a vibration results in the change in the molecular dipole moment, it is IR-active. In the character table, we can recognize the vibrational modes that are IR-active by those with symmetry of the x, y, and z axes.

In C_{2v}, any vibrations with A_1, B_1 or B_2 symmetry would be IR-active.

Raman selection rules:

If a vibration results in a change in the molecular polarizability, it will be Raman-active. In the character table, we can recognize the vibrational modes that are Raman-active by those with symmetry of any of the binary products (xy, xz, yz, x^2, y^2, and z^2) or a linear combination of binary products (e.g. $x^2 - y^2$).

In C_{2v}, any vibrations with A_1, A_2, B_1 or B_2 symmetry would be Raman-active.

In our H_2O example, we found that of the three vibrational modes, two have A_1 and one has B_1 symmetry. Both A_1 and B_1 are IR-active, and both are also Raman-active. ***There are two possible IR peaks and three possible Raman peaks expected for water***.*

*It is important to note that this prediction tells only what is possible, but not what we might actually see in the IR and Raman spectra. For example, if the two IR peaks overlap, we might actually notice only one peak in the spectrum. Or, if one or more peaks is off-scale, we wouldn't see it in actual data. Group theory tells us what is *possible and allows us to make predictions or interpretations of spectra*.

Summary of Analysis for Water

Each molecular motion for water, or any molecule, can be assigned a symmetry under the molecule's point group. For water, we found that there are a total of 9 molecular motions; $3A_1 + A_2 + 3B_1 + 2B_2$. Six of these motions are not the translations and rotations. The remaining motions are vibrations; two with A_1 symmetry and one with B_1 symmetry.

We can tell what these vibrations would look like based on their symmetries. The two A_1 vibrations must be completely symmetric, while the B_1 vibration is antisymmetric with respect to the principal C_2 axis.

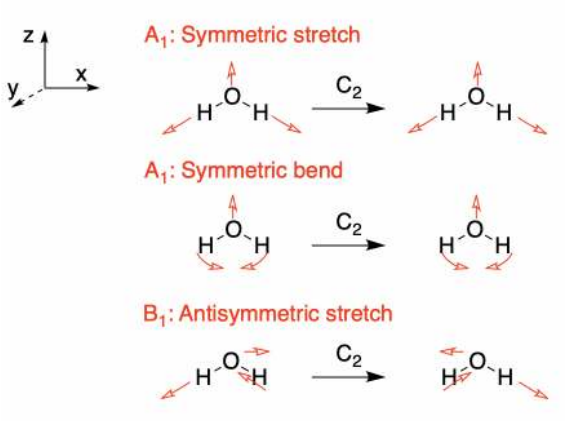


Figure 3.8.2: Illustration of the vibrational motions of water. The antisymmetric stretch has B_1 symmetry, while the symmetric stretch and symmetric bend both have A_1 symmetry. (Click here to see animation) (CC-BY-NC-SA; Kathryn Haas)

Table 3.8.1: 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 3.8.2

Find the symmetries of all motions of the square planar complex, tetrachloroplatinate (II). Determine which are rotations, translations, and vibrations. Determine which vibrations are IR and Raman active.

Answer

The point group of $[PtCl_4]^{2-}$ is D_{4h} (refer to its character table). There are five atoms and 15 vectors (x, y, z for each atom × 5 atoms).

STEP 1: The first major step is to **find a reducible representation (Γ)** for the movement of all atoms in the molecule.

C_{2v}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ_{modes}	15	1	−1	−3	−1	−3	−1	5	3	1

(3.8.4)

.

STEP 2: Break Γ_{modes} into its component irreducible representations.

Following the process described earlier, we come to $A_{1g} + A_{2g} + B_{1g} + B_{2g} + E_g + 2A_{2u} + B_{2u} + 3E_u$. This accounts for all modes of movement, including rotations and translations.

STEP 3: Subtract rotations and translations to find vibrational modes.

The translations are $A_{2u} + E_u$ and the rotations are $A_{2g} + E_g$.
The remaining normal modes are: $A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$

STEP 4: Determine which of the vibrational modes are IR-active and Raman-active:

$A_{2u} + E_u$ are IR-active. Since A_{2u} is singly degenerate and E_u is doubly degenerate, we expect three possible IR bands.
$A_{1g} + B_{1g} + B_{2g}$ are Raman-Active. Each of these is singly degenerate, so we expect three possible Raman bands.

Selected Vibrational Modes

The interpretation of CO stretching vibrations in an IR spectrum is particularly useful. Symmetry and group theory can be applied to predict the number of CO stretching bands that appear in a vibrational spectrum for a given metal coordination complex. A classic example of this application is in distinguishing isomers of metal-carbonyl complexes. For example, the *cis*- and *trans*-isomers of square planar metal dicarbonyl complexes ($ML_2(CO)_2$) have a different number of IR stretches that can be predicted and interpreted using symmetry and group theory. Another example is the case of *mer*- and *fac*- isomers of octahedral metal tricarbonyl complexes ($ML_3(CO)_3$). Structures of the two types of metal carbonyl configurations and their isomers are shown in Figure **3.8.1**. The isomers in each case can be distinguished using vibrational spectroscopy.

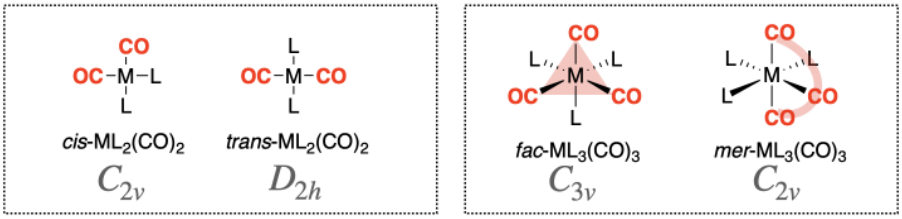


Figure **3.8.3**: Cis- and *trans*- isomers of square planar metal dicarbonyl complexes ($ML_2(CO)_2$) are shown in the left box. *Mer*- and *fac*- isomers of octahedral metal tricarbonyl complexes ($ML_3(CO)_3$) are shown in the right box. The point group for each of the general structures is also shown. (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 **3.8.1**. 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 **3.8.2** will be used here.



Figure **3.8.4**: 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 **3.8.2** (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}.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ_{cis-CO}	2	0	2	0

trans- $ML_2(CO)_2$:

For trans- $ML_2(CO)_2$, the point group is D_{2h} and so we use the operations under the D_{2h} character table to create the $\Gamma_{trans-CO}$.

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
$\Gamma_{trans-CO}$	2	0	0	2	0	2	2	0

Step 3: Break each Γ into its component irreducible representations

Each Γ can be reduced using inspection or by the systematic method described previously.

In the case of the *cis*- $ML_2(CO)_2$, the CO stretching vibrations are represented by A_1 and B_1 irreducible representations:

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
Γ_{cis-CO}	2	0	2	0		
A_1	1	1	1	1	z	x^2, y^2, z^2
B_1	1	−1	1	−1	x, R_y	xz

(3.8.5)

In the case of *trans*- $ML_2(CO)_2$, the CO stretching vibrations are represented by A_1 and B_{3u} irreducible representations:

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
$\Gamma_{trans-CO}$	2	0	0	2	0	2	2	0	
A_g	1	1	1	1	1	1	1	1	$x^2,\ y^2,\ z^2$
B_{3u}	1	−1	−1	1	−1	1	1	−1	x

These irreducible representations correspond to the symmetries of only the selected C—O vibrations. Since these motions are isolated to the C—O group, they do not include any rotations or translations of the entire molecule, and so we do not need to find and subtract rotationals or translations (unlike the previous cases where all motions were considered).

Step 4: Determine which vibrational modes are IR-active and/or Raman-active

Apply the infrared selection rules described previously to determine which of the CO vibrational motions are IR-active and Raman-active. The two isomers of $ML_2(CO)_2$ are described below.

In the case of the *cis*- $ML_2(CO)_2$, the CO stretching vibrations are represented by A_1 and B_1 irreducible representations. The characters of both representations and their functions are shown above, in 3.8.5 (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 3.8.5 (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 3.8.3

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 **3.8.1**) in both IR and Raman spectra. Could either of these vibrational spectroscopies be used to distinguish the two isomers?

Answer

Step 1: Assign the point group and Cartesian coordinates for each isomer.
The *fac*-isomer is C_{3v}. The *mer*-isomer is C_{2v}.

Step 2: Produce a reducible representation for CO stretches in each isomer.

Step 3: Break each into its component irreducible representations.

Step 4: Determine which vibrational modes are IR-active and/or Raman-active.

***For fac*-$ML_3(CO)_3$**, the point group is C_{3v} and so we use the operations under the C_{3v} character table to create the Γ_{fac-CO}. Then break it into its irreducible representations and determine which are IR and Raman active:

C_{3v}	E	$2C_2$	$3\sigma_v$
Γ_{fac-CO}	3	0	1

This reduces to $A_1 + E$. Both of these are IR active, and since one is singly degenerate while the other is doubly degenerate, we expect three possible IR bands from this isomer. Both vibrational modes are also Raman active, and again we would expect three possible bands in the Raman spectrum.

For mer-$ML_3(CO)_3$, the point group is C_{2v} and so we use the operations under the C_{2v} character table to create the Γ_{mer-CO}. Then break it into its irreducible representations and determine which are IR and Raman active:

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma'_v(yz)$
Γ_{mer-CO}	3	1	3	1

This reduces to $2A_1 + B_1$; both A_1 and B_1 are IR and Raman active. So this isomer would have three possible IR bands and three possible Raman Bands.

These two isomers have the same number of possible bands in both IR and Raman spectroscopy. It would not be straightforward to distinguish them from each other based on the number of possible bands in the vibrational spectrum.

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CHAPTER OVERVIEW

4: Acids, Bases, and Ions in Aqueous Solution

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4.1: The Equilibrium Constant Expression

Learning Objectives

- To know the relationship between the equilibrium constant and the rate constants for the forward and reverse reactions.
- To write an equilibrium constant expression for any reaction.

Because an equilibrium state is achieved when the forward reaction rate equals the reverse reaction rate, under a given set of conditions there must be a relationship between the composition of the system at equilibrium and the kinetics of a reaction (represented by rate constants). We can show this relationship using the system described in Equation 4.1.1, the decomposition of N_2O_4 to NO_2. Both the forward and reverse reactions for this system consist of a single elementary reaction, so the reaction rates are as follows:

$$\text{forward rate} = k_f[N_2O_4] \tag{4.1.1}$$

and

$$\text{reverse rate} = k_r[NO_2]^2 \tag{4.1.2}$$

At equilibrium, the forward rate equals the reverse rate (definition of equilibrium):

$$k_f[N_2O_4] = k_r[NO_2]^2 \tag{4.1.3}$$

so

$$\frac{k_f}{k_r} = \frac{[NO_2]^2}{[N_2O_4]} \tag{4.1.4}$$

The ratio of the rate constants gives us a new constant, the equilibrium constant (K), which is defined as follows:

$$K = \frac{k_f}{k_r} \tag{4.1.5}$$

Hence there is a fundamental relationship between chemical kinetics and chemical equilibrium: under a given set of conditions, the composition of the equilibrium mixture is determined by the magnitudes of the rate constants for the forward and the reverse reactions.

> The equilibrium constant is equal to the rate constant for the forward reaction divided by the rate constant for the reverse reaction.

Table 4.1.1 lists the initial and equilibrium concentrations from five different experiments using the reaction system described by Equation ???. At equilibrium the magnitude of the quantity $[NO_2]^2/[N_2O_4]$ is essentially the same for all five experiments. In fact, no matter what the initial concentrations of NO_2 and N_2O_4 are, at equilibrium the quantity $[NO_2]^2/[N_2O_4]$ will always be $6.53 \pm 0.03 \times 10^{-3}$ at 25°C, which corresponds to the ratio of the rate constants for the forward and reverse reactions. That is, at a given temperature, the equilibrium constant for a reaction always has the same value, even though the specific concentrations of the reactants and products vary depending on their initial concentrations.

Table 4.1.1: Initial and Equilibrium Concentrations for $NO_2 : N_2O_4$ Mixtures at 25°C

Initial Concentrations			Concentrations at Equilibrium		
Experiment	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$[N_2O_4]$ (M)	$[NO_2]$ (M)	$K = [NO_2]^2/[N_2O_4]$
1	0.0500	0.0000	0.0417	0.0165	6.54×10^{-3}
2	0.0000	0.1000	0.0417	0.0165	6.54×10^{-3}
3	0.0750	0.0000	0.0647	0.0206	6.56×10^{-3}
4	0.0000	0.0750	0.0304	0.0141	6.54×10^{-3}
5	0.0250	0.0750	0.0532	0.0186	6.50×10^{-3}



Introduction to Dynamic Equilibrium: https://youtu.be/4AJbFuzW2cs

Developing an Equilibrium Constant Expression

In 1864, the Norwegian chemists Cato Guldberg (1836–1902) and Peter Waage (1833–1900) carefully measured the compositions of many reaction systems at equilibrium. They discovered that for any reversible reaction of the general form

$$aA + bB \rightleftharpoons cC + dD \tag{4.1.6}$$

where A and B are reactants, C and D are products, and a, b, c, and d are the stoichiometric coefficients in the balanced chemical equation for the reaction, the ratio of the product of the equilibrium concentrations of the products (raised to their coefficients in the balanced chemical equation) to the product of the equilibrium concentrations of the reactants (raised to their coefficients in the balanced chemical equation) is always a constant under a given set of conditions. This relationship is known as the law of mass action and can be stated as follows:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{4.1.7}$$

where K is the equilibrium constant for the reaction. Equation 4.1.6 is called the equilibrium equation, and the right side of Equation 4.1.7 is called the equilibrium constant expression. The relationship shown in Equation 4.1.7 is true for any pair of opposing reactions regardless of the mechanism of the reaction or the number of steps in the mechanism.

The equilibrium constant can vary over a wide range of values. The values of K shown in Table 4.1.2, for example, vary by 60 orders of magnitude. Because products are in the numerator of the equilibrium constant expression and reactants are in the denominator, values of K greater than 10^3 indicate a strong tendency for reactants to form products. In this case, chemists say that equilibrium lies to the right as written, favoring the formation of products. An example is the reaction between H_2 and Cl_2 to produce HCl, which has an equilibrium constant of 1.6×10^{33} at 300 K. Because H_2 is a good reductant and Cl_2 is a good oxidant, the reaction proceeds essentially to completion. In contrast, values of K less than 10^{-3} indicate that the ratio of products to reactants

at equilibrium is very small. That is, reactants do not tend to form products readily, and the equilibrium lies to the left as written, favoring the formation of reactants.

Table 4.1.2: Equilibrium Constants for Selected Reactions*

Reaction	Temperature (K)	Equilibrium Constant (K)
$S(s) + O_2(g) \rightleftharpoons SO_2(g)$	300	4.4×10^{53}
$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g)$	500	2.4×10^{47}
$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$	300	1.6×10^{33}
$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$	300	4.1×10^{18}
$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$	300	4.2×10^{13}
$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$	300	2.7×10^{8}
$H_2(g) + D_2(g) \rightleftharpoons 2HD(g)$	100	1.92
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$	300	2.9×10^{-1}
$I_2(g) \rightleftharpoons 2I(g)$	800	$4.6 \times^{10-7}$
$Br_2(g) \rightleftharpoons 2Br(g)$	1000	4.0×10^{-7}
$Cl_2(g) \rightleftharpoons 2Cl(g)$	1000	1.8×10^{-9}
$F_2(g) \rightleftharpoons 2F(g)$	500	7.4×10^{-13}

*Equilibrium constants vary with temperature. The K values shown are for systems at the indicated temperatures.

You will also notice in Table 4.1.2 that equilibrium constants have no units, even though Equation 4.1.7 suggests that the units of concentration might not always cancel because the exponents may vary. **In fact, equilibrium constants are calculated using "effective concentrations," or activities, of reactants and products, which are the ratios of the measured concentrations to a standard state of 1 M.** As shown in Equation 4.1.8, the units of concentration cancel, which makes K unitless as well:

$$\frac{[A]_{measured}}{[A]_{standard\ state}} = \frac{\cancel{M}}{\cancel{M}} = \frac{\frac{\cancel{mol}}{\cancel{L}}}{\frac{\cancel{mol}}{\cancel{L}}} \tag{4.1.8}$$

Many reactions have equilibrium constants between 1000 and 0.001 ($10^3 \geq K \geq 10^{-3}$), neither very large nor very small. At equilibrium, these systems tend to contain significant amounts of both products and reactants, indicating that there is not a strong tendency to form either products from reactants or reactants from products. An example of this type of system is the reaction of gaseous hydrogen and deuterium, a component of high-stability fiber-optic light sources used in ocean studies, to form HD:

$$H_{2(g)} + D_{2(g)} \rightleftharpoons 2HD_{(g)} \tag{4.1.9}$$

The equilibrium constant expression for this reaction is

$$K = \frac{[HD]^2}{[H_2][D_2]} \tag{4.1.10}$$

with K varying between 1.9 and 4 over a wide temperature range (100–1000 K). Thus an equilibrium mixture of H_2, D_2, and HD contains significant concentrations of both product and reactants.

Figure 4.1.3 summarizes the relationship between the magnitude of K and the relative concentrations of reactants and products at equilibrium for a general reaction, written as

$$\text{reactants} \rightleftharpoons \text{products}. \tag{4.1.11}$$

Because there is a direct relationship between the kinetics of a reaction and the equilibrium concentrations of products and reactants (Equations 4.1.8 and 4.1.7), when $k_f \gg k_r$, K is a **large** number, and the concentration of products at equilibrium predominate. This corresponds to an essentially irreversible reaction. Conversely, when $k_f \ll k_r$, K is a very **small** number, and the reaction produces almost no products as written. Systems for which $k_f \approx k_r$ have significant concentrations of both reactants and products at equilibrium.

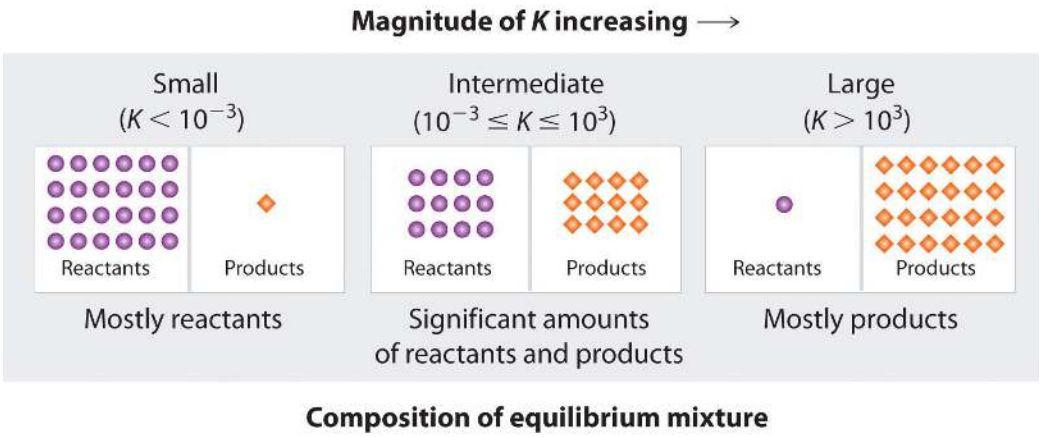


Figure **4.1.3**: The Relationship between the Composition of the Mixture at Equilibrium and the Magnitude of the Equilibrium Constant. The larger the K, the farther the reaction proceeds to the right before equilibrium is reached, and the greater the ratio of products to reactants at equilibrium.

A large value of the equilibrium constant K means that products predominate at equilibrium; a small value means that reactants predominate at equilibrium.

Example 4.1.1

Write the equilibrium constant expression for each reaction.

- $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$
- $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons CO_{2(g)}$
- $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}$

Given: balanced chemical equations

Asked for: equilibrium constant expressions

Strategy:

Refer to Equation 4.1.7. Place the arithmetic product of the concentrations of the products (raised to their stoichiometric coefficients) in the numerator and the product of the concentrations of the reactants (raised to their stoichiometric coefficients) in the denominator.

Solution:

The only product is ammonia, which has a coefficient of 2. For the reactants, N_2 has a coefficient of 1 and H2 has a coefficient of 3. The equilibrium constant expression is as follows:

$$\frac{[NH_3]^2}{[N_2][H_2]^3} \tag{4.1.12}$$

The only product is carbon dioxide, which has a coefficient of 1. The reactants are CO, with a coefficient of 1, and O_2, with a coefficient of $\frac{1}{2}$. Thus the equilibrium constant expression is as follows:

$$\frac{[CO_2]}{[CO][O_2]^{1/2}} \tag{4.1.13}$$

This reaction is the reverse of the reaction in part b, with all coefficients multiplied by 2 to remove the fractional coefficient for O_2. The equilibrium constant expression is therefore the inverse of the expression in part b, with all exponents multiplied by 2:

$$\frac{[CO]^2[O_2]}{[CO_2]^2} \tag{4.1.14}$$

Exercise 4.1.1

Write the equilibrium constant expression for each reaction.

a. $N_2O_{(g)} \rightleftharpoons N_{2(g)} + \frac{1}{2}O_{2(g)}$
b. $2C_8H_{18(g)} + 25O_{2(g)} \rightleftharpoons 16CO_{2(g)} + 18H_2O_{(g)}$
c. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

Answer:

a. $K = \frac{[N_2][O_2]^{1/2}}{[N_2O]}$
b. $K = \frac{[CO_2]^{16}[H_2O]^{18}}{[C_8H_{18}]^2[O_2]^{25}}$
c. $K = \frac{[HI]^2}{[H_2][I_2]}$

Example 4.1.2

Predict which systems at equilibrium will (a) contain essentially only products, (b) contain essentially only reactants, and (c) contain appreciable amounts of both products and reactants.

a. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)} \qquad K_{(700K)} = 54$
b. $2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)} \qquad K_{(1200K)} = 3.1 \times 10^{-18}$
c. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)} \qquad K_{(613K)} = 97$
d. $2O_{3(g)} \rightleftharpoons 3O_{2(g)} \qquad K_{(298K)} = 5.9 \times 10^{55}$

Given: systems and values of K

Asked for: composition of systems at equilibrium

Strategy:

Use the value of the equilibrium constant to determine whether the equilibrium mixture will contain essentially only products, essentially only reactants, or significant amounts of both.

Solution:

a. Only system 4 has $K \gg 10^3$, so at equilibrium it will consist of essentially only products.
b. System 2 has $K \ll 10^{-3}$, so the reactants have little tendency to form products under the conditions specified; thus, at equilibrium the system will contain essentially only reactants.
c. Both systems 1 and 3 have equilibrium constants in the range $10^3 \geq K \geq 10^{-3}$, indicating that the equilibrium mixtures will contain appreciable amounts of both products and reactants.

Exercise 4.1.2

Hydrogen and nitrogen react to form ammonia according to the following balanced chemical equation:

$$3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)} \tag{4.1.15}$$

Values of the equilibrium constant at various temperatures were reported as

- $K_{25°C} = 3.3 \times 10^8$,
- $K_{177°C} = 2.6 \times 10^3$, and
- $K_{327°C} = 4.1$.

At which temperature would you expect to find the highest proportion of H_2 and N_2 in the equilibrium mixture?

Assuming that the reaction rates are fast enough so that equilibrium is reached quickly, at what temperature would you design a commercial reactor to operate to maximize the yield of ammonia?

Answer:

a. 327°C, where K is smallest
b. 25°C

Variations in the Form of the Equilibrium Constant Expression

Because equilibrium can be approached from either direction in a chemical reaction, the equilibrium constant expression and thus the magnitude of the equilibrium constant depend on the form in which the chemical reaction is written. For example, if we write the reaction described in Equation 15.2.6 in reverse, we obtain the following:

$$cC + dD \rightleftharpoons aA + bB \tag{4.1.16}$$

The corresponding equilibrium constant K' is as follows:

$$K' = \frac{[A]^a[B]^b}{[C]^c[D]^d} \tag{4.1.17}$$

This expression is the inverse of the expression for the original equilibrium constant, so $K' = 1/K$. That is, when we write a reaction in the reverse direction, the equilibrium constant expression is inverted. For instance, the equilibrium constant for the reaction N_2O_4 \rightleftharpoons 2NO_2\) is as follows:

$$K = \frac{[NO_2]^2}{[N_2O_4]} \tag{4.1.18}$$

but for the opposite reaction, $2NO_2 \rightleftharpoons N_2O_4$, the equilibrium constant K′ is given by the inverse expression:

$$K' = \frac{[N_2O_4]}{[NO_2]^2} \tag{4.1.19}$$

Consider another example, the formation of water: $2H_{2(g)} + O_{2(g)} \rightleftharpoons 2H_2O_{(g)}$. Because H_2 is a good reductant and O_2 is a good oxidant, this reaction has a very large equilibrium constant ($K = 2.4 \times 10^{47}$ at 500 K). Consequently, the equilibrium constant for the reverse reaction, the decomposition of water to form O_2 and H_2, is very small: $K' = 1/K = 1/(2.4 \times 10^{47}) = 4.2 \times 10^{-48}$. As suggested by the very small equilibrium constant, and fortunately for life as we know it, a substantial amount of energy is indeed needed to dissociate water into H_2 and O_2.

The equilibrium constant for a reaction written in reverse is the *inverse* of the equilibrium constant for the reaction as written originally.

Writing an equation in different but chemically equivalent forms also causes both the equilibrium constant expression and the magnitude of the equilibrium constant to be different. For example, we could write the equation for the reaction

$$2NO_2 \rightleftharpoons N_2O_4 \tag{4.1.20}$$

as

$$NO_2 \rightleftharpoons \frac{1}{2}N_2O_4 \tag{4.1.21}$$

with the equilibrium constant K″ is as follows:

$$K'' = \frac{[N_2O_4]^{1/2}}{[NO_2]} \tag{4.1.22}$$

The values for K′ (Equation 4.1.19) and K″ are related as follows:

$$K'' = (K')^{1/2} = \sqrt{K'} \tag{4.1.23}$$

In general, if all the coefficients in a balanced chemical equation were subsequently multiplied by n, then the new equilibrium constant is the original equilibrium constant raised to the n^{th} power.

Example 4.1.3: The Haber Process

At 745 K, K is 0.118 for the following reaction:

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

What is the equilibrium constant for each related reaction at 745 K?

a. $2NH_{3(g)} \rightleftharpoons N2(g) + 3H_{2(g)}$
b. $\frac{1}{2}N_{2(g)} + \frac{3}{2}H_{2(g)} \rightleftharpoons NH_{3(g)}$

Given: balanced equilibrium equation, K at a given temperature, and equations of related reactions

Asked for: values of K for related reactions

Strategy:

Write the equilibrium constant expression for the given reaction and for each related reaction. From these expressions, calculate K for each reaction.

Solution:

The equilibrium constant expression for the given reaction of $N_{2(g)}$ with $H_{2(g)}$ to produce $NH_{3(g)}$ at 745 K is as follows:

$$K = \frac{[NH_3]^2}{[N_2][H_2]^3} = 0.118 \tag{4.1.24}$$

This reaction is the reverse of the one given, so its equilibrium constant expression is as follows:

$$K' = \frac{1}{K} = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{0.118} = 8.47 \tag{4.1.25}$$

In this reaction, the stoichiometric coefficients of the given reaction are divided by 2, so the equilibrium constant is calculated as follows:

$$K'' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = K^{1/2} = \sqrt{K} = \sqrt{0.118} = 0.344 \tag{4.1.26}$$

Exercise 4.1.3

At 527°C, the equilibrium constant for the reaction

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \tag{4.1.27}$$

is 7.9×10^4. Calculate the equilibrium constant for the following reaction at the same temperature:

$$SO_{3(g)} \rightleftharpoons SO_{2(g)} + \frac{1}{2}O_{2(g)} \tag{4.1.28}$$

Answer: 3.6×10^{-3}



Determining the Equilibrium Expression: https://youtu.be/ZK9cMIWFerY

Summary

- The law of mass action describes a system at equilibrium in terms of the concentrations of the products and the reactants.
- For a system involving one or more gases, either the molar concentrations of the gases or their partial pressures can be used.
- Definition of equilibrium constant in terms of forward and reverse rate constants:

$$K = \frac{k_f}{k_r}$$

- Equilibrium constant expression (law of mass action):

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- Equilibrium constant expression for reactions involving gases using partial pressures:

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

- Relationship between K_p and K:

$$K_p = K(RT)^{\Delta n}$$

The ratio of the rate constants for the forward and reverse reactions at equilibrium is the equilibrium constant (K), a unitless quantity. The composition of the equilibrium mixture is therefore determined by the magnitudes of the forward and reverse rate constants at equilibrium. Under a given set of conditions, a reaction will always have the same K. For a system at equilibrium, the law of mass action relates K to the ratio of the equilibrium concentrations of the products to the concentrations of the reactants raised to their respective powers to match the coefficients in the equilibrium equation. The ratio is called the equilibrium constant expression. When a reaction is written in the reverse direction, K and the equilibrium constant expression are inverted. For gases, the equilibrium constant expression can be written as the ratio of the partial pressures of the products to the partial pressures of the reactants, each raised to a power matching its coefficient in the chemical equation. An equilibrium constant calculated from partial pressures (K_p) is related to K by the ideal gas constant (R), the temperature (T), and the change in the number of moles of gas during the reaction. An equilibrium system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium. When a reaction can be expressed as the sum of two or more reactions, its equilibrium constant is equal to the product of the equilibrium constants for the individual reactions.

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4.2: 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:

$$\mathrm{HA\,(aq) + H_2O\,(l) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq)} \tag{4.2.1}$$

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 $\mathrm{pK_a}$ values for selected weak acids are given in Table 4.2.1.

Table 4.2.1: 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 $\mathbf{H_3O^+}$ in aqueous solution, Arrhenius bases decrease $\mathbf{H_3O^+}$. 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.

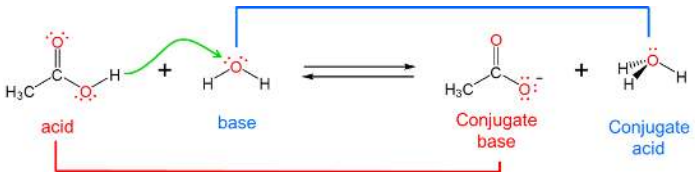
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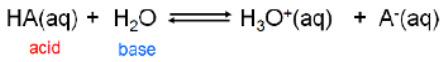
4.3: Brønsted-Lowry Concept

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.

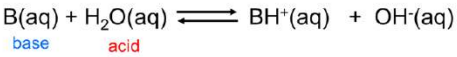


Because the Brønsted-Lowry concept is concerned with H^+ ion transfer rather than the creation of a particular chemical species, it is able to handle a diverse array of acid-base concepts. In fact, from the viewpoint of the Brønsted-Lowry concept, Arrhenius acids and bases are just a special case involving 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^+:



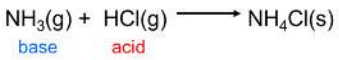
(4.3.1)

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.

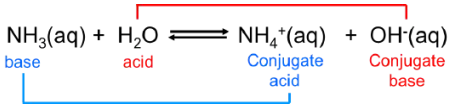
Becasue the Brønsted-Lowry concept can handle any sort of hydrogen ion transfer it readily accommodates many reactions that Arrhenius theory cannot, including those that take place outside of water, such as the reaction between gaseous hydrochloric acid and ammonia:



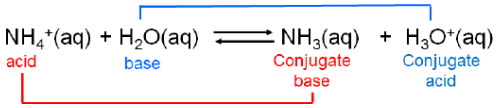
The classification of acids as strong or weak usually refers to their ability to donate or abstract hydrogen ions to or from water to give H_3O^+ and OH^-, respectively, *i.e.*, their Arrhenius acidity and basicity. However, acids and bases may be classified as strong and weak under the Brønsted-Lowry 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:

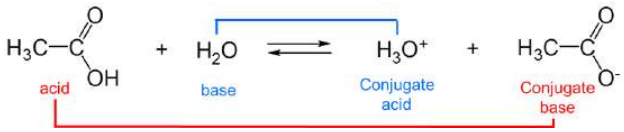


The ammonium ion is itself a weak acid that can undergo dissociation:

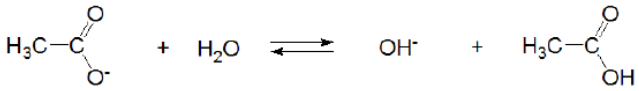


In this case ammonia and ammonium ion are acid-base conjugates. In general acids and bases that differ by a *single ionizable hydrogen ion* are said to be conjugates of one another.

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:



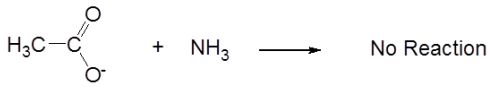
and acetic acid's conjugate base, acetate, acts as a weak Brønsted base.



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



while its conjugate base, acetate, is neutral.



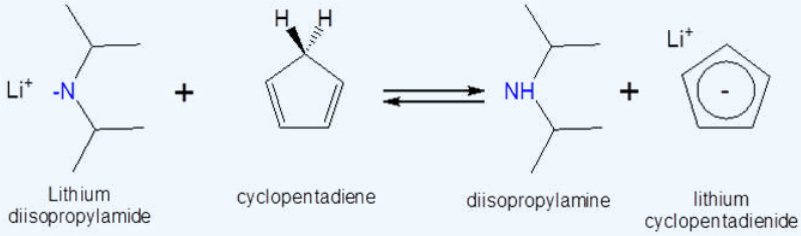
The reciprocal relationship between the strengths of acids and their conjugate bases has several consequences:

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 4.3.1

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



Solution:

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

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4.4: 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

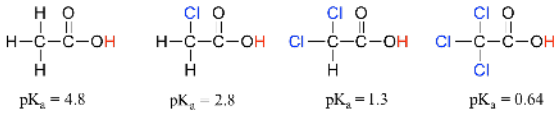
The weaker the bond to the ionizable hydrogen, the stronger the acid. Strongly bonded hydrogen ions are difficult to remove, weakly bonded ones much less so.

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.



- 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

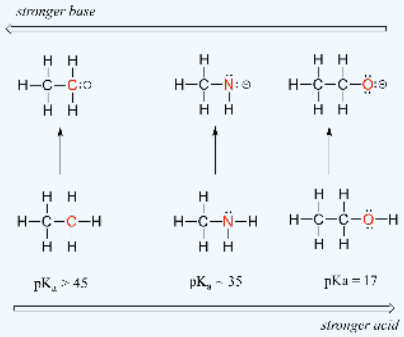
The more stable the acid's conjugate base, the stronger the Brønsted acid. All reactions are in theory reversible, and so when considering the propensity of an acid to donate hydrogen ions, it can be helpful to look at the reverse of hydrogen ion donation, namely, protonation of the acid's conjugate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

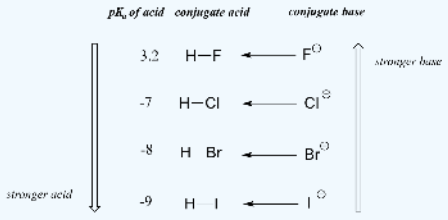
4. Size effects on Bond Strength and Charge Delocalization

There are two classes of size effects to be considered:

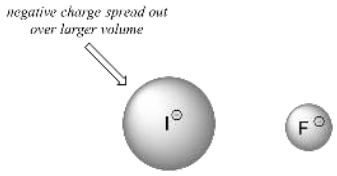
a. The larger the atom to which a H is bound in an E-H bond, the weaker the bond and the stronger the acid.
b. Increased charge delocalization with increasing size. Electrostatic charges, whether positive or negative, are more stable when they are ‘spread out’ over a larger area. The greater the volume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



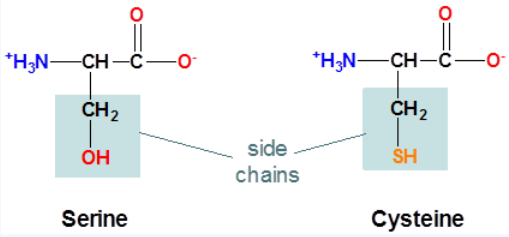
On going vertically down the halogen group from F to I the H-X bond strength decreases in the acid, making it easier to ionize, while the charge becomes more diffuse in the resultant X^- ion, making the conjugate base more stable.



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 Runaway argument for \eatSpaces?

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



Answer

Cysteine, since the cysteine side chain possesses an ionizable S-H bond while serine's side chain possesses an ionizable O-H bond. Since S is larger than O, cysteine's S-H bond will be weaker than serine's O-H bond, 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.

Contributors and Attributions

Stephen M. Contakes (Westmont College),

* who expanded this section from a combination of

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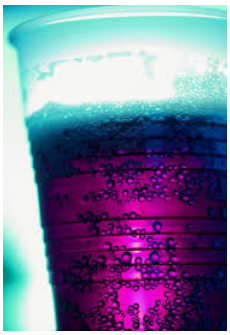
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4.5: Lewis Acids and Bases

Many oxyacids are rather unstable and cannot be isolated in pure form. An example is carbonic acid, H_2CO_3, which decomposes to water and carbon dioxide:

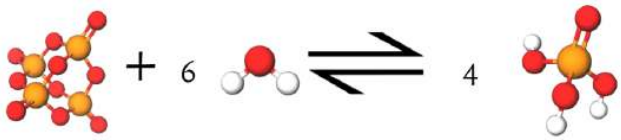
$$H_2CO_3(aq) \rightleftharpoons H_2O(l) + CO_2(g)$$

This decomposition process is familiar to us, as it is responsible for the fizzy nature of soda. When the CO_2 is dissolved in the soda, it becomes H_2CO_3, but when the soda is released from high pressure, the decomposition process occurs rapidly, forming bubbles of CO_2 and water.

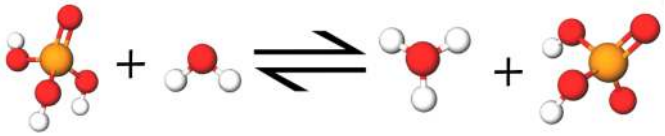


Since it can be made by removing H_2O from H_2CO_3, CO_2 is called the **acid anhydride** of H_2CO_3. (The term anhydride is derived from anhydrous, meaning "not containing water.") Acid anhydrides are usually oxides of nonmetallic elements. Some common examples and their corresponding oxyacids are SO_2—H_2SO_3; SO_3—H_2SO_4; P_4O_{10}—H_3PO_4; N_2O_5—HNO_3. Any of these anhydrides increases the hydronium-ion concentration when dissolved in water; for example,

$$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$$



$$H_3PO_4(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + H_2PO_4^-(aq)$$



In the Arrhenius sense, then, acid anhydrides are acids, but according to the Brönsted-Lowry definition, they are not acids because they contain no hydrogen.

In 1923, at the same time that the Brönsted-Lowry definition was proposed, G. N. Lewis suggested another definition which includes the acid anhydrides and a number of other substances as acids. According to the **Lewis definition**, an acid is any species which can accept a lone pair of electrons, and a base is any species which can donate a lone pair of electrons. An acid-base reaction in the Lewis sense involves formation of a coordinate covalent bond (where one atom provides both shared electrons).

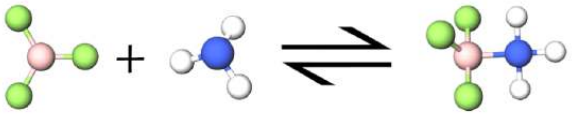
The Lewis definition has little effect on the types of molecules we expect to be basic. All the Brönsted-Lowry bases, for example, NH_3, O^{2-}, H^-, contain at least one lone pair. Lewis' idea does expand the number of acids, though. The proton is not the only species which can form a coordinate covalent bond with a lone pair. Cations of the transition metals, which are strongly hydrated, do the same thing:

$$\underset{\text{Lewis acid}}{Cr^{3+}} + \underset{\text{Lewis base}}{6H_2O} \rightarrow Cr(H_2O)_6^{3+} \quad (4.5.1)$$

$$\underset{\text{Lewis acid}}{Cu^{2+}} + \underset{\text{Lewis base}}{4NH_3} \rightarrow Cu(NH_3)_4^{2+} \quad (4.5.2)$$

So can electron deficient compounds such as boron trifluoride:

$$\underset{\text{Lewis acid}}{BF_3} + \underset{\text{Lewis base}}{:NH_3} \rightarrow F_3B{:}NH_3$$



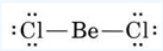
Many Lewis acid-base reactions occur in media other than aqueous solution. The Brönsted-Lowry theory accounts for almost all aqueous acid-base chemistry. Therefore the Brönsted-Lowry concept is most often intended when the words acid or base are used. The Lewis definition is useful when discussing transition-metal ions, however, and is discussed again in the sections on Metals.

Example 4.5.1 : Lewis Acids and Bases

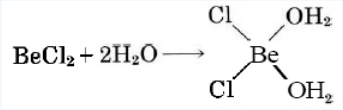
Identify the Lewis acids and bases in the following list. Write an equation for the combination of each acid with the Lewis base H_2O.(a) $BeCl_2(g)$; (b) CH_3OH; (c) SO_2; (d) CF_4.

Solution

a) The Lewis diagram

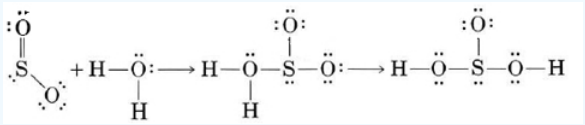


shows that Be is electron deficient. Therefore $BeCl_2(g)$ is a Lewis acid. Because of the lone pairs on the Cl atoms, $BeCl_2$ can also act as a Lewis base, but Cl is rather electronegative and reluctant to donate electrons, so the Lewis base strength of $BeCl_2$ is less than the Lewis acid strength.



b) There are lone pairs on O in CH_3OH, and so it can serve as a Lewis base.

c) The S atom in SO_2 can accept an extra pair of electrons, and so SO_2 is a Lewis acid. The O atoms have lone pairs but are only weakly basic for the same reason as the Cl atoms in part (a).



d) Although there are lone pairs on the F atoms, the high electronegativity of F prevents them from being donated to form coordinate covalent bonds. Consequently CF_4 has essentially no Lewis-base character.

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4.6: Lewis Concept of Acids and Bases

Acids and bases are an important part of chemistry. One of the most applicable theories is the Lewis acid/base motif that extends the definition of an acid and base beyond H^+ and OH^- ions as described by Brønsted-Lowry acids and bases.

The Brønsted acid-base theory has been used throughout the history of acid and base chemistry. However, this theory is very restrictive and focuses primarily on acids and bases acting as proton donors and acceptors. Sometimes conditions arise where the theory does not necessarily fit, such as in solids and gases. In 1923, G.N. Lewis from UC Berkeley proposed an alternate theory to describe acids and bases. His theory gave a generalized explanation of acids and bases based on structure and bonding. Through the use of the Lewis definition of acids and bases, chemists are now able to predict a wider variety of acid-base reactions. Lewis' theory used electrons instead of proton transfer and specifically stated that an acid is a species that accepts an electron pair while a base donates an electron pair.

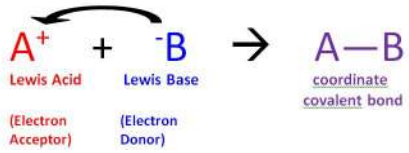


Figure **4.6.1**: A Lewis Base (B) donates it electrons to a Lewis Acid (A) resulting in a coordinate covalently bonded compound, also known as an adduct.

The reaction of a Lewis acid and a Lewis base will produce a coordinate covalent bond (Figure **4.6.1**). A coordinate covalent bond is just a type of covalent bond in which one reactant gives it electron pair to another reactant. In this case the lewis base donates its electrons to the Lewis acid. When they do react this way the resulting product is called an addition compound, or more commonly an adduct.

- Lewis Acid: a species that accepts an electron pair (i.e., an electrophile) and will have vacant orbitals
- Lewis Base: a species that donates an electron pair (i.e., a nucleophile) and will have lone-pair electrons

Lewis Acids

Lewis acids accept an electron pair. Lewis Acids are Electrophilic meaning that they are electron attracting. When bonding with a base the acid uses its lowest unoccupied molecular orbital or LUMO (Figure 2).

- Various species can act as Lewis acids. All cations are Lewis acids since they are able to accept electrons. (e.g., Cu^{2+}, Fe^{2+}, Fe^{3+})
- An atom, ion, or molecule with an incomplete octet of electrons can act as an Lewis acid (e.g., BF_3, AlF_3).
- Molecules where the central atom can have more than 8 valence shell electrons can be electron acceptors, and thus are classified as Lewis acids (e.g., $SiBr_4$, SiF_4).
- Molecules that have multiple bonds between two atoms of different electronegativities (e.g., CO_2, SO_2)

Lewis Bases

Lewis Bases donate an electron pair. Lewis Bases are Nucleophilic meaning that they “attack” a positive charge with their lone pair. They utilize the highest occupied molecular orbital or HOMO (Figure 2). An atom, ion, or molecule with a lone-pair of electrons can thus be a Lewis base. Each of the following anions can "give up" their electrons to an acid, e.g., OH^-, CN^-, CH_3COO^-, $:NH_3$, $H_2O:$, $CO:$. Lewis base's HOMO (highest occupied molecular orbital) interacts with the Lewis acid's LUMO (lowest unoccupied molecular orbital) to create bonded molecular orbitals. Both Lewis Acids and Bases contain HOMO and LUMOs but only the HOMO is considered for Bases and only the LUMO is considered for Acids (Figure **4.6.2**).

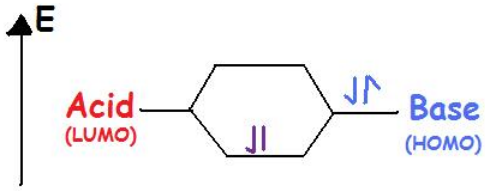


Figure **4.6.2**: Lewis Acids have vacant orbitals so they are in a lower energy level. While lewis bases have lone pair electrons to share and thus occupy a higher energy level.

Complex Ion / Coordination Compounds

Complex ions are polyatomic ions, which are formed from a central metal ion that has other smaller ions joined around it. While Brønsted theory can't explain this reaction Lewis acid-base theory can help. A Lewis Base is often the ligand of a coordination compound with the metal acting as the Lewis Acid (see Oxidation States of Transition Metals).

$$Al^{3+} + 6H_2O \rightleftharpoons [Al(H_2O)_6]^{3+} \tag{4.6.1}$$

The aluminum ion is the metal and is a cation with an unfilled valence shell, and it is a Lewis Acid. Water has lone-pair electrons and is an anion, thus it is a Lewis Base.

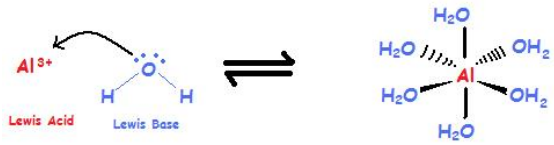


Figure **4.6.3**: Aluminum ion acts as a Lewis acid and accepts the electrons from water, which is acting as a Lewis base. This helps explain the resulting hexaaquaaluminum(III) ion.

The Lewis Acid accepts the electrons from the Lewis Base which donates the electrons. Another case where Lewis acid-base theory can explain the resulting compound is the reaction of ammonia with Zn^{2+}.

$$Zn^{2+} + 4NH_3 \rightarrow [Zn(NH_3)_4]^{4+} \tag{4.6.2}$$

Similarly, the Lewis Acid is the zinc Ion and the Lewis Base is NH_3. Note how Brønsted Theory of Acids and Bases will not be able to explain how this reaction occurs because there are no H^+ or OH^- ions involved. Thus, Lewis Acid and Base Theory allows us to explain the formation of other species and complex ions which do not ordinarily contain hydronium or hydroxide ions. One is able to expand the definition of an acid and a base via the Lewis Acid and Base Theory. The lack of H^+ or OH^- ions in many complex ions can make it harder to identify which species is an acid and which is a base. Therefore, by defining a species that donates an electron pair and a species that accepts an electron pair, the definition of a acid and base is expanded.

Amphoterism

As of now you should know that acids and bases are distinguished as two separate things however some substances can be both an acid and a base. You may have noticed this with water, which can act as both an acid or a base. This ability of water to do this makes it an amphoteric molecule. Water can act as an acid by donating its proton to the base and thus becoming its conjugate acid, OH-. However, water can also act as a base by accepting a proton from an acid to become its conjugate base, H_3O^+.

- Water acting as an Acid:

$$H_2O + NH_3 \rightarrow NH_4^+ + OH^- \tag{4.6.3}$$

- Water acting as a Base:

$$H_2O + HCl \rightarrow Cl^- + H_3O^+ \tag{4.6.4}$$

You may have noticed that the degree to which a molecule acts depends on the medium in which the molecule has been placed in. Water does not act as an acid in an acid medium and does not act as a base in a basic medium. Thus, the medium which a molecule is placed in has an effect on the properties of that molecule. Other molecules can also act as either an acid or a base. For example,

$$Al(OH)_3 + 3H^+ \rightarrow Al^{3+} + 3H_2O \tag{4.6.5}$$

- where $Al(OH)_3$ is acting as a Lewis Base.

$$Al(OH)_3 + OH^- \rightarrow Al(OH)_4^- \tag{4.6.6}$$

- where $Al(OH)_3$ is acting as an Lewis Acid.

Note how the amphoteric properties of the $Al(OH)_3$ depends on what type of environment that molecule has been placed in.

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4.7: Acid-Base Chemistry in Amphoteric Solvents and the Solvent Levelling 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.

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

For example, sulfuric acid ionizes according to the equation:

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

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 $H_3SO_4^+$ and HSO_4^- present in pure sulfuric acid are ~0.02 *M*, much greater than the 10^{-7} *M* H_3O^+ and OH^- present in pure water.

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

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

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):

$$HA + S \rightleftharpoons HS^+ + A^-$$

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

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

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

$$B + HS \rightleftharpoons BH^+ + S^-$$

The position of this equilibrium depends on whether B or S^- is the stronger base. If the solvent's conjugate base, S^-, is stronger, then the base B will remain unprotonated and available to act as a base. However, if B is a stronger base than S^-, it will deprotonate the solvent to give BH^+ and S^-. In this way the strongest base that can exist in a given solvent is the solvent's conjugate base.

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

It is important to consider the 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:

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

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 $LiAlH_4$).

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4.8: Thermodynamics

Thermodynamic parameters on changes of state are necessary to describe chemical bonding, structure, and reaction. This is true also in inorganic chemistry, and the most important concepts in thermodynamics are described in this section. Even simple thermodynamic knowledge is considerably useful for judging whether structures of compounds are stable and the likelihood of spontaneous reactions, and for the calculations of reaction heat, determination of reaction mechanism, and understanding of electrochemistry.

Enthalpy

Since enthalpy is the heat content of a system under constant pressure, the changeΔH is negative in an exothermic reaction, and positive in an endothermic reaction. The standard reaction enthalpy, ΔH^0, is the enthalpy change between 1 mol of products and reactants in the standard state (10^5 Pa and 298.15 K). The **standard enthalpy of formation**, ΔH_f^0, of a compound is the standard reaction enthalpy for the formation of the compound from its constituent elements. Since enthalpy is a state function, the standard reaction enthalpy is calculated by defining the standard enthalpy of formation of simple substances to be zero. Namely,

$$\Delta H^0 = \Sigma n \Delta H_f^0 \,(product) - \Sigma n \Delta H_f^0 \,(reactant)$$

Entropy

Entropy is a state function, and is a criterion determining whether one state can be reached spontaneously from another state. The 2nd law of thermodynamics states that the entropy, S, of an isolated system increases upon a spontaneous change. Namely,

$$\Delta S > 0$$

A thermodynamically irreversible process produces entropy. Entropy is related to the disorder of a system in statistical themodynamics as follows:

$$S = k \ln W$$

k is the Boltzmann constant, and W is the number of the arrangements of atoms or molecules of the system with the same energy, and corresponds to the extent of disorder. As entropy becomes larger, the larger the disorder of a system.

Gibbs energy

This quantity is defined as

$$\Delta G = \Delta H - T\Delta S$$

A spontaneous reaction occurs when Gibbs energy of a reaction is negative at constant temperature and pressure. The standard Gibbs free energy ΔG^0 is related to the equilibrium constant K of the reaction

$$A \overset{K}{\rightleftharpoons} B.$$

$$\Delta G^0 = -RT \ln K$$

K is larger than 1 when ΔG^0 becomes negative, and the reaction proceeds to the right.

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4.9: Ligands

A metal ion in solution does not exist in isolation, but in combination with ligands (such as solvent molecules or simple ions) or chelating groups, giving rise to complex ions or coordination compounds. These complexes contain a central atom or ion, often a transition metal, and a cluster of ions or neutral molecules surrounding it. Ligands are ions or neutral molecules that bond to a central metal atom or ion. Ligands act as Lewis bases (electron pair donors), and the central atom acts as a Lewis acid (electron pair acceptor). Ligands have at least one donor atom with an electron pair used to form covalent bonds with the central atom.

The term ligand come from the latin word *ligare* (which meaning to bind) was first used by Alfred Stock in 1916 in relation to silicon chemistry. Ligands can be anions, cations, or neutral molecules. Ligands can be further characterized as monodentate, bidentate, tridentate etc. where the concept of teeth **(dent)** is introduced, hence the idea of bite angle etc. A monodentate ligand has only one donor atom used to bond to the central metal atom or ion.

Monodentate Ligands

The term "monodentate" can be translated as "one tooth," referring to the ligand binding to the center through only one atom. Some examples of monodentate ligands are: chloride ions (referred to as chloro when it is a ligand), water (referred to as aqua when it is a ligand), hydroxide ions (referred to as hydroxo when it is a ligand), and ammonia (referred to as ammine when it is a ligand).

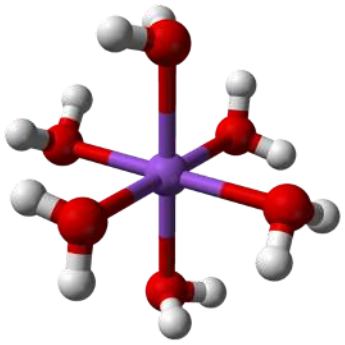


Figure **4.9.1**: Central atom with six monodentate ligands attached. (Image courtesy of Wikimedia Commons.)

Bidentate Ligands

Bidentate ligands have two donor atoms which allow them to bind to a central metal atom or ion at two points. Common examples of bidentate ligands are ethylenediamine (en), and the oxalate ion (ox). Shown below is a diagram of ethylenediamine: the nitrogen (blue) atoms on the edges each have two free electrons that can be used to bond to a central metal atom or ion.

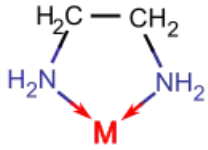


Figure **4.9.2**: Ethylenediamine (en) is an example of a bidentate ligand. (Image courtesy of Wikimedia Commons.). Ethylenediamine (en) is a bidentate ligand that forms a five-membered ring in coordinating to a metal ion M

Polydentate Ligands

Polydentate ligands range in the number of atoms used to bond to a central metal atom or ion. EDTA, a hexadentate ligand, is an example of a polydentate ligand that has six donor atoms with electron pairs that can be used to bond to a central metal atom or ion.

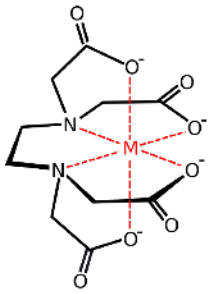
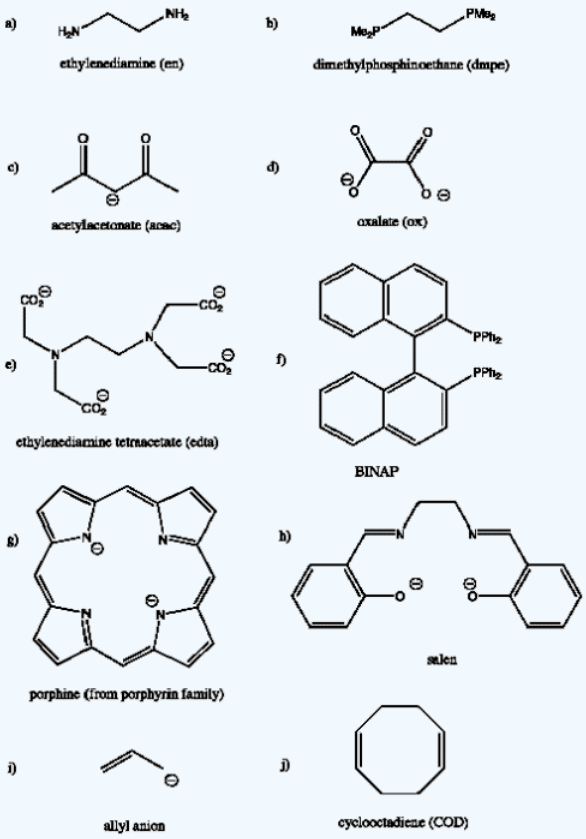


Figure **4.9.3**: Ethylenediaminetetraaceticacid acid (EDTA) is a hexadentate ligand and can bind a Metal via multiple "teeth" (left) Unbound EDTA ion and (right) EDTA bound to a generic transition metal. (Images courtesy of Wikimedia Commons.)

Unlike polydentate ligands, ambidentate ligands can attach to the central atom in two places. A good example of this is thiocyanate, SCN^-, which can attach at either the sulfur atom or the nitrogen atom.

Example 4.9.1

Draw metal complexes using the ligands below and metal ions of your choice.



Chelation

Chelation is a process in which a polydentate ligand bonds to a metal ion, forming a ring. The complex produced by this process is called a chelate, and the polydentate ligand is referred to as a chelating agent. The term chelate was first applied in 1920 by Sir Gilbert T. Morgan and H.D.K. Drew, who stated: "The adjective chelate, derived from the great claw or chela (chely- Greek) of the lobster or other crustaceans, is suggested for the caliperlike groups which function as two associating units and fasten to the central atom so as to produce heterocyclic rings." As the name implies, chelating ligands have high affinity for metal ions relative to ligands with only one binding group (which are called monodentate = "single tooth") ligands. Both Ethylenediamine (Figure **4.9.2**) and Ethylenediaminetetraaceticacid acid (Figure **4.9.3**) are examples of chelating agents, but many others are commonly found in the inorganic laboratory.

The Chelate Effect

The chelate effect is the enhanced affinity of chelating ligands for a metal ion compared to the affinity of a collection of similar nonchelating (monodentate) ligands for the same metal.

The **macrocyclic effect** follows the same principle as the chelate effect, but the effect is further enhanced by the cyclic conformation of the ligand. Macrocyclic ligands are not only multi-dentate, but because they are covalently constrained to their cyclic form, they allow less conformational freedom. The ligand is said to be "pre-organized" for binding, and there is little entropy penalty for wrapping it around the metal ion. For example heme b is a tetradentate cyclic ligand that strongly complexes transition metal ions, including Fe^{+2} in hemogloben (Figure 4.9.4).

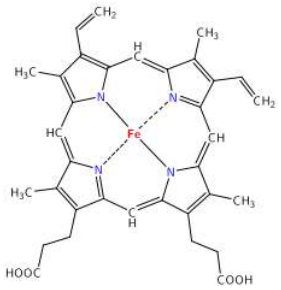
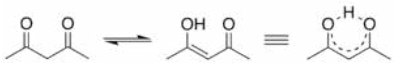


Figure 4.9.4: Heme b macrocyclic ligand that binds iron in hemoglobin

Some other common chelating and cyclic ligands are shown below:

- **Acetylacetonate** ($acac^-$, top) is an anionic bidentate ligand that coordinates metal ions through two oxygen atoms. $Acac^-$ is a hard base so it prefers hard acid cations. With divalent metal ions, $acac^-$forms neutral, volatile complexes such as $Cu(acac)_2$ and $Mo(acac)_2$ that are useful for chemical vapor deposition (CVD) of metal thin films.



- **2,2'-Bipyridine 2,2'-Bipyridine** (Figure 4.9.5*:* left) and related bidentate ligands such as 1,10-phenanthroline form propeller-shaped complexes with metals such as Ru^{2+}. The $[Ru(bpy)_3]^{2+}$ complex is photoluminescent and can also undergo photoredox reactions, making it an interesting compound for both photocatalysis and artificial photosynthesis.
- **Crown ethers** such as 18-crown-6 **2,2'-Bipyridine** (Figure 4.9.5: center) are cyclic hard bases that can complex alkali metal cations. Crowns can selectively bind Li^+, Na^+, or K^+ depending on the number of ethylene oxide units in the ring.
- The chelating properties of crown ethers are mimetic of the natural antibiotic **valinomycin** (**2,2'-Bipyridine** (Figure 4.9.5: right), which selectively transports K^+ ions across bacterial cell membranes, killing the bacterium by dissipating its membrane potential. Like crown ethers, valinomycin is a cyclic hard base.

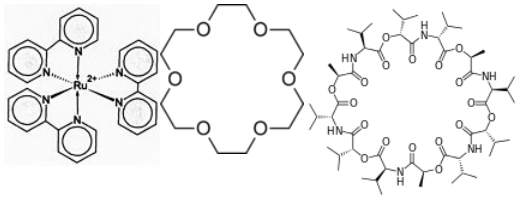


Figure 4.9.5: (let) 2,2'-Bipyridine, (center) 18-crown-6 2,2'-Bipyridine (right) valinomycin

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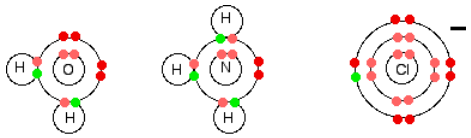
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4.10: What is a Complex Ion?

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



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

Bonding in Simple Complex Ions

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

Example 4.10.1: $Al(H_2O)_6^{3+}$

Aluminum has the electronic structure

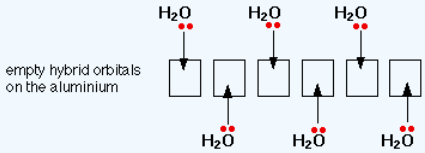
$$1s^2 2s^2 2p^6 3s^2 3p_x^1$$

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

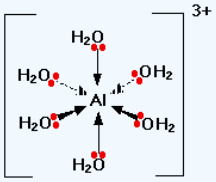
$$1s^2 2s^2 2p^6$$

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

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



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



Because of the movement of electrons towards the center of the ion, the 3+ charge is no longer located entirely on the aluminum, but is now spread over the whole of the ion. Because the aluminum is forming 6 bonds, the co-ordination number of the aluminum is said to be 6. The co-ordination number of a complex ion counts the number of co-ordinate bonds being formed by the metal ion at its center.

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

Example **4.10.2** is chosen because it is very similar to the last one - except that it involves a transition metal.

Example 4.10.2: $Fe(H_2O)_6^{3+}$

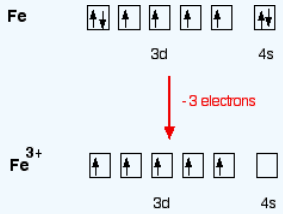
Iron has the electronic structure

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

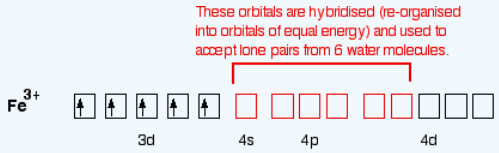
When it forms an Fe^{3+} ion it loses the 4s electrons and one of the 3d electrons to leave

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

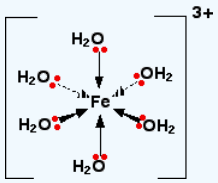
Looking at this as electrons-in-boxes, at the bonding level:



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



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



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

Example **4.10.3** demonstrates the formation of a complex ion with a negative charge.

Example 4.10.3: $CuCl_4^{2-}$

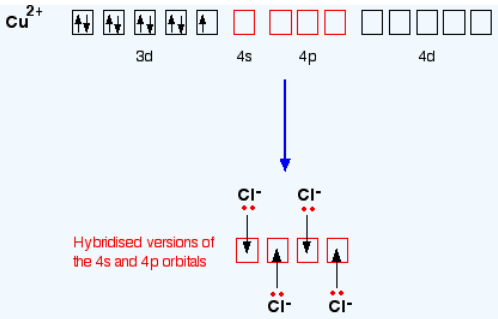
Copper has the electronic structure

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

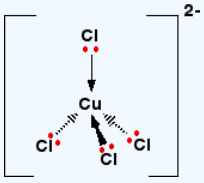
When it forms a Cu^{2+} ion it loses the 4s electron and one of the 3d electrons to leave

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

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



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



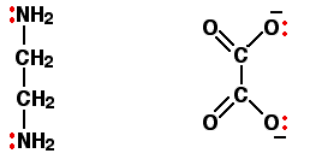
The ion carries 2 negative charges overall. That comes from a combination of the 2 positive charges on the copper ion and the 4 negative charges from the 4 chloride ions. In this case, the co-ordination number of the copper is 4.

Complex metal ions containing more complicated ligands

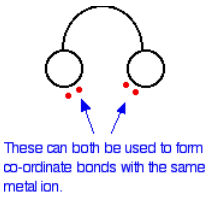
In the examples we've already looked at, each ligand only forms one bond with the central metal ion to give the complex ion. Such a ligand is said to be unidentate. That means literally that it only has one tooth! It only has one pair of electrons that it can use to bond to the metal - any other lone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

Bidentate ligands

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



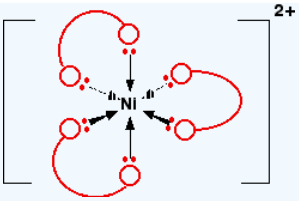
In the ethanedioate ion, there are lots more lone pairs than the two shown, but these are the only ones we are interested in. You can think of these bidentate ligands rather as if they were a pair of headphones, carrying lone pairs on each of the "ear pieces". These will then fit snuggly around a metal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



Example 4.10.4: $Ni(NH_2CH_2CH_2NH_2)_3^{2+}$

You might find this abbreviated to $[Ni(en)_3]^{2+}$.

The structure of the ion looks like this:



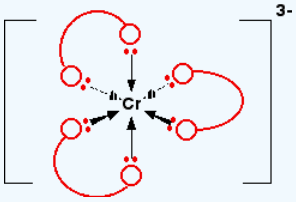
In this case, the "ear pieces" are the nitrogen atoms of the NH_2 groups - and the "bit that goes over your head " is the - CH_2CH_2- group. If you were going to draw this in an exam, you would obviously want to draw it properly - but for learning purposes, drawing all the atoms makes the diagram look unduly complicated!

Notice that the arrangement of the bonds around the central metal ion is exactly the same as it was with the ions with 6 water molecules attached. The only difference is that this time each ligand uses up two of the positions - at right angles to each other. Because the nickel is forming 6 co-ordinate bonds, the coordination number of this ion is 6, despite the fact that it is only joined to 3 ligands. Coordination number counts the **number of bonds**, not the number of ligands.

Example 4.10.5: $Cr(C_2O_4)_3^{3-}$

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

The structure of the ion looks like this:

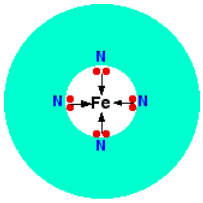


Again, if you drew this in an exam, you would want to show all the atoms properly. If you need to be able to do this, practice drawing it so that it looks clear and tidy! Refer back to the diagram of the ethanedioate ion further up the page to help you.

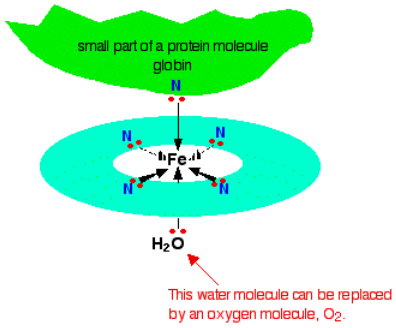
A Quadridentate Ligand

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

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



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

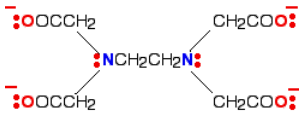


Overall, the complex ion has a co-ordination number of 6 because the central metal ion is forming 6 co-ordinate bonds. The water molecule which is bonded to the bottom position in the diagram is easily replaced by an oxygen molecule (again via a lone pair on one of the oxygens in O_2) - and this is how oxygen gets carried around the blood by the haemoglobin. When the oxygen gets to where it is needed, it breaks away from the haemoglobin which returns to the lungs to get some more.

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

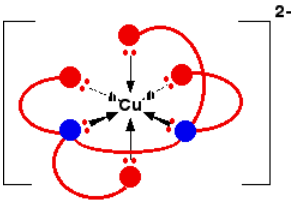
A Hexadentate Ligand

A hexadentate ligand has 6 lone pairs of electrons - all of which can form co-ordinate bonds with the same metal ion. The best example is EDTA, which is used as a negative ion - $EDTA^{4-}$. The diagram shows the structure of the ion with the important atoms and lone pairs picked out.



the $EDTA^{4-}$ ion

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



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

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

Contributors and Attributions

- Jim Clark (Chemguide.co.uk)

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4.11: Chelating Ligands

Introduction

Each ligand that binds to a transition metal donates a pair of its electrons to the metal, sharing those electrons in a metal-ligand bond. Counting the total number of electrons in the metal's valence shell is fairly easy when you know that each ligand contributes two electrons.

But what if a ligand could contribute more than two electrons? Take a look at the following table. Each of the ligands shown here can bind to a metal twice. The ligand forms two bonds to the metal, donating two pairs of electrons. It might seem obvious, but forming two bonds to the metal means the ligand binds more tightly to the metal. Remember the lego-like nature of transition metal complexes: ligands can come and go, but these ligands are less likely to go; they hold on.

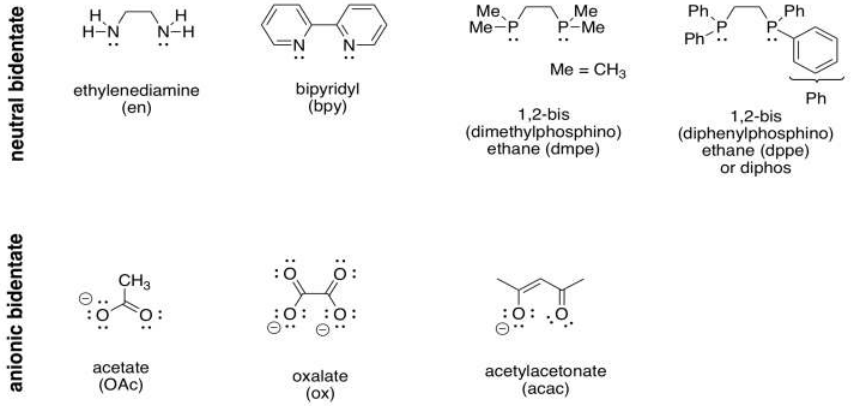


Figure 4.11.1:

These ligands are called *bidentate* ligands. That means, literally, that they have two teeth. That does not sound like much, but the ligands we have seen previously are described as *monodentate*; they have only one tooth. Bidentate ligands can bite into and hold onto the metal more strongly than monodentate ligands.

Another term used for these kinds of ligands is derived from the Greek *chele*, for claw. These ligands grab onto the metal like the claw of a lobster or crab; they *chelate*. The "chelate effect" (see next section) is the tendency of these ligands to bind firmly to a metal, whereas monodentate ligands might come off more easily.

Denticity

Denticity refers to the number of atoms with which a ligand binds to a metal ion. A ligand could be **mono*dentate***, meaning it binds through a lone pair on a single atom. It could be **bi*dentate***, meaning it binds through lone pairs on two different atoms. It could even be **tri*dentate***, with three atoms bearing their own lone pairs, **tetra*dentate***, and so on. The words, **poly*dentate*** and **multi*dentate***, are two general terms for ligands that bind through more than one atom. The words ***chelator*** and ***chelating ligand*** are also general terms used to refer to these ligands.

Figures **4.11.2** and **4.11.3** Examples of polydentate ligands.

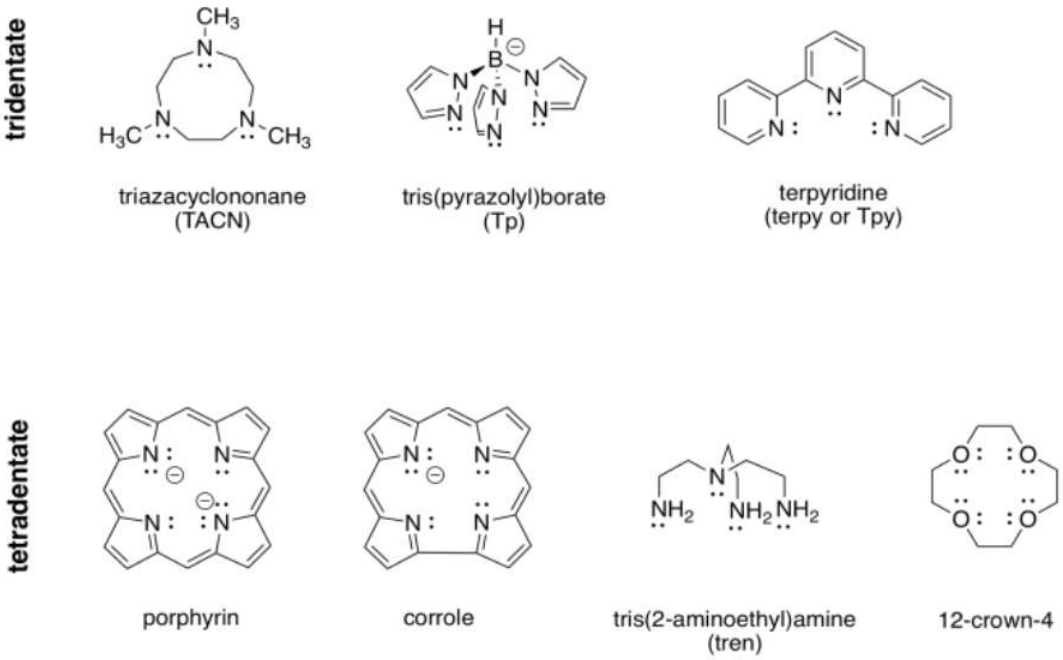


Figure **4.11.2**:

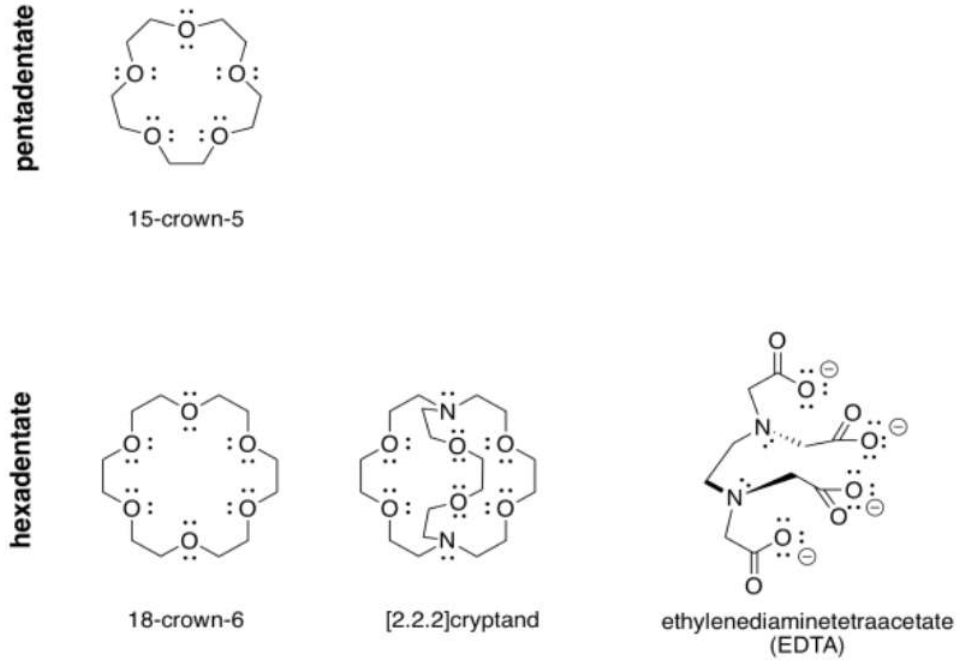


Figure **4.11.3**:

There is a symbol for denticity, κ (it's a Greek letter, pronounced "kappa"), which simply describes how many atoms are bound to the metal. For example, in ethylenediamine or 1,2-diaminoethane, $NH_2CH_2CH_2NH_2$, the two nitrogen atoms can be bound to the metal at the same time, although none of the other atoms in

between would be directly attached to the metal. This donor is capable of binding in a κ^2 mode. However, if for some reason one of the nitrogen atoms lets go of the metal so that the ethylenediamine is hanging on by only one nitrogen, we would say that the ligand is binding in κ^1 mode.

? Exercise 4.11.1

In each of the following cases,

i) describe the denticity;

ii) indicate the charge on the ligand and on the metal.

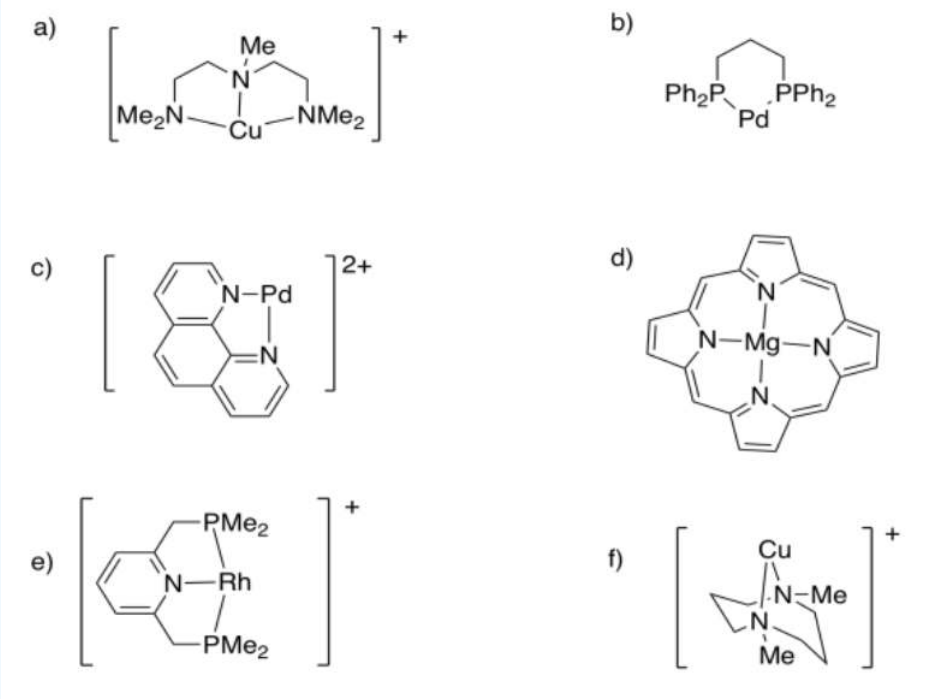


Figure 4.11.4:

Answer a):

tridentate or κ^3; ligand = 0; metal = 1+

Answer b):

bidentate or κ^2; ligand = 1-; metal = 0

Answer c):

bidentate or κ^2; ligand = 0; metal = 2+

Answer d):

tetradentate or κ^4; ligand = 2-; metal = 2+

Answer e):

tridentate or κ^3; ligand = 0; metal = 1+

Answer f):

bidentate or κ^2; ligand = 0; metal = 1+

Isomers

Coordination isomers in polydentate ligands

Now, just because a ligand could bind through multiple atoms does not mean that it always binds that way. That's often true with the acetate ligand, for example, because the four-membered ring that forms when it binds through both oxygen atoms is a little too strained. Consequently, there are examples of binding through both oxygen atoms, and there are also examples of binding through only one. Sometimes, acetate uses one oxygen to bind to one metal atom and the other oxygen to bind to a second metal atom, forming a bridge.

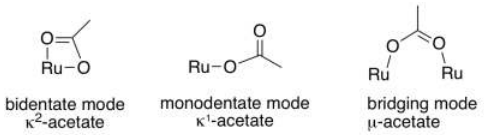


Figure 4.11.6:

Usually, if a ligand is capable of chelation, assume it binds that way. However, there may be cases in which you are asked specifically to draw it binding in one way or another.

? Exercise 4.11.2

In the following cases, the ligand has slipped so that it isn't binding as tightly as it possibly could. In each case,

i) describe the denticity as drawn;

ii) state the maximum denticity possible;

iii) indicate the charge on the ligand and on the metal.

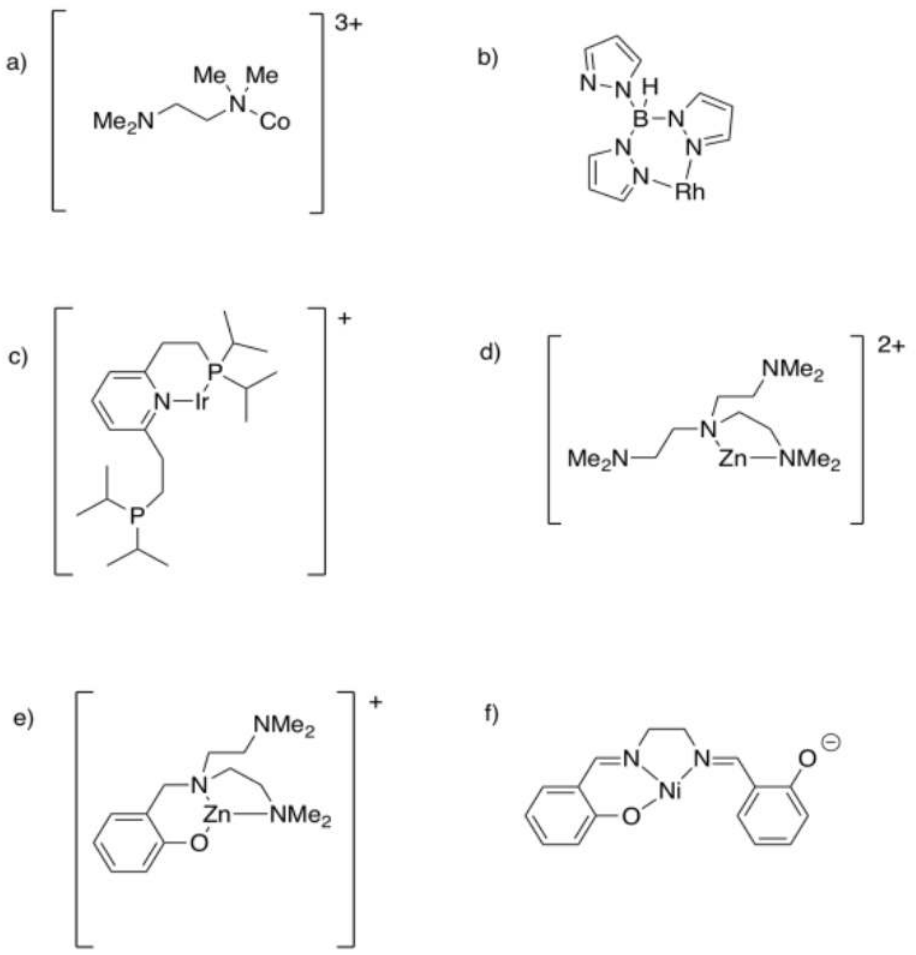


Figure 4.11.5:

Answer a):

monodentate or κ^1; maximum bidentate or κ^2; ligand = 0; metal = 2+

Answer b):

bidentate or κ^2; maximum tridentate or κ^3; ligand = 1-; metal = 1+

Answer c):

bidentate or κ^2; maximum tridentate or κ^3; ligand = 0; metal = 1+

Answer d):

bidentate or κ^2; maximum tetradentate or κ^4; ligand = 0; metal = 2+

Answer e):

tridentate or κ^3; maximum tetradentate or κ^4; ligand = 1-; metal = 2+

Answer f):

tridentate or κ^3; maximum tetradentate or κ^4; ligand = 2-; metal = 2+

? Exercise 4.11.3

Determine the denticity of each ligand in the following complexes.

a) $[Cu(en)_2(OH)_2]$ b) $[RuCl_2(dmpe)(bpy)]$ c) $[Ni(acac)_2(OH_2)_2]$ d) $K_2[Cu(ox)_2(OH_2)_2]$

e) $[FeH_2(dmpe)_2]$ f) $[RuH(OAc)(PPh_3)_3]$ g) $[Co(en)_2Cl_2]BF_4$ h) $[Ru(bpy)_2(HOCH_2CH_3)_2](ClO_4)_2$

Answer a):

en = bidentate; OH = monodentate

Answer b):

dmpe = bidentate; bpy = bidentate; Cl = monodentate

Answer c):

acac = bidentate; H_2O = monodentate

Answer d):

ox = bidentate; H_2O = monodentate

Answer e):

dmpe = bidentate; H = monodentate

Answer f):

H = monodentate; PPh3 = monodentate; OAc = bidentate. In this case, the acetate gets the complex to 18 electrons by binding twice.

Answer g):

en = bidentate; Cl = monodentate

Answer h):

bpy = bidentate; $HOCH_2CH_3$ = monodentate

Exercise 4.11.4

Determine the charges (or oxidation states) on the metals in the following complexes:

a) $K[Cr(ox)_2(OH_2)_2]$ b) $K[Mn(acac)_3]$ c) $[Cr(en)_2Cl_2]PF_6$ d) $[Co(en)_2(OH)Cl]ClO_4$

e) $Na_3[Mn(ox)_3]$ f) $K_3[Cr(ox)_3]$ g) $Na[Au(bpy)(CN)_2]$

Answer a):

Overall charge = 1-; ligands charge = 4-; charge on Cr = 3+

Answer b):

Overall charge = 1-; ligands charge = 3-; charge on Mn = 2+

Answer c):

Overall charge = 1+; ligands charge = 2-; charge on Cr = 3+

Answer d):

Overall charge = 1+; ligands charge = 2-; charge on Co = 3+

Answer e):

Overall charge = 3-; ligands charge = 6-; charge on Mn = 3+

Answer f):

Overall charge = 3-; ligands charge = 6-; charge on Cr = 3+

Answer g):

Overall charge = 1-; ligands charge = 2-; charge on Au = 1+

? Exercise 4.11.5

Determine the electron count on the metal in each of the complexes from the previous problem.

Answer a):

Cr = d^6; Cr^{3+} = d^3; ox = 2 x $4e^-$ = 8 e^-; water = 2 x $2e^-$ = 4 e-; total = 15 e^-

Answer b):

Mn = d^7; Mn^{2+} = d^5; acac = 3 x $4e^-$ = 12 e^-; total = 17 e^-

Answer c):

Cr = d^6; Cr^{3+} = d^3; en = 2 x $4e^-$ = 8 e^-; Cl = 2 x $2e^-$ = 4 e-; total = 15 e^-

Answer d):

Co = d^9; Co^{3+} = d^6; en = 2 x $4e^-$ = 8 e^-; OH = $2e^-$; Cl = 2 e-; total = 15 e^-

Answer e):

Mn = d^7; Mn^{3+} = d^4; ox = 3 x $4e^-$ = 12 e^-; total = 16 e^-

Answer f):

Cr = d^6; Cr^{3+} = d^3; ox = 3 x $4e^-$ = 12 e^-; total = 15 e^-

Answer g):

Au = s^1d^{10}; Au^{1+} = d^{10}; bpy = 2 x $2e^-$ = 4 e^-; cyanide = 2 x $2e^-$ = 4 e-; total = 18 e^-

Stereoisomers in polydentate ligands

Polydentate ligands can give **Λ**\(\Delta\) isomers and mer\fac isomers, respectively. See the examples below.



Figure 4.11.7: The two molecules shown on the left are **Λ** and **Δ** stereoisomers of tris(ethylenediamine)cobalt(III). The two molecules on the right are fac and mer isomers of diethylenetriaminetrichlorocobalt(III).

More details on isomers are provided in a more advanced course.

Bite Angle

There are more subtle aspects of chelation. For example, two different bidentate ligands may not necessarily bind to the metal in exactly the same way. In the drawing below, it's apparent that the three bidentate phosphine ligands, bis(dimethylphosphino)methane, bis(dimethylphosphino)ethane, and bis(dimethylphosphino)propane, do not all bind the metal with the same geometry. In each case, the metal forms a different angle with the two phosphines.

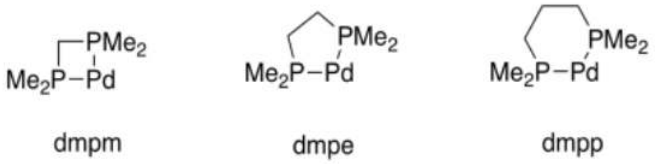


Figure **4.11.8**:

The term "bite angle" is frequently used to describe how different bidentate ligands will attach to metals at different angles. In the picture, the P-Pd-P angle appears to be about 90 degrees when dmpm is bound; in reality it is even smaller. With dmpe, the bite angle appears larger in the picture than the one for dmpm, and in reality it is larger, although not quite as large as it appears here. Two different ligands that bind with two different bite angles will have different influences on the complex that forms. In fact, chemists often use these differences to "tune" the behavior of transition metals that are used as catalysts for important properties. They might add similar ligands with different bite angles to see which one best promotes the desired catalytic reaction.

Many factors can influence the bite angle, including structural features of the bidentate ligand itself, the metal, and other ligands bound to the metal. However, a particular ligand will usually have a normal range of bite angles that it will be able to adopt under different circumstances.

? Exercise 4.11.6

Certain ligands may have natural bite angles that work better in some cases than in others. Propose the optimum bite angle in each of the following geometries.

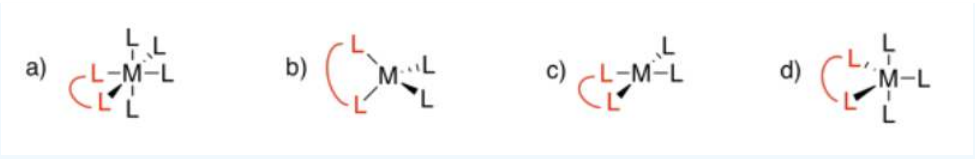
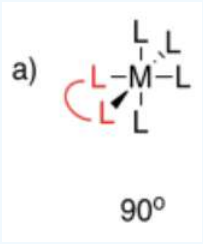
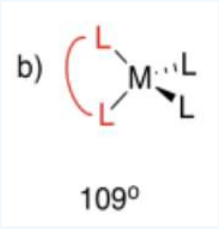


Figure **4.11.9**:

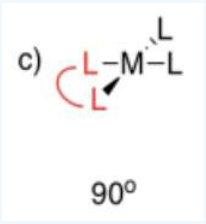
Answer a):



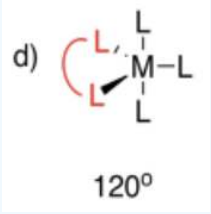
Answer b):



Answer c):



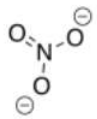
Answer d):

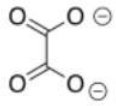


? Exercise 4.11.7

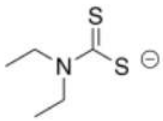
Certain ligands tend to give a certain range of bite angles. Use the suggested criterion to predict which ligand in each pair would give the larger bite angle.

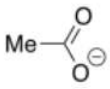
a) nitrate vs. oxalate, based on **ring size**



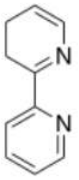


b) dithiocarbamatre vs. acetate, based on **bond lengths**





c) bipyridyl vs. ethylenediamine, based on **hybridization / bond angles**



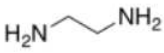
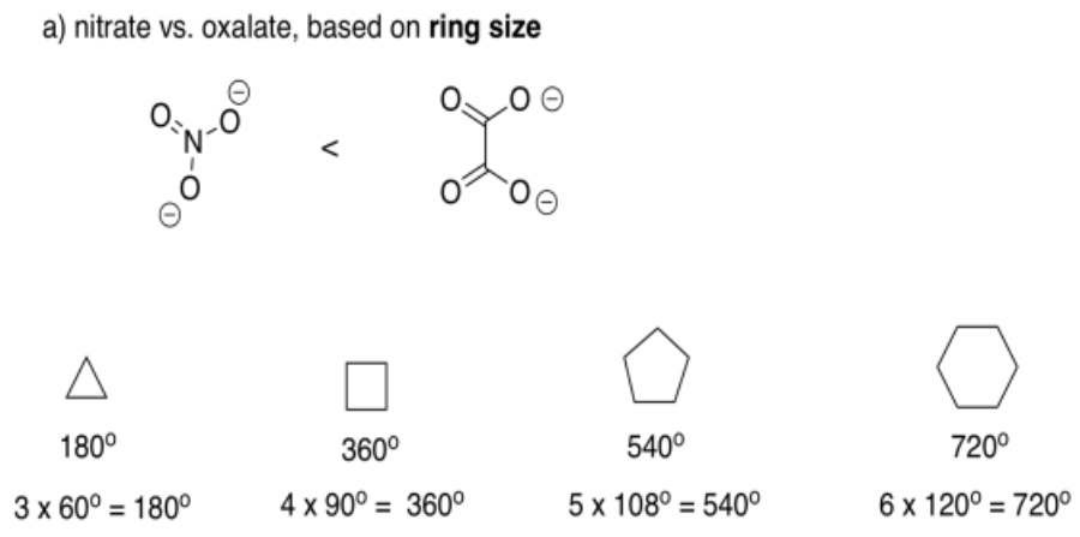


Figure 4.11.10:

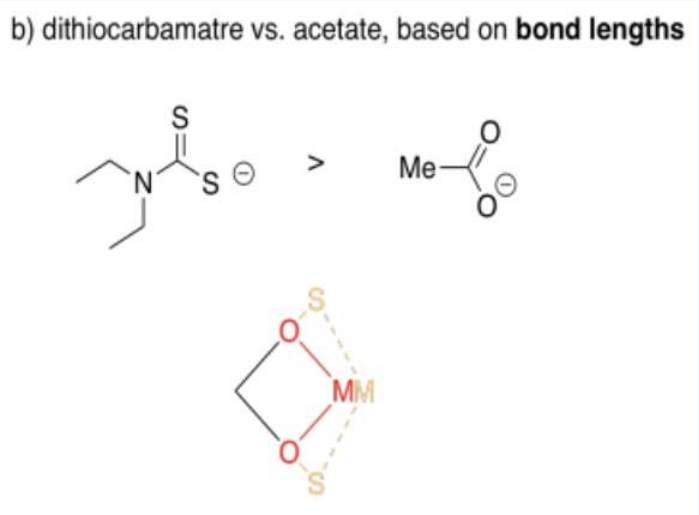
Answer a):



The total of the interior angles of a regular polyhedron is given by $(n\text{-}2)180^{o}$, in which n is the number of sides in the polyhedron. Assuming the ring formed by the bidentate ligand and the metal is a regular polyhedron (it won't be, but we are simplifying), then nitrate gives a triangle with 60° angles, including a 60° O-M-O bite angle. Oxalate gives a square with a larger, 90° bite angle.

In reality, the bite angle for nitrate varies with the complex that is formed, but it is usually somewhere around sixty degrees, whereas oxalate usually gives somewhere around eighty five degrees (see, for example, Alvarez, *Chem. Rev*. **2015**, *115*, 13447-13483). The smaller ring size gives a smaller bite angle.

Answer b):

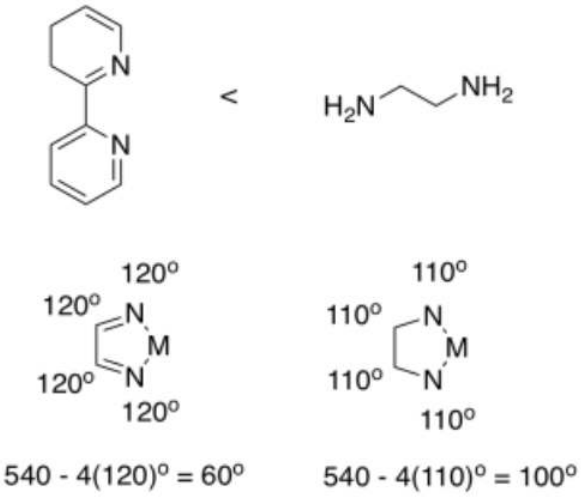


Sulfur is larger than oxygen, so its bonds will be a little longer. As a result, you can imagine those two sides of the square being a little longer with sulfur than with oxygen. From the perspective of the metal, the gap between the two donor atoms widens out a little.

Acetate forms bite angles of around sixty degrees, but dithiocarbamate forms larger bite angles of seventy or seventy five degrees.

Answer c):

c) bipyridyl vs. ethylenediamine, based on **hybridization / bond angles**



There are lots of differences between these two ligands, but if we simplify and only consider bond angle, we can make a prediction. If the atoms in bipridyl can be considered sp^2 hybridised, then they form 120° bond angles. The atoms in ethylenediamine could be considered sp^3 hybridised, forming approximately 110° angles. The angle N-M-N still has to complete the shape of the regular pentagon, so if all of the other angles are bigger in the bipyridyl complex, we would expect the bite angle to be smaller.

Really, the bite angles are much closer than this rough estimate suggests. Bipyridyl forms average bite angles of around eighty degrees, whereas ethylenediamine forms average bite angles of around eighty-five degrees. Keep in mind that those are just averages, though. These two values are close enough that their ranges overlap; lots of bipyridyl complexes would have bite angles smaller than ethylenediamine complexes.

? Exercise 4.11.8

Suggest which ligand in each pair would have the larger bite angle, and why.

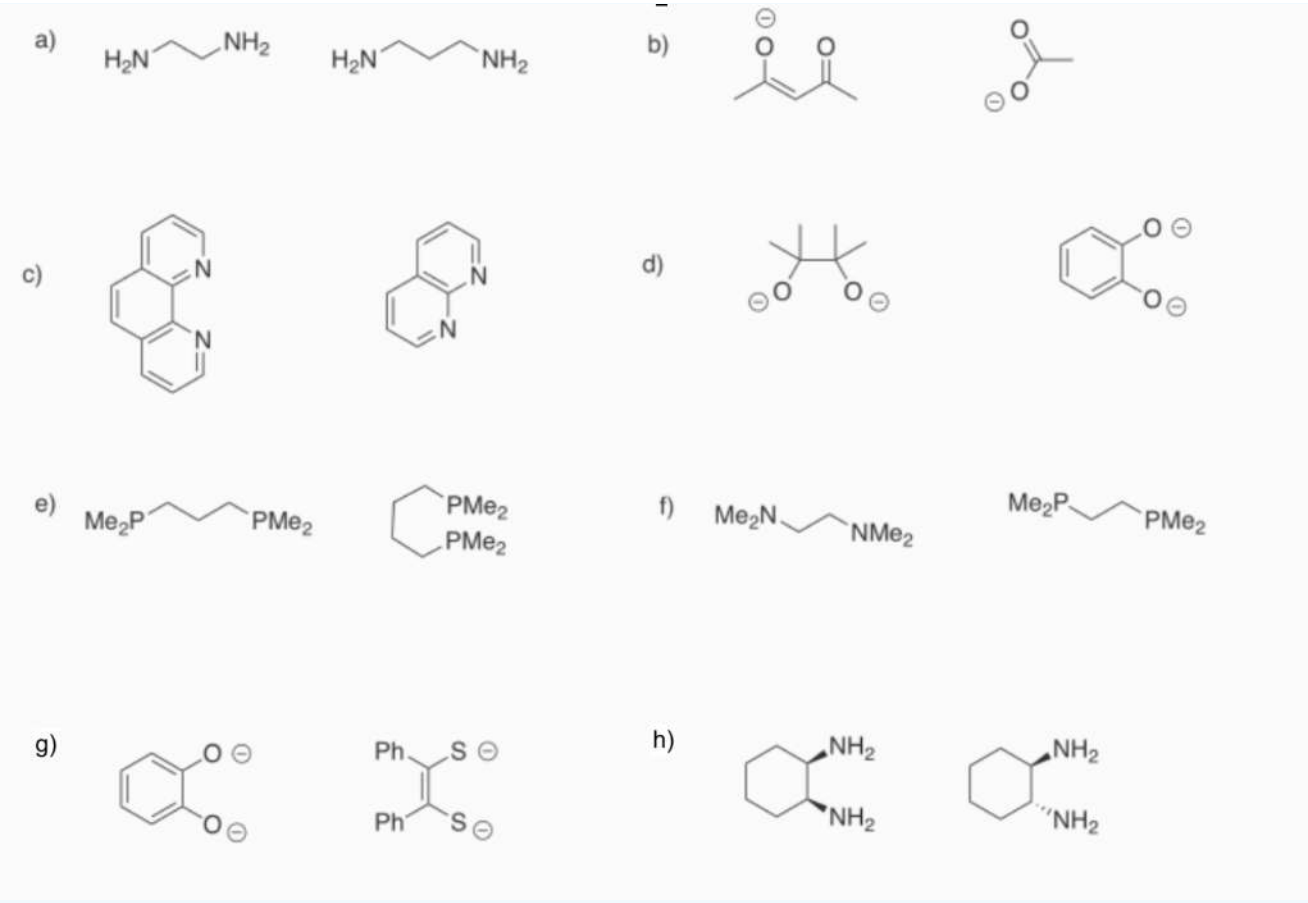
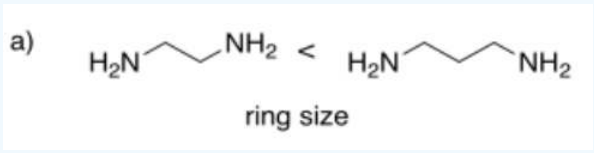
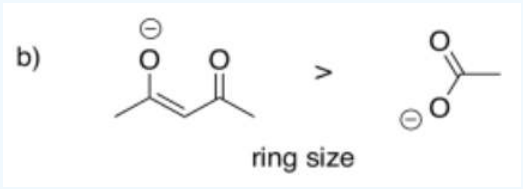


Figure **4.11.11**:

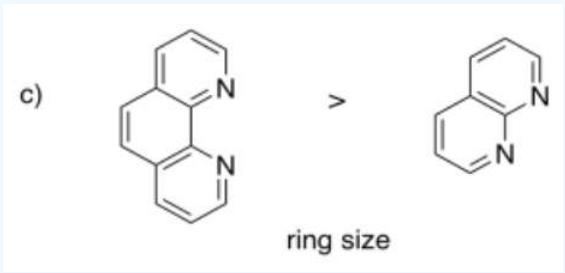
Answer a):



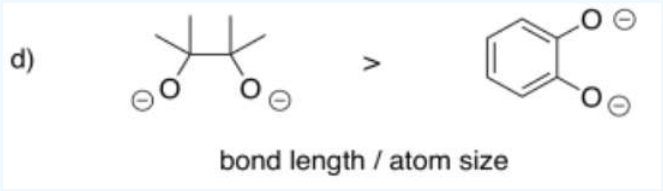
Answer b):



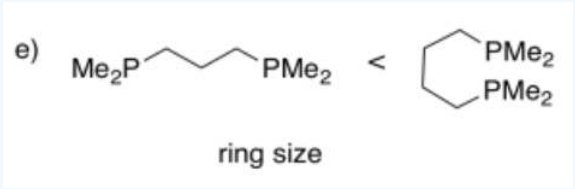
Answer c):



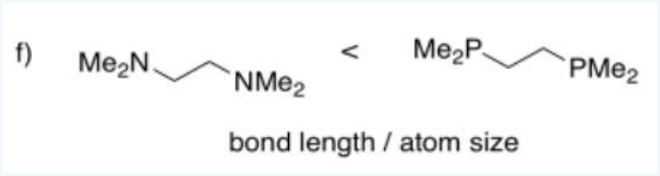
Answer d):



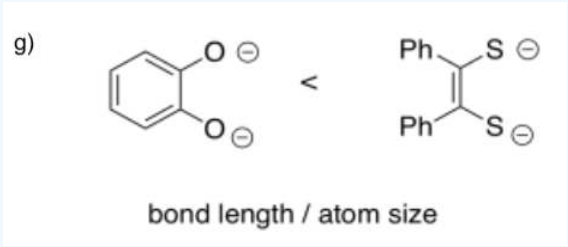
Answer e):



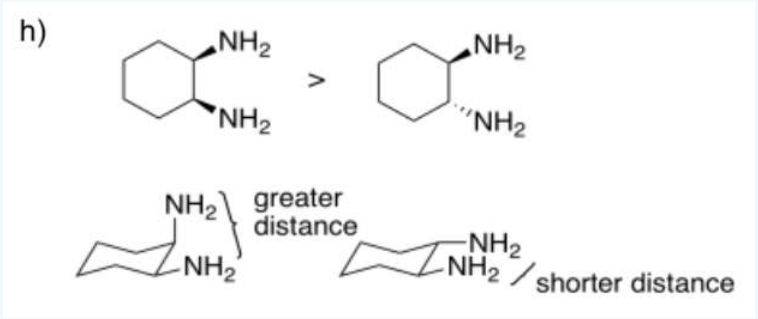
Answer f):



Answer g):



Answer h):



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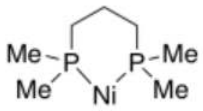
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4.12: The Chelate Effect (and Macrocycle Effect)

Introduction

Monodentate ligands bind through only one donor atom. Monodentate means "one-toothed". The halides, phosphines, ammonia and amines seen previously are monodentate ligands.

Bidentate ligands bind through two donor sites. Bidentate means "two-toothed". An example of a bidentate ligand is bis(dimethylphosphino)propane. It can bind to a metal via two donor atoms at once: it uses one lone pair on each phosphorus atom.



an example of a bidentate donor coordinating to a metal

Figure **4.12.1**:

More examples of bidentate ligands are shown below. They all have at least two different atoms with lone pairs. In some cases, there are additional atoms with lone pairs, but only two of them are able to face the metal at one time. Oxalate and glycinate would act as bidentate donors, donating up to two sets of lone pairs at the same time.

Table CC 4.12.1 Some common bidentate ligands

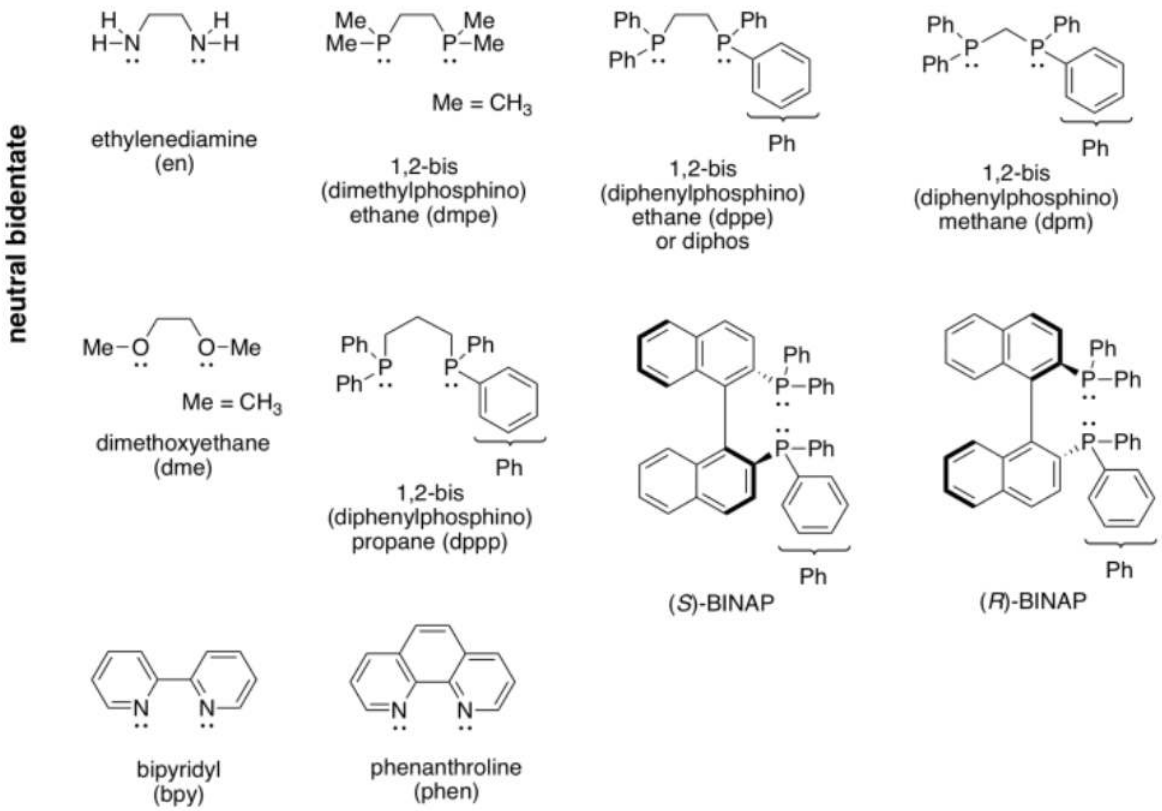


Figure **4.12.2**:

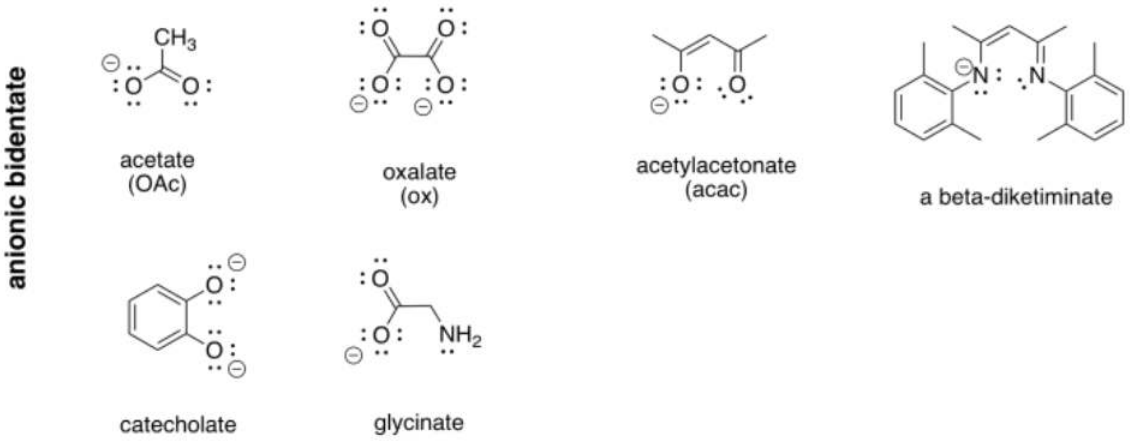


Figure 4.12.3:

The Chelate Effect

Chelating ligands have higher affinity for a metal ion than analogous monodentate ligands. The **chelate effect** is the enhanced affinity of a chelating ligand for a metal ion compared to its monodentate ligand counterpart(s). This term comes from the Greek chelos, meaning "crab". A crab does not have any teeth at all, but it does have two claws for tightly holding onto something. A very simple analogy is that, if you are holding something with two hands rather than one, you are not as likely to drop it. For example, ethylenediamine (en, $H_2NCH_2CH_2NH_2$) is a bidentate ligand that binds metal ions more strongly than monodentate amine ligands like ammonia (NH_3) and methylamine (CH_3NH_2). Tridentate ligands, which bind through three donors, can bind even more tightly than bidentate, and so on.

> *Multidentate ligands bind more tightly because of the chelate effect*

Chemical reasoning for the Chelate Effect

The chelate effect can be explained using principles of thermodynamics. Recall that reactions are spontaneous when the Gibbs Free Energy change is negative $-\Delta G$; this is true when change in enthalpy is negative ($-\Delta H$) and the change in entropy is positive (disorder increases, $+\Delta S$. (From the equation $\Delta G = \Delta H - T\Delta S$.)

Consider the reaction shown below:

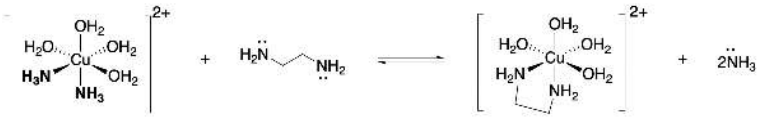


Figure 4.12.4: A reaction where one ethylenediamine (en) ligand replaces two ammonia ligands in a Cu(II) complex. The equilibrium constant for this reaction is approximately 1000 ($K \approx 10^3$), and so the equilibrium lies to the right.

Enthalpy

In each the reactant Cu complex and product Cu-complex in Figure 4.12.4, there are two N-Cu bonds. Electronically, the ammonia and en ligands are very similar, since both bind through N and since the Lewis base strengths of their nitrogen atoms are similar. The enthalpy change due to breaking two H_3N-Cu bonds and replacing them with two new N(en)-C bonds is almost zero. Thus, *enthalpy is not a major driving factor in the chelate effect.*

Entropy

In terms of entropy (disorder) there are two things to consider:

(1) The entropy from free rotation of the chelator. The chelator becomes somewhat constrained upon binding to the metal, and so this would result in small entropic penalty (loss in entropy). This is worth noting, but is a relatively small effect.

(2) The entropy from change in the number of molecules that can move freely. When a chelating ligand replaces several monodentate ligands, the result is an increase in the number of free molecules in the system, meaning a relatively large

increase in entropy. This is the major energetic factor driving the chelate effect.

> *When a chelating ligand replaces monodentate ligands, there is a relatively large increase in entropy ($+\Delta S$). This is the primary driving factor for the Chelate Effect.*

For example, when en replaces two ammonia ligands (Figure **4.12.4**), the number of total molecules increases from two to three. Increasing the number of molecules by just one is enough to drive the reaction forward.

The example above gives a case when just one bidentate ligand is involved. When multiple bidentate ligands are involved, or when denticity increases, the chelate effect is enhanced further. Consider the two complexation equilibria in aqueous solution, between the cobalt (II) ion, Co^{2+}(aq) and ethylenediamine (en) on the one hand and ammonia, NH_3, on the other.

$$[Co(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{2+} + 6H_2O \ (1) \tag{4.12.1}$$

$$[Co(H_2O)_6]^{2+} + 3en \rightleftharpoons [Co(en)_3]^{2+} + 6H_2O \ (2) \tag{4.12.2}$$

This means that ΔH must be very similar for the two reactions, since six Co-N bonds are formed in each case. Interestingly however, we observe that the equilibrium constant is *100,000 times larger* for the second reaction than it is for the first.

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

$$K_f(en)/K_f(NH_3) = e^{-\Delta\Delta G^\circ/RT} \approx e^{+\Delta\Delta S^\circ/R} \approx e^{12} \approx 10^5 \tag{4.12.3}$$

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

? Exercise 4.12.1

Draw metal complexes using the ligands below, binding to Ni(2+) in a bidentate mode.

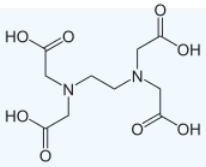
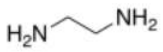
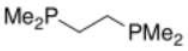


Figure **4.12.5**: Ethylenediaminetetraaceticacid acid (EDTA), a hexadentate ligand

a) 

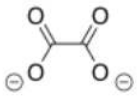
ethylenediamine (en)

b) 

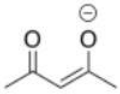
dimethylphoshinoethane (dmpe)

c) 

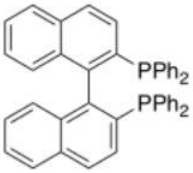
acetate (OAc)

d) 

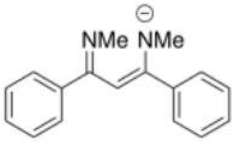
oxalate (ox)

e) 

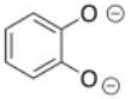
acetylacetonate (acac)

f) 

BINAP

g) 

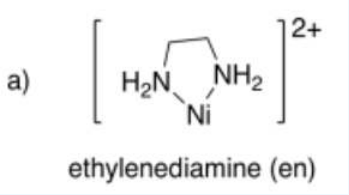
beta-diketiminate

h) 

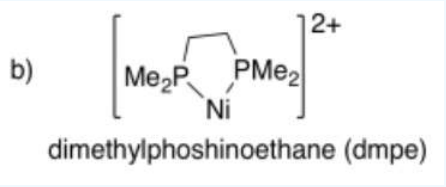
catecholate

Figure 4.12.1:

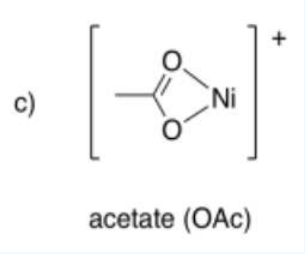
Answer a):



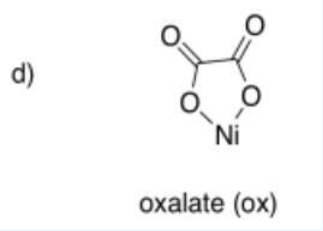
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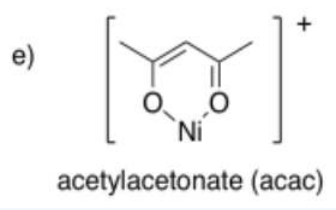
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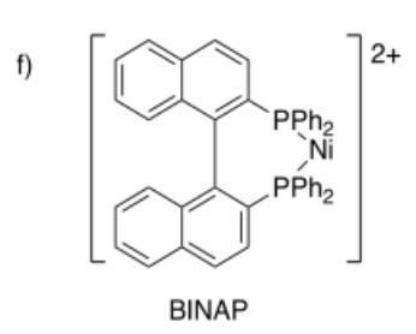
Answer d):



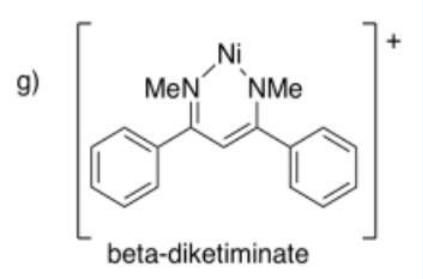
Answer e):



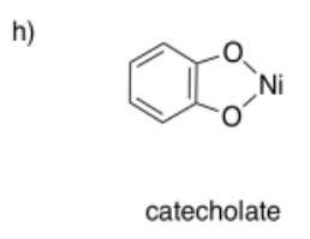
Answer f):



Answer g):



Answer h):



The Macrocycle Effect

The **macrocyclic effect** follows the same principle as the chelate effect, but the effect is further enhanced by the cyclic conformation of the ligand. Macrocyclic ligands are not only multi-dentate, but because they are covalently constrained to their cyclic form, they also allow less conformational freedom. The ligand is said to be "**pre-organized**" for binding, and there is little entropy penalty for the ligand to wrap around the metal ion. For example heme b is a tetradentate cyclic ligand which strongly complexes transition metal ions, including (in biological systems) Fe^{+2}.

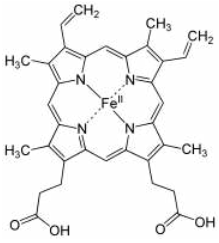


Figure 5.10.3: Heme b

Some other common cyclic ligands are shown below:

- **Crown ethers** such as 18-crown-6 (below left) are cyclic hard bases that can complex alkali metal cations. Crowns can selectively bind Li^+, Na^+, or K^+ depending on the number of ethylene oxide units in the ring.
- The chelating properties of crown ethers are mimetic of the natural antibiotic **valinomycin** (below right), which selectively transports K^+ ions across bacterial cell membranes and kills the bacterium by dissipating its membrane potential. Like crown ethers, valinomycin is a cyclic hard base.

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4.13: Equilibria Involving Complex Ions

Learning Objectives

- To be introduced to complex ions, including ligands.

Previously, you learned that metal ions in aqueous solution are hydrated—that is, surrounded by a shell of usually four or six water molecules. A hydrated ion is one kind of a **complex ion** (or, simply, complex), a species formed between a central metal ion and one or more surrounding **ligands**, molecules or ions that contain at least one lone pair of electrons, such as the $[Al(H_2O)_6]^{3+}$ ion.

A complex ion forms from a metal ion and a ligand because of a Lewis acid–base interaction. The positively charged metal ion acts as a Lewis acid, and the ligand, with one or more lone pairs of electrons, acts as a Lewis base. Small, highly charged metal ions, such as Cu^{2+} or Ru^{3+}, have the greatest tendency to act as Lewis acids, and consequently, they have the greatest tendency to form complex ions.

As an example of the formation of complex ions, consider the addition of ammonia to an aqueous solution of the hydrated Cu^{2+} ion $\{[Cu(H_2O)_6]^{2+}\}$. Because it is a stronger base than H_2O, ammonia replaces the water molecules in the hydrated ion to form the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion. Formation of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex is accompanied by a dramatic color change, as shown in Figure **4.13.1**. The solution changes from the light blue of $[Cu(H_2O)_6]^{2+}$ to the blue-violet characteristic of the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ion.



Figure **4.13.1**: The Formation of Complex Ions. An aqueous solution of $CuSO_4$ consists of hydrated Cu^{2+} ions in the form of pale blue $[Cu(H_2O)_6]^{2+}$ (left). The addition of aqueous ammonia to the solution results in the formation of the intensely blue-violet $[Cu(NH_3)_4(H_2O)_2]^{2+}$ ions, usually written as $[Cu(NH_3)_4]^{2+}$ ion (right) because ammonia, a stronger base than H_2O, replaces water molecules from the hydrated Cu^{2+} ion. For a more complete description, see https://www.youtube.com/watch?v=IQNcLH6OZK0.

The Formation Constant

The replacement of water molecules from $[Cu(H_2O)_6]^{2+}$ by ammonia occurs in sequential steps. Omitting the water molecules bound to Cu^{2+} for simplicity, we can write the equilibrium reactions as follows:

$$Cu^{2+}(aq) + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)]^{2+}_{(aq)} \quad K_1 \tag{4.13.1}$$

$$[Cu(NH_3)]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_2]^{2+}_{(aq)} \quad K_2 \tag{4.13.2}$$

$$[Cu(NH_3)_2]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_3]^{2+}_{(aq)} \quad K_3 \tag{4.13.3}$$

$$[Cu(NH_3)_3]^{2+}_{(aq)} + NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)} \quad K_4 \tag{4.13.4}$$

The sum of the stepwise reactions is the overall equation for the formation of the complex ion: The hydrated Cu^{2+} ion contains six H_2O ligands, but the complex ion that is produced contains only four NH_3 ligands, not six.

$$Cu^{2+}_{(aq)} + 4NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)} \tag{4.13.5}$$

The equilibrium constant for the formation of the complex ion from the hydrated ion is called the **formation constant (K_f)**. The equilibrium constant expression for K_f has the same general form as any other equilibrium constant expression. In this case, the expression is as follows:

$$K_f = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4} = 2.1 \times 10^{13} = K_1K_2K_3K_4 \tag{4.13.6}$$

> *The formation constant (K_f) has the same general form as any other equilibrium constant expression.*

Water, a pure liquid, does not appear explicitly in the equilibrium constant expression, and the hydrated $Cu^{2+}(aq)$ ion is represented as Cu^{2+} for simplicity. As for any equilibrium, the larger the value of the equilibrium constant (in this case, K_f), the more stable the product. With $K_f = 2.1 \times 10^{13}$, the $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion is very stable. The formation constants for some common complex ions are listed in Table **4.13.1**.

Table **4.13.1**: Formation Constants for Selected Complex Ions in Aqueous Solution*

	Complex Ion	Equilibrium Equation	K_f
Ammonia Complexes	$[Ag(NH_3)_2]^+$	$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$	1.1×10^7
	$[Cu(NH_3)_4]^{2+}$	$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	2.1×10^{13}
	$[Ni(NH_3)_6]^{2+}$	$Ni^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+}$	5.5×10^8
Cyanide Complexes	$[Ag(CN)_2]^-$	$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$	1.1×10^{18}
	$[Ni(CN)_4]^{2-}$	$Ni^{2+} + 4CN^- \rightleftharpoons [Ni(CN)_4]^{2-}$	2.2×10^{31}
	$[Fe(CN)_6]^{3-}$	$Fe^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-}$	1×10^{42}
Hydroxide Complexes	$[Zn(OH)_4]^{2-}$	$Zn^{2+} + 4OH^- \rightleftharpoons [Zn(OH)_4]^{2-}$	4.6×10^{17}
	$[Cr(OH)_4]^-$	$Cr^{3+} + 4OH^- \rightleftharpoons [Cr(OH)_4]^-$	8.0×10^{29}
Halide Complexes	$[HgCl_4]^{2-}$	$Hg^{2+} + 4Cl^- \rightleftharpoons [HgCl_4]^{2-}$	1.2×10^{15}
	$[CdI_4]^{2-}$	$Cd^{2+} + 4I \rightleftharpoons [CdI_4]^{2-}$	2.6×10^5
	$[AlF_6]^{3-}$	$Al^{3+} + 6F^- \rightleftharpoons [AlF_6]^{3-}$	6.9×10^{19}
Other Complexes	$[Ag(S_2O_3)_2]^{3-}$	$Ag^+ + 2S_2O_3^{2-} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}$	2.9×10^{13}
	$[Fe(C_2O_4)_3]^{3-}$	$Fe^{3+} + 3C_2O_4^{2-} \rightleftharpoons [Fe(C_2O_4)_3]^{3-}$	2.0×10^{20}

*Reported values are overall formation constants. Source: Data from *Lange's Handbook of Chemistry*, 15th ed. (1999).

Example 4.13.1

If 12.5 g of $Cu(NO_3)_2 \cdot 6H_2O$ is added to 500 mL of 1.00 M aqueous ammonia, what is the equilibrium concentration of $Cu^{2+}(aq)$?

Given: mass of Cu^{2+} salt and volume and concentration of ammonia solution

Asked for: equilibrium concentration of $Cu^{2+}(aq)$

Strategy:

A. Calculate the initial concentration of Cu^{2+} due to the addition of copper(II) nitrate hexahydrate. Use the stoichiometry of the reaction shown in Equation 4.13.5 to construct a table showing the initial concentrations, the changes in concentrations, and the final concentrations of all species in solution.

B. Substitute the final concentrations into the expression for the formation constant (Equation 4.13.6) to calculate the equilibrium concentration of $Cu^{2+}(aq)$.

Solution

Adding an ionic compound that contains Cu^{2+} to an aqueous ammonia solution will result in the formation of $[Cu(NH_3)_4]^{2+}(aq)$, as shown in Equation 4.13.5. We assume that the volume change caused by adding solid copper(II) nitrate to aqueous ammonia is negligible.

A The initial concentration of Cu^{2+} from the amount of added copper nitrate prior to any reaction is as follows:

$$12.5\ \cancel{g}\ Cu(NO_3)_2 \cdot 6H_2O \left(\frac{1\ mol}{295.65\ \cancel{g}}\right)\left(\frac{1}{500\ \cancel{mL}}\right)\left(\frac{1000\ \cancel{mL}}{1\ L}\right) = 0.0846\ M \tag{4.13.7}$$

Because the stoichiometry of the reaction is four NH_3 to one Cu^{2+}, the amount of NH_3 required to react completely with the Cu^{2+} is 4(0.0846) = 0.338 M. The concentration of ammonia after complete reaction is 1.00 M − 0.338 M = 0.66 M. These results are summarized in the first two lines of the following table. Because the equilibrium constant for the reaction is large (2.1×10^{13}), the equilibrium will lie far to the right. Thus we will assume that the formation of $[Cu(NH_3)_4]^{2+}$ in the first step is complete and allow some of it to dissociate into Cu^{2+} and NH_3 until equilibrium has been reached. If we define x as the amount of Cu^{2+} produced by the dissociation reaction, then the stoichiometry of the reaction tells us that the change in the concentration of $[Cu(NH_3)_4]^{2+}$ is $-x$, and the change in the concentration of ammonia is $+4x$, as indicated in the table. The final concentrations of all species (in the bottom row of the table) are the sums of the concentrations after complete reaction and the changes in concentrations.

$$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$$

	$[Cu^{2+}]$	$[NH_3]$	$[[Cu(NH_3)_4]^{2+}]$
initial	0.0846	1.00	0
after complete reaction	0	0.66	0.0846
change	$+x$	$+4x$	$-x$
final	x	$0.66 + 4x$	$0.0846 - x$

B Substituting the final concentrations into the expression for the formation constant (Equation 4.13.6) and assuming that x << 0.0846, which allows us to remove x from the sum and difference,

$$K_f = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}][NH_3]^4} = \frac{0.0846 - x}{x(0.66 + 4x)^4} \approx \frac{0.0846}{x(0.66)^4} = 2.1 \times 10^{13} \tag{4.13.8}$$

$$x = 2.1 \times 10^{-14} \tag{4.13.9}$$

The value of x indicates that our assumption was justified. The equilibrium concentration of $Cu^{2+}(aq)$ in a 1.00 M ammonia solution is therefore 2.1×10^{-14} M.

? Exercise 4.13.1

The ferrocyanide ion $\{[Fe(CN)_6]^{4-}\}$ is very stable, with a K_f of 1×10^{35}. Calculate the concentration of cyanide ion in equilibrium with a 0.65 M solution of $K_4[Fe(CN)_6]$.

Answer 2×10^{-6} M

The Effect of the Formation of Complex Ions on Solubility

What happens to the solubility of a sparingly soluble salt if a ligand that forms a stable complex ion is added to the solution? One such example occurs in conventional black-and-white photography. Recall that black-and-white photographic film contains light-sensitive microcrystals of AgBr, or mixtures of AgBr and other silver halides. AgBr is a sparingly soluble salt, with a K_{sp} of 5.35×10^{-13} at 25°C. When the shutter of the camera opens, the light from the object being photographed strikes some of the crystals on the film and initiates a photochemical reaction that converts AgBr to black Ag metal. Well-formed, stable negative images appear in tones of gray, corresponding to the number of grains of AgBr converted, with the areas exposed to the most light being darkest. To fix the image and prevent more AgBr crystals from being converted to Ag metal during processing of the film, the unreacted AgBr on the film is removed using a complexation reaction to dissolve the sparingly soluble salt.

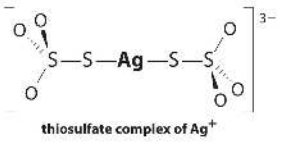
The reaction for the dissolution of silver bromide is as follows:

$$AgBr_{(s)} \rightleftharpoons Ag^+_{(aq)} + Br^-_{(aq)} \tag{4.13.10}$$

with

$$K_{sp} = 5.35 \times 10^{-13} \text{ at } 25°C \tag{4.13.11}$$

The equilibrium lies far to the left, and the equilibrium concentrations of Ag^+ and Br^- ions are very low (7.31×10^{-7} M). As a result, removing unreacted AgBr from even a single roll of film using pure water would require tens of thousands of liters of water and a great deal of time. Le Chatelier's principle tells us, however, that we can drive the reaction to the right by removing one of the products, which will cause more AgBr to dissolve. Bromide ion is difficult to remove chemically, but silver ion forms a variety of stable two-coordinate complexes with neutral ligands, such as ammonia, or with anionic ligands, such as cyanide or thiosulfate ($S_2O_3^{2-}$). In photographic processing, excess AgBr is dissolved using a concentrated solution of sodium thiosulfate.



thiosulfate complex of Ag^+

The reaction of Ag^+ with thiosulfate is as follows:

$$Ag^+_{(aq)} + 2S_2O^{2-}_{3(aq)} \rightleftharpoons [Ag(S_2O_3)_2]^{3-}_{(aq)} \tag{4.13.12}$$

with

$$K_f = 2.9 \times 10^{13} \tag{4.13.13}$$

The magnitude of the equilibrium constant indicates that almost all Ag^+ ions in solution will be immediately complexed by thiosulfate to form $[Ag(S_2O_3)_2]^{3-}$. We can see the effect of thiosulfate on the solubility of AgBr by writing the appropriate reactions and adding them together:

$$\mathrm{AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq) \quad} K_{sp} = 5.35 \times 10^{-13} \tag{4.13.14}$$

$$\mathrm{Ag^+(aq) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq) \quad} K_f = 2.9 \times 10^{13} \tag{4.13.15}$$

$$\mathrm{AgBr(s) + 2S_2O_3^{2-}(aq) \rightleftharpoons [Ag(S_2O_3)_2]^{3-}(aq) + Br^-(aq) \quad} K = K_{sp}K_f = 15 \tag{4.13.16}$$

Comparing K with K_{sp} shows that the formation of the complex ion increases the solubility of AgBr by approximately 3×10^{13}. The dramatic increase in solubility combined with the low cost and the low toxicity explains why sodium thiosulfate is almost universally used for developing black-and-white film. If desired, the silver can be recovered from the thiosulfate solution using any of several methods and recycled.

> *If a complex ion has a large K_f, the formation of a complex ion can dramatically increase the solubility of sparingly soluble salts.*

Example 4.13.2

Due to the common ion effect, we might expect a salt such as AgCl to be much less soluble in a concentrated solution of KCl than in water. Such an assumption would be incorrect, however, because it ignores the fact that silver ion tends to form a two-coordinate complex with chloride ions ($AgCl_2^-$). Calculate the solubility of AgCl in each situation:

a. in pure water
b. in 1.0 M KCl solution, ignoring the formation of any complex ions
c. the same solution as in part (b) except taking the formation of complex ions into account, assuming that $AgCl_2^-$ is the only Ag^+ complex that forms in significant concentrations

At 25°C, $K_{sp} = 1.77 \times 10^{-10}$ for AgCl and $K_f = 1.1 \times 10^5$ for $AgCl_2^-$.

Given: K_{sp} of AgCl, K_f of $AgCl_2^-$, and KCl concentration

Asked for: solubility of AgCl in water and in KCl solution with and without the formation of complex ions

Strategy:

A. Write the solubility product expression for AgCl and calculate the concentration of Ag^+ and Cl^- in water.
B. Calculate the concentration of Ag^+ in the KCl solution.
C. Write balanced chemical equations for the dissolution of AgCl and for the formation of the $AgCl_2^-$ complex. Add the two equations and calculate the equilibrium constant for the overall equilibrium.
D. Write the equilibrium constant expression for the overall reaction. Solve for the concentration of the complex ion.

Solution

a. **A** If we let x equal the solubility of AgCl, then at equilibrium $[Ag+] = [Cl^-] = x$ M. Substituting this value into the solubility product expression,

$$K_{sp} = [Ag^+][Cl^-] = (x)(x) = x^2 = 1.77\times10^{-10}$$
$$x = 1.33\times10^{-5}$$

Thus the solubility of AgCl in pure water at 25°C is 1.33×10^{-5} M.

b. **B** If x equals the solubility of AgCl in the KCl solution, then at equilibrium $[Ag^+] = x$ M and $[Cl^-] = (1.0 + x)$ M. Substituting these values into the solubility product expression and assuming that $x << 1.0$,

$$K_{sp} = [Ag^+][Cl^-] = (x)(1.0 + x) \approx x(1.0) = 1.77\times10^{-10} = x$$

If the common ion effect were the only important factor, we would predict that AgCl is approximately five orders of magnitude less soluble in a 1.0 M KCl solution than in water.

c. **C** To account for the effects of the formation of complex ions, we must first write the equilibrium equations for both the dissolution and the formation of complex ions. Adding the equations corresponding to K_{sp} and K_f gives us an equation that describes the dissolution of AgCl in a KCl solution. The equilibrium constant for the reaction is therefore the product of K_{sp} and K_f:

$$\mathrm{AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)} \quad K_{sp} = 1.77 \times 10^{-10} \tag{4.13.17}$$
$$\mathrm{Ag^+(aq) + 2Cl^- \rightleftharpoons [AgCl_2]^-} \quad K_f = 1.1 \times 10^5 \tag{4.13.18}$$
$$\mathrm{AgCl(s) + Cl^- \rightleftharpoons [AgCl_2]^-} \quad K = K_{sp}K_f = 1.9 \times 10^{-5} \tag{4.13.19}$$

D If we let x equal the solubility of AgCl in the KCl solution, then at equilibrium $[AgCl_2^-] = x$ and $[Cl^-] = 1.0 - x$. Substituting these quantities into the equilibrium constant expression for the net reaction and assuming that $x << 1.0$,

$$K = \frac{[\mathrm{AgCl_2^-}]}{[\mathrm{Cl^-}]} = \frac{x}{1.0 - x} \approx 1.9 \times 10^{-5} = x$$

That is, AgCl dissolves in 1.0 M KCl to produce a 1.9×10^{-5} M solution of the $AgCl_2^-$ complex ion. Thus we predict that AgCl has approximately the same solubility in a 1.0 M KCl solution as it does in pure water, which is 10^5 times greater than that predicted based on the common ion effect. (In fact, the measured solubility of AgCl in 1.0 M KCl is almost a factor of 10 greater than that in pure water, largely due to the formation of other chloride-containing complexes.)

? Exercise 4.13.2

Calculate the solubility of mercury(II) iodide (HgI_2) in each situation:

a. pure water
b. a 3.0 M solution of NaI, assuming $[HgI_4]^{2-}$ is the only Hg-containing species present in significant amounts

$K_{sp} = 2.9 \times 10^{-29}$ for HgI_2 and $K_f = 6.8 \times 10^{29}$ for $[HgI_4]^{2-}$.

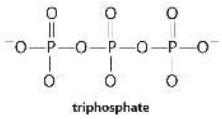
Answer

a. 1.9×10^{-10} M
b. 1.4 M



Solubility of Complex Ions: https://youtu.be/f4pkKDg2XTA

Complexing agents, molecules or ions that increase the solubility of metal salts by forming soluble metal complexes, are common components of laundry detergents. Long-chain carboxylic acids, the major components of soaps, form insoluble salts with Ca^{2+} and Mg^{2+}, which are present in high concentrations in "hard" water. The precipitation of these salts produces a bathtub ring and gives a gray tinge to clothing. Adding a complexing agent such as pyrophosphate ($O_3POPO_3^{4-}$, or $P_2O_7^{4-}$) or triphosphate ($P_3O_{10}^{5-}$) to detergents prevents the magnesium and calcium salts from precipitating because the equilibrium constant for complex-ion formation is large:



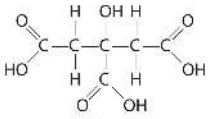
triphosphate

$$Ca^{2+}_{(aq)} + O_3POPO^{4-}_{4(aq)} \rightleftharpoons [Ca(O_3POPO_3)]^{2-}_{(aq)} \tag{4.13.20}$$

with

$$K_f = 4 \times 10^4 \tag{4.13.21}$$

However, phosphates can cause environmental damage by promoting eutrophication, the growth of excessive amounts of algae in a body of water, which can eventually lead to large decreases in levels of dissolved oxygen that kill fish and other aquatic organisms. Consequently, many states in the United States have banned the use of phosphate-containing detergents, and France has banned their use beginning in 2007. "Phosphate-free" detergents contain different kinds of complexing agents, such as derivatives of acetic acid or other carboxylic acids. The development of phosphate substitutes is an area of intense research.



Citric acid,
a hydroxy polycarboxylic acid

Commercial water softeners also use a complexing agent to treat hard water by passing the water over ion-exchange resins, which are complex sodium salts. When water flows over the resin, sodium ion is dissolved, and insoluble salts precipitate onto the resin surface. Water treated in this way has a saltier taste due to the presence of Na^+, but it contains fewer dissolved minerals.

Another application of complexing agents is found in medicine. Unlike x-rays, magnetic resonance imaging (MRI) can give relatively good images of soft tissues such as internal organs. MRI is based on the magnetic properties of the ^1H nucleus of hydrogen atoms in water, which is a major component of soft tissues. Because the properties of water do not depend very much on whether it is inside a cell or in the blood, it is hard to get detailed images of these tissues that have good contrast. To solve this problem, scientists have developed a class of metal complexes known as "MRI contrast agents." Injecting an MRI contrast agent into a patient selectively affects the magnetic properties of water in cells of normal tissues, in tumors, or in blood vessels and

allows doctors to “see” each of these separately (Figure **4.13.2**). One of the most important metal ions for this application is Gd^{3+}, which with seven unpaired electrons is highly paramagnetic. Because $Gd^{3+}(aq)$ is quite toxic, it must be administered as a very stable complex that does not dissociate in the body and can be excreted intact by the kidneys. The complexing agents used for gadolinium are ligands such as $DTPA^{5-}$ (diethylene triamine pentaacetic acid), whose fully protonated form is shown here.

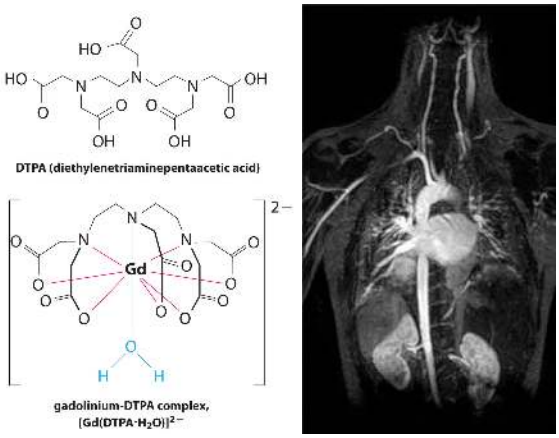


Figure **4.13.2**: An MRI Image of the Heart, Arteries, and Veins. When a patient is injected with a paramagnetic metal cation in the form of a stable complex known as an MRI contrast agent, the magnetic properties of water in cells are altered. Because the different environments in different types of cells respond differently, a physician can obtain detailed images of soft tissues.

Summary

The formation of complex ions can substantially increase the solubility of sparingly soluble salts if the complex ion has a large K_f. A complex ion is a species formed between a central metal ion and one or more surrounding ligands, molecules or ions that contain at least one lone pair of electrons. Small, highly charged metal ions have the greatest tendency to act as Lewis acids and form complex ions. The equilibrium constant for the formation of the complex ion is the formation constant (K_f). The formation of a complex ion by adding a complexing agent increases the solubility of a compound.

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4.14: Hard and Soft Acid and Base Theory

A note from Dr. Haas: Hard and Soft Acid and Base (HSAB) theory allows us to predict which acids and bases prefer to interact. Recall that Lewis acid-base theory can be applied to describe metal-ligand interactions. Metal ions are electron pair acceptors, and thus are Lewis Acids. So when we discuss hard or soft "acids" in this course, we are discussing metal ions. Ligands are electron pair donors, and thus are Lewis bases. When we discuss hard or soft "bases", we are discussing ligands.

Softness roughly refers to the polarizability of an acid or base. The larger and more neutral any species, the softer it is. Conversely, the smaller and more charged a species is, the harder it is.

HSAB theory is a useful tool to predict thermodynamic stability or kinetic lability of Metal-Ligand complexes. But, other important factors like the chelate effect or ligand field stabilization energy (LFSE) must also be considered and may outweigh the effects of HSAB.

Introduction

Certain metal ions form stronger interactions with certain ligands. This observation led to a classification system called **Hard and Soft Acids and Bases (HSAB)**, developed by Pearson. It is a theory that you can use to predict which metal ions and ligands will interact most favorably.

Hard/Soft Acid/Base

Classification

Lewis acids and bases can be classified by designating them as hard or soft. Acids and bases are not strictly hard or soft, since many ions and compounds are classified as intermediate. The categorizations are based on three factors: (1) charge density, or charge-to-size ratio (2) polarizability (3) covalent vs. ionic nature of interactions.

Hard Acids/Bases:

In general, "Hard" acids and bases have a high charge density, are not very polarizable, and form bonding interactions that are more ionic in nature. These atoms and ions tend to have high charge and/or small radius.

- **Typical Hard Acids:** metal ions with high positive charges and smaller ionic sizes tend to be hard acids. Early transition metal ions in the 3d series tend to be hard Lewis acids.
- **Typical Hard Bases**: Small anions and neutral molecules; heteroatoms of the second row of the periodic table are typically hard (N,O,F). Some examples of hard acids and bases include: H^+, O^{2-}, OH^-, F^-, Fe^{3+}, and Al^{3+}. Oxygen atoms are always hard, and N atoms are *usually* hard.

Soft Acids/Bases:

In general, "Soft" acids or bases have a low charge density, are more polarizable, and form bonds that are more covalent in nature. These atoms/ions tend to have low charge and/or large radius.

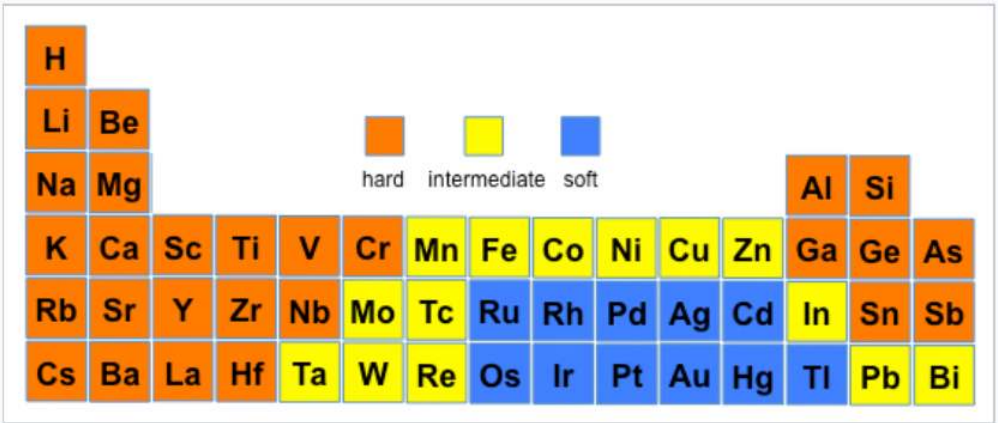
- **Typical Soft Acids**: Transition metals with (+1) charge (such as Cu^+) or that are in the late 4d and 5d series (like Cd^{2+} and Hg^{2+}), are classified as soft. Soft acids often include transition metals in the second and third row of the periodic table that have a +1 or +2 charge, as well as late transition metals (especially those in the 4d and 5d series) with filled or almost completely filled *d* orbitals.
- **Typical Soft Bases:** Larger anions and neutral molecules. For example, I^- and S^{2-} are soft bases.

Intermediate Acids/Bases:

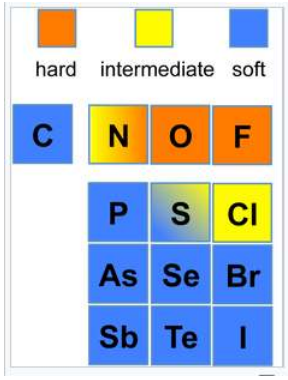
These are acids and bases with intermediate character, between hard and soft. For example, trimethylborane, Fe^{2+}, and Pb^{2+} cations are intermediate acids, and pyridine and aniline are examples of intermediate bases.

An element can have different hard/soft character depending on its oxidation state and whether or not its polarizability is affected by surrounding atoms and bonds. The most extreme example is hydrogen, where H^+ is a hard acid and H^- is a soft base. Ni^{3+} (as in the layered compound NiOOH) is a hard acid, but Ni^0 (as in $Ni(CO)_4$) is a soft acid. Nitrogen is hard when it is an ammine ($-NH_2$),

but the nitrogen in pyridine is borderline due to increased polarizability imparted by the aromatic ring. The figures below show hard/soft trends for acids (left) and bases (right) in the periodic table. For bases, the major hard/soft discontinuity is between the 2nd row (N,O,F) and the rows below.



Hard-soft trends for acids



Hard-soft trends for bases

Like binds with Like

Hard acids interact more strongly with hard bases than they do with soft bases, and soft acids interact more strongly with soft bases than hard bases. Thus, the most stable complexes are those with hard-hard and soft-soft interactions. This tendency is illustrated in the table below, which shows the trend in formation constants for hard and soft acids. Hard acids bind halides in the order $F^- > Cl^- > Br^- > I^-$, whereas soft acids follow the opposite trend.

Log K_1	fluoride	chloride	bromide	iodide	acid classification
Fe^{3+}	6.0	1.4	0.5	-	Hard
Pb^{2+}	1.3	0.9	1.1	1.3	Intermediate
Ag^+	0.4	3.3	4.7	6.6	Soft
Hg^{2+}	1.0	6.7	8.9	12.9	Soft

The softest metal ion in the periodic table is $Au^+(aq)$. It forms stable complexes with soft bases such as phosphines and CN^-, but not with hard bases such as O^{2-} or F^-. The affinity of Au^+ for the soft base CN^- is high, and the resulting $[Au(CN)_2]^-$ complex is so stable that gold (which is normally very difficult to oxidize) can be oxidized by oxygen in the air:

$$4\,Au_{(s)} + 8\,CN^-_{(aq)} + O_{2\,(g)} + 2\,H_2O = 4\,[Au(CN)_2]^-_{(aq)} + 4\,OH^- \qquad (4.14.1)$$

This reaction is used in gold mining to separate small flakes of Au from large volumes of sand and other oxides. Ag is similarly dissolved by air oxidation in cyanide solutions. The precious metals are then isolated from the solution using chemical reducing agents or by electroplating. The use of cyanide ion on a large scale in mining, however, creates a potentially serious environmental hazard. In 2000, a spill at Baia Mare, Romania resulted in the worst environmental disaster in Europe since Chernobyl. Cyanide, which is highly toxic, is gradually oxidized by air to the less toxic cyanate (OCN^-) ion. On the laboratory scale, cyanide plating solutions are typically disposed of by using bleach to oxidize CN^- to OCN^-, and the metal is recovered as an insoluble chloride salt.



Netted solution pond next to cyanide heap leaching of gold ore near Elko, Nevada (1992).

The Au^{3+} ion, because of its higher positive charge, is a harder acid than Au^+ and can form complexes with harder bases such as H_2O and amines. In keeping with the "like binds like" principle, the compound AuI (soft-soft) is stable, but AuI_3 (hard-soft) is unknown. Conversely, AuF has never been isolated but AuF_3 (hard-hard) is stable.

? Exercise 4.14.1

Suggest which of the following ions is harder.

a) zinc(II) or mercury(II)

b) potassium(I) or copper(I)

c) iron(II) or iron(III)

Answer a:

Zn(II), because it is smaller and less polarizable.

Answer b:

K^+, because it is less electronegative.

Answer c:

Fe(III), because of the higher charge.

? Exercise 4.14.2

Suggest which of the following bases is softer.

a) Me_3P or Me_3N

b) chloride or iodide

c) amide (NH_2^-) or azide (N_3^-)

Answer a:

Me_3P, because phosphorus is larger and more polarizable than nitrogen.

Answer b:

Iodide, which is larger and more polarizable than chloride.

Answer c:

Azide, which has a more polarizable, delocalized pi bonding system.

There are some obvious HSAB applications in metallurgy and geology. Some common minerals of hard metals are rutile (titanium oxide, TiO_2), dolomite (magnesium and calcium carbonate $CaMg(CO_3)_2$) and chromite (iron chromium oxide, $FeCrO_4$). Fluoride, carbonates, oxides, phosphates and sulfates are examples of hard bases.

Some prevalent minerals of soft metals are galena (lead sulfide, PbS_2) and cinnabar (mercury sulfide, HgS). Sulfides are the most common soft bases in geology, although the larger halides, like bromide and iodide, are also soft.

Some metals can pair with either hard or soft bases, particularly those metals from the middle of the transition metal group. For example, iron(III) is often found as hematite (iron oxide, Fe_2O_3), whereas iron(II) can also be found as pyrite (iron sulfide, FeS). Molybdenum(VI) can be found as powellite (calcium molybdenum oxide, $CaMoO_4$), but the most commonly mined ore contains molybdenum(IV), found in molybdenite (MoS_2).

? Exercise 4.14.3

Propose a formula for a plausible mineral containing each of the following ions.

a) zirconium(IV)

b) cadmium(II)

c) tungsten(VI)

d) zinc(II)

e) copper(I)

Answer a:

ZrO_2

Answer b:

CdS

Answer c:

WO_3

Answer d:

ZnS

Answer e:

Cu_2S

In biology, metals display aspects of hard & soft acid & base chemistry. Relatively hard potassium ions bind to oxygen atoms in DNA to help stabilize the helix structure. Calmodulin, which aids in calcium uptake, uses hard oxygen donors in aspartate and glutamate to bind to the Ca^{2+}.

On the other hand, copper(I) is a soft acid. In poplar plastocyanin, which aids in transferring electrons during reactions in the plant cell, the copper ion is coordinated to two nitrogen-

donating histidines and two sulfur donors, a cysteine and a methionine.

Many biologically important metal ions fall under the "borderline" category between hard and soft. Iron is one of the most abundant elements on earth, and many iron compounds play important roles in biology. Many biological compounds contain iron(II), which is able to bind well to both hard and soft ligands. Consequently, it is found with anionic oxygen carboxylate donors in methane monooxygenase, neutral and anionic nitrogen porphyrin donors in heme proteins, and sulfur cysteines and sulfides in ferridoxins and other iron-sulfur clusters.

Hard and soft acid and base phenomena have been studied using molecular orbital theory and other quantitative approaches. In MO theory, it has been shown that interactions between hard anions and cations are characterized by large HOMO-LUMO separations, whereas interactions between soft anions and cations are characterized by small HOMO-LUMO separations. In other words, hard acid-base interactions are dominated by more strongly ionic character, but soft acid-base interactions are dominated by more strongly covalent character.

? Exercise 4.14.4

Mercury ions, Hg(I) and Hg(II), are particularly poisonous. They can displace other metals from enzymes, so that the enzymes stop working.

a) are these ions hard or soft?

b) what amino acid residues would most likely bind to them?

Answer a:

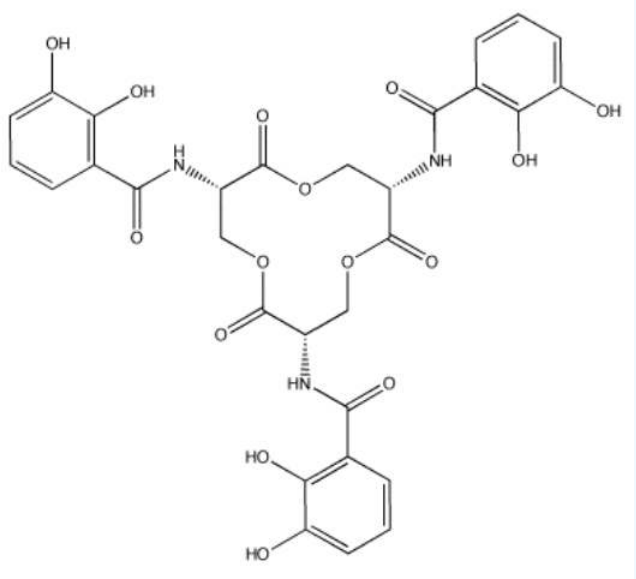
Hg(I) and Hg(II) are both large, polarizable ions. They are soft cations and should bind well to soft donors.

Answer b:

The most common soft donor is a sulfur atom or sulfide ion; in amino acids, that suggests cysteine or methionine.

? Exercise 4.14.5

Enterobactin (below) is a molecule used by certain bacteria to bind iron(III) and transport it into the cell. The formation constant for the iron(III)-enterobactin complex is about 10^{49}. Provide reasons why the formation constant is so high.



Answer

Fe(III) is a hard cation and should bind well to oxygen donors. Enterobactin has several oxygen donors it could provide to the iron. In fact, there is a pair of OH groups on each of the benzene rings in enterobactin. These benzene rings with two OH groups next to each other are called "catechols". Because there are three of these groups in enterobactin, and there is enough space in between for the groups to fold around a central atom, enterobactin is a chelating (hexadentate) donor with a high binding constant.

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CHAPTER OVERVIEW

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5.1: Oxidation States of Transition Metals

The oxidation state of an element is related to the number of electrons that an atom loses, gains, or appears to use when joining with another atom in compounds. It also determines the ability of an atom to oxidize (to lose electrons) or to reduce (to gain electrons) other atoms or species. Almost all of the transition metals have multiple oxidation states experimentally observed.

Introduction

Filling atomic orbitals requires a set number of electrons. The s-block is composed of elements of Groups I and II, the alkali and alkaline earth metals (sodium and calcium belong to this block). Groups XIII through XVIII comprise of the p-block, which contains the nonmetals, halogens, and noble gases (carbon, nitrogen, oxygen, fluorine, and chlorine are common members). Transition metals reside in the d-block, between Groups III and XII. If the following table appears strange, or if the orientations are unclear, please review the section on atomic orbitals.

Table **5.1.1**

s Orbital	p Orbitals	d Orbitals
1 orbital, 2 electrons	3 orbitals: p_x, p_y, p_z; 6 electrons	5 orbitals: $d_{x^2-y^2}$, d_{z^2}, d_{xy}, d_{yz}, d_{xz}; 10 electrons
	Highest energy orbital for a given quantum number n	Degenerate with s-orbital of quantum number n+1

The key thing to remember about electronic configuration is that the most stable noble gas configuration is ideal for any atom. Forming bonds are a way to approach that configuration. In particular, the transition metals form more lenient bonds with anions, cations, and neutral complexes in comparison to other elements. This is because the d orbital is rather diffused (the f orbital of the lanthanide and actinide series more so).

Neutral-Atom Electron Configurations

Counting through the periodic table is an easy way to determine which electrons exist in which orbitals. As mentioned before, by counting protons (atomic number), you can tell the number of electrons in a neutral atom. Organizing by block quickens this process. For example, if we were interested in determining the electronic organization of **Vanadium** (atomic number 23), we would start from hydrogen and make our way down the the Periodic Table).

1s (H, He), 2s (Li, Be), 2p (B, C, N, O, F, Ne), 3s (Na, Mg), 3p (Al, Si, P, S, Cl, Ar), 4s (K, Ca), 3d (Sc, Ti, V).

If you do not feel confident about this counting system and how electron orbitals are filled, please see the section on electron configuration.

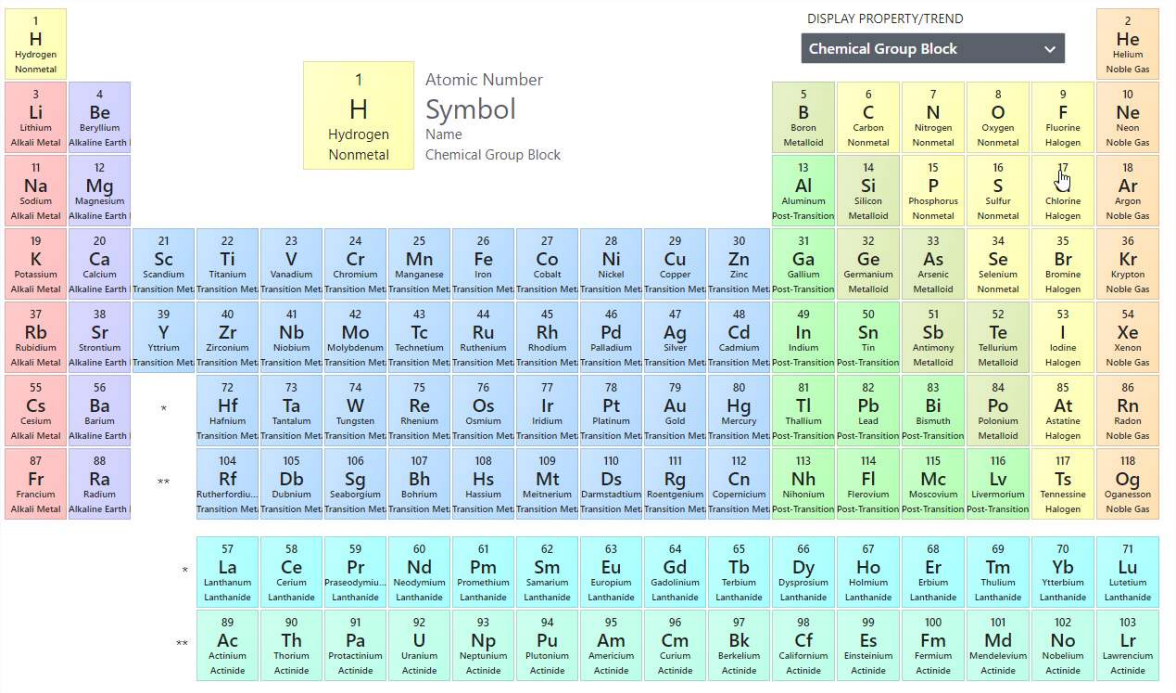


Figure 5.1.1: Periodic Table (Public Domain; PubChem)

Referring to the periodic table below confirms this organization. We have three elements in the 3d orbital. Therefore, we write in the order the orbitals were filled.

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

or

$$[Ar]\ 4s^2\ 3d^3.$$

The neutral atom configurations of the fourth period transition metals are in Table 5.1.2.

Table 5.1.2

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
[Ar] $4s^2 3d^1$	[Ar] $4s^2 3d^2$	[Ar] $4s^2 3d^3$	[Ar] ~~$4s^2 3d^4$~~	[Ar] $4s^2 3d^5$	[Ar] $4s^2 3d^6$	[Ar] $4s^2 3d^7$	[Ar] $4s^2 3d^8$	[Ar] ~~$4s^2 3d^9$~~	[Ar] $4s^2 3d^{10}$
			[Ar] $4s^1 3d^5$					[Ar] $4s^1 3d^{10}$	

Chromium and copper appear anomalous. Take a brief look at where the element **Chromium** (atomic number 24) lies on the Periodic Table (Figure 5.1.1). The electronic configuration for chromium is not [Ar] $4s^2 3d^4$ but instead it is [Ar] $4s^1 3d^5$. This is because the half-filled 3d manifold (with one 4s electron) is more stable than a partially filled d-manifold (and a filled 4s manifold). You will notice from Table 5.1.2 that the copper exhibits a similar phenomenon, although with a fully filled d-manifold.

Oxidation States of Transition Metal Ions

When considering ions, we add or subtract negative charges from an atom. Keeping the atomic orbitals when assigning oxidation numbers in mind helps in recognizing that transition metals pose a special case, but not an exception to this convenient method. An atom that accepts an electron to achieve a more stable configuration is assigned an oxidation number of -1. The donation of an electron is then +1. When a transition metal loses electrons, it tends to lose it's s orbital electrons before any of its d orbital electrons. For more discussion of these compounds form, see formation of coordination complexes.

Example 5.1.1

Write the electronic configurations of:

a. neutral iron,
b. iron(II) ion, and
c. iron(III) ion.

Answer

The atomic number of iron is 26 so there are 26 protons in the species.

a. Fe: [Ar] $4s^2$ $3d^6$
b. Fe^{2+}: [Ar] $3d^6$
c. Fe^{3+}: [Ar] $3d^5$

Note that the s-orbital electrons are lost **first**, then the d-orbital electrons.

Example 5.1.2

Determine the more stable configuration between the following pair:

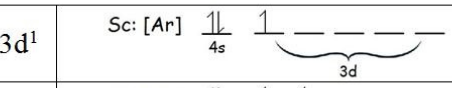
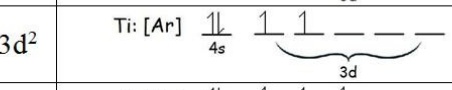
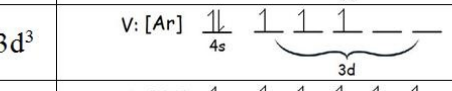
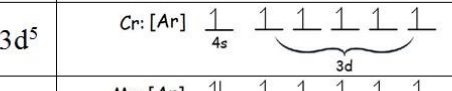
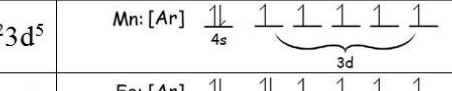
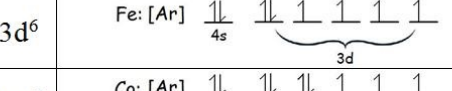
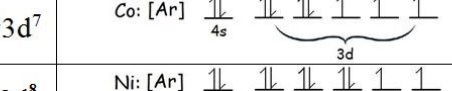
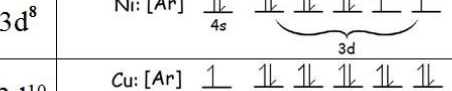
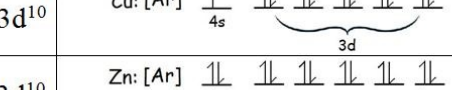
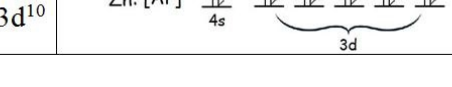
a. [Kr] $5s^2$ $4d^6$ vs. [Kr] $5s^1$ $4d^7$
b. Ag^{1+} vs. Ag^{2+}

Answer

a. This describes Ruthenium. There is only one 5s electron.
b. Once-oxidized silver ([Kr] $4d^{10}$) is more stable than twice- ([Kr] $4d^9$).

Multiple Oxidation States

Most transition metals have multiple oxidation states, since it is relatively easy to lose electron(s) for transition metals compared to the alkali metals and alkaline earth metals. Alkali metals have one electron in their valence s-orbital and their ions almost always have oxidation states of +1 (from losing a single electron). Similarly, alkaline earth metals have two electrons in their valences s-orbitals, resulting in ions with a +2 oxidation state (from losing both). However, transitions metals are more complex and exhibit a range of observable oxidation states due primarily to the removal of d-orbital electrons. The following chart describes the most common oxidation states of the period 3 elements.

Element Name and Symbol	Atomic Number	Common Oxidation States	Electron Configuration	
Scandium (Sc)	21	+3	Sc: [Ar] $4s^2 3d^1$	
Titanium (Ti)	22	+4	Ti: [Ar] $4s^2 3d^2$	
Vanadium (V)	23	+2, +3, +4, +5	V: [Ar] $4s^2 3d^3$	
Chromium (Cr)	24	+2, +3, +6	Cr: [Ar] $4s^1 3d^5$	
Manganese (Mn)	25	+2, +3, +4, +6, +7	Mn: [Ar] $4s^2 3d^5$	
Iron (Fe)	26	+2, +3	Fe: [Ar] $4s^2 3d^6$	
Cobalt (Co)	27	+2, +3	Co: [Ar] $4s^2 3d^7$	
Nickel (Ni)	28	+2	Ni: [Ar] $4s^2 3d^8$	
Copper (Cu)	29	+1,+2	Cu: [Ar] $4s^1 3d^{10}$	
Zinc (Zn)	30	+2	Zn: [Ar] $4s^2 3d^{10}$	

Scandium is one of the two elements in the first transition metal period which has only one oxidation state (zinc is the other, with an oxidation state of +2). All the other elements have at least two different oxidation states. Manganese, which is in the middle of the period, has the highest number of oxidation states, and indeed the highest oxidation state in the whole period since it has five unpaired electrons (see table below).

To help remember the stability of higher oxidation states for transition metals it is important to know the trend: the stability of the higher oxidation states progressively increases down a group. For example, in group 6, (chromium) Cr is most stable at a +3 oxidation state, meaning that you will not find many stable forms of Cr in the +4 and +5 oxidation states. By contrast, there are many stable forms of molybdenum (Mo) and tungsten (W) at +4 and +5 oxidation states.

Example 5.1.3

What makes zinc stable as Zn^{2+}? What makes scandium stable as Sc^{3+}?

Answer

Zinc has the neutral configuration $[Ar]4s^2 3d^{10}$. Losing 2 electrons does not alter the complete d orbital. Neutral scandium is written as $[Ar]4s^2 3d^1$. Losing 3 electrons brings the configuration to the noble state with valence $3p^6$.

Example 5.1.4

Why is iron almost always Fe^{2+} or Fe^{3+}?

Answer

Iron is written as $[Ar]4s^2 3d^6$. Losing 2 electrons from the s-orbital ($3d^6$) or 2 s- and 1 d-orbital ($3d^5$) electron are fairly stable oxidation states.

Example 5.1.5

Write manganese oxides in a few different oxidation states. Which ones are possible and/or reasonable?

Answer

Although Mn^{+2} is the most stable ion for manganese, the d-orbital can be made to remove 0 to 7 electrons. Compounds of manganese therefore range from Mn(0) as $Mn_{(s)}$, Mn(II) as MnO, Mn(II,III) as Mn_3O_4, Mn(IV) as MnO_2, or manganese dioxide, Mn(VII) in the permanganate ion MnO_4^-, and so on.

Oxidation State of Transition Metals in Compounds

When given an ionic compound such as $\mathbf{AgCl}$, you can easily determine the oxidation state of the transition metal. In this case, you would be asked to determine the oxidation state of silver (Ag). Since we know that chlorine (Cl) is in the halogen group of the periodic table, we then know that it has a charge of -1, or simply Cl^-. In addition, by seeing that there is no overall charge for $\mathbf{AgCl}$, (which is determined by looking at the top right of the compound, i.e., $AgCl^{\#}$, where # represents the overall charge of the compound) we can conclude that silver (**Ag**) has an oxidation state of +1. This gives us Ag^+ and Cl^-, in which the positive and negative charge cancels each other out, resulting with an overall neutral charge; therefore +1 is verified as the oxidation state of silver (Ag).

Example 5.1.6

Determine the oxidation state of cobalt in $\mathbf{CoBr_2}$.

Answer

Similar to chlorine, bromine (**Br**) is also a halogen with an oxidation charge of -1 ($\mathbf{Br^-}$). Since there are two bromines each with a charge of -1. In addition, we know that $\mathbf{CoBr_2}$ has an overall neutral charge, therefore we can conclude that the cation (cobalt), **Co** must have an oxidation state of +2 to neutralize the -2 charge from the two bromine anions.

Example 5.1.7

What is the oxidation state of zinc in $\mathbf{ZnCO_3}$. (Note: the $\mathbf{CO_3}$ anion has a charge state of -2)

Answer

Knowing that $\mathbf{CO_3}$ has a charge of -2 and knowing that the overall charge of this compound is neutral, we can conclude that zinc has an oxidation state of +2. This gives us $\mathbf{Zn^{2+}}$ and $\mathbf{CO_3^{-2}}$, in which the positive and negative charges from zinc and carbonate will cancel with each other, resulting in an overall neutral charge expected of a compound.

Polyatomic Transition Metal Ions

Consider the manganese (**Mn**) atom in the permanganate ($\mathbf{MnO_4^-}$) ion. Since oxygen has an oxidation state of -2 and we know there are four oxygen atoms. In addition, this compound has an overall charge of -1; therefore the overall charge is not neutral in this example. Thus, since the oxygen atoms in the ion contribute a total oxidation state of -8, and since the overall charge of the ion is -1, the sole manganese atom must have an oxidation state of +7. This gives us $\mathbf{Mn^{7+}}$ and $\mathbf{4\,O^{2-}}$, which will result as $\mathbf{MnO_4^-}$.

> *This example also shows that manganese atoms can have an oxidation state of +7, which is the highest possible oxidation state for the fourth period transition metals.*

Manganese: A Case Study

Manganese is widely studied because it is an important reducing agent in chemical analysis and is also studied in biochemistry for catalysis and in metallurgy in fortifying alloys. In plants, manganese is required in trace amounts; stronger doses begin to react with enzymes and inhibit some cellular function. Due to manganese's flexibility in accepting many oxidation states, it becomes a good example to describe general trends and concepts behind electron configurations.



Figure 5.1.2: (left) A rough fragment of lustrous silvery metal (CC BY-SA 3.0; Tomihahndorf via Wikipedia) (right) Some of the Lascaux cave paintings use manganese-based pigments. (Public Domain; Prof saxx via Wikipedia)

Electron configurations of unpaired electrons are said to be **paramagnetic** and respond to the proximity of magnets. Fully paired electrons are **diamagnetic** and do not feel this influence. Manganese, in particular, has paramagnetic and diamagnetic orientations depending on what its oxidation state is.

$\mathbf{Mn_2O_3}$ is manganese(III) oxide with manganese in the +3 state. 4 unpaired electrons means this complex is paramagnetic.

$$[Ar]4s^0 3d^4$$

$\mathbf{MnO_2}$ is manganese(IV) oxide, where manganese is in the +4 state. 3 unpaired electrons means this complex is less paramagnetic than Mn^{3+}.

$$[Ar]4s^0 3d^3$$

$\mathbf{KMnO_4}$ is potassium permanganate, where manganese is in the +7 state with no electrons in the 4s and 3d orbitals.

$$[Ar]4s^0 3d^0$$

Since the 3p orbitals are all paired, this complex is diamagnetic.

Summary

Oxidation states of transition metals follow the general rules for most other ions, except for the fact that the d orbital is degenerated with the s orbital of the higher quantum number. Transition metals achieve stability by arranging their electrons accordingly and are oxidized, or they lose electrons to other atoms and ions. These resulting cations participate in the formation of coordination complexes or synthesis of other compounds.

Questions

Determine the oxidation states of the transition metals found in these neutral compounds. Note: The transition metal is underlined in the following compounds.

(A) Copper(I) Chloride: $\underline{Cu}Cl$	(B) Copper(II) Nitrate: $\underline{Cu}(NO_3)_2$	(C) Gold(V) Fluoride: $\underline{Au}F_5$
(D) Iron(II) Oxide: $\underline{Fe}O$	(E) Iron(III) Oxide: $\underline{Fe}_2O_3$	(F) Lead(II) Chloride: $\underline{Pb}Cl_2$
(G) Lead(II) Nitrate: $\underline{Pb}(NO_3)_2$	(H) Manganese(II) Chloride: $\underline{Mn}Cl_2$	(I) Molybdenum trioxide: $\underline{Mo}O_3$
(J) Nickel(II) Hydroxide: $\underline{Ni}(OH)_2$	(K) Platinum(IV) Chloride: $\underline{Pt}Cl_4$	(L) Silver Sulfide: $\underline{Ag}_2S$
(M) Tungsten(VI) Fluoride: $\underline{W}F_6$	(N) Vanadium(III) Nitride: $\underline{V}N$	(O) Zirconium Hydroxide: $\underline{Zr}(OH)_4$

1. Determine the oxidation state of the transition metal for an overall non-neutral compound: Manganate ($\underline{Mn}O_4^{2-}$)
2. Why do transition metals have a greater number of oxidation states than main group metals (i.e. alkali metals and alkaline earth metals)?
3. Which transition metal has the most number of oxidation states?

4. Why does the number of oxidation states for transition metals increase in the middle of the group?
5. What two transition metals have only one oxidation state?

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5.2: General Properties of Transition Metals

We have daily contact with many transition metals. Iron occurs everywhere—from the rings in your spiral notebook and the cutlery in your kitchen to automobiles, ships, buildings, and in the hemoglobin in your blood. Titanium is useful in the manufacture of lightweight, durable products such as bicycle frames, artificial hips, and jewelry. Chromium is useful as a protective plating on plumbing fixtures and automotive detailing.

Transition metals are defined as those elements that have (or readily form) partially filled *d* orbitals. As shown in Figure **5.2.2**, the *d*-block elements in groups 3–11 are transition elements. The *f*-block elements, also called *inner transition metals* (the lanthanides and actinides), also meet this criterion because the *d* orbital is partially occupied before the *f* orbitals. The *d* orbitals fill with the copper family (group 11); for this reason, the next family (group 12) are technically not transition elements. However, the group 12 elements do display some of the same chemical properties and are commonly included in discussions of transition metals. Some chemists do treat the group 12 elements as transition metals.

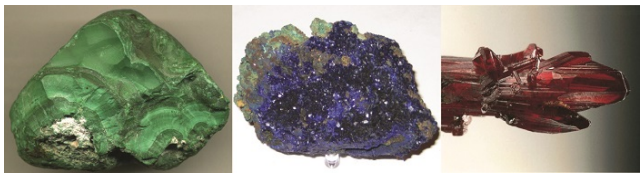


Figure **5.2.1**: Transition metals often form vibrantly colored complexes. The minerals malachite (green), azurite (blue), and proustite (red) are some examples. (credit left: modification of work by James St. John; credit middle: modification of work by Stephanie Clifford; credit right: modification of work by Terry Wallace)

The *d*-block elements are divided into the first transition series (the elements Sc through Cu), the second transition series (the elements Y through Ag), and the third transition series (the element La and the elements Hf through Au). Actinium, Ac, is the first member of the fourth transition series, which also includes Rf through Rg.

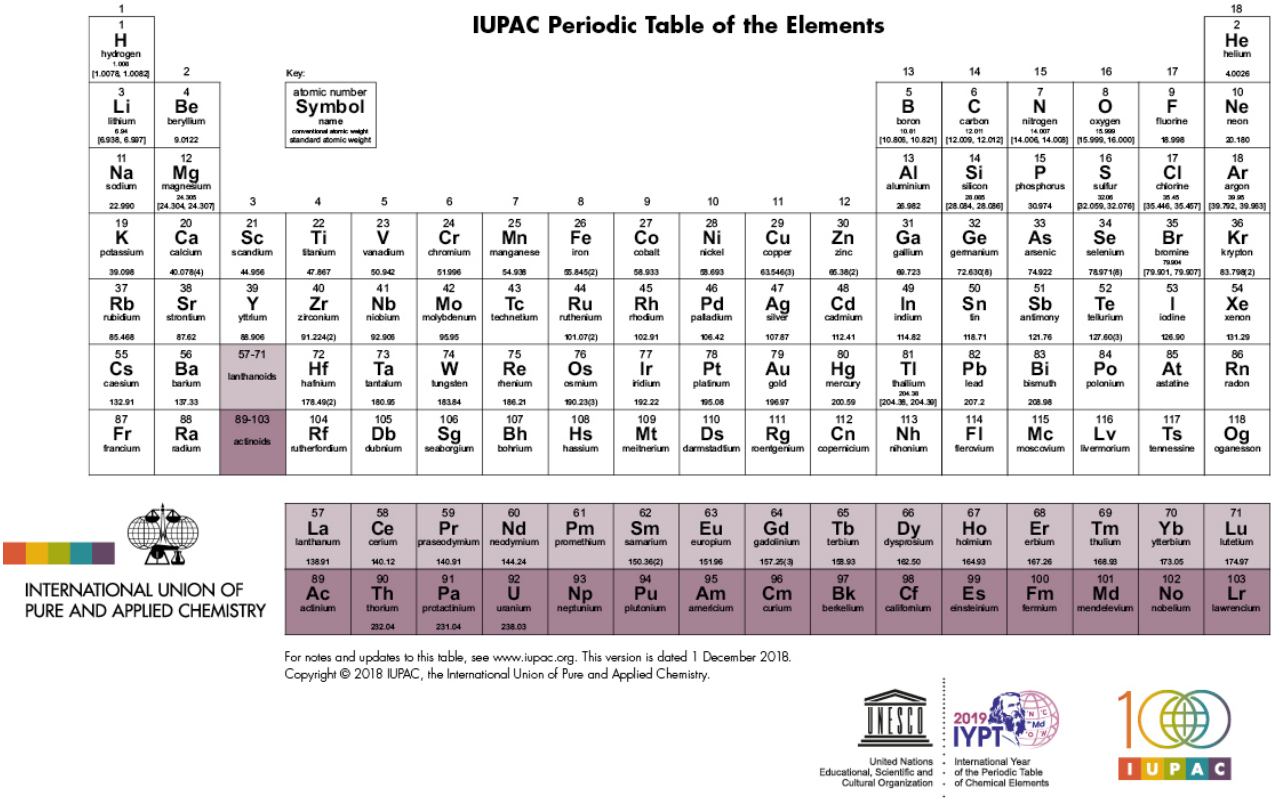


Figure **5.2.2**: The transition metals are located in groups 3–11 of the periodic table. The inner transition metals are in the two rows below the body of the table.

The *f*-block elements are the elements Ce through Lu, which constitute the lanthanide series (or lanthanoid series), and the elements Th through Lr, which constitute the actinide series (or actinoid series). Because lanthanum behaves very much like the lanthanide elements, it is considered a lanthanide element, even though its electron configuration makes it the first member of the third transition series. Similarly, the behavior of actinium means it is part of the actinide series, although its electron configuration makes it the first member of the fourth transition series

Properties and Trends in Transition Metals

The elements of the second and third rows of the Periodic Table show gradual changes in properties across the table from left to right as expected. Electrons in the outer shells of the atoms of these elements have little shielding effects resulting in an increase in effective nuclear charge due to the addition of protons in the nucleus. Consequently, the effects on atomic properties are: smaller atomic radius, increased first ionization energy, enhanced electronegativity and more nonmetallic character. This trend continues until one reaches calcium (Z=20). There is an abrupt break at this point. The next ten elements called the first transition series are remarkably similar in their physical and chemical properties. This general similarity in properties has been explained in terms of their relatively small difference in effective nuclear charge over the series. This occurs because each additional electron enters the penultimate 3d shell providing an effective shield between the nucleus and the outer 4s shell.

What is a Transition Metal?

Thus, the transition elements can be defined as those in which the d electron shells are being filled and so we generally ignore Sc and Zn where Sc(III) is d^0 and Zn(II) is d^{10}.

It is useful, at the beginning, to identify the physical and chemical properties of transition elements which differ from main group elements (s-block). Properties of transition elements include:

- have large charge/radius ratio;
- are hard and have high densities;
- have high melting and boiling points;
- form compounds which are often paramagnetic;
- show variable oxidation states;
- form coloured ions and compounds;
- form compounds with profound catalytic activity;
- form stable complexes.

Table **5.2.1** : Summary of select physical properties of transition elements:

Element	Group	density /g cm^{-3}	m. p. / °C	b.p. / °C	radius / pm	free atom configuration	ionization energy / kJ mol^{-1}	Uses
Sc	3	2.99	1541	2831	164	[Ar] $3d^1 4s^2$	631	
Ti	4	4.50	1660	3287	147	[Ar]$3d^2 4s^2$	658	-engines/aircraft industry-density is 60% of iron
V	5	5.96	1890	3380	135	[Ar]$3d^3 4s^2$	650	-stainless steel, 19% Cr, 9% Ni the rest Fe
Cr	6	7.20	1857	2670	129	[Ar]$3d^5 4s^1$	653	-alloys eg with C steel, the most significant use
Mn	7	7.20	1244	1962	137	[Ar]$3d^5 4s^2$	717	-alloys eg with Cu
Fe	8	7.86	1535	2750	126	[Ar]$3d^6 4s^2$	759	-alloys eg with C steel, the most significant use
Co	9	8.90	1495	2870	125	[Ar]$3d^7 4s^2$	758	-alloys eg with Cr and W for hardened drill bits
Ni	10	8.90	1455	2730	125	[Ar]$3d^8 4s^2$	737	-alloys Fe/Ni armor plating, resists corrosion
Cu	11	8.92	1083	2567	128	[Ar]$3d^{10} 4s^1$	746	-high electrical conductivity (2nd to Ag), wiring
Zn	12	7.14	420	907	137	[Ar]$3d^{10} 4s^2$	906	

Densities and Metallic Radii

The transition elements are much denser than the s-block elements and show a gradual increase in density from scandium to copper. This trend in density can be explained by the small and irregular decrease in metallic radii coupled with the relative increase in atomic mass.

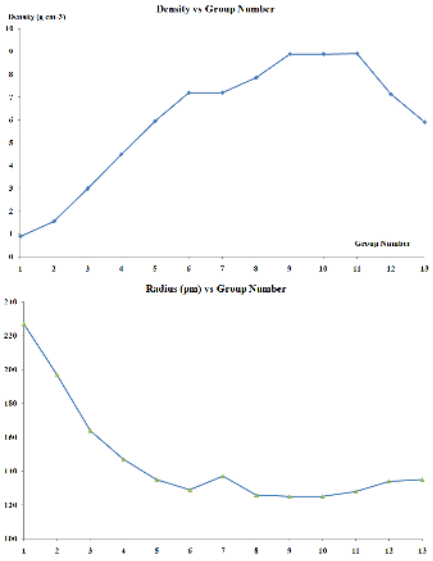


Figure **5.2.3**: Variations of the density (leff) and metallic radius (right) in the first row transition metals.

Melting and Boiling points

The melting points and the molar enthalpies of fusion of the transition metals are both high in comparison to main group elements. This arises from strong metallic bonding in transition metals which occurs due to delocalization of electrons facilitated by the availability of both d and s electrons.

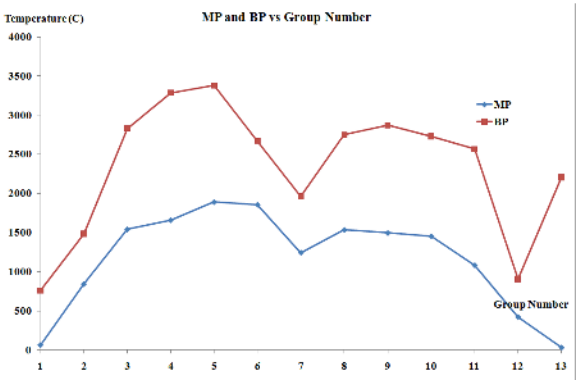


Figure **5.2.4**: Variations of the melting point (blue curve) and boiling points (red) in the first row transition metals.

Ionization Energies

In moving across the series of metals from scandium to zinc a small change in the values of the first and second ionization energies is observed. This is due to the build-up of electrons in the immediately underlying d-sub-shells that efficiently shields the 4s electrons from the nucleus and minimizing the increase in effective nuclear charge Z_{eff} from element to element. The increases in third and fourth ionization energy values are more rapid. However, the trends in these values show the usual discontinuity half way along the series. The reason is that the five d electrons are all unpaired, in singly occupied orbitals. When the sixth and subsequent electrons enter, the electrons have to share the already occupied orbitals resulting in inter-electron repulsions, which would require less energy to remove an electron. Hence, the third ionization energy curve for the last five elements is identical in shape to the curve for the first five elements, but displaced upwards by 580 kJ mol^{-1}.

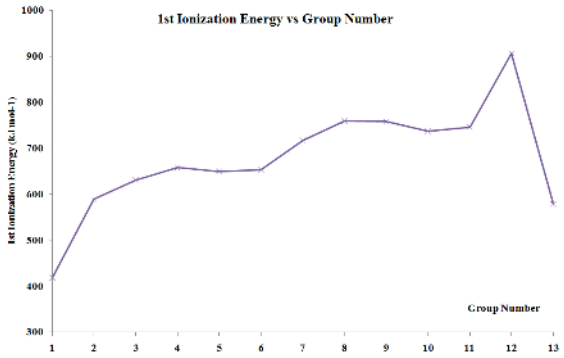


Figure **5.2.4**: Variations of the first ionization energy in the first row transition metals.

Oxidation States

Transition metals can form compounds with a wide range of oxidation states. Some of the observed oxidation states of the elements of the first transition series are shown in Figure **5.2.5**. As we move from left to right across the first transition series, we see that the number of common oxidation states increases at first to a maximum towards the middle of the table, then decreases. The values in the table are typical values; there are other known values, and it is possible to synthesize new additions. For example, in 2014, researchers were successful in synthesizing a new oxidation state of iridium (9+).

21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
								1+	
		2+	2+	2+	2+	2+	2+	2+	2+
3+	3+	3+	3+	3+	3+	3+	3+	3+	
	4+	4+	4+	4+					
		5+							
			6+	6+	6+				
				7+					

Figure **5.2.5**:Transition metals of the first transition series can form compounds with varying oxidation states.

For the elements scandium through manganese (the first half of the first transition series), the highest oxidation state corresponds to the loss of all of the electrons in both the *s* and *d* orbitals of their valence shells. The titanium(IV) ion, for example, is formed when the titanium atom loses its two 3*d* and two 4*s* electrons. These highest oxidation states are the most stable forms of scandium, titanium, and vanadium. However, it is not possible to continue to remove all of the valence electrons from metals as we continue through the series. Iron is known to form oxidation states from 2+ to 6+, with iron(II) and iron(III) being the most common. Most of the elements of the first transition series form ions with a charge of 2+ or 3+ that are stable in water, although those of the early members of the series can be readily oxidized by air.

The elements of the second and third transition series generally are more stable in higher oxidation states than are the elements of the first series. In general, the atomic radius increases down a group, which leads to the ions of the second and third series being larger than are those in the first series. Removing electrons from orbitals that are located farther from the nucleus is easier than removing electrons close to the nucleus. For example, molybdenum and tungsten, members of group 6, are limited mostly to an oxidation state of 6+ in aqueous solution. Chromium, the lightest member of the group, forms stable Cr^{3+} ions in water and, in the absence of air, less stable Cr^{2+} ions. The sulfide with the highest oxidation state for chromium is Cr_2S_3, which contains the Cr^{3+} ion. Molybdenum and tungsten form sulfides in which the metals exhibit oxidation states of 4+ and 6+.

Electronic Configurations

The electronic configuration of the atoms of the first row transition elements are basically the same. It can be seen in the Table above that there is a gradual filling of the 3d orbitals across the series starting from scandium. This filling is, however, not regular, since at chromium and copper the population of 3d orbitals increase by the acquisition of an electron from the 4s shell. This illustrates an important generalization about orbital energies of the first row transition series. At chromium, both the 3d and 4s orbitals are occupied, but neither is completely filled in preference to the other. This suggests that the energies of the 3d and 4s orbitals are relatively close for atoms in this row.

In the case of copper, the 3d level is full, but only one electron occupies the 4s orbital. This suggests that in copper the 3d orbital energy is lower than the 4s orbital. Thus the 3d orbital energy has passed from higher to lower as we move across the period from

potassium to zinc. However, the whole question of preference of an atom to adopt a particular electronic configuration is not determined by orbital energy alone. In chromium it can be shown that the 4s orbital energy is still below the 3d which suggests a configuration [Ar] $3d^4 4s^2$. However due to the effect of electronic repulsion between the outer electrons the actual configuration becomes [Ar]$3d^5 4s^1$ where all the electrons in the outer orbitals are unpaired. It should be remembered that the factors that determine electronic configuration in this period are indeed delicately balanced.

Redox Couple	E°/V
Mn^{2+}(aq.)/Mn(s)	-1.18
H^+(aq.)/H_2(g)	0.00

This shows that elemental Mn is a stronger reductant than molecular hydrogen and hence should be able to displace hydrogen gas from 1 mol dm^{-3} hydrochloric acid.

Valence Electrons in Transition Metals

Review how to write electron configurations, covered in the chapter on electronic structure and periodic properties of elements. Recall that for the transition and inner transition metals, it is necessary to remove the *s* electrons before the *d* or *f* electrons. Then, for each ion, give the electron configuration:

a. cerium(III)
b. lead(II)
c. Ti^{2+}
d. Am^{3+}
e. Pd^{2+}

For the examples that are transition metals, determine to which series they belong.

Solution

For ions, the *s*-valence electrons are lost prior to the *d* or *f* electrons.

a. Ce^{3+}[Xe]$4f^1$; Ce^{3+} is an inner transition element in the lanthanide series.
b. Pb^{2+}[Xe]$6s^2 5d^{10} 4f^{14}$; the electrons are lost from the *p* orbital. This is a main group element.
c. titanium(II) [Ar]$3d^2$; first transition series
d. americium(III) [Rn]$5f^6$; actinide
e. palladium(II) [Kr]$4d^8$; second transition series

Exercise 5.2.1

Check Your Learning Give an example of an ion from the first transition series with no *d* electrons.

Answer

V^{5+} is one possibility. Other examples include Sc^{3+}, Ti^{4+}, Cr^{6+}, and Mn^{7+}.

Chemical Reactivity

Transition metals demonstrate a wide range of chemical behaviors. As can be seen from their reduction potentials (Table P1), some transition metals are strong reducing agents, whereas others have very low reactivity. For example, the lanthanides all form stable 3+ aqueous cations. The driving force for such oxidations is similar to that of alkaline earth metals such as Be or Mg, forming Be^{2+} and Mg^{2+}. On the other hand, materials like platinum and gold have much higher reduction potentials. Their ability to resist oxidation makes them useful materials for constructing circuits and jewelry.

Ions of the lighter *d*-block elements, such as Cr^{3+}, Fe^{3+}, and Co^{2+}, form colorful hydrated ions that are stable in water. However, ions in the period just below these (Mo^{3+}, Ru^{3+}, and Ir^{2+}) are unstable and react readily with oxygen from the air. The majority of

simple, water-stable ions formed by the heavier *d*-block elements are oxyanions such as MoO_4^{2-} and ReO_4^-.

Ruthenium, osmium, rhodium, iridium, palladium, and platinum are the *"platinum metals"*. With difficulty, they form simple cations that are stable in water, and, unlike the earlier elements in the second and third transition series, they do not form stable oxyanions.

Both the *d*- and *f*-block elements react with nonmetals to form binary compounds; heating is often required. These elements react with halogens to form a variety of halides ranging in oxidation state from 1+ to 6+. On heating, oxygen reacts with all of the transition elements except palladium, platinum, silver, and gold. The oxides of these latter metals can be formed using other reactants, but they decompose upon heating. The *f*-block elements, the elements of group 3, and the elements of the first transition series except copper react with aqueous solutions of acids, forming hydrogen gas and solutions of the corresponding salts.

✔ Activity of the Transition Metals

Which is the strongest oxidizing agent in acidic solution: dichromate ion, which contains chromium(VI), permanganate ion, which contains manganese(VII), or titanium dioxide, which contains titanium(IV)?

Solution

First, we need to look up the reduction half reactions (Table P1) for each oxide in the specified oxidation state:

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O \quad +1.33\,V \tag{5.2.1}$$

$$MnO_4^- + 8\,H^+ + 5\,e^- \longrightarrow Mn^{2+} + H_2O \quad +1.51\,V \tag{5.2.2}$$

$$TiO_2 + 4\,H^+ + 2\,e^- \longrightarrow Ti^{2+} + 2\,H_2O \quad -0.50\,V \tag{5.2.3}$$

A larger reduction potential means that it is easier to reduce the reactant. Permanganate, with the largest reduction potential, is the strongest oxidizer under these conditions. Dichromate is next, followed by titanium dioxide as the weakest oxidizing agent (the hardest to reduce) of this set.

? Exercise 5.2.2

Predict what reaction (if any) will occur between HCl and Co(*s*), and between HBr and Pt(*s*). You will need to use the standard reduction potentials from (Table P1).

Answer

$Co(s) + 2\,HCl \longrightarrow H_2 + CoCl_2(aq)$; no reaction because Pt(*s*) will not be oxidized by H^+

Contributors and Attributions

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- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)

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5.3: Introduction to Transition Metals I

The elements of the second and third rows of the Periodic Table show gradual changes in properties across the table from left to right as expected. Electrons in the outer shells of the atoms of these elements have little shielding effects resulting in an increase in effective nuclear charge due to the addition of protons in the nucleus. Consequently, the effects on atomic properties are: smaller atomic radius, increased first ionization energy, enhanced electronegativity and more nonmetallic character. This trend continues until one reaches calcium (Z=20). There is an abrupt break at this point. The next ten elements called the first transition series are remarkably similar in their physical and chemical properties. This general similarity in properties has been explained in terms of their relatively small difference in effective nuclear charge over the series. This occurs because each additional electron enters the penultimate 3d shell providing an effective shield between the nucleus and the outer 4s shell.

Thus, the transition elements can be defined as those in which the d electron shells are being filled and so we generally ignore Sc and Zn where Sc(III) is d^0 and Zn(II) is d^{10}.

Physical Properties

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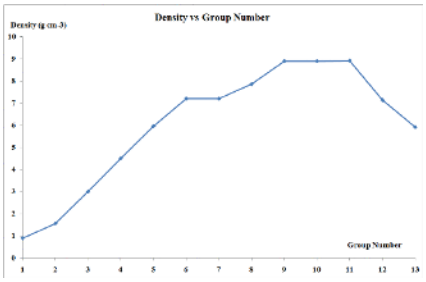
- have large charge/radius ratio;
- are hard and have high densities;
- have high melting and boiling points;
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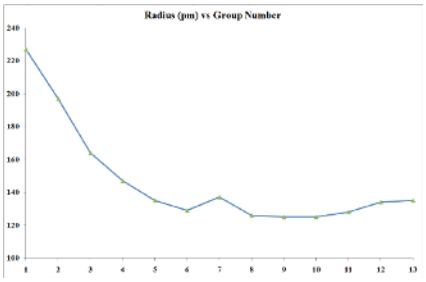
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V	5	5.96	1890	3380	135	[Ar]$3d^3 4s^2$	650	-stainless steel, 19% Cr, 9% Ni the rest Fe
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Densities and metallic radii

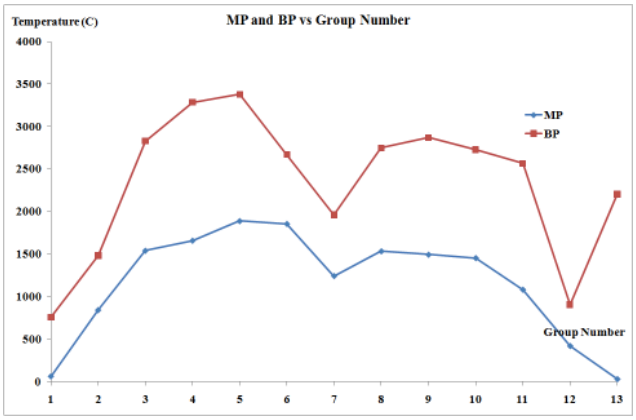
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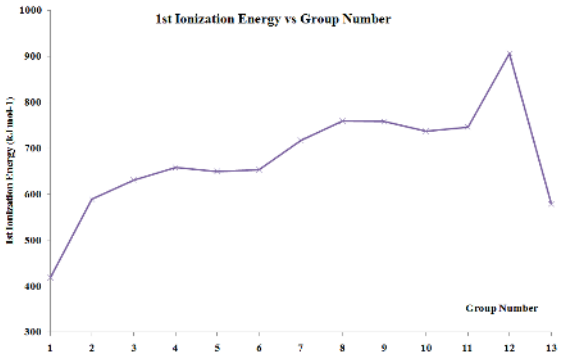
Melting and boiling points

The melting points and the molar enthalpies of fusion of the transition metals are both high in comparison to main group elements. This arises from strong metallic bonding in transition metals which occurs due to delocalization of electrons facilitated by the availability of both d and s electrons.



Ionization Energies

In moving across the series of metals from scandium to zinc a small change in the values of the first and second ionization energies is observed. This is due to the build-up of electrons in the immediately underlying d-sub-shells that efficiently shields the 4s electrons from the nucleus and minimizing the increase in effective nuclear charge from element to element. The increases in third and fourth ionization energy values are more rapid. However, the trends in these values show the usual discontinuity half way along the series. The reason is that the five d electrons are all unpaired, in singly occupied orbitals. When the sixth and subsequent electrons enter, the electrons have to share the already occupied orbitals resulting in inter-electron repulsions, which would require less energy to remove an electron. Hence, the third ionization energy curve for the last five elements is identical in shape to the curve for the first five elements, but displaced upwards by 580 kJ mol^{-1}.



Electronic Configurations

The electronic configuration of the atoms of the first row transition elements are basically the same. It can be seen in the Table above that there is a gradual filling of the 3d orbitals across the series starting from scandium. This filling is, however, not regular, since at chromium and copper the population of 3d orbitals increase by the acquisition of an electron from the 4s shell. This illustrates an important generalization about orbital energies of the first row transition series. At chromium, both the 3d and 4s orbitals are occupied, but neither is completely filled in preference to the other. This suggests that the energies of the 3d and 4s orbitals are relatively close for atoms in this row.

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Redox Couple	E°/V
$Mn^{2+}(aq.)/Mn(s)$	-1.18
$H^+(aq.)/H_2(g)$	0.00

This shows that elemental Mn is a stronger reductant than molecular hydrogen and hence should be able to displace hydrogen gas from 1 mol dm^{-3} hydrochloric acid.

Contributors and Attributions

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5.4: Introduction to Transition Metals II

This page explains what a transition metal is in terms of its electronic structure, and then goes on to look at the general features of transition metal chemistry. These include variable oxidation state (oxidation number), complex ion formation, colored ions, and catalytic activity.

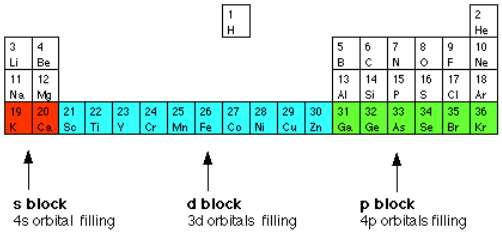
What is a transition metal?

The terms transition metal (or element) and d block element are sometimes used as if they mean the same thing. They don't - there's a subtle difference between the two terms. We'll explore d block elements first:

d-block elements

You will remember that when you are building the Periodic Table and working out where to put the electrons using the Aufbau Principle, something odd happens after argon.

At argon, the 3s and 3p levels are full, but rather than fill up the 3d levels next, the 4s level fills instead to give potassium and then calcium. Only after that do the 3d levels fill. The elements in the Periodic Table which correspond to the d levels filling are called **d block elements**. The first row of these is shown in the shortened form of the Periodic Table below.



The electronic structures of the d block elements shown are:

Sc	[Ar] $\mathbf{3d^1}4s^2$
Ti	[Ar] $\mathbf{3d^2}4s^2$
V	[Ar] $\mathbf{3d^3}4s^2$
Cr	[Ar] $\mathbf{3d^5 4s^1}$
Mn	[Ar] $\mathbf{3d^5 4s^2}$
Fe	[Ar] $\mathbf{3d^6}4s^2$
Co	[Ar] $\mathbf{3d^7}4s^2$
Ni	[Ar] $\mathbf{3d^8}4s^2$
Cu	[Ar] $\mathbf{3d^{10} 4s^1}$
Zn	[Ar] $\mathbf{3d^{10} 4s^2}$

You will notice that the pattern of filling is not entirely tidy! It is broken at both chromium and copper.

Transition metals

> Not all d block elements count as transition metals! There are two slightly different definitions in use at the moment both of which crop up in various uses:
>
> *The official IUPAC definition:*

> **A transition metal is one which has an atom with an incompletely filled d orbital or which forms one or more stable ions with incompletely filled d orbitals.**
>
> *The older definition:*
>
> **A transition metal is one which forms one or more stable ions which have *incompletely* filled d orbitals.**

Notice how similar these two definitions are. The only difference is that the IUPAC definition allows for the atom itself having incompletely filled d levels as well as the ions.

The problem lies only at the extreme left-hand end of the d block with, for example, scandium: Scandium has the electronic structure [Ar] $3d^1 4s^2$. When it forms ions, it always loses the 3 outer electrons and ends up with an argon structure. The Sc^{3+} ion has **no d electrons** and so does not meet the second (older) definition.

Zinc has the electronic structure [Ar] $3d^{10} 4s^2$. When it forms ions, it always loses the two 4s electrons to give a 2+ ion with the electronic structure [Ar] $3d^{10}$. The zinc ion has **full d levels** and does not meet either definition.

By contrast, copper, [Ar] $3d^{10} 4s^1$, forms two ions. In the Cu^+ ion the electronic structure is [Ar] $3d^{10}$. However, the more common Cu^{2+} ion has the structure [Ar] $3d^9$. Copper is definitely a transition metal because the Cu^{2+} ion has an incomplete d level.

Transition metal ions

Here you are faced with one of the most irritating facts in chemistry at this level! When you work out the electronic structures of the first transition series (from scandium to zinc) using the Aufbau Principle, you do it on the basis that the 3d orbitals have higher energies than the 4s orbitals.

That means that you work on the assumption that the 3d electrons are added after the 4s ones. However, in all the chemistry of the transition elements, the 4s orbital behaves as the outermost, highest energy orbital.

> It is important to note that when d block elements form ions, the 4s electrons are always lost first.

To write the electronic structure for Co^{2+}:

Co		[Ar] $3d^7 4s^2$
Co^{2+}		[Ar] $3d^7$

The 2+ ion is formed by the loss of the two 4s electrons.

To write the electronic structure for V^{3+}:

V		[Ar] $3d^3 4s^2$
V^{3+}		[Ar] $3d^2$

The 4s electrons are lost first followed by one of the 3d electrons.

Variable oxidation state (number)

One of the key features of transition metal chemistry is the wide range of oxidation states (oxidation numbers) that the metals can show. It would be wrong, though, to give the impression that only transition metals can have variable oxidation states. For example, elements like Sulfur or nitrogen or chlorine have a very wide range of oxidation states in their compounds - and these obviously aren't transition metals. However, this variability is less common in metals apart from the transition elements. Of the familiar metals from the main groups of the Periodic Table, only lead and tin show variable oxidation state to any extent.

Examples of variable oxidation states in the transition metals

- **Iron:** Iron has two common oxidation states (+2 and +3) in, for example, Fe^{2+} and Fe^{3+}. It also has a less common +6 oxidation state in the ferrate(VI) ion, FeO_4^{2-}.
- **Manganese:** Manganese has a very wide range of oxidation states in its compounds. For example:

+2	in Mn^{2+}
+3	in Mn_2O_3
+4	in MnO_2
+6	in MnO_4^{2-}
+7	in MnO_4^-

You will find the above examples and others looked at in detail if you explore the chemistry of individual metals from the transition metal menu. There is a link to this menu at the bottom of the page.

Explaining the variable oxidation states in the transition metals

We'll look at the formation of simple ions like Fe^{2+} and Fe^{3+}. When a metal forms an ionic compound, the formula of the compound produced depends on the energetics of the process. On the whole, the compound formed is the one in which most energy is released. The more energy released, the more stable the compound. There are several energy terms to think about, but the key ones are:

- The amount of energy needed to ionize the metal (the sum of the various ionization energies)
- The amount of energy released when the compound forms. This will either be lattice enthalpy if you are thinking about solids, or the hydration enthalpies of the ions if you are thinking about solutions.

The more highly charged the ion, the more electrons you have to remove and the more ionization energy you will have to provide. But off-setting this, the more highly charged the ion, the more energy is released either as lattice enthalpy or the hydration enthalpy of the metal ion.

Thinking about a typical non-transition metal (calcium)

The formula for Calcium chloride is $CaCl_2$. Why is that? If you tried to make CaCl, (containing a Ca^+ ion), the overall process is slightly exothermic. By making a Ca^{2+} ion instead, you have to supply more ionization energy, but you get out lots more lattice energy. There is much more attraction between chloride ions and Ca^{2+} ions than there is if you only have a 1+ ion. The overall process is very exothermic. Because the formation of $CaCl_2$ releases much more energy than making CaCl, then $CaCl_2$ is more stable - and so forms instead.

What about $CaCl_3$? This time you have to remove yet another electron from calcium. The first two come from the 4s level. The third one comes from the 3p. That is much closer to the nucleus and therefore much more difficult to remove. There is a large jump in ionization energy between the second and third electron removed. Although there will be a gain in lattice enthalpy, it is not anything like enough to compensate for the extra ionization energy, and the overall process is very endothermic. It definitely is not energetically sensible to make $CaCl_3$!

Thinking about a typical transition metal (iron)

Here are the changes in the electronic structure of iron to make the 2+ or the 3+ ion.

Fe		[Ar] $3d^6 4s^2$
Fe^{2+}		[Ar] $3d^6$
Fe^{3+}		[Ar] $3d^5$

The 4s orbital and the 3d orbitals have very similar energies. There is not a huge jump in the amount of energy you need to remove the third electron compared with the first and second. The figures for the first three ionization energies (in kJ mol^{-1}) for iron compared with those of calcium are:

metal	1st IE	2nd IE	3rd IE
Ca	590	1150	4940
Fe	762	1560	2960

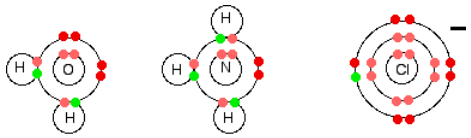
There is an increase in ionization energy as you take more electrons off an atom because you have the same number of protons attracting fewer electrons. However, there is much less increase when you take the third electron from iron than from calcium.

In the iron case, the extra ionization energy is compensated more or less by the extra lattice enthalpy or hydration enthalpy evolved when the 3+ compound is made. The net effect of all this is that the overall enthalpy change is not vastly different whether you make, say, $FeCl_2$ or $FeCl_3$. That means that it is not too difficult to convert between the two compounds.

The formation of complex ions

What is a complex ion?

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



What all these have got in common is active lone pairs of electrons in the outer energy level. These are used to form co-ordinate bonds with the metal ion.

Some examples of complex ions formed by transition metals

$[Fe(H_2O)_6]^{2+}$

$[Co(NH_3)_6]^{2+}$

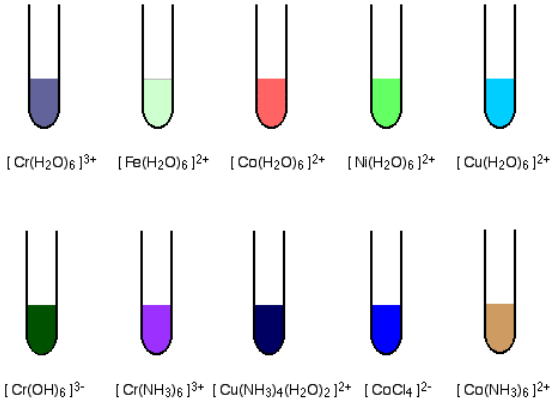
$[Cr(OH)_6]^{3-}$

$[CuCl_4]^{2-}$

Other metals also form complex ions - it is not something that only transition metals do. Transition metals do, however, form a very wide range of complex ions.

The formation of colored compounds

The diagrams show approximate colors for some common transition metal complex ions.



You will find these and others discussed if you follow links to individual metals from the transition metal menu (link at the bottom of the page). Alternatively, you could explore the complex ions menu (follow the link in the help box which has just disappeared off the top of the screen).

The origin of color in the transition metal ions

When white light passes through a solution of one of these ions, or is reflected off it, some colors in the light are absorbed. The color you see is how your eye perceives what is left. Attaching ligands to a metal ion has an effect on the energies of the d orbitals. Light is absorbed as electrons move between one d orbital and another. This is explained in detail on another page.

Catalytic Activity

Transition metals and their compounds are often good catalysts. A few of the more obvious cases are mentioned below, but you will find catalysis explored in detail elsewhere on the site (follow the link after the examples). Transition metals and their compounds function as catalysts either because of their ability to change oxidation state or, in the case of the metals, to adsorb other substances on to their surface and activate them in the process. All this is explored in the main catalysis section.

Iron in the Haber Process

The Haber Process combines hydrogen and nitrogen to make ammonia using an iron catalyst.

$$N_{2(g)} + 3H_{2(g)} \underset{}{\overset{Fe}{\rightleftharpoons}} 2NH_{3(g)}$$

Nickel in the hydrogenation of C=C bonds

This reaction is at the heart of the manufacture of margarine from vegetable oils. However, the simplest example is the reaction between ethene and hydrogen in the presence of a nickel catalyst.

$$CH_2{=}CH_2 + H_2 \xrightarrow{Ni} CH_3CH_3$$

Transition metal compounds as catalysts

Vanadium(V) oxide in the Contact Process

At the heart of the Contact Process is a reaction which converts Sulfur dioxide into Sulfur trioxide. Sulfur dioxide gas is passed together with air (as a source of oxygen) over a solid vanadium(V) oxide catalyst.

$$2SO_{2(g)} + O_{2(g)} \underset{}{\overset{V_2O_5}{\rightleftharpoons}} 2SO_{3(g)}$$

Iron ions in the reaction between persulfate ions and iodide ions

Persulphate ions (peroxodisulphate ions), $S_2O_8^{2-}$, are very powerful oxidizing agents. Iodide ions are very easily oxidized to iodine. And yet the reaction between them in solution in water is very slow. The reaction is catalyzed by the presence of either iron(II) or iron(III) ions.

$$S_2O_8^{2-} + 2I^- \rightarrow 2SO_4^{2-} + I_2$$

Contributors and Attributions

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5.5: Werner's Theory of Coordination Compounds

Learning Objectives

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

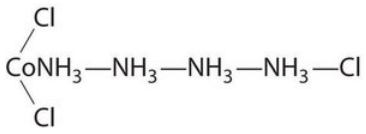
One of the most important properties of metallic elements is their ability to act as Lewis acids that form complexes with a variety of Lewis bases. A metal complex consists of a central metal atom or ion that is bonded to one or more ligands (from the Latin ligare, meaning "to bind"), which are ions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

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

History of the Coordination Compounds

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

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



$\mathbf{CoCl_3 \cdot 4NH_3}$

The modern theory of coordination chemistry is based largely on the work of Alfred Werner (1866–1919; Nobel Prize in Chemistry in 1913). In a series of careful experiments carried out in the late 1880s and early 1890s, he examined the properties of several series of metal halide complexes with ammonia. For example, five different "adducts" of ammonia with $PtCl_4$ were known at the time: $PtCl_4 \cdot nNH_3$ (n = 2–6). Some of Werner's original data on these compounds are shown in Table **5.5.1**. The electrical conductivity of aqueous solutions of these compounds was roughly proportional to the number of ions formed per mole, while the number of chloride ions that could be precipitated as AgCl after adding $Ag^+(aq)$ was a measure of the number of "free" chloride

ions present. For example, Werner's data on $PtCl_4 \cdot 6NH_3$ in Table **5.5.1** showed that all the chloride ions were present as free chloride. In contrast, $PtCl_4 \cdot 2NH_3$ was a neutral molecule that contained no free chloride ions.

Alfred Werner (1866–1919)

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

Table **5.5.1**: Werner's Data on Complexes of Ammonia with $PtCl_4$

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

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

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

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

Werner's studies on the analogous Co^{3+} complexes also allowed him to propose a structural model for metal complexes with a coordination number of 6. Thus he found that $[Co(NH_3)_6]Cl_3$ (yellow) and $[Co(NH_3)_5Cl]Cl_2$ (purple) were 1:3 and 1:2 electrolytes. Unexpectedly, however, two different $[Co(NH_3)_4Cl_2]Cl$ compounds were known: one was red, and the other was green (Figure **5.5.1***a*). Because both compounds had the same chemical composition and the same number of groups of the same kind attached to the same metal, there had to be something different about the arrangement of the ligands around the metal ion. Werner's key insight was that the six ligands in $[Co(NH_3)_4Cl_2]Cl$ had to be arranged at the vertices of an octahedron because that was the only structure consistent with the existence of two, and only two, arrangements of ligands (Figure **5.5.1***b*. His conclusion was corroborated by the existence of only two different forms of the next compound in the series: $Co(NH_3)_3Cl_3$.

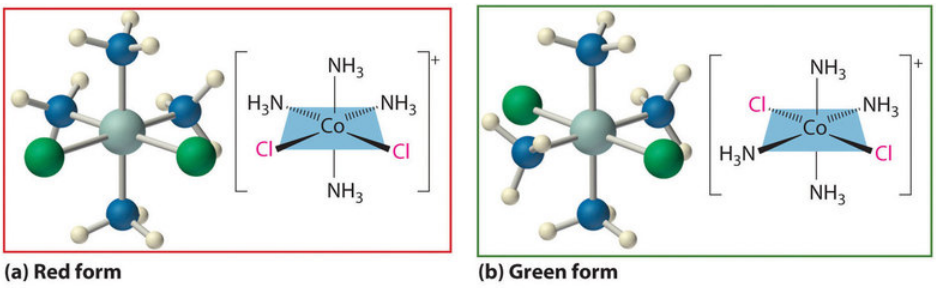


Figure **5.5.1**: Complexes with Different Arrangements of the Same Ligands Have Different Properties. The $[Co(NH_3)_4Cl_2]^+$ ion can have two different arrangements of the ligands, which results in different colors: if the two Cl^- ligands are next to each other, the complex is red (a), but if they are opposite each other, the complex is green (b).

Example 5.5.1

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

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

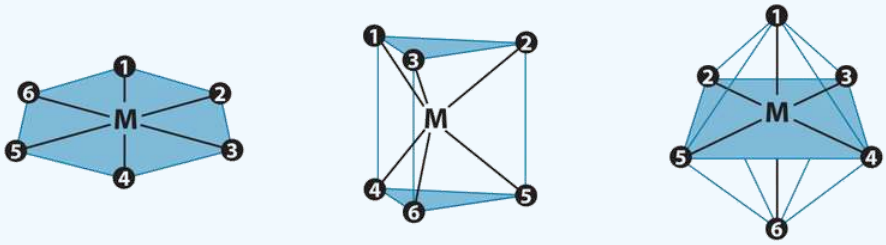
Asked for: number of different arrangements of ligands for MA_4B_2 complex for each structure

Strategy:

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

Solution

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



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

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

In the octahedron, however, if we place the first B ligand at position 1, then we have only two choices for the second B ligand: at position 2 (or 3 or 4 or 5) or position 6. In the latter, the two B ligands are at opposite vertices of the octahedron, with the

metal lying directly between them. Although there are four possible arrangements for the former, they are chemically identical because in all cases the two B ligands are adjacent to each other.

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

? Exercise 5.5.1

Determine the maximum number of structures that are possible for a four-coordinate MA_2B_2 complex with either a square planar or a tetrahedral symmetrical structure.

Answer

square planar, 2; tetrahedral, 1

Structures of Metal Complexes

The coordination numbers of metal ions in metal complexes can range from 2 to at least 9. In general, the differences in energy between different arrangements of ligands are greatest for complexes with low coordination numbers and decrease as the coordination number increases. Usually only one or two structures are possible for complexes with low coordination numbers, whereas several different energetically equivalent structures are possible for complexes with high coordination numbers (n > 6). The following presents the most commonly encountered structures for coordination numbers 2–9. Many of these structures should be familiar to you from our discussion of the valence-shell electron-pair repulsion (VSEPR) model because they correspond to the lowest-energy arrangements of n electron pairs around a central atom.

> *Compounds with low coordination numbers exhibit the greatest differences in energy between different arrangements of ligands.*

Coordination Number 2

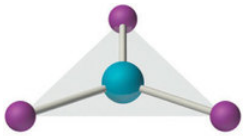
Although it is rare for most metals, this coordination number is surprisingly common for d^{10} metal ions, especially Cu^+, Ag^+, Au^+, and Hg^{2+}. An example is the $[Au(CN)_2]^-$ ion, which is used to extract gold from its ores. As expected based on VSEPR considerations, these complexes have the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



Linear ML_2

Coordination Number 3

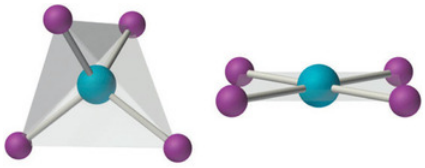
Although it is also rare, this coordination number is encountered with d^{10} metal ions such as Cu^+ and Hg^{2+}. Among the few known examples is the HgI_3^- ion. Three-coordinate complexes almost always have the trigonal planar structure expected from the VSEPR model.



Trigonal planar ML_3

Coordination Number 4

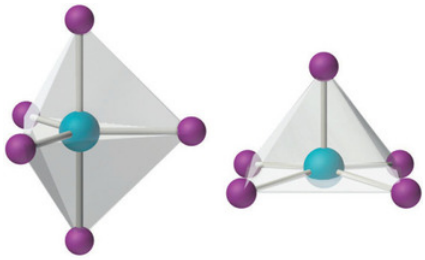
Two common structures are observed for four-coordinate metal complexes: tetrahedral and square planar. The tetrahedral structure is observed for all four-coordinate complexes of nontransition metals, such as $[BeF_4]^{2-}$, and d^{10} ions, such as $[ZnCl_4]^{2-}$. It is also found for four-coordinate complexes of the first-row transition metals, especially those with halide ligands (e.g., $[FeCl_4]^-$ and $[FeCl_4]^{2-}$). In contrast, square planar structures are routinely observed for four-coordinate complexes of second- and third-row transition metals with d^8 electron configurations, such as Rh^+ and Pd^{2+}, and they are also encountered in some complexes of Ni^{2+} and Cu^{2+}.



Tetrahedral and square planar ML_4

Coordination Number 5

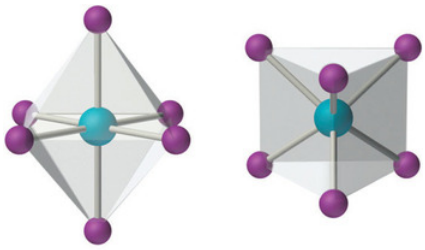
This coordination number is less common than 4 and 6, but it is still found frequently in two different structures: trigonal bipyramidal and square pyramidal. Because the energies of these structures are usually rather similar for most ligands, many five-coordinate complexes have distorted structures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



Trigonal bipyramidal and square pyramidal ML_5

Coordination Number 6

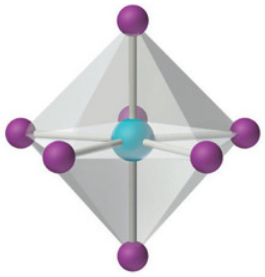
This coordination number is by far the most common. The six ligands are almost always at the vertices of an octahedron or a distorted octahedron. The only other six-coordinate structure is the trigonal prism, which is very uncommon in simple metal complexes.



Octahedral and trigonal prismatic ML_6

Coordination Number 7

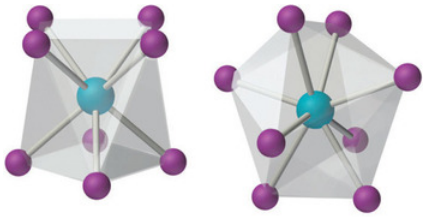
This relatively uncommon coordination number is generally encountered for only large metals (such as the second- and third-row transition metals, lanthanides, and actinides). At least three different structures are known, two of which are derived from an octahedron or a trigonal prism by adding a ligand to one face of the polyhedron to give a “capped” octahedron or trigonal prism. By far the most common, however, is the pentagonal bipyramid.



Pentagonal bipyramidal ML_7

Coordination Number 8

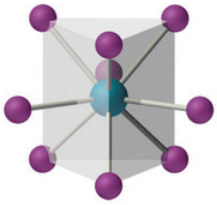
This coordination number is relatively common for larger metal ions. The simplest structure is the cube, which is rare because it does not minimize interligand repulsive interactions. Common structures are the square antiprism and the dodecahedron, both of which can be generated from the cube.



Square antiprismatic and trigonal dodecahedral ML_8

Coordination Number 9

This coordination number is found in larger metal ions, and the most common structure is the tricapped trigonal prism, as in $[Nd(H_2O)_9]^{3+}$.



Tricapped trigonal prismatic ML_9

Key Takeaways

- Coordination compounds are a major feature of the chemistry of over half the elements.
- Coordination compounds have important roles as industrial catalysts in controlling reactivity, and they are essential in biochemical processes.

Summary

Transition metals form metal complexes, polyatomic species in which a metal ion is bound to one or more ligands, which are groups bound to a metal ion. Complex ions are electrically charged metal complexes, and a coordination compound contains one or more metal complexes. Metal complexes with low coordination numbers generally have only one or two possible structures, whereas those with coordination numbers greater than six can have several different structures. Coordination numbers of two and three are common for d^{10} metal ions. Tetrahedral and square planar complexes have a coordination number of four; trigonal bipyramidal and square pyramidal complexes have a coordination number of five; and octahedral complexes have a coordination

number of six. At least three structures are known for a coordination number of seven, which is generally found for only large metal ions. Coordination numbers of eight and nine are also found for larger metal ions.

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5.6: 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 **5.6.1**. 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).

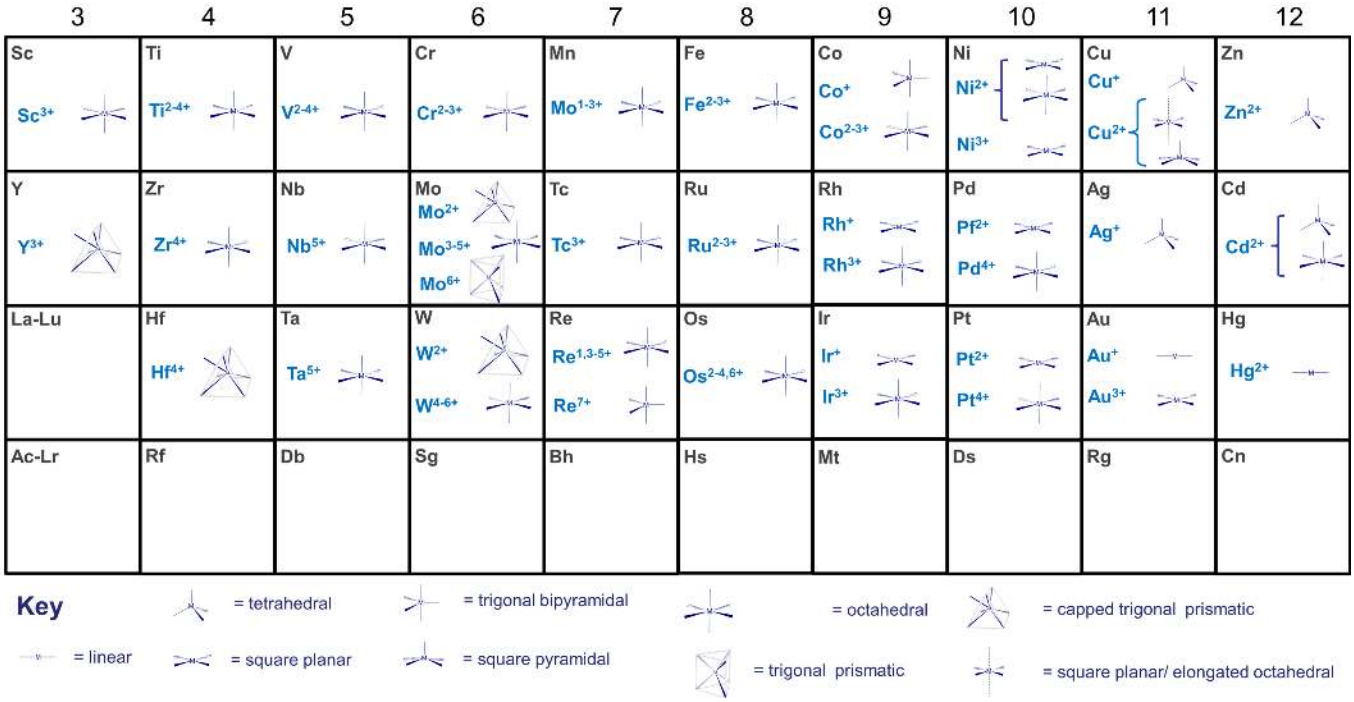


Figure **5.6.1**. Preferred coordination geometries of the transition elements. Assignments are as reported in reference 1 except for Cu^{2+}, which is assigned above as square planar/elongated octahedral instead of the square planar assignment given in that work. This work by Stephen Contakes is licensed 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 **5.6.2**. As may be seen from the geometries listed in Figure **5.6.2**, 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 **5.6.2**.

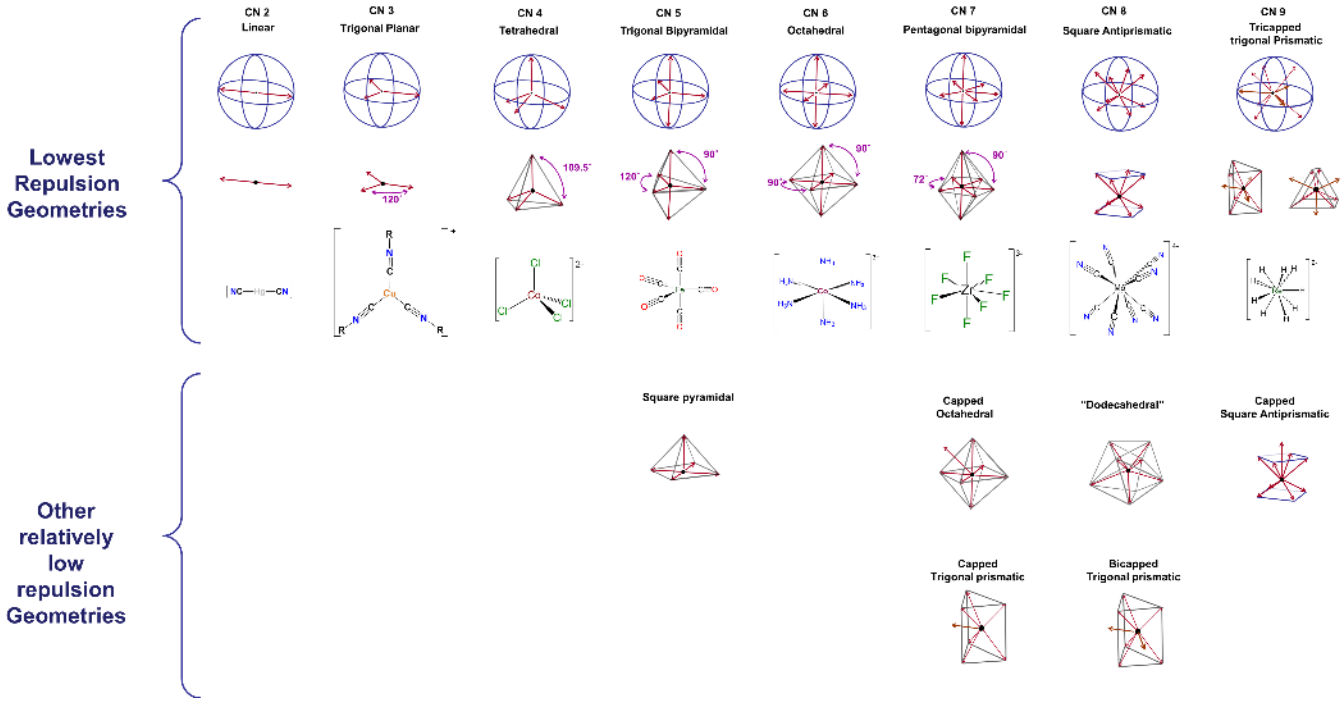


Figure **5.6.2**. Coordination geometries predicted by the Kepert model for coordination numbers two through nine along with other coordination geometries similar in energy to the lowest repulsion geometry. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

d-electron effects

A few coordination geometries are noticeably absent from the Kepert-preferred and Kepert-accessible geometries in Figure **5.6.1**. 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 **5.6.2** may be extended to that shown in Figure **5.6.3**.

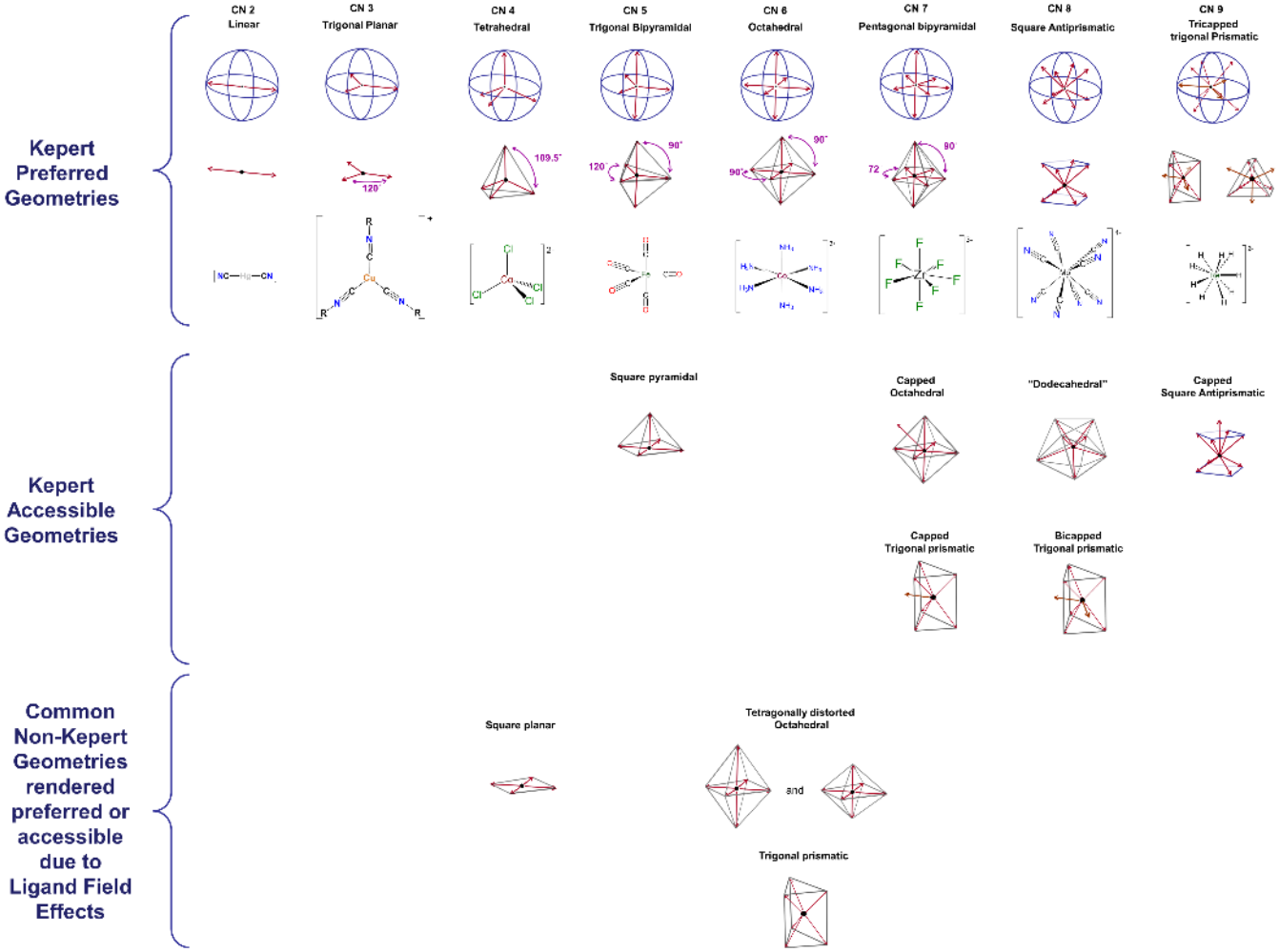


Figure **5.6.3**. Coordination geometries accessible for 2-9 coordinate complexes even without constraint by rigid or semirigid ligands. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

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 **5.6.4**.

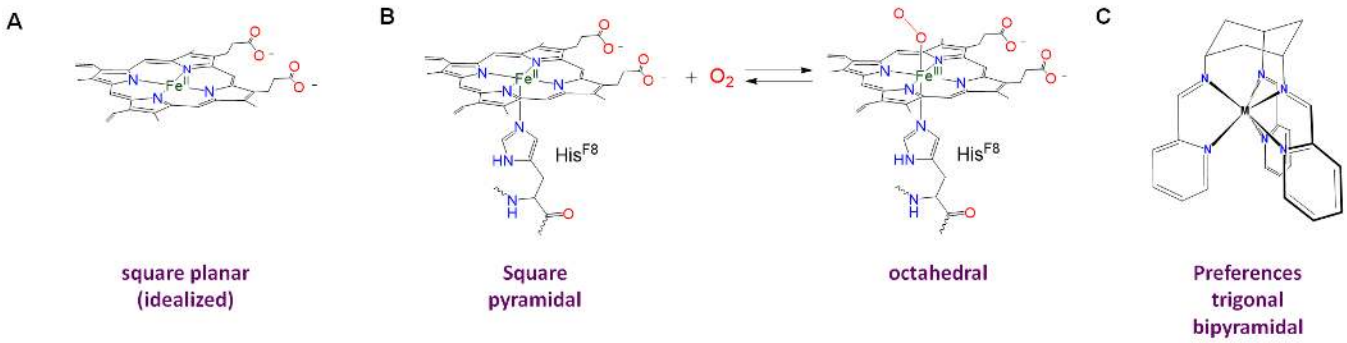


Figure **5.6.4**. Examples of rigid/semirigid ligands that can impose their preferred coordination geometry on a metal center. Porphyrins, phyhalocyanines and related macrocycles tend to impose a slightly bent square planar coordination geometry, although (B) many such complexes, including the iron of 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]
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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 **5.6.5**.

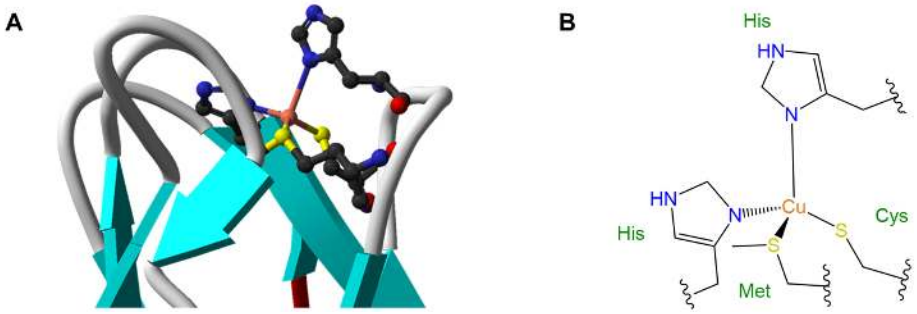


Figure **5.6.5**. (A) Structure and (B) schematic of the plastocyanin active site showing the distorted tetrahedral coordination environment that the protein imposes on the copper center (tan), which is most evident from the long vertically oriented Cu-Histidine bond. The image in part A is cropped from an original image by Ben Mills - Own work, Public Domain, https://commons.wikimedia.org/w/inde...?curid=6202620. 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 **5.6.5**, 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 **5.6.6A**.

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 **5.6.6B**, the relative closeness in energy of the 6*s* 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.

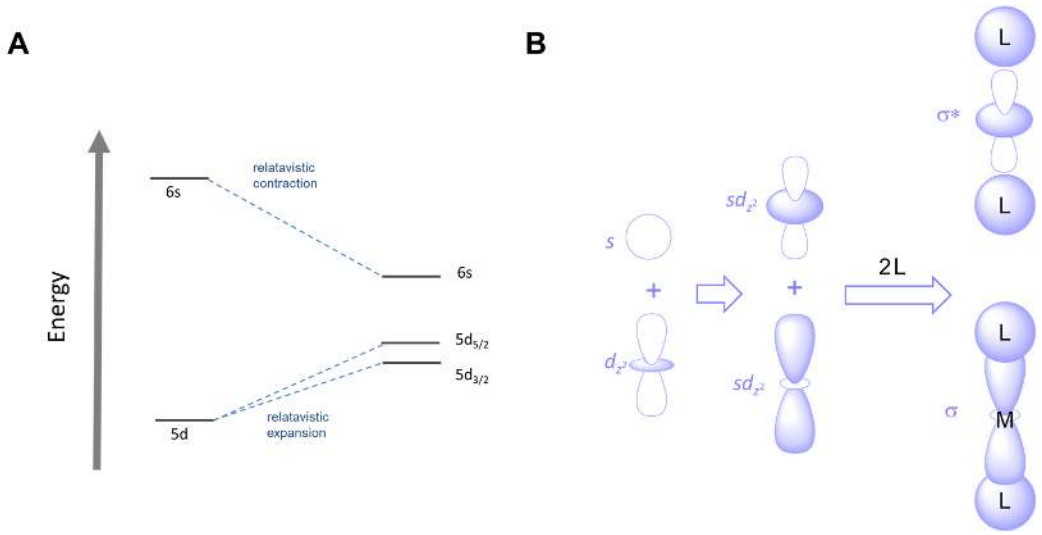


Figure **5.6.6**. (A) Gold experiences relativistic expansion and contraction of its 5*d* and 6*s* orbitals, resulting in shifts to their relative energies. (B) This makes mixing of these orbitals more favorable, facilitating the ability of gold to form two-coordinate complexes with strong sigma bonds 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 **5.6.7**.

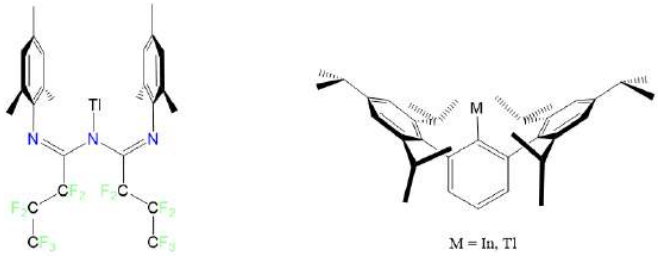
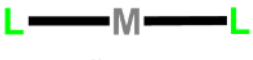


Figure **5.6.7**. No monocoordinate transition metal complexes are known, but Tl^{+} and In^{+} form monocoordinate complexes with extremely bulky ligands. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

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.**



linear

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 **5.6.8**. 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.

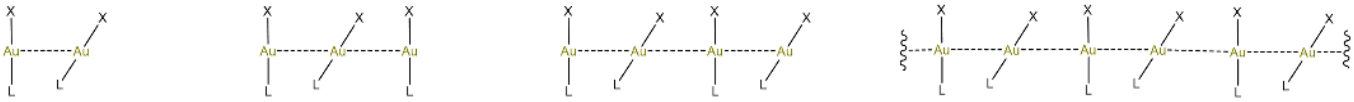
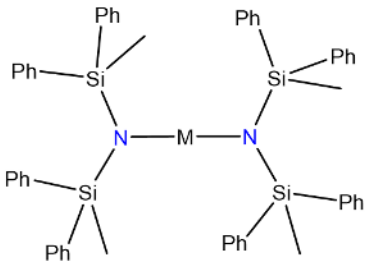


Figure **5.6.8**. Many "linear" gold complexes associate side-on to form dimers, trimers, tetramers, and chains. Although in this chapter L is usually taken to represent a generic ligand, in this scheme L represents a neutral ligand that donates two electrons to the metal (py, PR_3, CO, etc.) and X an 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 **5.6.9**.

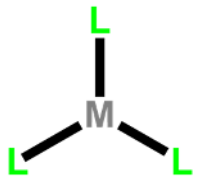


M = Mn, Fe, Co

Figure **5.6.9**. 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.



Trigonal planar

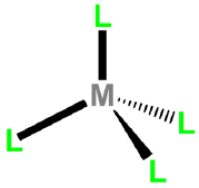
Figure **5.6.10**.



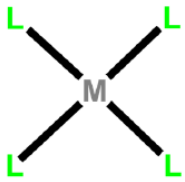
Figure **5.6.10**. Three-coordinate complexes prepared using bulky and semirigid ligands. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

Coordination Number 4

The two common four-coordinate geometries are tetrahedral and square planar.



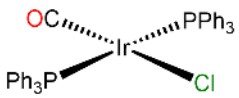
tetrahedral



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*-$[Ir(CO)Cl(PPh_3)_2]$.



Vaska's Complex

Coordination Number 5

The two common coordination geometries for five-coordinate complexes are trigonal bipyramidal and square pyramidal.



Figure **5.6.11**.

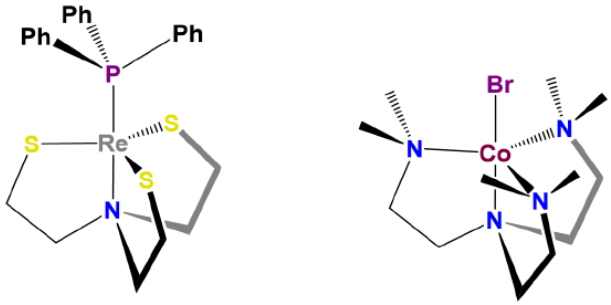


Figure **5.6.11**. Some tripodal ligands preference the formation of trigonal bipyramidal complexes. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

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 **5.6.4** and for complexes containing oxo and nitrido ligands, examples of which are shown in Figure **5.6.12**.

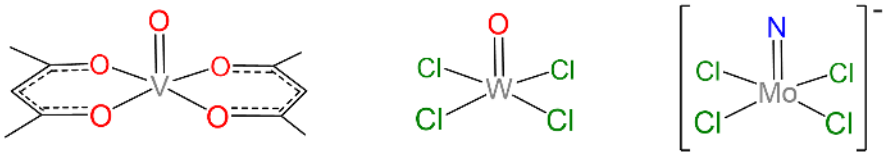


Figure **5.6.12**. Some square pyramidal oxo and nitrido complexes. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

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 **5.6.13**.

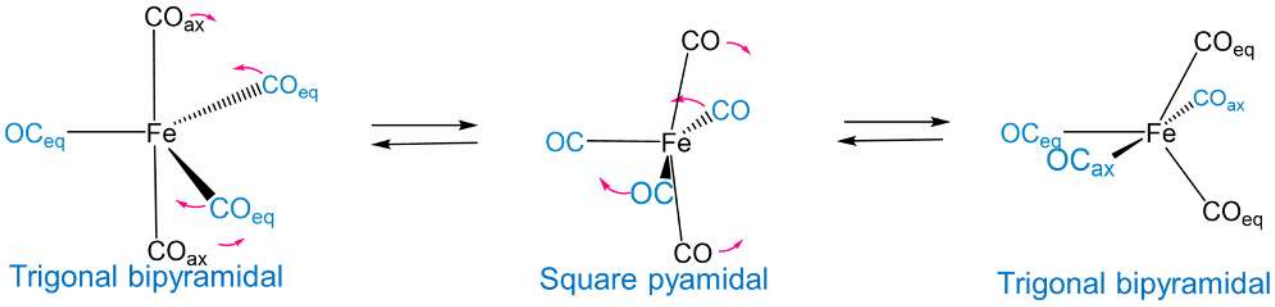


Figure **5.6.13**. Fluxionality in pentacarbonyliron(0) involves exchange of axial and equatorial carbonyl ligands via Berry pseudorotation. Interconversion of the axial and equatorial carbonyl groups occurs faster than the NMR timescale at room temperature. As a result the ^{13}C NMR spectrum of $Fe(CO)_5$ 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.

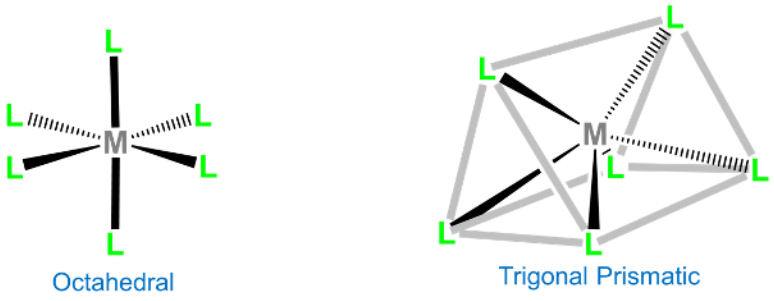


Figure **5.6.14**.

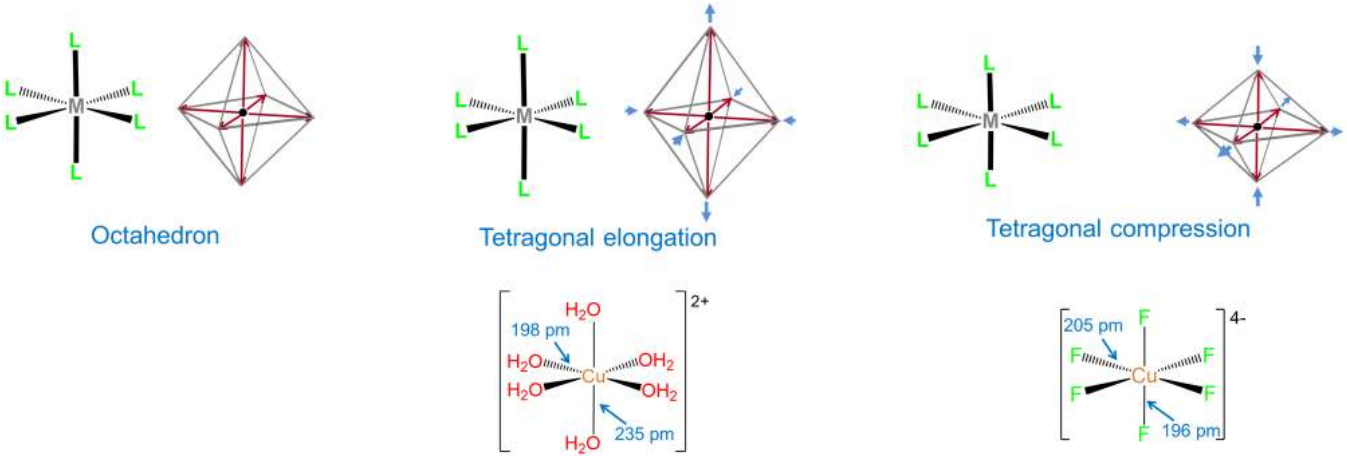


Figure **5.6.14**. Tetragonal distortions commonly occur for d^4, d^7 , and d^9 octahedral complexes. The most common type involves axial elongation in which the octahedron is stretched along a single *trans*-L-M-L axis, but axial compressions in which the octahedron is compressed along such an axis 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 **5.6.15**. As may be seen in Figure **5.6.15**, 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.

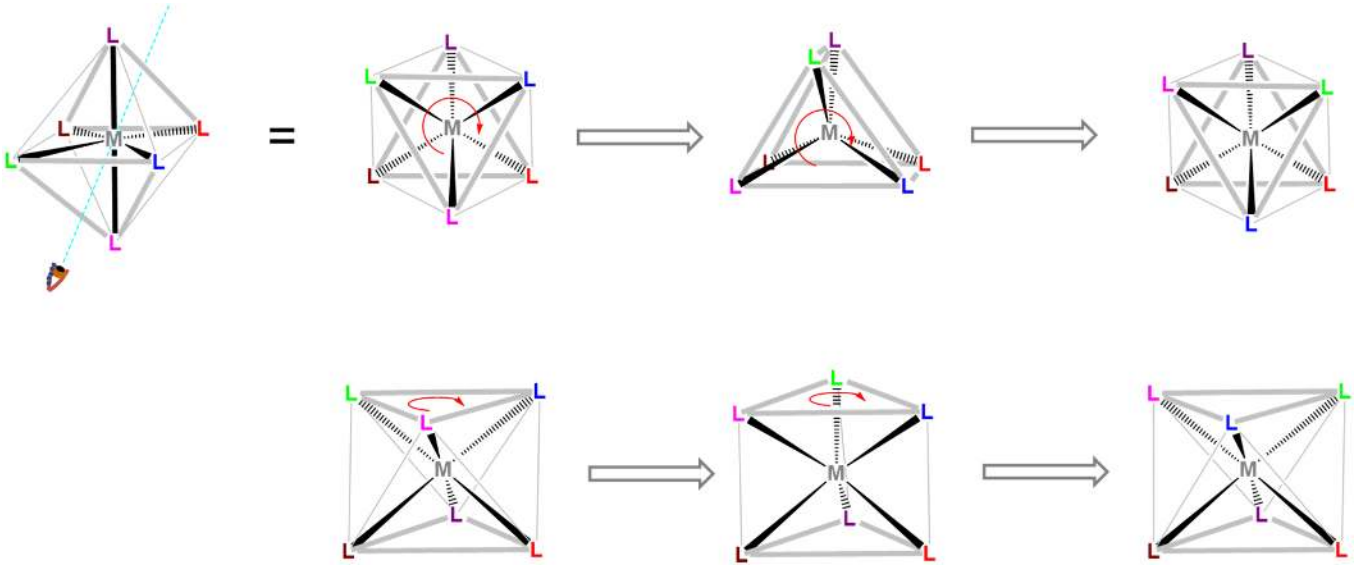


Figure 5.6.15. Since an octahedron is a trigonal antiprism, a trigonal prism may be produced by rotating or "twisting" one face of the octahedron relative to its opposite. Since continuation of the rotation gives an isomer of the original octahedron, when the energy landscape for twists like these is 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 5.6.16. Semirigid ligands like that shown in Figure 5.6.4C 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.

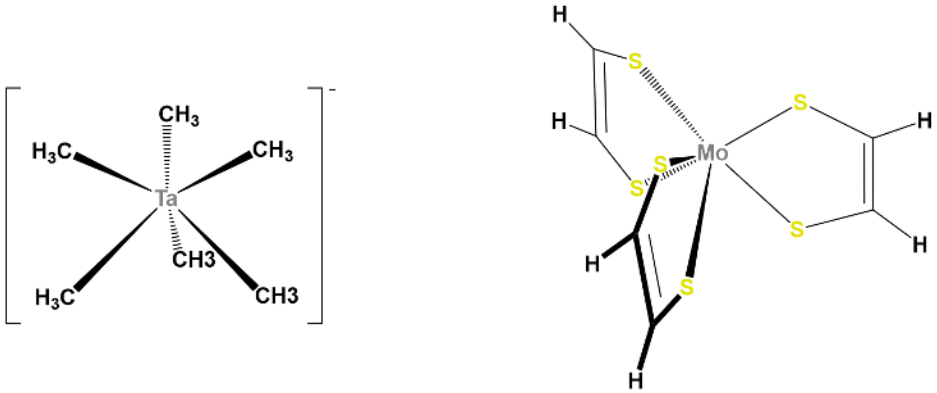
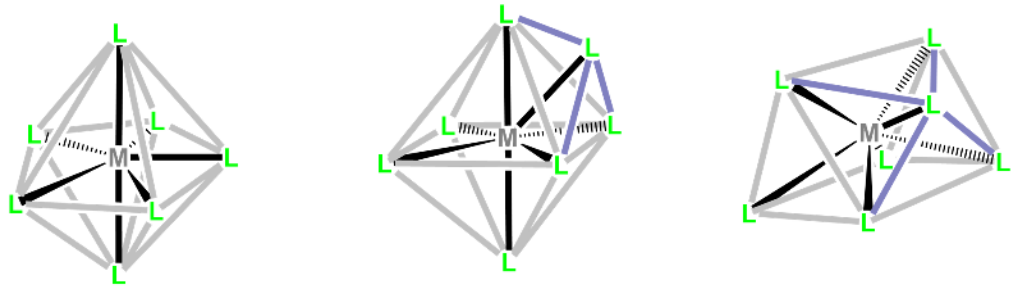


Figure 5.6.16. The complexes $[Ta(CH_3)_6]^-$ and $[Mo(S_2C_2H_2)_3]$ adopt a trigonal prismatic geometry. Trigonal prismatic coordination is common for d^0 and d^1 complexes with alkyl and dithiolene ligands. It is also typical for the dithiolene ligands to coordinate along the rectangular edges of 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.



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 **5.6.17**.

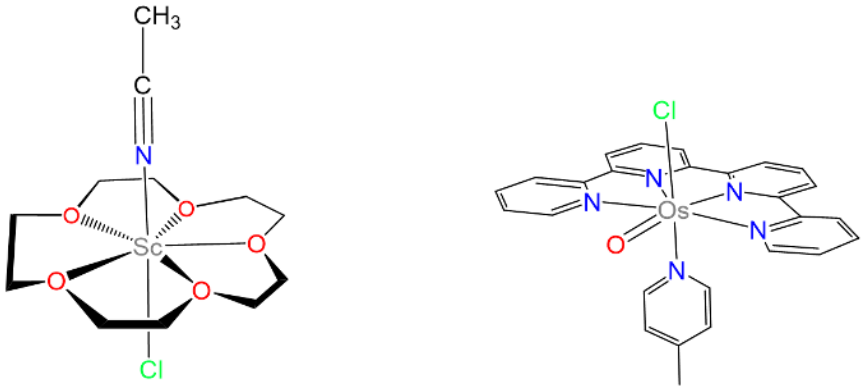


Figure **5.6.17**. Seven-coordinate complexes containing ligands that encourage the formation of seven-coordinate geometries. Note that while in $[NbOF_6]^{3-}$ and $[UO_2F_5]^{3-}$ the oxo ligands occupy axial positions, the Osmium complex shown possesses an oxo ligand in an equatorial position. This 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 **5.6.18**.

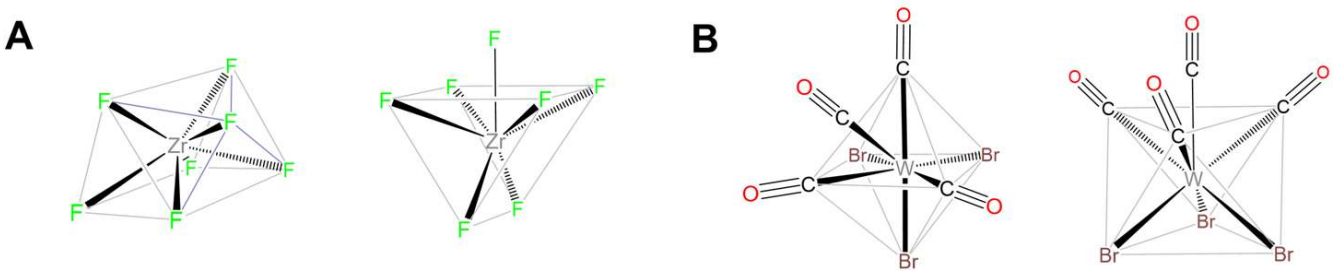


Figure **5.6.18**. Examples of complexes that adopt monocapped triconal prismatic and monocapped octahedral geometries.(A) Two views of the structure of (A) capped trigonalprismatic $[ZrF_7]^{3-}$ and (B) capped octahedral $[WBr_3(CO)_4]$. This work by Stephen Contakes is licensed under a Creative Commons 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 **5.6.19**).

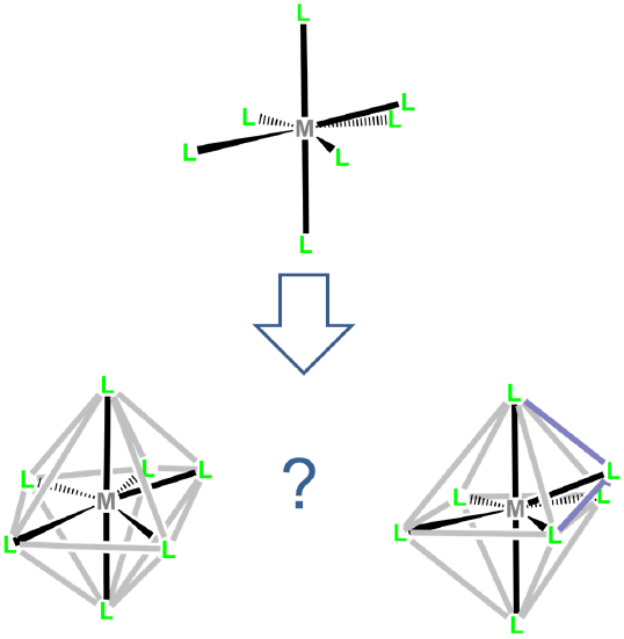


Figure **5.6.19**. Many seven-coordinate structures are distorted and can be difficult to classify. For example, how should the geometry of this complex be described - as distorted trigonal bipyramidal or distorted monocapped octahedral? This work by Stephen Contakes is licensed under a Creative Commons 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 $Na_3[UF_8]$.

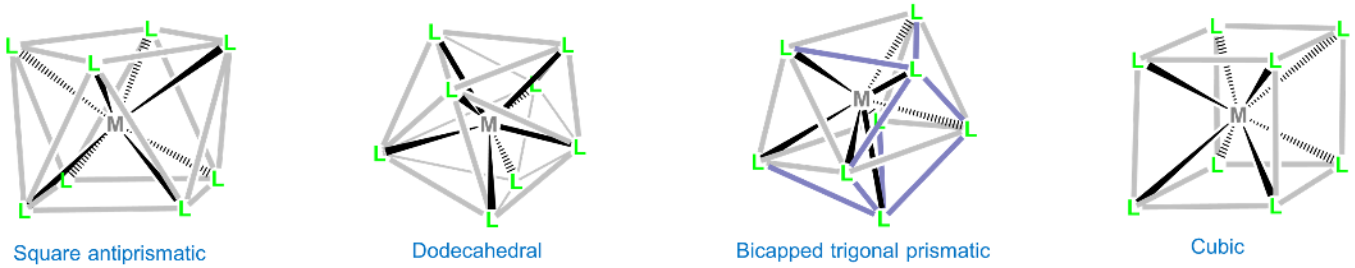


Figure **5.6.20**. The square antiprism may be made by twisting one face of a cube relative to another, and the dodecahedron by folding opposing faces towards one another.

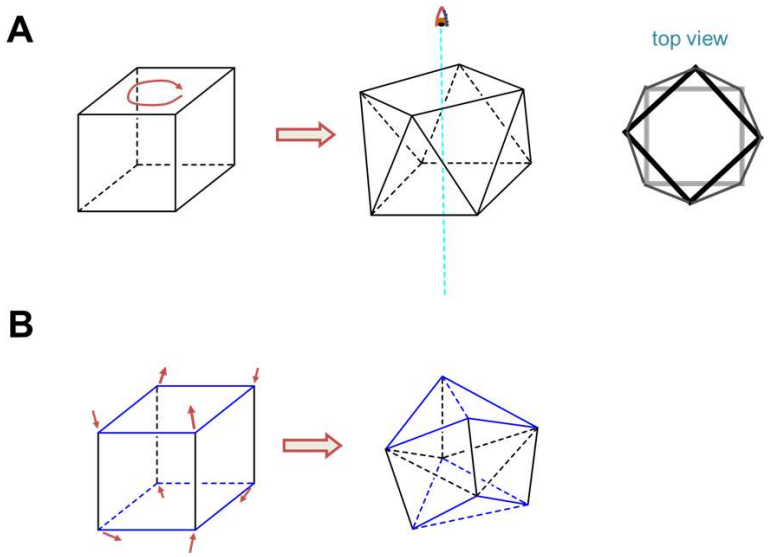


Figure **5.6.20**. The (A) square antiprismatic and (B) dodecahedral coordination geometries are distorted cubic geometries. (A) The square antiprismatic coordination geometry is just a cubic coordination geometry in which one face has been rotated 45° relative to its opposite (and for which the distance 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 **5.6.21**.

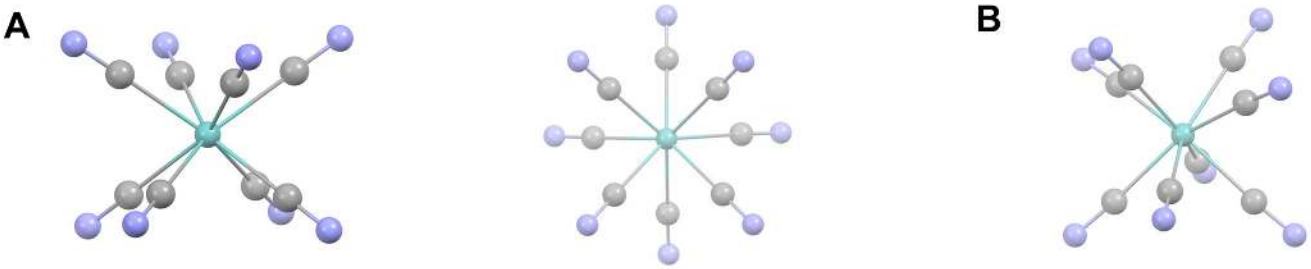


Figure **5.6.21**: Structures reported for (A) square antiprismatic $[Mo(CN)_8]^{3-}$ as a solid 4,4'-Diazenediyldipyridinium salt and (B) dodecahedral $[Mo(CN)_8]^{4-}$ as a solid tetra-n-butylammonium salt.

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 $[ReH_9]^{2-}$.

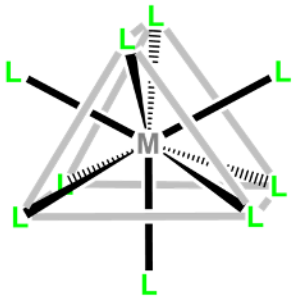


Figure **5.6.22**.

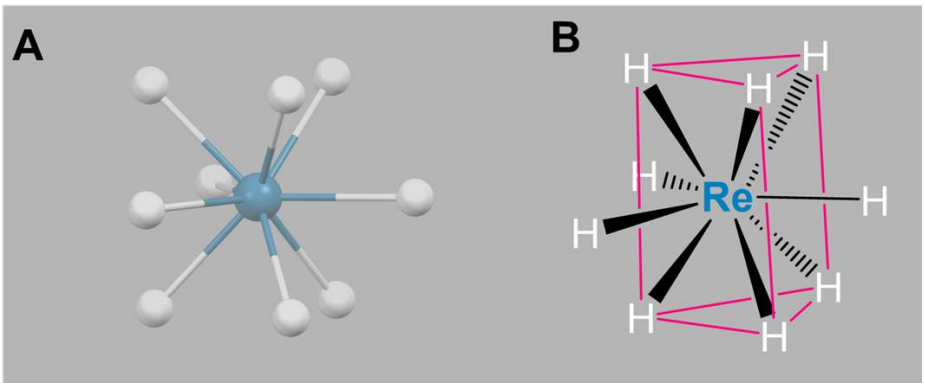


Figure **5.6.22**. (A) Structure of $[ReH_9]^{2-}$ in $K_2[ReH_9]$ and (B) schematic showing how the structure maps onto a tricapped trigonal pyramidal coordination geometry. This work by Stephen Contakes is licensed under a Creative Commons Attribution 4.0 International License.

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 **5.6.23**, $[Hf(BH_4)_4]$ 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.

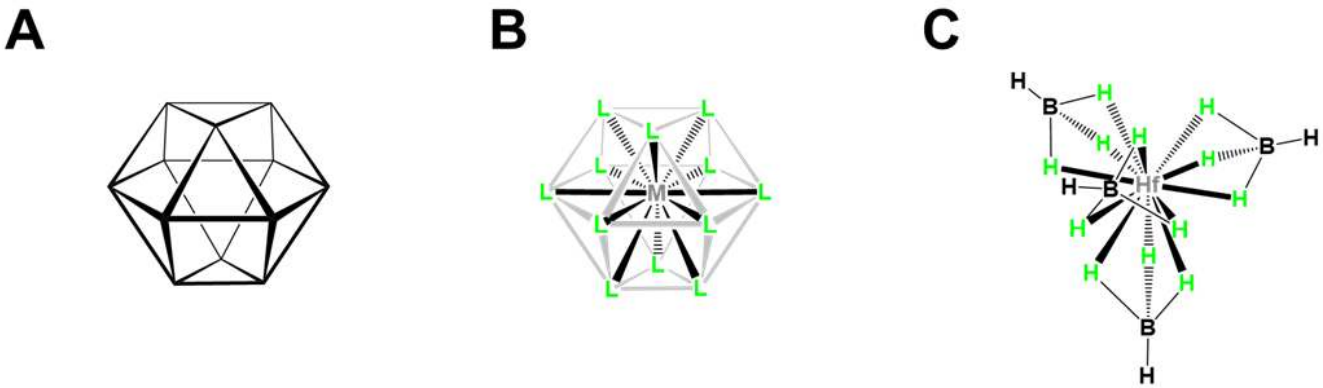


Figure **5.6.23**. The anticubooctahedral coordination geometry is observed for $[Hf(BH_4)_4]$. (A) An anticubooctahedron consists of a hexagonal ring capped with antiparallel triangles above and below the ring. (B) Idealized anticubooctahedral complex. (C) Structure of $[Hf(BH_4)_4]$. This work by Stephen 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 **5.6.24**. The nitrates in the structure bind the Ce center in bidentate fashion in an octahedral array.

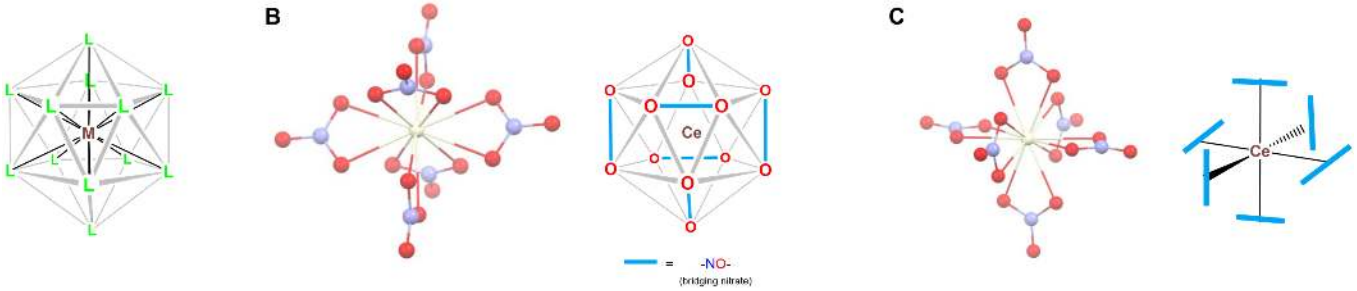


Figure **5.6.24**. Coordination geometry of $[Ce(NO_3)_6]^{2-}$ in $[Mg(H_2O)_6][Ce(NO_3)_6]\cdot H_2O$. (A) Idealized icosahedral coordination. (B) View of the structure of $[Ce(NO_3)_6]^{2-}$ showing how it maps onto the icosahedral coordination geometry. (C) The structure may also be thought of as 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 **5.6.25**. 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.

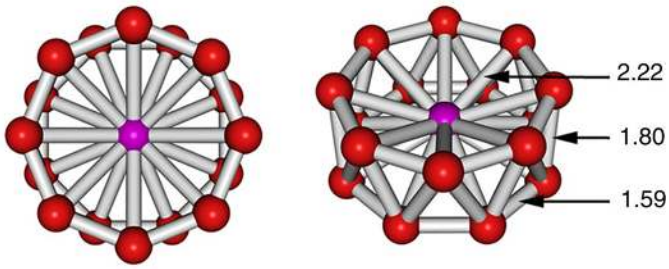


Figure 2A from Popov, I., Jian, T., Lopez, G. *et al.* Cobalt-centered boron molecular drums with the highest coordination number in the CoB_{16}^- cluster. *Nat Commun* **6,** 8654 (2015). https://doi.org/10.1038/ncomms9654, which is is licensed in that publication under a Creative Commons Attribution 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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5.7: Structural Isomers- Ionization Isomerism in Transition Metal Complexes

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

Introduction

Ionization isomers are identical except for a ligand has exchanged places with an anion or neutral molecule that was originally outside the coordination complex. The central ion and the other ligands are identical. For example, an octahedral isomer will have five ligands that are identical, but the sixth will differ. The non-matching ligand in one compound will be outside of the coordination sphere of the other compound. Because the anion or molecule outside the coordination sphere is different, the chemical properties of these isomers is different.

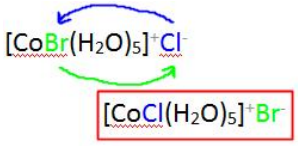


Figure 5.7.1: Two Ionization isomers. The two isomers differ only which ligands are actually bound to the center metal. These two isomers are called pentaaquabromocobaltate(II) chloride and pentaaquachlorocobaltate(II) bromide.

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

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

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

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

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

Note

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

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

$$[PtBr(NH_3)_3]NO_2(s) \rightarrow [PtBr(NH_3)_3]^+(aq) + NO_2^-(aq) \quad (5.7.1)$$

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

$$[Pt(NO_2)(NH_3)_3]Br(s) \rightarrow [Pt(NO_2)(NH_3)_3]^+(aq) + Br^-(aq) \quad (5.7.2)$$

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

Equations 5.7.1 and 5.7.2 are valid under the assumption that the platinum-ligand bonds of the complexes are stable (i.e., not labile). Otherwise, they may break and other ligands (e.g., water) may bind.

Example 5.7.1

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

Solution

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

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

Now, let's look at what these two compounds look like (Figure **5.7.2**). The sulfate group is a ligand with a dative bond to the chromium atom and the bromide counter ion ($[Cr(NH_3)_5(OSO_3)]Br$). For $[Cr(NH_3)_5Br]SO_4$, this is the the reverse.

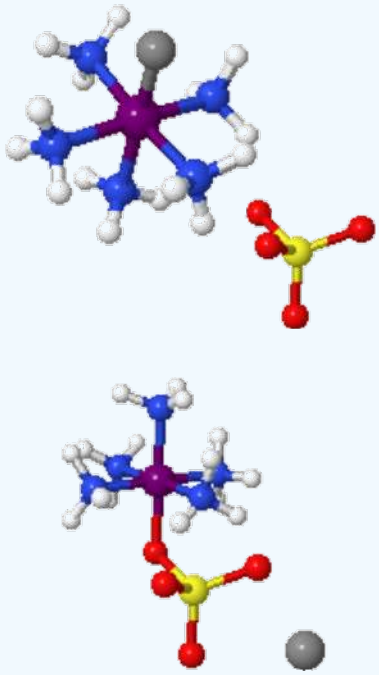


Figure **5.7.2**: $[Cr(NH_3)_5(OSO_3)]Br$ (left) and $[Cr(NH_3)_5Br]SO_4$ (right) are coordination isomers.

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

? Exercise 5.7.1

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

Solution

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

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

Solvate or Hydrate Isomerization: A Special kind of Ionization Isomer

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

- $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$: bright-green colored
- $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$: grey-green colored
- $[Cr(H_2O)_6]Cl_3$: violet colored

These isomers have very different chemical properties and on reaction with $AgNO_3$ to test for Cl^- ions, would find 1, 2, and 3 Cl^- ions in solution respectively.

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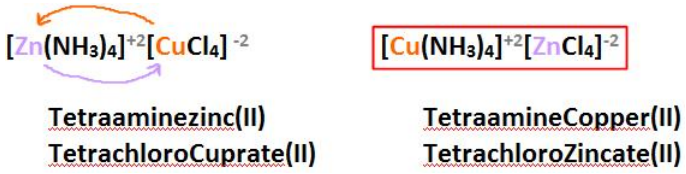
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5.8: Structural Isomers- Coordination Isomerism in Transition Metal Complexes

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



? Exercise 5.8.1

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

Solution

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

Yes, they are coordination isomers.

? Exercise 5.8.2

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

Solution

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

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

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5.9: Structural Isomers- Linkage Isomerism in Transition Metal Complexes

Linkage isomerism occurs with *ambidentate* ligands that are capable of coordinating in more than one way. The best known cases involve the monodentate ligands: SCN^-/NCS^- and NO_2^-/ONO^-. The only difference is what **atoms the molecular ligands bind to the central ion**. The ligand(s) must have more than one donor atom, but bind to ion in only one place. For example, the (NO_2^-) ion is a ligand can bind to the central atom through the nitrogen or the oxygen atom, but cannot bind to the central atom with both oxygen and nitrogen at once, in which case it would be called a *polydentate* rather than an *ambidentate* ligand.

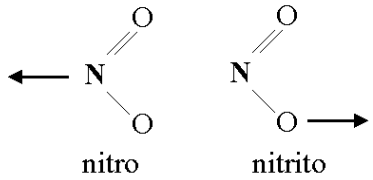
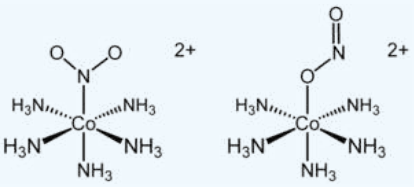


Figure 5.9.1: Linkage Isomerism in the NO_2 ligand. This occurs when a particular ligand is capable of coordinating to a metal in two different and distinct ways. from Angel C. de Dios.

The names used to specify the changed ligands are changed as well. For example, the (NO_2^-) ion is called *nitro* when it binds with the N atom and is called *nitrito* when it binds with the O atom.

Example 5.9.1: Nitro- vs. Nitrito- Linkage Isomers

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



(left) The nitro isomer (Co-NO_2) and (right) the nitrito isomer (Co-ONO)

When donation is from nitrogen to a metal center, the complex is known as a *nitro-* complex and when donation is from one oxygen to a metal center, the complex is known as a *nitrito-* complex. An alternative formula structure to emphasize the different coordinate covalent bond for the two isomers

- $[Co(ONO)(NH_3)_5]Cl$: the *nitrito* isomer -O attached
- $[Co(NO_2)(NH_3)_5]Cl$: the *nitro* isomer - N attached.

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

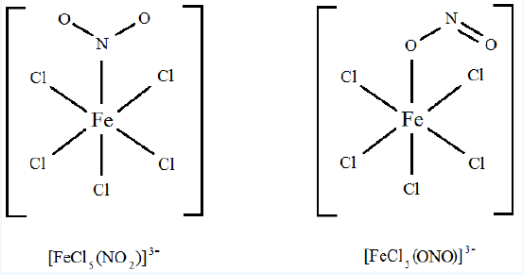
Another example of an ambidentate ligans is thiocyanate, SCN^-, which can attach at either the sulfur atom or the nitrogen atom. Such compounds give rise to linkage isomerism. Polyfunctional ligands can bond to a metal center through different ligand atoms to form various isomers. Other ligands that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

Exercise 5.9.1

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

Solution

Here, the difference is in how the ligand bonds to the metal. In the first isomer, the ligand bonds to the metal through an electron pair on the nitrogen. In the second isomer, the ligand bonds to the metal through an electron pair on one of the oxygen atoms. It's easier to see it:



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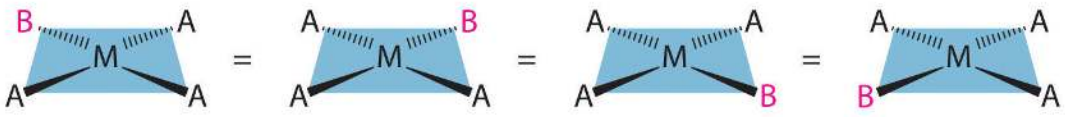
5.10: Stereoisomers- Geometric Isomers in Transition Metal Complexes

The existence of coordination compounds with the same formula but different arrangements of the ligands was crucial in the development of coordination chemistry. Two or more compounds with the same formula but different arrangements of the atoms are called **isomers**. Because isomers usually have different physical and chemical properties, it is important to know which isomer we are dealing with if more than one isomer is possible. Recall that in many cases more than one structure is possible for organic compounds with the same molecular formula; examples discussed previously include n-butane versus isobutane and cis-2-butene versus trans-2-butene. As we will see, coordination compounds exhibit the same types of isomers as organic compounds, as well as several kinds of isomers that are unique.

Planar Isomers

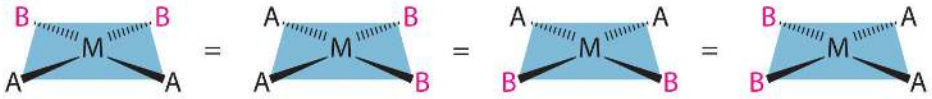
Metal complexes that differ only in which ligands are adjacent to one another (**cis**) or directly across from one another (**trans**) in the coordination sphere of the metal are called geometrical isomers. They are most important for square planar and octahedral complexes.

Because all vertices of a square are equivalent, it does not matter which vertex is occupied by the ligand B in a square planar MA_3B complex; hence only a single geometrical isomer is possible in this case (and in the analogous MAB_3 case). All four structures shown here are chemically identical because they can be superimposed simply by rotating the complex in space:

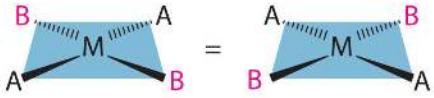


MA_3B square planar complex

For an MA_2B_2 complex, there are two possible isomers: either the A ligands can be adjacent to one another (cis), in which case the B ligands must also be cis, or the A ligands can be across from one another (trans), in which case the B ligands must also be trans. Even though it is possible to draw the cis isomer in four different ways and the trans isomer in two different ways, all members of each set are chemically equivalent:

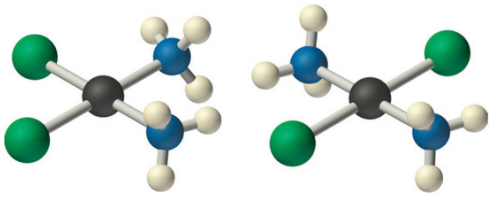


MA_2B_2 square planar complex, *cis* isomer



MA_2B_2 square planar complex, *trans* isomer

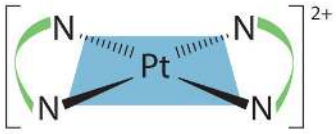
Because there is no way to convert the cis structure to the trans by rotating or flipping the molecule in space, they are fundamentally different arrangements of atoms in space. Probably the best-known examples of cis and trans isomers of an MA_2B_2 square planar complex are cis-$Pt(NH_3)_2Cl_2$, also known as cisplatin, and trans-$Pt(NH_3)_2Cl_2$, which is actually toxic rather than therapeutic.



cis-$Pt(NH_3)_2Cl_2$ *trans*-$Pt(NH_3)_2Cl_2$

The anticancer drug cisplatin and its inactive trans isomer. Cisplatin is especially effective against tumors of the reproductive organs, which primarily affect individuals in their 20s and were notoriously difficult to cure. For example, after being diagnosed with metastasized testicular cancer in 1991 and given only a 50% chance of survival, Lance Armstrong was cured by treatment with cisplatin.

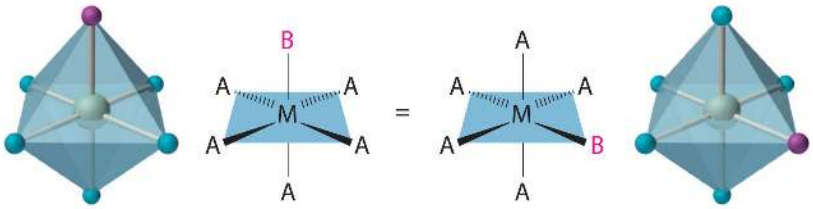
Square planar complexes that contain symmetrical bidentate ligands, such as $[Pt(en)_2]^{2+}$, have only one possible structure, in which curved lines linking the two N atoms indicate the ethylenediamine ligands:



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

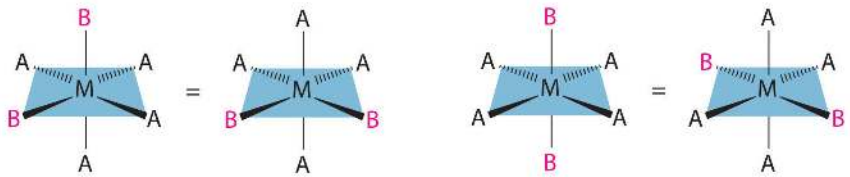
Octahedral Isomers

Octahedral complexes also exhibit cis and trans isomers. Like square planar complexes, only one structure is possible for octahedral complexes in which only one ligand is different from the other five (MA_5B). Even though we usually draw an octahedron in a way that suggests that the four "in-plane" ligands are different from the two "axial" ligands, in fact all six vertices of an octahedron are equivalent. Consequently, no matter how we draw an MA_5B structure, it can be superimposed on any other representation simply by rotating the molecule in space. Two of the many possible orientations of an MA_5B structure are as follows:



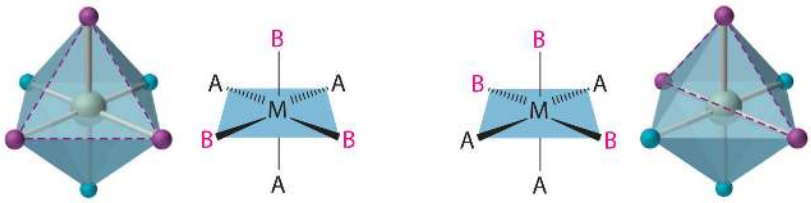
MA_5B octahedral complex

If two ligands in an octahedral complex are different from the other four, giving an MA_4B_2 complex, two isomers are possible. The two B ligands can be cis or trans. Cis- and trans-$[Co(NH_3)_4Cl_2]Cl$ are examples of this type of system:



MA_4B_2 octahedral complex, *cis* isomer **MA_4B_2 octahedral complex, *trans* isomer**

Replacing another A ligand by B gives an MA_3B_3 complex for which there are also two possible isomers. In one, the three ligands of each kind occupy opposite triangular faces of the octahedron; this is called the fac isomer (for facial). In the other, the three ligands of each kind lie on what would be the meridian if the complex were viewed as a sphere; this is called the mer isomer (for meridional):



MA_3B_3 octahedral complex, *fac* isomer

MA_3B_3 octahedral complex, *mer* isomer

Example 5.10.1

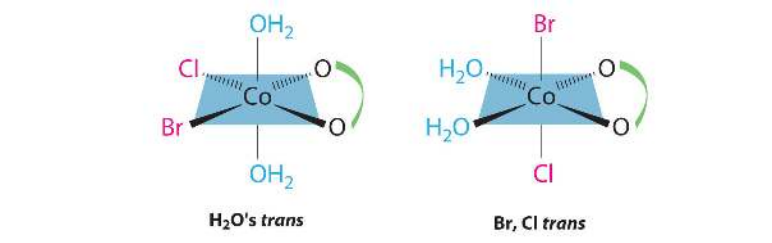
Draw all the possible geometrical isomers for the complex $[Co(H_2O)_2(ox)BrCl]^-$, where ox is $^-O_2CCO_2^-$, which stands for oxalate.

Given: formula of complex

Asked for: structures of geometrical isomers

Solution

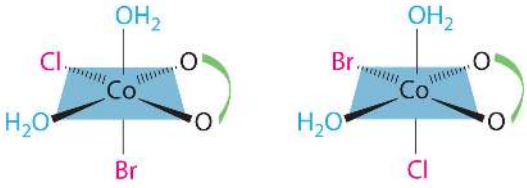
This complex contains one bidentate ligand (oxalate), which can occupy only adjacent (cis) positions, and four monodentate ligands, two of which are identical (H_2O). The easiest way to attack the problem is to go through the various combinations of ligands systematically to determine which ligands can be trans. Thus either the water ligands can be trans to one another or the two halide ligands can be trans to one another, giving the two geometrical isomers shown here:



H_2O's *trans*

Br, Cl *trans*

In addition, two structures are possible in which one of the halides is trans to a water ligand. In the first, the chloride ligand is in the same plane as the oxalate ligand and trans to one of the oxalate oxygens. Exchanging the chloride and bromide ligands gives the other, in which the bromide ligand is in the same plane as the oxalate ligand and trans to one of the oxalate oxygens:



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

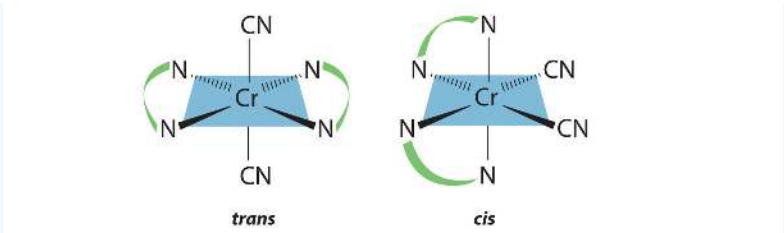
H_2O's *cis*; Br, Cl *cis*; Br *trans* to O

This complex can therefore exist as four different geometrical isomers.

Exercise 5.10.1

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

Answer



Two geometrical isomers are possible: trans and cis.

Summary

Many metal complexes form isomers, which are two or more compounds with the same formula but different arrangements of atoms. Structural isomers differ in which atoms are bonded to one another, while geometrical isomers differ only in the arrangement of ligands around the metal ion. Ligands adjacent to one another are cis, while ligands across from one another are trans.

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5.11: Stereoisomers- Geometric Isomers in Transition Metal Complexes II

Geometric Isomers are isomers that differ in the arrangement of the ligands around the metal or the central atom. In other words, these isomers differ from each other based on where the ligands are placed in the coordinate compound. This will be much easier to understand as examples will be considered. There are 2 main types of geometric isomers:

- Cis-Trans Isomers (referencing the spatial arrangement of two species)
- Mer-Fac Isomers (referencing the spatial arrangement of three species)

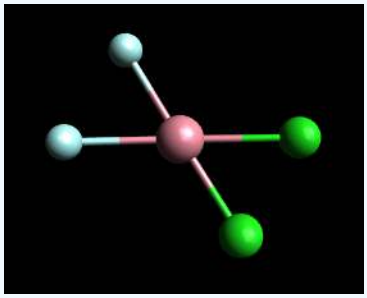
Cis-Trans Isomers

Cis-Trans Isomers are isomers that differ in the arrangement of two ligands in square planar and octahedral geometry. Cis isomers are isomers where the two ligands are 90 degrees apart from one another in relation to the central molecule. This is because Cis isomers have a bond angle of 90º, between two same atoms. Trans isomers, on the other hand, are isomers where the two ligands are on opposite sides in a molecule because trans isomers have a bond angle of 180º, between the two same atoms. When naming cis or trans isomers, the name begins either with cis or trans, whichever applies, followed by a hyphen and then the name of a molecule. For example a cis isomer of $CoCl_2F_2$ would be called cis-$CoCl_2F_2$. Finally, the last thing to keep in mind when examining cis and trans isomers is that **only square planar and octahedral** geometries can have cis or trans isomers. Examples of both isomers are provided below.

Example 5.11.1: cis Isomer

$CoCl_2F_2$:

(Color scheme: pink=cobalt, blue=fluorine, green=chlorine)



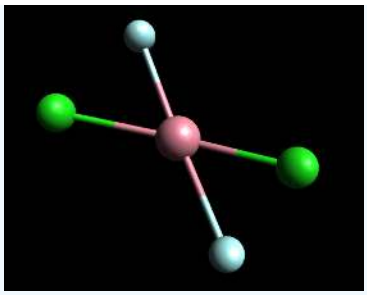
This above is an example of the molecule cis-$CoCl_2F_2$ or cis-dichlorodifluorocobalt (IV). The molecule pictured above is a cis isomer because both fluorine and chlorine ligands, respectively, are on the same side of the molecule. Additionally, one can approximate that the bond angle between each of the chlorine atoms and between each of the fluorine atoms is 90º.

Isomer

$CoCl_2F_2$:

(Color scheme: pink=cobalt, blue=fluorine, green=chlorine)

(Note, the differences in the length of the bond between the two pictures are not intentional and have nothing to do with cis-trans isomerism)

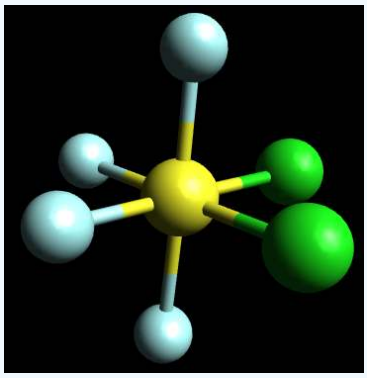


This above is an example of the molecule trans-$CoCl_2F_2$ or trans-dichlorodifluorocobalt (IV).

We know the above molecule is a trans isomer because the two same chlorine atoms and the two same fluorine atoms are opposite each other. Furthermore, the bond angle between the two chlorine atoms and between the two fluorine atoms is 180^o. The above examples were all for square planar geometry but as the examples below illustrate, cis-trans isomerism can also occur in octahedral geometry. Both the molecules below are isomers of the molecule SCl_2F_4 (color scheme: yellow=sulfur, blue=fluorine, green=chlorine).

Example 5.11.3: Octahedral cis Isomer

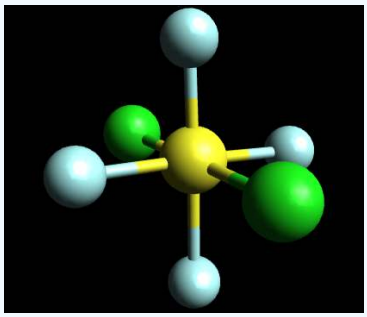
SCl_2F_4:



We know this isomer above is a cis isomer because both the chlorine ligands are on the same side and the bond angle between the chlorine atoms appears to be 90^o.

Example 5.11.4: Octahedral trans Isomer

SCl_2F_4:



The isomer above is a trans isomer because the chlorine ligands are on opposite sides and the bond angle between the chlorine atoms is 180^o. All other isomers are essentially just rotations of these two isomers. Once again when trying to find cis and trans isomers look at the arrangement of the ligands. If two same ligands are on the same side, it is a cis isomer and if the ligands are

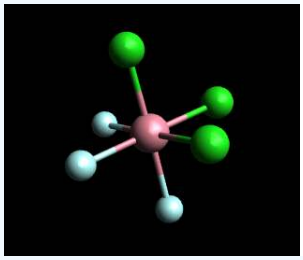
on opposite sides, it is a trans isomer. Another way to tell the isomers apart is the bond angles: cis isomers have a 90^o bond angle whereas trans isomers have a 180^o bond angle.

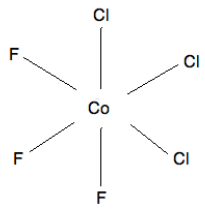
Mer-Fac Isomers

Mer-Fac isomers are easier to notice than cis-trans isomers in the sense that they only exist in octahedral geometry. Just like cis-trans isomers, mer-fac isomers are determined based on whether or not the ligands exist on the same side. Instead of dealing with 2 ligands, mer-fac isomers deal with 3 ligands. If the 3 ligands are all on the same side, the isomer is called a fac-isomer. Another way to identify fac isomers is to look at the bond angle between the ligands because fac isomers have a 90^o bond angle between each of the 3 atoms. The mer isomer on the other hand is where only 2 of the 3 ligands are on the same side. In mer isomers, there exists a 90^o-90^o-180^o bond angle between the 3 same ligands. In terms of nomenclature, mer-fac isomers follow the same rule as cis-trans isomers where you put the isomer type, followed by a hyphen, followed by the molecular formula. Examples have been provided below.

Example 5.11.5: fac Isomer

Below is an example of the fac isomer, fac-$CoCl_3F_3$:



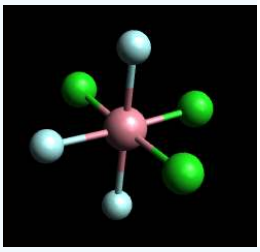


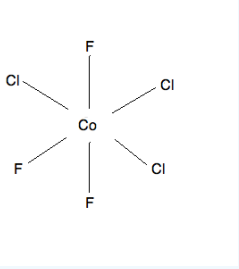
(note the color scheme: pink=cobalt, green=chlorine, blue=fluorine)

Through the 2d version, it is easier to see how the ligands are all on the same side. Nonetheless, in the 3D version, one can observe that the bond angle between the 3 same ligands is 90^o, thus making this isomer a fac-isomer.

Example 5.11.6: mer Isomer

Below is an example of the mer isomer, mer-$CoCl_3F_3$:





(note the color scheme: pink=cobalt, green=chlorine, blue=fluorine)

Its hard to tell in the 3D version but in the 2D version, one can easily tell how the same ligands are not on the same side. Additionally, one can approximate that the bond angle between the three chlorine atoms and between the three fluorine atoms is 90^o-90^o-180^o, thus making the above molecule a mer isomer.

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5.12: Optical Isomers in Inorganic Complexes

Optical activity refers to whether or not a compound has optical isomers. A coordinate compound that is optically active **has** optical isomers and a coordinate compound that is not optically active does **not have** optical isomers. As we will discuss later, optical isomers have the unique property of rotating light. When light is shot through a polarimeter, optical isomers can rotate the light so it comes out in a different direction on the other end. Armed with the knowledge of symmetry and mirror images, optical isomers should not be very difficult. There are two ways optical isomers can be determined: using mirror images or using planes of symmetry.

Optical isomers do not exhibit symmetry and do not have identical mirror images. Let's go through a quick review of symmetry and mirror images. A *mirror image* of an object is that object flipped or the way the object would look in front of a mirror. For example, the mirror image of your left hand would be your right hand. Symmetry on the other hand refers to when an object looks exactly the same when sliced in a certain direction with a plane. For example imagine the shape of a square. No matter in what direction it is sliced, the two resulting images will be the same.

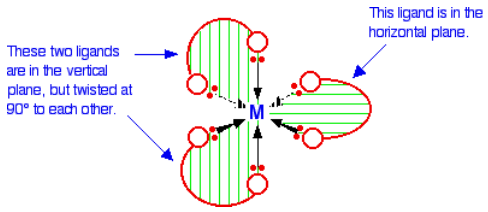
Method 1: The "Mirror Image Method"

The mirror images method uses a mirror image of the molecule to determined whether optical isomers exist or not. If the mirror image **can** be rotated in such a way that it looks identical to the original molecule, then the molecule is said to be superimposable and has no optical isomers. On the other hand, if the mirror image **cannot** be rotated in any way such that it looks identical to the original molecule, then the molecule is said to be non-superimposable and the molecule has optical isomers. Once again, if the mirror image is superimposable, then no optical isomers but if the mirror image is non-superimposable, then optical isomers exist.

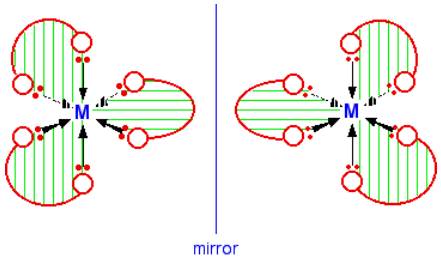
Definition: Non-superimposable

Non-superimposable means the structure cannot be rotated in a way that one can be put on top of another. This means that no matter how the structure is rotated, it cannot be put on top of another with all points matching. An example of this is your hands. Both left and right hands are identical, but they cannot be put on top of each other with all points matching.

The examples you are most likely to need occur in octahedral complexes which contain bidentate ligands - ions like $[Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$ or $[Cr(C_2O_4)_3]^{3-}$. The diagram below shows a simplified view of one of these ions. Essentially, they all have the same shape - all that differs is the nature of the "headphones".



A substance with *no plane of symmetry is going to have optical isomers* - one of which is the mirror image of the other. One of the isomers will rotate the plane of polarization of plane polarised light clockwise; the other rotates it counter-clockwise. In this case, the two isomers are:



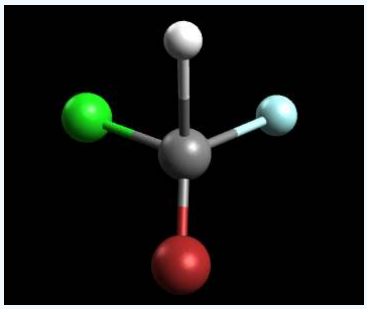
You may be able to see that there is no way of rotating the second isomer in space so that it looks exactly the same as the first one. As long as you draw the isomers carefully, with the second one a true reflection of the first, the two structures will be different.

Method 2: The "Plane of Symmetry Method"

The plane of symmetry method uses symmetry, as it's name indicates, to identify optical isomers. In this method, one tries to see if such a plane exists which when cut through the coordinate compound produces two exact images. In other words, one looks for the existence of a plane of symmetry within the coordinate compound. If a plane of symmetry exists, then no optical isomers exist. On the other hand, if there is no plane of symmetry, the coordinate compound has optical isomers. Furthermore, if a plane of symmetry exists around the central atom, then that molecule is called **achiral** but if a plane of symmetry does not exist around the central molecule, then that molecule has chiral center.

Example 5.12.1: CHBrClF

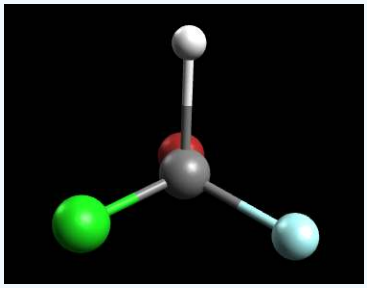
Consider the tetrahedral molecule, CHBrClF (note the color scheme: grey=carbon, white=hydrogen, green=chlorine, blue=fluorine, red=bromine)



Is this molecule optically active? In other words, does this molecule have optical isomers?

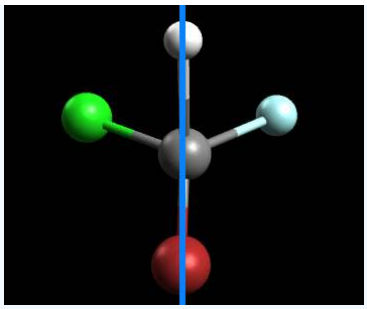
Solution

First take the Mirror-image method. The mirror image of the molecule is:



Note that this mirror image is not superimposable. In other words, the mirror image above cannot be rotated in any such way that it looks identical to the original molecule. Remember, if the mirror image is not superimposable, then optical isomers exist. Thus we know that this molecule has optical isomers.

Let's try approaching this problem using the symmetry method. If we take the original molecule and draw an axis or plane of symmetry down the middle, this is what we get:



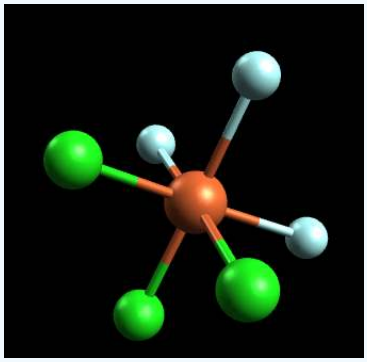
Since the left side is not identical to the right, this molecule does not have a symmetrical center and thus can be called chiral.Additionally, because it does not have a symmetrical center, we can conclude that this molecule has optical isomers. In general, when dealing with a tetrahedral molecule that has 4 different ligands, optical isomers will exist most of the time.

No matter which method you use, the answer will end up being the same.

Optical isomers because they have no plane of symmetry. In the organic case, for tetrahedral complexes, this is fairly easy to recognize the possibility of this by looking for a center atom with **four** different things attached to it. Unfortunately, this is not quite so easy with more complicated geometries!

Example 5.12.1: $PFeCl_3F_3$

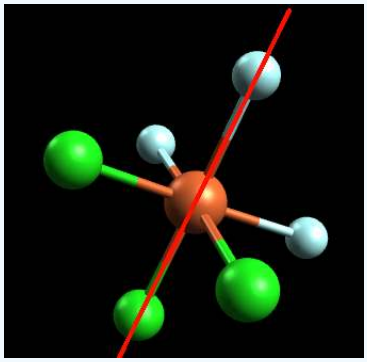
This time we will be analyzing the octahedral compound $FeCl_3F_3$. Is this molecule optically active?



(note the color scheme: orange=iron, blue=fluorine, green=chlorine):

Solution

If we try to attempt this problem using the mirror image method, we notice that the mirror image is essentially identical to the original molecule. In other words, the mirror image can be placed on top of the original molecule and is thus superimposable. Since the mirror image is superimposable, this molecule does not have any optical isomers. Let's attempt this same problem using the symmetry method. If we draw an axis or plane of symmetry, this is what we get:



Since the left side is identical to the right side, this molecule has a symmetrical center and is an achiral molecule. Thus, it has no optical isomers.

What is a Polarimeter?

A polarimeter is a scientific instrument used to measure the angle of rotation caused by passing polarized light through an optically active substance. Some chemical substances are optically active, and polarized (uni-directional) light will rotate either to the left (counter-clockwise) or right (clockwise) when passed through these substances. The amount by which the light is rotated is known as the *angle of rotation*. The angle of rotation is basically known as observed angle.

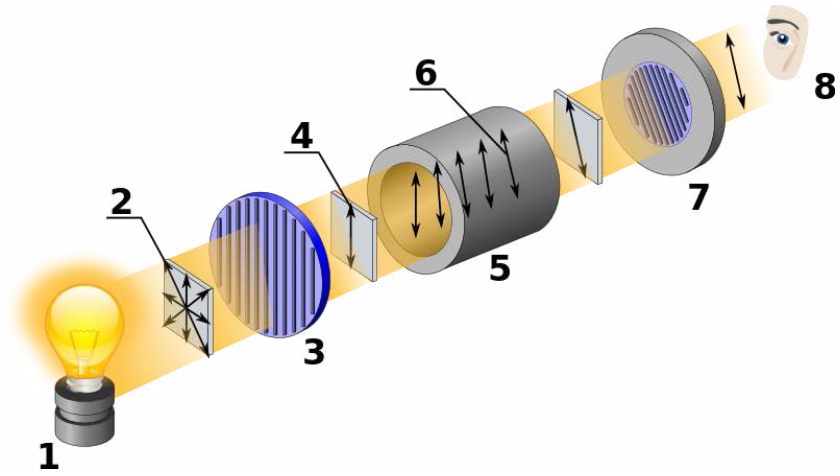


Figure 5.12.1: Schematic of a polarimeter showing the principles behind it's operation. Unpolarized light is passed through a polarizing filter before traveling through a sample. The degree of rotation of polarization is determined by a second, rotatable filter. (CC AS 3.0; Kaidor).

The polarimeter is made up of a polarizer (#3 on Figure 5.12.1) and an analyzer (#7 on Figure 5.12.1). The polarizer allows only those light waves which move in a single plane. This causes the light to become plane polarized. When the analyzer is also placed in a similar position it allows the light waves coming from the polarizer to pass through it. When it is rotated through the right angle no waves can pass through the right angle and the field appears to be dark. If now a glass tube containing an optically active solution is placed between the polarizer and analyzer the light now rotates through the plane of polarization through a certain angle, the analyzer will have to be rotated in same angle.

Nomenclature of Optical Isomers

Various methods have been used to denote the absolute configuration of optical isomers such as R or S, Λ or Δ, or C and A. The IUPAC rules suggest that for general octahedral complexes C/A scheme is convenient to use and that for bis and tris bidentate complexes the absolute configuration be designated Lambda Λ (left-handed) and Delta Δ (right-handed).

Priorities are assigned for mononuclear coordination systems based on the standard sequence rules developed for enantiomeric carbon compounds by Cahn, Ingold and Prelog (CIP rules). These rules use the coordinating atom to arrange the ligands into a priority order such that the highest atomic number gives the highest priority number (smallest CIP number). For example the hypothetical complex [Co Cl Br I NH_3 NO_2 SCN]$^{2-}$ would assign the I- as 1, Br as 2, Cl as 3, SCN as 4, NO_2 as 5 and NH_3 as 6.

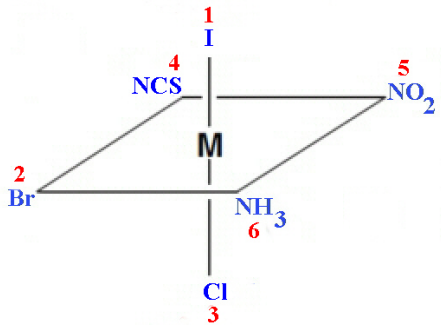
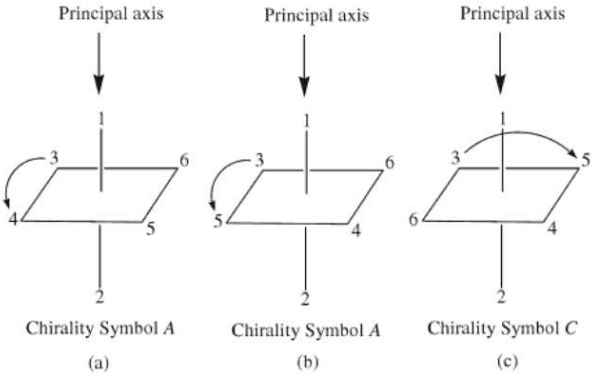


Figure* 5.12.2*: *Here is one isomer where the I and Cl, and Br and NO_2 were found to be trans- to each other.*

The reference axis for an octahedral center is that axis containing the ligating atom of CIP priority 1 and the trans ligating atom of lowest possible priority (highest numerical value). The atoms in the coordination plane perpendicular to the reference axis are viewed from the ligand having that highest priority (CIP priority 1) and the clockwise and anticlockwise sequences of priority numbers are compared. The structure is assigned the symbol C or A, according to whether the clockwise (C) or anticlockwise (A) sequence is lower at the first point of difference. In the example shown above this would be C.



The two optical isomers of $[Co(en)_3]^{3+}$ have identical chemical properties and just denoting their absolute configuration does NOT give any information regarding the direction in which they rotate plane-polarised light. This can ONLY be determined from measurement and then the isomers are further distinguished by using the prefixes (-) and (+) depending on whether they rotate left or right.

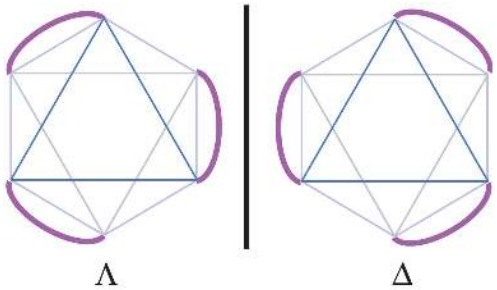


Figure **5.12.3**: left-handed Λ isomer (left) and right-handed Δ isomer (right)

To add to the confusion, when measured at the sodium D line (589 nm), the tris(1,2-diaminoethane)M(III) complexes (M= Rh(III) and Co(III)) with **IDENTICAL** absolute configuration, rotate plane polarized light in **OPPOSITE** directions! The left-handed (Λ)-$[Co(en)_3]^{3+}$ isomer gives a rotation to the right and therefore corresponds to the (+) isomer. Since the successful resolution of an entirely inorganic ion (containing no C atoms) (hexol) only a handful of truly inorganic complexes have been isolated as their optical isomers e.g. $(NH_4)_2Pt(S_5)_3.2H_2O$.

For tetrahedral complexes, R and S would be used in a similar method to tetrahedral Carbon species and although it is predicted that tetrahedral complexes with 4 different ligands should be able to give rise to optical isomers, in general they are too labile and can not be isolated.

Contributors and Attributions

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- Jim Clark (Chemguide.co.uk)

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5.12.1: Enantiomers in Octahedral Complexes with Bidentate Ligands

Enantiomers are another kind of isomer that occur in octahedral metal complexes. Like the square planar platinum complexes seen before, these compounds consist of metal ions with other atoms or groups bound to them. More information about the binding of ligands to metals is found in the section on Lewis acids and bases. These groups that bind to metal ions are called ligands. One example of a type of octahedral compounds that can form enantiomers is bidentate complexes. In bidentate complexes (from the Greek two teeth) or chelating complexes (from the Greek crab), a ligand binds very tightly to the metal because it holds onto the metal via more than one atom. Ethylenediamine is one example of a bidentate ligand.



Figure SC18a: Ethylenediamine (sometimes abbreviated en).

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

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

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



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

These shapes are alternatively described as a left-handed screw and a right handed screw. If you can picture turning the shape so that it screws into the page behind it, which direction would you turn the screwdriver? If you would twist the screwdriver clockwise, then you have a right handed screw. If you would twist the screwdriver counter-clockwise, then you have a left handed screw.

What do we know about enantiomers?

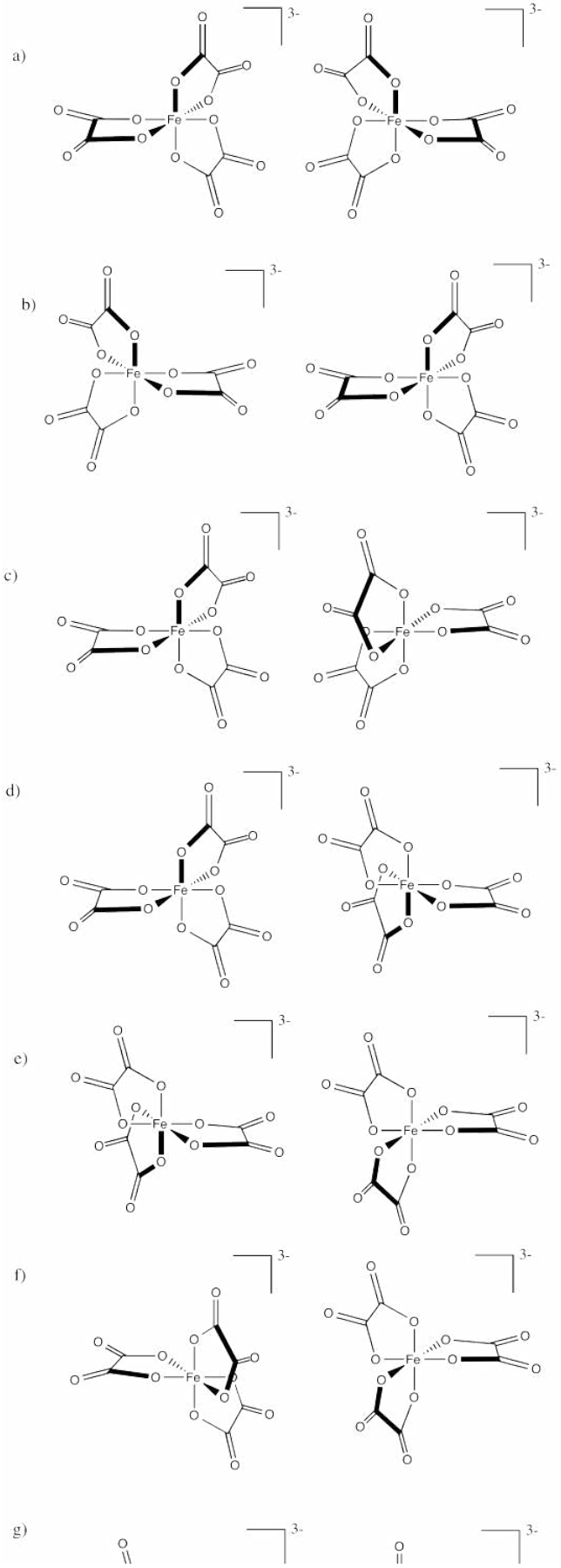
- enantiomers have identical physical properties, except...
- enantiomers have opposite optical rotation.

These kinds of complexes were historically important in demonstrating how small molecules and ions bound to metal cations. By showing that some metal complexes were chiral and displayed optical activity, early 20th century workers such as Alfred Werner were able to rule out some competing ideas about the structures of metal compounds. Today, we know that metal complexes play important roles in enzymes in biology, and Werner's work on metal complexes laid the groundwork for how we think about these complexes.

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

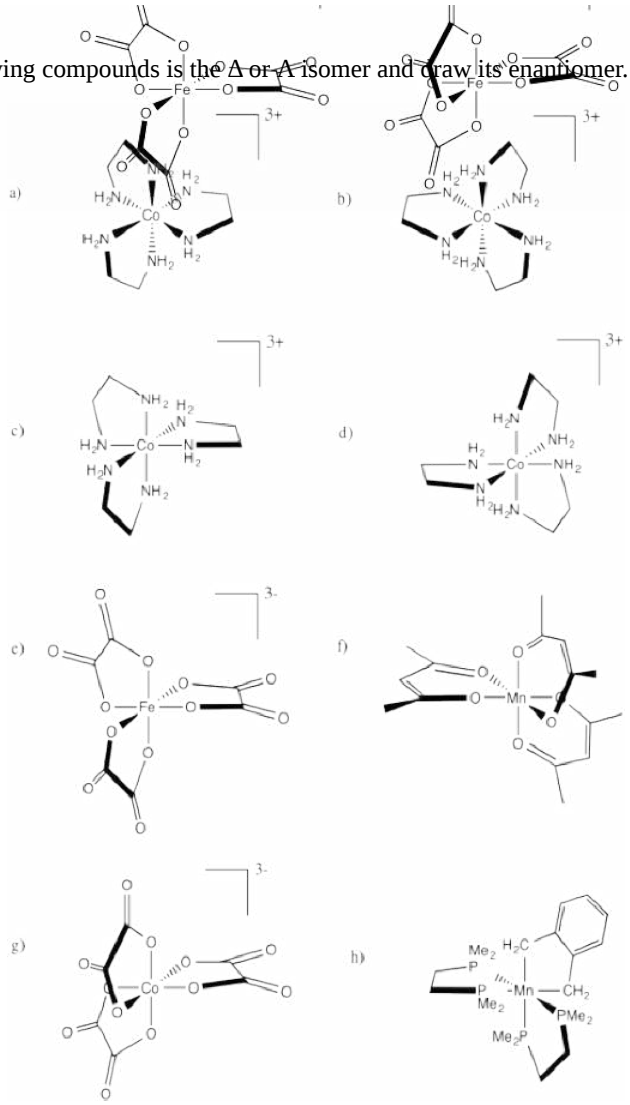
Problem SC18.1.

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


a)
b)
c)
d)
e)
f)
g)
3-

Problem SC18.2.

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



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

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5.12.2: Identifying Planes of Symmetry in Octahedral Complexes

The symmetry of a molecule is determined by the existence of **symmetry operations** performed with respect to **symmetry elements**. A symmetry element is a line, a plane or a point in or through an object, about which a rotation or reflection leaves the object in an orientation indistinguishable from the original. A plane of symmetry and the reflection operation is the coincidence of atoms on one side of the plane with corresponding atoms on the other side, as though reflected in a mirror.

Nine Planes of Potential Symmetry

Identifying planes of symmetry in an octahedral geometry can be daunting in evaluating if a molecule is chiral or not. There is a simple approach, which requires identying and testing six possible planes of symmetry that may exist for this geometry. To demonstrated this, we will consider the $[Cr(CO)_6]$ complex in Figure **5.12.2.1**.

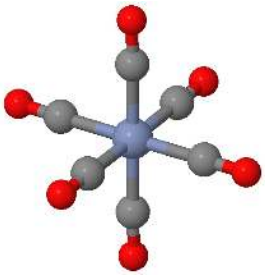


Figure **5.12.2.1**: Octahedral Structure of the $[Cr(CO_6]$ complex. Image made with Otterbein University's Symmetry page (symmetry.otterbein.edu/gallery/index.html).

While you can no doubt recognize at least one plane of symmetry to confirm that this is an achiral complex, let's identify all six of them. First we have the three planes that include the Cr metal center (as they all do) and four of the attached ligands (Figure **5.12.2.2**). These are often the easy planes to identify.

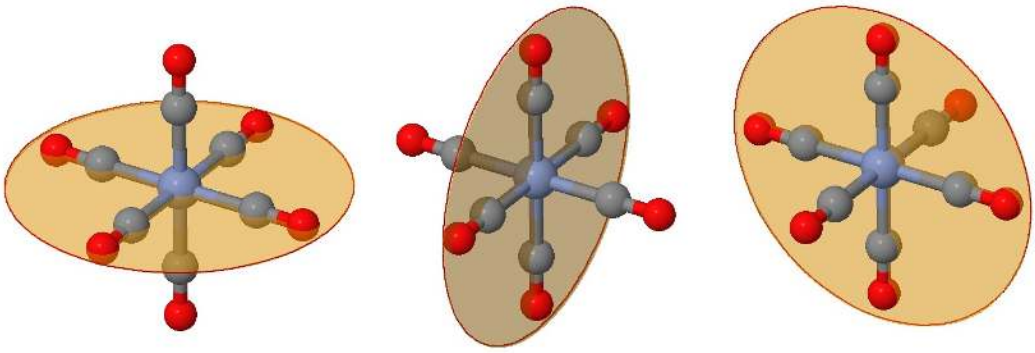


Figure **5.12.2.2**: Three potential planes of symmetry for an octahedral complex. These planes have four ligands on the plane and two off. The perspective makes it difficulty to resolve, but the atoms behind the plane are lighter colored and the slope of the plane can be identified by the projection through the central Cr atom. Image made with Otterbeins University's Symmetry page (symmetry.otterbein.edu/gallery/index.html).

The next six planes are harder to identify and can be viewed as rotations of those in Figure **5.12.2.2** by 45°. These planes bisect one angle between ligands, but still have two ligands on the plane (instead of four in the planes of Figure **5.12.2.2**).

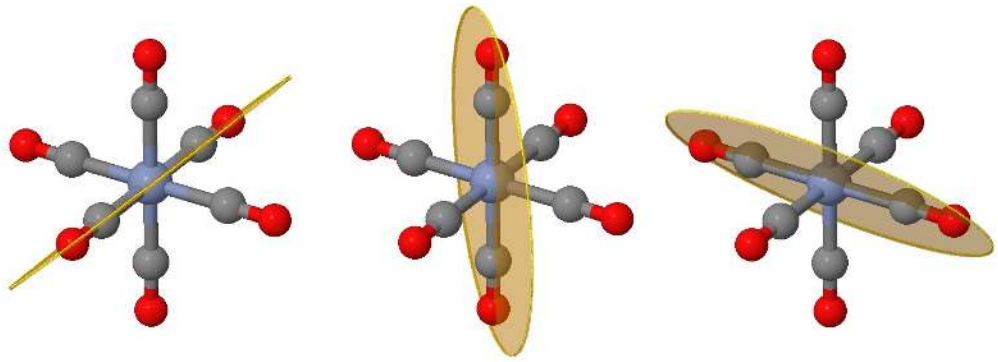


Figure 5.12.2.3: Three potential planes of symmetry for an octahedral complex. These planes have two ligands on the plane and four off. The perspective makes it difficulty to resolve, but the atoms behind the plane are lighter colored and the slope of the plane can be identified by the projection through the central Cr atom. Image made with Otterbein University's Symmetry page (symmetry.otterbein.edu/gallery/index.html).

The next three planes are even harder to view on the same perspective but are also rotations of those in Figure 5.12.2.2 by 45° in the perpendicular direction. These planes bisect an angle between ligands, but still have two ligands on the plane.

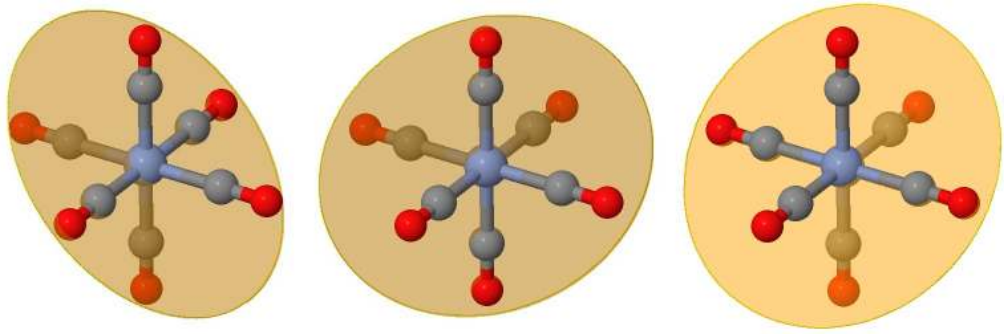


Figure 5.12.2.4: Three potential planes of symmetry for an octahedral complex. These planes have two ligands on the plane and four off. The perspective makes it difficulty to resolve, but the atoms behind the plane are lighter colored and the slope of the plane can be identified by the projection through the central Cr atom. Image made with Otterbein University's Symmetry page (symmetry.otterbein.edu/gallery/index.html).

All nine planes, in each of planes are combined in the images below.

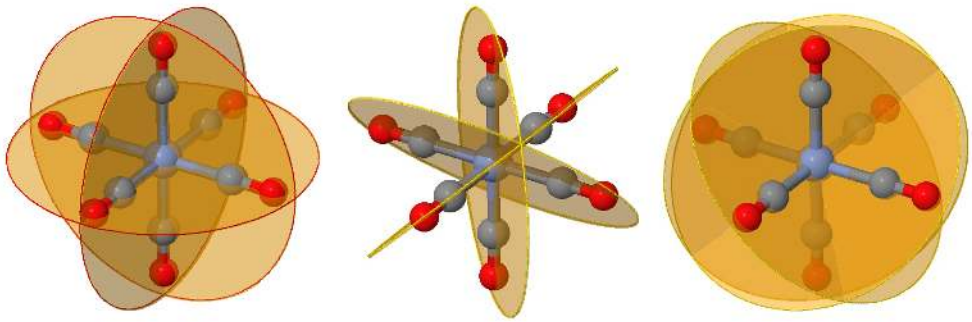


Figure 5.12.2.4 have two ligands on the plane and four off. The perspective makes it difficulty to resolve, but the atoms behind the plane are lighter colored and the slope of the plane can be identified by the projection through the central Cr atom. Image made with Otterbein University's Symmetry page (symmetry.otterbein.edu/gallery/index.html).

Now that can you identify these nine planes that may be mirror planes in an octahedral complex, you have to evaluate if they truly are mirror planes. That is simply asking if the ligand fields above the plane is IDENTICAL to the ligand field below. For the [Cr(CO)] complex discussed above, all nine planes are indeed mirror planes. However, in other complexes that may not be the case. Fortunately, to determine if a complex is chiral (optically active), then only one plane needs to be identified.

Contributors and Attributions

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CHAPTER OVERVIEW

6: d-Block Metal Chemistry- Coordination Compounds

6.1: Crystal Field Theory

6.2: Additional Resources- High and Low Spin

6.3: Ligand Field Theory Fundamentals

6.4: Spectrochemical Series

6.5: Jahn-Teller Distortions

6.6: Electronic Spectroscopy- Interpretation

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6.1: Crystal Field Theory

Crystal field theory (CFT) describes the breaking of orbital degeneracy in transition metal complexes due to the presence of ligands. CFT qualitatively describes the strength of the metal-ligand bonds. Based on the strength of the metal-ligand bonds, the energy of the system is altered. This may lead to a change in magnetic properties as well as color. This theory was developed by Hans Bethe and John Hasbrouck van Vleck.

Basic Concept

In Crystal Field Theory, it is assumed that the ions are **simple point charges** (a simplification). When applied to alkali metal ions containing a symmetric sphere of charge, calculations of bond energies are generally quite successful. The approach taken uses classical potential energy equations that take into account the attractive and repulsive interactions between charged particles (that is, Coulomb's Law interactions).

$$E \propto \frac{q_1 q_2}{r}$$

with

- E the bond energy between the charges and
- q_1 and q_2 are the charges of the interacting ions and
- r is the distance separating them.

This approach leads to the correct prediction that large cations of low charge, such as K^+ and Na^+, should form few coordination compounds. For transition metal cations that contain varying numbers of d electrons in orbitals that are NOT spherically symmetric, however, the situation is quite different. The shapes and occupations of these d-orbitals then become important in building an accurate description of the bond energy and properties of the transition metal compound.

When examining a single transition metal ion, the five *d*-orbitals have the same energy (Figure **6.1.1**). When ligands approach the metal ion, some experience more opposition from the *d*-orbital electrons than others based on the geometric structure of the molecule. Since ligands approach from different directions, not all *d*-orbitals interact directly. These interactions, however, create a splitting due to the electrostatic environment.

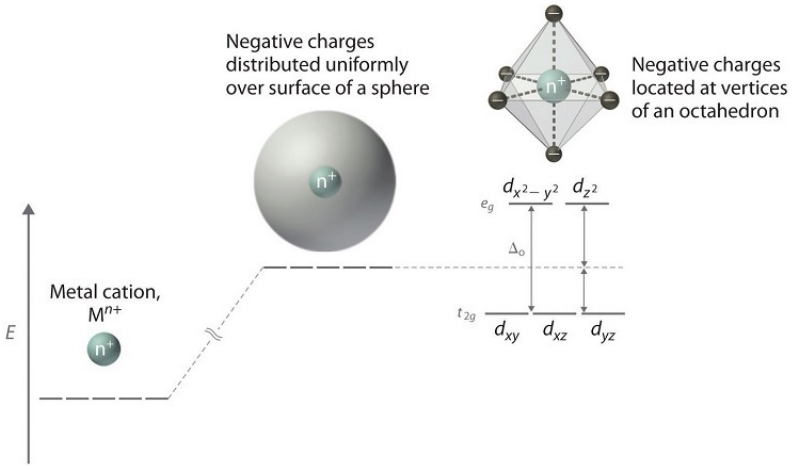


Figure **6.1.1**: Distributing a charge of −6 uniformly over a spherical surface surrounding a metal ion causes the energy of all five d orbitals to increase due to electrostatic repulsions, but the five d orbitals remain degenerate. Placing a charge of −1 at each vertex of an octahedron causes the d orbitals to split into two groups with different energies: the $d_{x^2-y^2}$ and d_{z^2} orbitals increase in energy, while the, d_{xy}, d_{xz}, and d_{yz} orbitals decrease in energy. The average energy of the five d orbitals is the same as for a spherical distribution of a −6 charge, however. Attractive electrostatic interactions between the negatively charged ligands and the positively charged metal ion (far right) cause all five d orbitals to decrease in energy but does not affect the splittings of the orbitals. The two e_g orbitals point directly at the six negatively charged ligands, which increases their energy compared with a spherical distribution of negative charge. In contrast, the three t_{2g} orbitals point between the negatively charged ligands, which decreases their energy compared with a spherical distribution of charge.

For example, consider a molecule with octahedral geometry. Ligands approach the metal ion along the x, y, and z axes. Therefore, the electrons in the d_{z^2} and $d_{x^2-y^2}$ orbitals (which lie along these axes) experience greater repulsion. It requires more energy to have an electron in these orbitals than it would to put an electron in one of the other orbitals. This causes a splitting in the energy levels of the *d*-orbitals. This is known as **crystal field splitting**. For octahedral complexes, crystal field splitting is denoted by Δ_o (or Δ_{oct}). The energies of the d_{z^2} and $d_{x^2-y^2}$ orbitals increase due to greater interactions with the ligands. The d_{xy}, d_{xz}, and d_{yz} orbitals decrease with respect to this normal energy level and become more stable.

Electrons in Orbitals

According to the Aufbau principle, electrons are filled from lower to higher energy orbitals (Figure **6.1.1**). For the octahedral case above, this corresponds to the d_{xy}, d_{xz}, and d_{yz} orbitals. Following Hund's rule, electrons are filled in order to have the highest number of unpaired electrons. For

example, if one had a d^3 complex, there would be three unpaired electrons. If one were to add an electron, however, it has the ability to fill a higher energy orbital (d_{z^2} or $d_{x^2-y^2}$) or pair with an electron residing in the d_{xy}, d_{xz}, or d_{yz} orbitals. This pairing of the electrons requires energy (spin pairing energy). If the pairing energy is less than the crystal field splitting energy, Δ_o, then the next electron will go into the d_{xy}, d_{xz}, or d_{yz} orbitals due to stability. This situation allows for the least amount of unpaired electrons, and is known as low spin. If the pairing energy is greater than Δ_o, then the next electron will go into the d_{z^2} or $d_{x^2-y^2}$ orbitals as an unpaired electron. This situation allows for the most number of unpaired electrons, and is known as high spin. Ligands that cause a transition metal to have a small crystal field splitting, which leads to high spin, are called weak-field ligands. Ligands that produce a large crystal field splitting, which leads to low spin, are called **strong field ligands**.

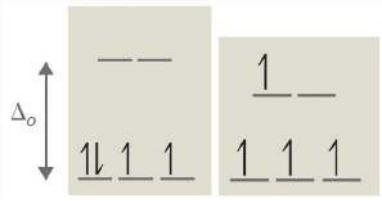


Figure **6.1.2**: Low Spin, Strong Field ($\Delta_o > P$) High Spin, Weak Field ($\Delta_o < P$)Splitting for a d^4 complex under a strong field (left) and a weak field (right). The strong field is a low spin complex, while the weak field is a high spin complex.

As mentioned above, CFT is based primarily on symmetry of ligands around a central metal/ion and how this anisotropic (properties depending on direction) ligand field affects the metal's atomic orbitals; the energies of which may increase, decrease or not be affected at all. Once the ligands' electrons interact with the electrons of the *d*-orbitals, the electrostatic interactions cause the energy levels of the d-orbital to fluctuate depending on the orientation and the nature of the ligands. For example, the oxidation state and the strength of the ligands determine splitting; the higher the oxidation state or the stronger the ligand, the larger the splitting. Ligands are classified as strong or weak based on the spectrochemical series:

$$I^- < Br^- < Cl^- < \underline{S}CN^- < F^- < OH^- < ox^{2-} < \underline{O}NO^- < H_2O < SC\underline{N}^- < EDTA^{4-} < NH_3 < en < \underline{N}O_2^- < CN^-$$

Note that SCN^- and NO_2- ligands are represented twice in the above spectrochemical series since there are two different Lewis base sites (e.g., free electron pairs to share) on each ligand (e.g., for the SCN^- ligand, the electron pair on the sulfur or the nitrogen can form the coordinate covalent bond to a metal). The specific atom that binds in such ligands is underlined.

In addition to octahedral complexes, two common geometries observed are that of tetrahedral and square planar. These complexes differ from the octahedral complexes in that the orbital levels are raised in energy due to the interference with electrons from ligands. For the tetrahedral complex, the d_{xy}, d_{xz}, and d_{yz} orbitals are raised in energy while the d_{z^2}, $d_{x^2-y^2}$ orbitals are lowered. For the square planar complexes, there is greatest interaction with the $d_{x^2-y^2}$ orbital and therefore it has higher energy. The next orbital with the greatest interaction is d_{xy}, followed below by d_{z^2}. The orbitals with the lowest energy are the d_{xz} and d_{yz} orbitals. There is a large energy separation between the d_{z^2} orbital and the d_{xz} and d_{yz} orbitals, meaning that the crystal field splitting energy is large. We find that the square planar complexes have the greatest crystal field splitting energy compared to all the other complexes. This means that most square planar complexes are low spin, strong field ligands.

Description of *d*-Orbitals

To understand CFT, one must understand the description of the lobes:

- d_{xy}: lobes lie in-between the x and the y axes.
- d_{xz}: lobes lie in-between the x and the z axes.
- d_{yz}: lobes lie in-between the y and the z axes.
- $d_{x^2-y^2}$: lobes lie on the x and y axes.
- d_{z^2}: there are two lobes on the z axes and there is a donut shape ring that lies on the xy plane around the other two lobes.

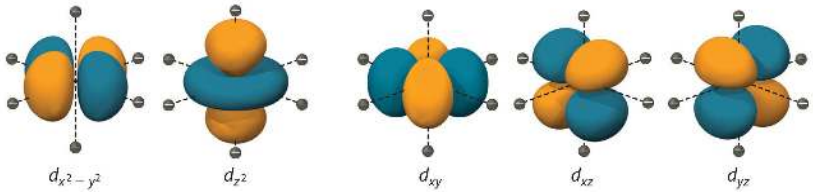


Figure **6.1.3**: Spatial arrangement of ligands in the an octahedral ligand field with respect to the five d-orbitals.

Octahedral Complexes

In an octahedral complex, there are six ligands attached to the central transition metal. The d-orbital splits into two different levels (Figure **6.1.4**). The bottom three energy levels are named d_{xy}, d_{xz}, and d_{yz} (collectively referred to as t_{2g}). The two upper energy levels are named $d_{x^2-y^2}$, and d_{z^2} (collectively referred to as e_g).

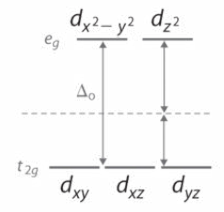


Figure **6.1.4**.

The reason they split is because of the electrostatic interactions between the electrons of the ligand and the lobes of the d-orbital. In an octahedral, the electrons are attracted to the axes. Any orbital that has a lobe on the axes moves to a higher energy level. This means that in an octahedral, the energy levels of e_g are higher ($0.6\Delta_o$) while t_{2g} is lower ($0.4\Delta_o$). The distance that the electrons have to move from t_{2g} from e_g and it dictates the energy that the complex will absorb from white light, which will determine the color. Whether the complex is paramagnetic or diamagnetic will be determined by the spin state. If there are unpaired electrons, the complex is paramagnetic; if all electrons are paired, the complex is diamagnetic.

Tetrahedral Complexes

In a tetrahedral complex, there are four ligands attached to the central metal. The d orbitals also split into two different energy levels. The top three consist of the d_{xy}, d_{xz}, and d_{yz} orbitals. The bottom two consist of the $d_{x^2-y^2}$ and d_{z^2} orbitals. The reason for this is due to poor orbital overlap between the metal and the ligand orbitals. The orbitals are directed on the axes, while the ligands are not.

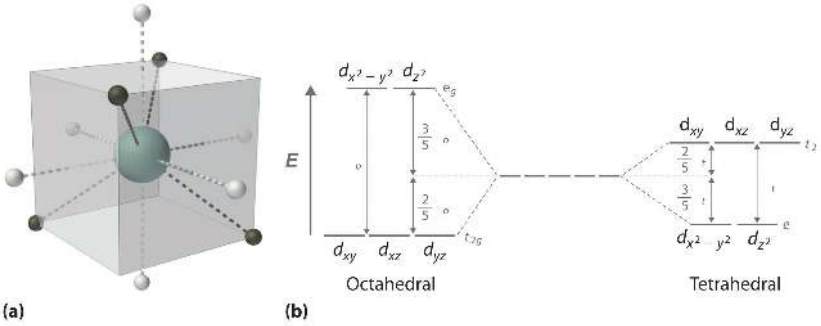


Figure **6.1.5**: (a) Tetraheral ligand field surrounding a central transition metal (blue sphere). (b) Splitting of the degenerate d-orbitals (without a ligand field) due to an octahedral ligand field (left diagram) and the tetrahedral field (right diagram).

The difference in the splitting energy is tetrahedral splitting constant (Δ_t), which less than (Δ_o) for the same ligands:

$$\Delta_t = 0.44\,\Delta_o \tag{6.1.1}$$

Consequentially, Δ_t is typically smaller than the spin pairing energy, so tetrahedral complexes are usually **high spin**.

Square Planar Complexes

In a square planar, there are four ligands as well. However, the difference is that the electrons of the ligands are only attracted to the xy plane. Any orbital in the xy plane has a higher energy level (Figure **6.1.6**). There are four different energy levels for the square planar (from the highest energy level to the lowest energy level): $d_{x^2-y^2}$, d_{xy}, d_{z^2}, and both d_{xz} and d_{yz}.

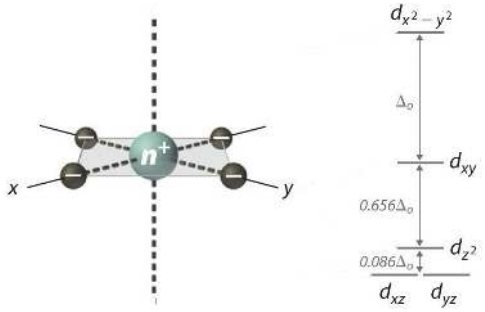


Figure **6.1.6**: Splitting of the degenerate d-orbitals (without a ligand field) due to an square planar ligand field.

The splitting energy (from highest orbital to lowest orbital) is Δ_{sp} and tends to be larger then Δ_o

$$\Delta_{sp} = 1.74\,\Delta_o \tag{6.1.2}$$

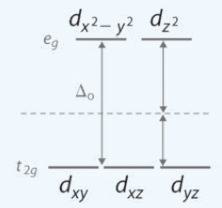
Moreover, Δ_{sp} is also larger than the pairing energy, so the square planar complexes are usually **low spin** complexes.

Example 6.1.1

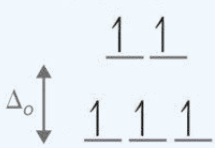
For the complex ion $[Fe(Cl)_6]^{3-}$ determine the number of d electrons for Fe, sketch the d-orbital energy levels and the distribution of d electrons among them, list the number of lone electrons, and label whether the complex is paramagnetic or diamagnetic.

Solution

- Step 1: Determine the oxidation state of Fe. Here it is Fe^{3+}. Based on its electron configuration, Fe^{3+} has **5 d-electrons**.
- Step 2: Determine the geometry of the ion. Here it is an octahedral which means the energy splitting should look like:



- Step 3: Determine whether the ligand induces is a strong or weak field spin by looking at the spectrochemical series. Cl^- is a weak field ligand (i.e., it induces high spin complexes). Therefore, electrons fill all orbitals before being paired.



- Step four: Count the number of lone electrons. Here, there are **5 electrons**.
- Step five: The five unpaired electrons means this complex ion is **paramagnetic** (and strongly so).

Example 6.1.2

A *tetrahedral* complex absorbs at 545 nm. What is the respective octahedral crystal field splitting (Δ_o)? What is the color of the complex?

Solution

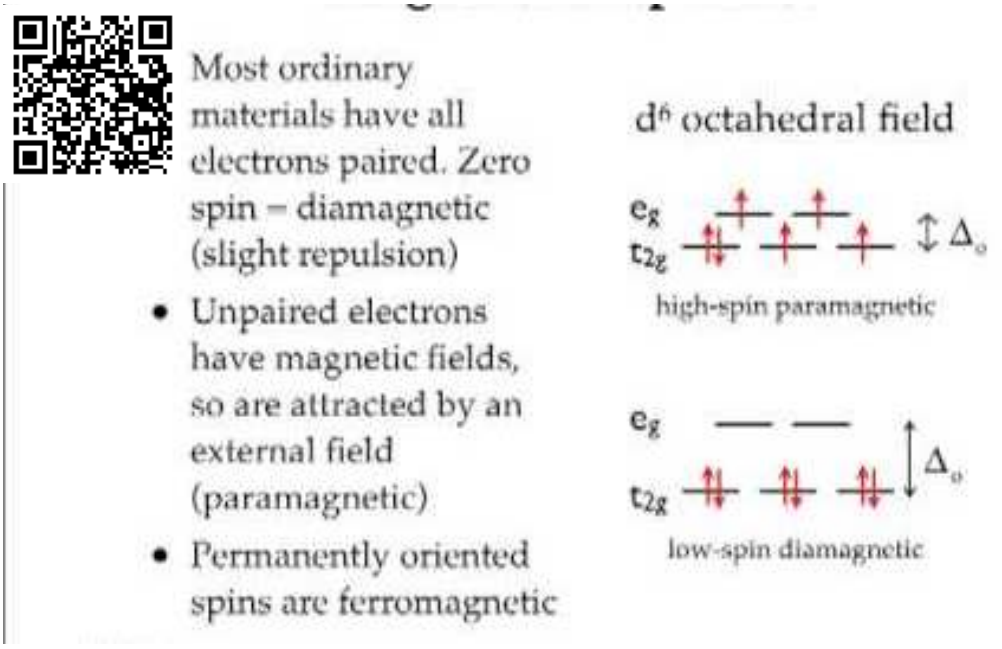
$$\begin{aligned}\Delta_t &= \frac{hc}{\lambda} \\ &= \frac{(6.626 \times 10^{-34} J \cdot s)(3 \times 10^8 m/s)}{545 \times 10^{-9} m} \\ &= 3.65 \times 10^{-19}\ J\end{aligned}$$

However, the *tetrahedral* splitting (Δ_t) is ~4/9 that of the *octahedral* splitting (Δ_o).

$$\begin{aligned}\Delta_t &= 0.44\Delta_o \\ \Delta_o &= \frac{\Delta_t}{0.44} \\ &= \frac{3.65 \times 10^{-19} J}{0.44} \\ &= 8.30 \times 10^{-18} J\end{aligned}$$

This is the energy needed to promote *one* electron in *one* complex. Often the crystal field splitting is given per mole, which requires this number to be multiplied by Avogadro's Number (6.022×10^{23}).

This complex appears red, since it absorbs in the complementary green color (determined via the color wheel).



Video:

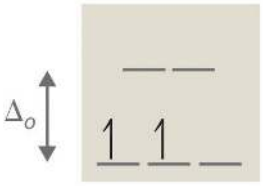
Problems

For each of the following, sketch the d-orbital energy levels and the distribution of d electrons among them, state the geometry, list the number of d-electrons, list the number of lone electrons, and label whether they are paramagnetic or dimagnetic:

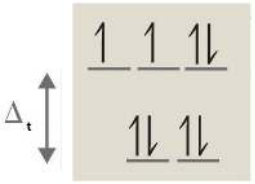
1. $[Ti(H_2O)_6]^{2+}$
2. $[NiCl_4]^{2-}$
3. $[CoF_6]^{3-}$ (also state whether this is low or high spin)
4. $[Co(NH_3)_6]^{3+}$ (also state whether this is low or high spin)
5. True or False: Square Planer complex compounds are usually low spin.

Answers

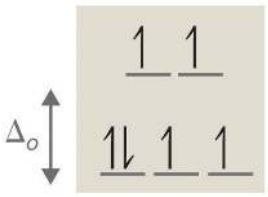
1. octahedral, 2, 2, paramagnetic



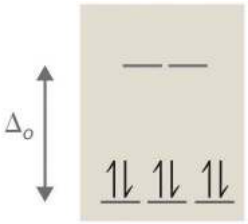
2. tetrahedral, 8, 2, paramagnetic (see Octahedral vs. Tetrahedral Geometries)



3. octahedral, 6, 4, paramagnetic, high spin



4. octahedral, 6, 0, diamagnetic, low spin



5. True

Contributors and Attributions

- Asadullah Awan (UCD), Hong Truong (UCD)
- Prof. Robert J. Lancashire (The Department of Chemistry, University of the West Indies)

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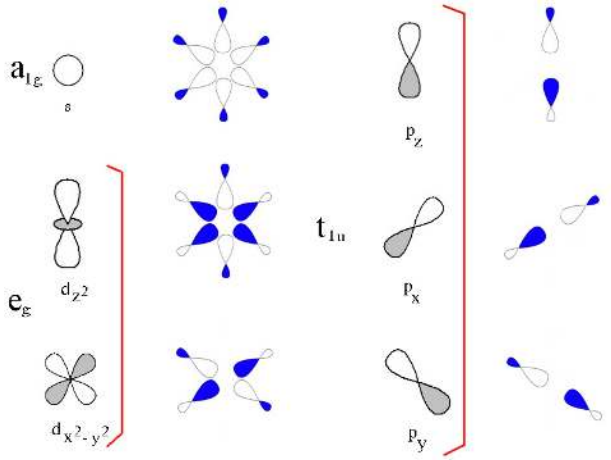
6.2: Additional Resources- High and Low Spin

Additional Resources: High and Low Spin

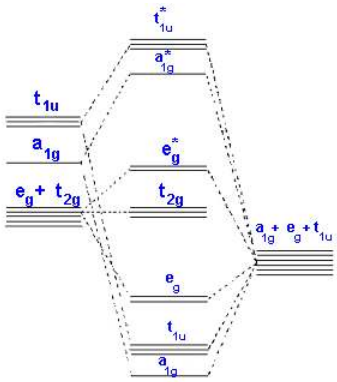
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6.3: Ligand Field Theory Fundamentals

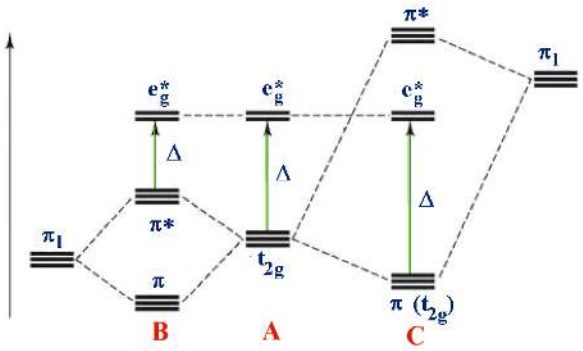
Ligand Field Theory can be considered an extension of Crystal Field Theory such that all levels of covalent interactions can be incorporated into the model. Treatment of the bonding in LFT is generally done using Molecular Orbital Theory. A qualitative approach that can be used for octahedral metal complexes is given in the following 3 diagrams.



In the first diagram, the 3d, 4s and 4p metal ion atomic orbitals are shown together with the ligand group orbitals that would have the correct symmetry to be able to overlap with them. The symmetry adapted linear comination of ligand orbitals are generated by taking 6 sigma orbitals from the ligands, designated as σ_x, σ_{-x}, σ_y, σ_{-y}, σ_z, σ_{-z} and then combining them to make 6 ligand group orbitals. (labelled e_g, a_{1g}, t_{1u})



In the second diagram only sigma bonding is considered and it shows the combination of the metal 3d, 4s and 4p orbitals with OCCUPIED ligand group orbitals (using 1 orbital from each ligand). The result is that that the metal electrons would be fed into t2g and eg* molecular orbitals which is similar to the CFT model except that the eg orbital is now eg*.



For example: B - $[M(II)I_6]^{4-}$ A - $[M(II)(H_2O)_6]^{2+}$ C - $[M(II)(CN)_6]^{4-}$

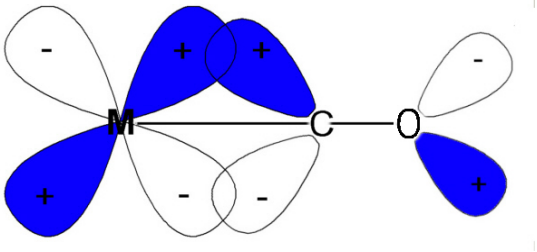
In the third diagram, π (pi) bonding is considered. In general π bonds are weaker than σ (sigma) bonds and so the effect is to modify rather than dramatically alter the description. 2 orbitals from each ligand are combined to give a total of 12 which are subdivided into four sets with three ligand group orbitals in each set. These are labelled t_{1g}, t_{1u}, t_{2g} and t_{2u}. The metal t_{2g} orbital is the most suitable for interaction and this is shown in the 2 cases above.
Case A is the same as above, ignoring π interactions.

- For case B, the ligand π orbitals are full and at lower energy than the metal t_{2g}. This causes a decrease in the size of Δ.
- For case C, the ligand π orbitals are empty and at higher energy than the metal t_{2g}. This causes an increase in the size of Δ.

Returning to the problem of correctly placing ligands in the Spectrochemical series, the halides are examples of case A and groups like CN- and CO are examples of case B. It is possible then to explain the Spectrochemical series once covalent effects are considered.

Some convincing arguments for covalency and effects on Δ come from a study of the IR spectra recorded for simple carbonyl compounds e.g. $M(CO)_6$.

- The CO molecule has a strong triple bond which in the IR gives rise to a strong absorption at ~2140 cm^{-1}. For the series $[Mn(CO)_6]^+$, $[Cr(CO)_6]$ and $[V(CO)_6]^-$, which are isoelectronic, the IR bands for the CO have shifted to 2090, 2000 and 1860 cm^{-1} respectively. Despite the fact that the metals have the same number of electrons (isoelectronic) the frequency of force constant of the CO bond is seen to vary $Mn^+ > Cr > V^-$.
- This can not be explained on an ionic basis but is consistent with the π bonding scheme since the greater the positive charge on the metal, the less readily the metal can delocalize electrons back into the π^* orbitals of the CO group.



Note that the IR values we are dealing with relate to the CO bond and not the M-C so when the CO frequency gets less then it is losing triple bond character and becoming more like a double bond. This is expected if electrons are pushed back from the metal into what were empty π^* antibonding orbitals.

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6.4: Spectrochemical Series

Strong and weak field ligands. The spectrochemical series ranks ligands according the **energy difference Δ_O** between the t_{2g} and e_g orbitals in their octahedral complexes. This energy difference is measured in the spectral transition between these levels, which often lies in the visible part of the spectrum and is responsible for the colors of complexes with partially filled d-orbitals. Ligands that produce a large splitting are called **strong field** ligands, and those that produce a small splitting are called **weak field** ligands.



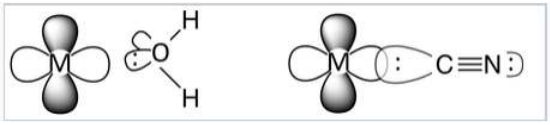
An abbreviated spectrochemical series is:

Weak field $I^- < Br^- < Cl^- < NO_3^- < F^- < OH^- < H_2O <$ Pyridine $< NH_3 < NO_2^- < CN^- <$ CO **Strong field**

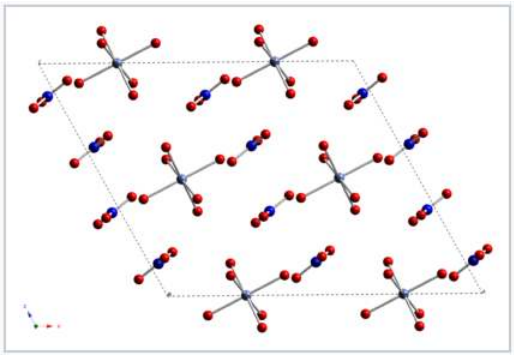
Orbital overlap

Referring to the molecular orbital diagram above, we see that the splitting between d-electron levels reflects the antibonding interaction between the e_g metal orbitals and the ligands. Thus, we expect ligand field strength to correlate with metal-ligand orbital overlap. Ligands that bind through very electronegative atoms such as **O and halogens** are thus expected to be **weak field**, and

ligands that bind through **C or P** are typically **strong field**. Ligands that bind through **N** are **intermediate** in strength. Another way to put this is that hard bases tend to be weak field ligands and soft bases are strong field ligands.



Water is a weak field ligand. The electronegative O atom is strongly electron-withdrawing, so there is poor orbital overlap between the electron pair on O and a metal d-orbital. The more electropositive C atom in the strong field ligand CN^- allows better orbital overlap and sharing of the electron pair. Note that CN^- typically coordinates metal ions through the C atom rather than the N atom.



Cobalt (II) complexes have different colors depending on the nature of the ligand. In crystals of the red compound cobalt(II) nitrate dihydrate, each cobalt ion is coordinated by six water molecules. The $[Co(H_2O)_6]^{2+}$ cations and NO_3^- anions crystallize to make a salt. When the complex is dissolved in water, Co(II) retains its coordination shell of six water molecules and the solution has the same red color as the crystal.

Energy units

Energy can be calculated in a number of ways and it is useful to try to relate the splitting energy Δ_O to more familiar quantities like bond energies.

$$E = h\nu = h\frac{c}{\lambda} = hc\tilde{\nu} \tag{6.4.1}$$

Here ν is the frequency of the electromagnetic radiation, h is Planck's constant (6.626×10^{-34} J*s), and c is the speed of light. $\tilde{\nu}$ is called the "wavenumber" and is the inverse of the wavelength, usually measured in cm^{-1}. Energy gaps are often expressed by spectroscopists in terms of wavenumbers.

For example, a red photon has a wavelength of about 620 nm and a wavenumber of about 16,000 cm^{-1}. In other energy units, the same red photon has an energy of 2.0 eV (1 eV = 1240 nm) or 193 kJ/mol (1 eV = 96.5 kJ/mol). If we compare this to the dissociation energy of a carbon-carbon single bond (350 kJ/mol), we see that the C-C bond has about twice the energy of a red photon. We would need an ultraviolet photon (E > 350 kJ/mol = 3.6 eV = 345 nm = 29,000cm^{-1}) to break a C-C bond.

We will see that Δ_O varies widely for transition metal complexes, from near-infrared to ultraviolet wavelengths. Thus the energy difference between the t_{2g} and e_g orbitals can range between the energy of a rather weak to a rather strong covalent bond.

Δ_O depends on both the metal and the ligand. We can learn something about trends in Δ_O by comparing a series of d^6 metal complexes

Complex	Δ_O (cm^{-1})
$[Co(H_2O)_6]^{2+}$	9,300
$[Co(H_2O)_6]^{3+}$	18,200
$[Co(CN)_6]^{3-}$	33,500
$[Rh(H_2O)_6]^{3+}$	27,000
$[Rh(CN)_6]^{3-}$	45,500

Important trends in Δ_O:

- **Co^{3+}** complexes have larger Δ_O than **Co^{2+}** complexes with the same ligand. This reflects the **electrostatic** nature of the crystal field splitting.
- **Rh^{3+}** complexes have larger Δ_O than **Co^{3+}** complexes. In general, elements in the 2nd and 3rd transition series (the **4d and 5d elements)** have **larger splitting** than those in the 3d series.

For a given metal in one oxidation state (e.g., Co^{3+}), the trend in Δ_O follows the **spectrochemical series**. Thus Δ_O is larger for $[Co(CN)_6]^{3-}$, which contains the strong field CN^- ligand, than it is for $[Co(H_2O)_6]^{3+}$ with the weak field ligand H_2O.

The 4d and 5d elements are similar in their size and their chemistry. In comparing Δ_O values for complexes in the 3d, 4d, and 5d series (e.g., comparing elements in the triads Co,Rh,Ir or Fe,Ru,Os), we always find 3d << 4d $\lesssim$ 5d. This trend reflects the spatial extent of the d-orbitals and thus their overlap with ligand orbitals. The 3d orbitals are smaller, and they are less effective in bonding than the 4d or 5d. The 4d and 5d orbitals are similar to each other because of the lanthanide contraction. At the beginning of the 5d series (between ^{56}Ba and ^{72}Hf) are the fourteen lanthanide elements (^{57}La - ^{71}Lu).

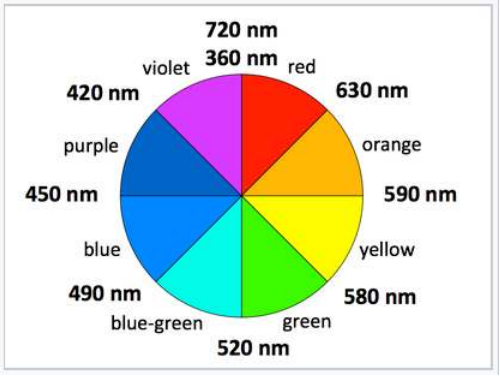
Although the valence orbitals of the 5d elements are in a higher principal quantum shell than those of the 4d elements, the addition of 14 protons to the nucleus in crossing the lanthanide series contracts the sizes of the atomic orbitals. The important result is that the **valence orbitals of the 4d and 5d elements have similar sizes** and thus the elements resemble each other in their chemistry much more than they resemble their cousins in the 3d series. For example, the chemistry of Ru is very similar to that of Os, as illustrated below, but quite different from that of Fe.



Both Os and Ru form volatile, molecular tetroxides MO_4. OsO_4 is used in epoxidation reactions and as a stain in electron microscopy. In contrast, the highest binary oxide of iron is Fe_2O_3.

Colors of transition metal complexes

A simple, qualitative way to see the relative crystal field splitting energy, Δ_O, is to observe the color of a transition metal complex. The higher the energy of the absorbed photon, the larger the energy gap. However, the color a complex absorbs is **complementary** to the color it appears (i.e., the color of light it reflects), which is **opposite** the absorbed color on the color wheel.



Complementary colors are across the color wheel from each other

Examples: (all d^7 Co^{2+} complexes)

$[Co(H_2O)_6]^{2+}$ looks purple in its salts and in concentrated solution because it absorbs in the green range.

$[Co(NH_3)_6]^{2+}$ is straw-colored because it absorbs in the blue range.

$[Co(CN)_6]^{4-}$, looks red, absorbs in the violet and ultra-violet part of the spectrum. This is consistent with the idea that CN^- is a stronger field ligand than NH_3, because the energy of a UV photon is higher than that of a red-orange photon.

This method is applicable to most transition metal complexes, as the majority of them absorb somewhere in the visible range (400-700 nm = 25,000 to 14,300 cm^{-1}), or have UV transitions that tail into the visible, making them appear yellow; however there are complexes such as $[Rh(CN)_6]^{3-}$ that appear colorless because their d-d transitions are in the ultraviolet. Other complexes such as $[Mn(H_2O)]_6^{2+}$ are weakly colored because their d-d transitions involve a change in the spin state of the complex.

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6.5: Jahn-Teller Distortions

The Jahn-Teller effect is a geometric distortion of a non-linear molecular system that reduces its symmetry and energy. This distortion is typically observed among octahedral complexes where the two axial bonds can be shorter or longer than those of the equatorial bonds. This effect can also be observed in tetrahedral compounds. This effect is dependent on the electronic state of the system.

Introduction

In 1937, Hermann Jahn and Edward Teller postulated a theorem stating that "stability and degeneracy are not possible simultaneously unless the molecule is a linear one," in regards to its electronic state.[1] This leads to a break in degeneracy which stabilizes the molecule and by consequence, reduces its symmetry. Since 1937, the theorem has been revised which Housecroft and Sharpe have eloquently phrased as "any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy, thereby removing the degeneracy."[2] This is most commonly observed with transition metal octahedral complexes, however, it can be observed in tetrahedral compounds as well.

For a given octahedral complex, the five d atomic orbitals are split into two degenerate sets when constructing a molecular orbital diagram. These are represented by the sets' symmetry labels: t_{2g} (d_{xz}, d_{yz}, d_{xy}) and e_g (d_{z^2} and $d_{x^2-y^2}$). When a molecule possesses a degenerate electronic ground state, it will distort to remove the degeneracy and form a lower energy (and by consequence, lower symmetry) system. The octahedral complex will either elongate or compress the z ligand bonds as shown in Figure **6.5.1** below:

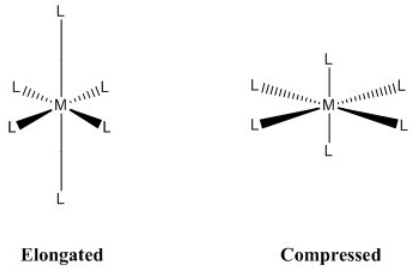


Figure **6.5.1**: Jahn-Teller distortions for an octahedral complex.

When an octahedral complex exhibits elongation, the axial bonds are longer than the equatorial bonds. For a compression, it is the reverse; the equatorial bonds are longer than the axial bonds. Elongation and compression effects are dictated by the amount of overlap between the metal and ligand orbitals. Thus, this distortion varies greatly depending on the type of metal and ligands. In general, the stronger the metal-ligand orbital interactions are, the greater the chance for a Jahn-Teller effect to be observed.

Elongation

Elongation Jahn-Teller distortions occur when the degeneracy is broken by the stabilization (lowering in energy) of the d orbitals with a *z* component, while the orbitals without a *z* component are destabilized (higher in energy) as shown in Figure **6.5.2** below:

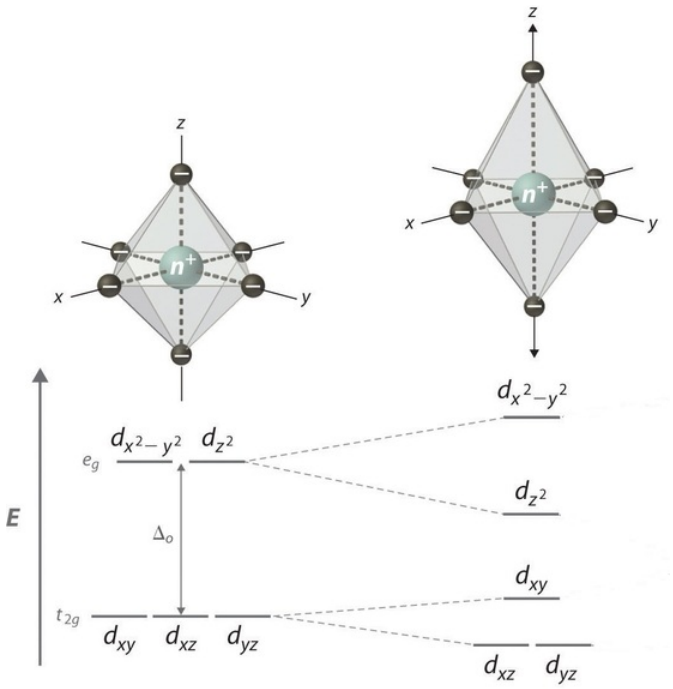


Figure **6.5.2**: Illustration of tetragonal distortion (elongation) for an octahedral complex.

This is due to the d_{xy} and $d_{x^2-y^2}$ orbitals having greater overlap with the ligand orbitals, resulting in the orbitals being higher in energy. Since the $d_{x^2-y^2}$ orbital is antibonding, it is expected to increase in energy due to elongation. The d_{xy} orbital is still nonbonding, but is destabilized due to the interactions. Jahn-Teller elongations are well-documented for copper(II) octahedral compounds. A classic example is that of copper(II) fluoride as shown in Figure **6.5.3**.

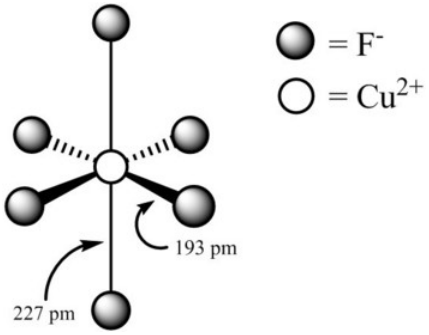


Figure **6.5.3**: Structure of octahedral copper(II) fluoride.[3]

Notice that the two axial bonds are both elongated and the four shorter equatorial bonds are the same length as each other. According the theorem, the orbital degeneracy is eliminated by distortion, making the molecule more stable based on the model presented in Figure **6.5.2**.

Compression

Compression Jahn-Teller distortions occur when the degeneracy is broken by the stabilization (lowering in energy) of the d orbitals *without* a *z* component, while the orbitals with a *z* component are destabilized (higher in energy) as shown in Figure **6.5.4** below:

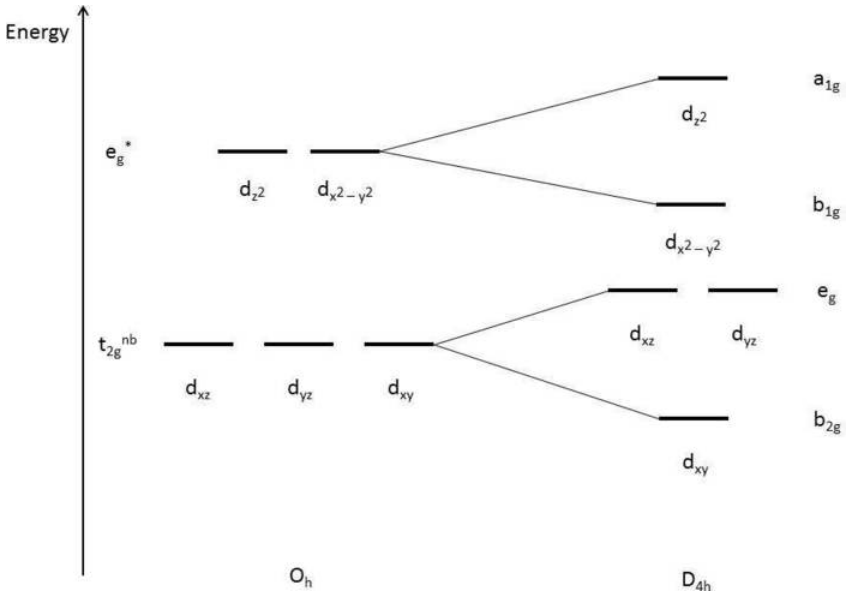


Figure **6.5.4**: Illustration of tetragonal distortion (compression) for an octahedral complex.

This is due to the *z*-component d orbitals having greater overlap with the ligand orbitals, resulting in the orbitals being higher in energy. Since the d_{z^2} orbital is antibonding, it is expected to increase in energy due to compression. The d_{xz} and d_{yz} orbitals are still nonbonding, but are destabilized due to the interactions.

Electronic Configurations

For Jahn-Teller effects to occur in transition metals there must be degeneracy in either the t_{2g} or e_g orbitals. The electronic states of octahedral complexes depend on the number of d-electrons and the splitting energy, **Δ**. When **Δ** is large and is greater than the energy required to pair electrons, electrons pair in t_{2g} before occupying e_g. On the other hand, when ***Delta*** small and is less than the pairing energy, electrons will occupy e_g before pairing in t_{2g}. The **Δ** of an octahedral complex is dictated by the chemical environment (ligand identity), and the identity and charge of the metal ion. If there electron configurations for any d-electron count is different depending on **Δ**, the configuration with more paired electrons is called low spin while the one with more unpaired electrons is called high spin.

The electron configurations diagrams for d1 through d10 with large and small ***δ*** are illustrated in the figures below. Notice that the electron configurations for d^1, d^2, d^3, d^8, d^9, and d^{10} are the same no matter what the magnitude of **Δ**. Low spin and high spin configurations exist only for the electron counts d^4, d^5, d^6, and d^7.

Large Δ

Figure **6.5.5** (below) shows the various electronic configurations for octahedral complexes with large **Δ**, including the low-spin configurations of d^4, d^5, d^6, and d^7:

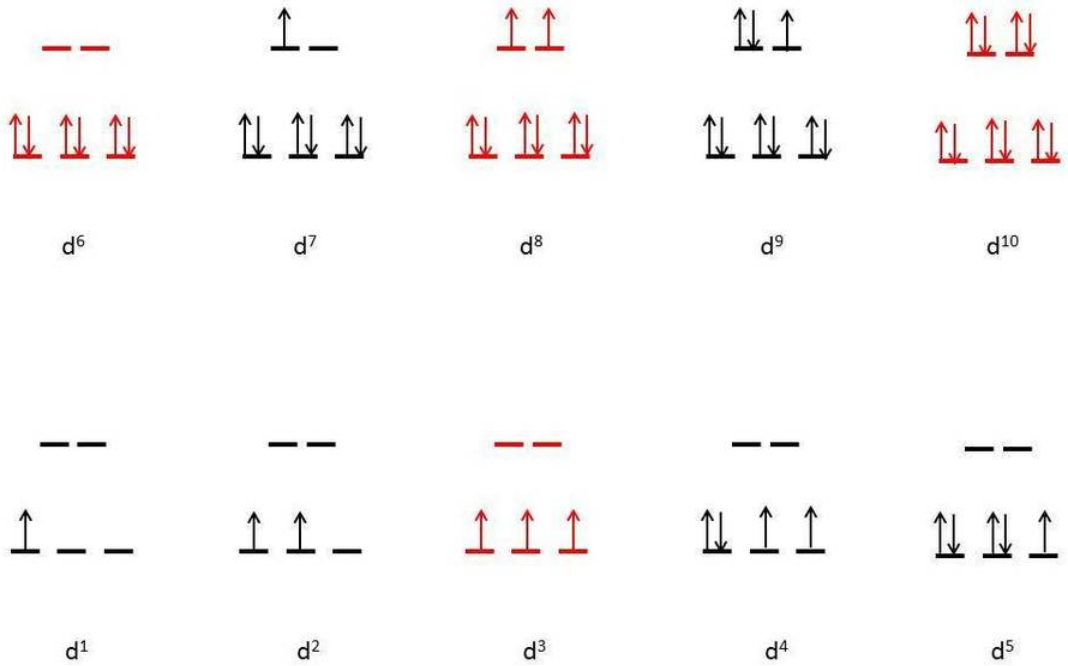


Figure **6.5.5**: Electron configuration diagram of octahedral complexes (red indicates no degeneracies possible, thus no Jahn-Teller effects).

The figure illustrates the electron configurations in the case of large **Δ**. The electron configurations highlighted in red (d^3, low spin d^6, d^8, and d^{10}) **do not** exhibit Jahn-Teller distortions. On the other hand d^1, d^2, low spin d^4, low spin d^5, low spin d^7, and d^9, would be expected to exhibit Jhan-Teller distortion. These electronic configurations correspond to a variety of transition metals. Some common examples include Cr^{3+}, Co^{3+}, and Ni^{2+}.

Small Δ

Figure **6.5.6** (below) shows the various electronic configurations for octahedral complexes with small **Δ**, including the high-spin configurations of d^4, d^5, d^6, and d^7::

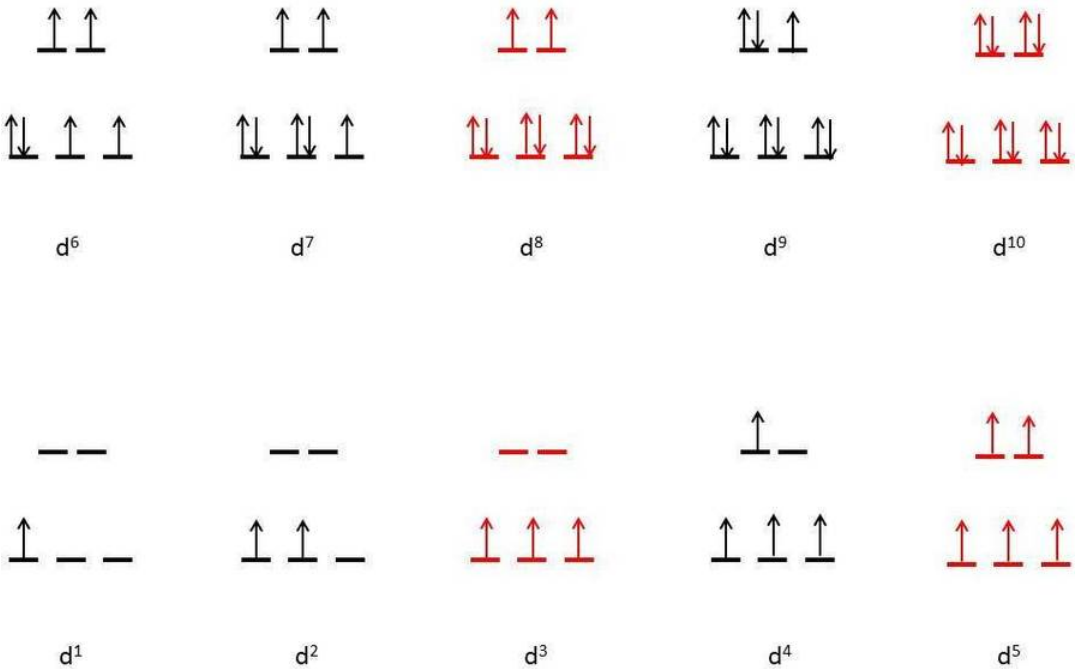


Figure **6.5.6**: High spin octahedral coordination diagram (red indicates no degeneracies possible, thus no Jahn-Teller effects).

The figure illustrates the electron configurations in the case of small Δ. The electron configurations highlighted in red (d^3, high spin d^5, d^8, and d^{10}) **do not** exhibit Jahn-Teller distortions. In general, degenerate electronic states occupying the e_g orbital set tend to show stronger Jahn-Teller effects. This is primarily caused by the occupation of these high energy orbitals. Since the system is more stable with a lower energy configuration, the degeneracy of the e_g set is broken, the symmetry is reduced, and occupations at lower energy orbitals occur.

Spectroscopic Observation

Jahn-Teller distortions can be observed using a variety of spectroscopic techniques. In UV-VIS absorption spectroscopy, distortion causes splitting of bands in the spectrum due to a reduction in symmetry (O_h to D_{4h}). Consider a hypothetical molecule with octahedral symmetry showing a single absorption band. If the molecule were to undergo Jahn-Teller distortion, the number of bands would increase as shown in Figure **6.5.7** below:

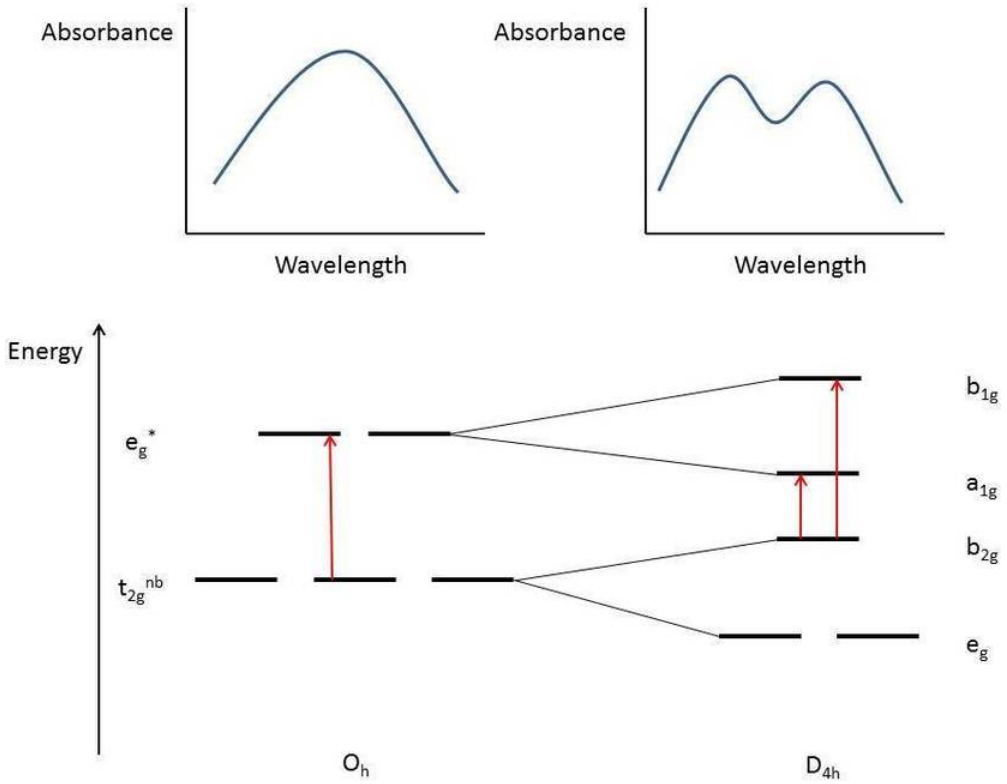


Figure **6.5.7**: Hypothetical absorption spectra of an octahedral molecule (left) and the same molecule with Jahn-Teller elongation (right). The red arrows indicate electronic transitions.

A similar phenomenon can be seen with IR and Raman vibrational spectroscopy. The number of vibrational modes for a molecule can be calculated using the 3n - 6 rule (or 3n - 5 for linear geometry) rule. If a molecule exhibits an O_h symmetry point group, it will have fewer bands than that of a Jahn-Teller distorted molecule with D_{4h} symmetry. Thus, one could observe Jahn-Teller effects through either IR or Raman techniques. This effect can also be observed in EPR experiments as long as there is at least one unpaired electron.

Table **6.5.1**: Examples of Jahn-Teller distorted complexes

$CuBr_2$	4 Br at 240 pm 2 Br at 318 pm
$CuCl_2$	4 Cl at 230 pm 2 Cl at 295 pm
$CuCl_2.2H_2O$	2 O at 193 pm 2 Cl at 228 pm 2 Cl at 295 pm
$CsCuCl_3$	4 Cl at 230 pm 2 Cl at 265 pm
CuF_2	4 F at 193 pm 2 F at 227 pm
$CuSO_4.4NH_3.H_2O$	4 N at 205 pm 1 O at 259 pm 1 O at 337 pm
K_2CuF_4	4 F at 191 pm 2 F at 237 pm
$KCuAlF_6$	2 F at 188 pm 4 F at 220 pm
CrF_2	4 F at 200 pm 2 F at 243 pm
$KCrF_3$	4 F at 214 pm 2 F at 200 pm
MnF_3	2 F at 209 pm 2 F at 191 pm 2 F at 179 pm

The Jahn-Teller Theorem predicts that distortions should occur for *any degenerate state*, including degeneracy of the t_{2g} level, however distortions in bond lengths are much more distinctive when the degenerate electrons are in the e_g level.

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Practice Questions

1. Why do d^3 complexes not show Jahn-Teller distortions?
2. Does the spin system (high spin v. low spin) of a molecule play a role in Jahn-Teller effects?
3. What spectroscopic method would one utilize in order to observe Jahn-Teller distortions in a diamagnetic molecule?
4. What spectroscopic method(s) would one utilize in order to observe Jahn-Teller distortions in a paramagnetic molecule?
5. Why are Jahn-Teller effects most prevalent in inorganic (transition metal) compounds?

Answers

1. Complexes with d^3 electron configurations do not show Jahn-Teller distortions because there is no ground state degeneracy.
2. Yes. Examining the d^5 electron configuration, one finds that the high spin scenario contains all singly occupied d orbitals (no degeneracy). However, the low spin d^5 electron configuration shows degeneracy, which then leads to possible Jahn-Teller effects.
3. UV-VIS absorption spectroscopy is one of the most common techniques for observing these effects. In general, it is independent of magnetism (diamagnetic v. paramagnetic). Thus, one would see the effect in the spectrum of UV-VIS absorption analysis. Note that EPR requires at least one unpaired electron, and therefore not EPR active.
4. Inorganic, specifically transition metal, complexes are most prevalent in showing Jahn-Teller distortions due to the availability of d orbitals. The most common geometry that the Jahn-Teller effect is observed is in octahedral complexes (see **Figures 2, 4, 5** and **6** above) due to the splitting of d orbitals into two degenerate sets. Due to stabilization, the degeneracies are removed, making a lower symmetry and lower energy molecule.

5. In addition to UV-VIS absorption, one can also employ EPR spectroscopy if a molecule possesses and unpaired electron.

Contributors and Attributions

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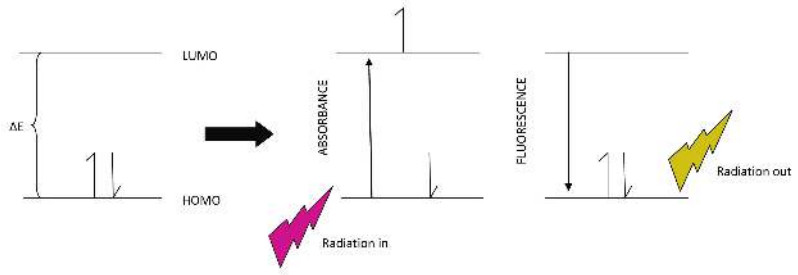
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6.6: Electronic Spectroscopy- Interpretation

Electronic Spectroscopy relies on the quantized nature of energy states. Given enough energy, an electron can be excited from its initial ground state or initial excited state (hot band) and briefly exist in a higher energy excited state. Electronic transitions involve exciting an electron from one principle quantum state to another. Without incentive, an electron will not transition to a higher level. Only by absorbing energy, can an electron be excited. Once it is in the excited state, it will relax back to it's original more energetically stable state, and in the process, release energy as photons.

Introduction

Often, during electronic spectroscopy, the electron is excited first from an initial low energy state to a higher state by absorbing photon energy from the spectrophotometer. If the wavelength of the incident beam has enough energy to promote an electron to a higher level, then we can detect this in the absorbance spectrum. Once in the excited state, the electron has higher potential energy and will relax back to a lower state by emitting photon energy. This is called fluorescence and can be detected in the spectrum as well.



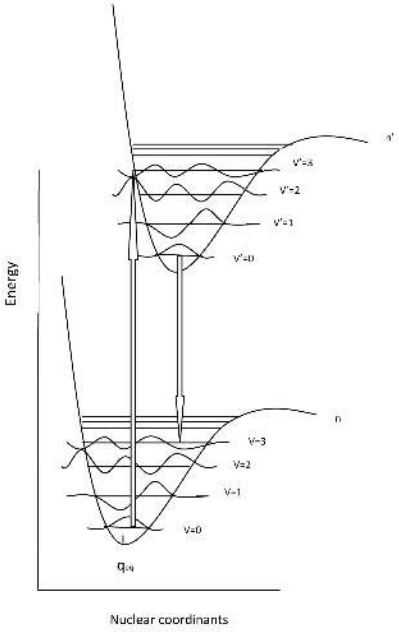
Embedded into the electronic states (n=1,2,3...) are vibrational levels (v=1,2,3...) and within these are rotational energy levels (j=1,2,3...). Often, during electronic transitions, the initial state may have the electron in a level that is excited for both vibration and rotation. In other words, n=0, v does not = 0 and r does not =0. This can be true for the ground state and the excited state. In addition, due to the Frank Condon Factor, which describes the overlap between vibrational states of two electronic states, there may be visible vibrational bands within the absorption bands. Therefore, vibrational fine structure that can be seen in the absorption spectrum gives some indication of the degree of Frank Condon overlap between electronic states.

When interpreting the absorbance and fluorescence spectra of a given molecule, compound, material, or an elemental material, understanding the possible electronic transitions is crucial. Assigning the peaks in the absorption spectrum can become easier when considering which transitions are allowed by symmetry, the Laporte Rules, electron spin, or vibronic coupling. Knowing the degree of allowedness, one can estimate the intensity of the transition, and the extinction coefficient associated with that transition. These guidelines are a few examples of the selection rules employed for interpreting the origin of spectral bands. Only a complete model of molecular energy diagrams for the species under investigation can make clear the possible electronic transitions. Every different compound will have unique energy spacing between electronic levels, and depending on the type of compound, one can categorize these spacings and find some commonality. For example, aromatic compounds pi to pi* and n to pi* transitions where as inorganic compounds can have similar transitions with Metal to Ligand Charge Transfer (MLCT) and Ligand to Metal Charge Transfer (LMCT) in addition to d-d transitions, which lead to the bright colors of transition metal complexes. Although surprises in science often lead to discovery, it is more fortuitous for the interpreter to predict the spectra rather than being baffled by the observation.

The following section will discuss the interpretation of electronic absorption spectra given the nature of the chemical species being studied. This includes an understanding of the molecular or elemental electronic state symmetries, Russell-Sanders states, spin multiplicities, and forbidden and allowed transitions of a given species.

As the light passes through the monochrometer of the spectrophotometer, it hits the sample with some wavelength and corresponding energy. The ratio of the initial intensity of this light and the final intensity after passing through the sample is measured and recorded as absorbance (Abs). When absorbance is measured at different wavelengths, an absorbance spectrum of Abs vs wavelength can be obtained. This spectra reveals the wavelengths of light that are absorbed by the chemical specie, and is specific for each different chemical. Many electronic transitions can be visible in the spectrum if the energy of the incident light

matches or surpasses the quantum of energy separating the ground state and that particular excited state. An example of an absorbance spectrum is given below.



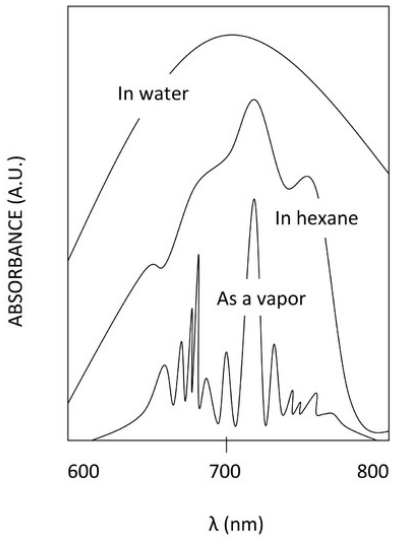


Figure 3.

Temperature Effects

Here we can see the effect of temperature and also the effect of solvents on the clarity of the spectrum. We can see from these anonymous compounds that decreasing the temperature allows the vibrational fine structure to emerge. These vibrational bands embedded within the electronic bands represent the transitions from v=n to v'=n. Generally, the v=0 to v'=0 transition is the one with the lowest frequency. From there, increasing energy, the transitions can be from v=0 to v'=n, where n=1,2,3... With a higher temperature, the vibrational transitions become averaged in the spectrum due to the presence of vibrational hot bands and Fermi Resonance, and with this, the vibrational fine structure is lost at higher temperatures.

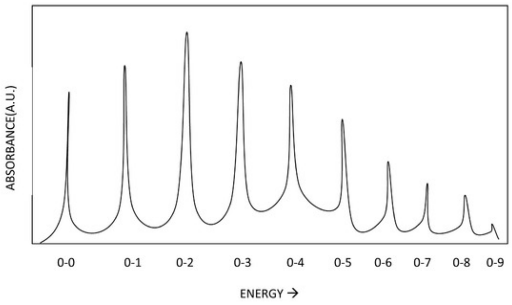


Figure 2.

Solvent Effects

The effect that the solvent plays on the absorption spectrum is also very important. It is clear that polar solvents give rise to broad bands, non-polar solvents show more resolution, though, completely removing the solvent gives the best resolution. This is due to solvent-solute interaction. The solvent can interact with the solute in its ground state or excited state through intermolecular bonding. For example, a polar solvent like water has the ability of hydrogen bonding with the solute if the solute has a hydrogen bonding component, or simply through induced dipole-dipole interactions. The non-polar solvents can interact though polarizability via London interactions also causing a blurring of the vibronic manifold. This is due to the solvent's tendency to align its dipole moment with the dipole moment of the solute. Depending on the interaction, this can cause the ground state and the excited state of the solute to increase or decrease, thus changing the frequency of the absorbed photon. Due to this, there are many different transition energies that become average together in the spectra. This causes peak-broadening. The effects of peak broadening are most severe for polar solvent, less so for non-polar solvents, and absent when the solute is in vapor phase.

Group Theory and The Transition Moment Integral

When estimating the intensities of the absorption peaks, we use the molar absorptivity constant (epsilon). If the transition is "allowed" then the molar absorptivity constant from the Beer's Law Plot will be high. This means that the probability of transition is large. If the transition is not allowed, then there will be no intensity and no peak on the spectrum. Transitions can be "partially allowed" as well, and these bands appear with a lower intensity than the full allowed transitions. One way to decide whether a transition will be allowed or not is to use symmetry arguments with Group Theory.

If the symmetries of the ground and final state of a transition are correct, then the transition is symmetry allowed. We express this by modifying the transition moment integral from an integral of eigenstates to an orthogonally expressed direct product of the symmetries of the states.

$$\int \psi_2 \mu \psi_1 d\mathcal{T} \longrightarrow \Gamma_2 \otimes \Gamma \mu_{xyz} \otimes \Gamma_1 \tag{6.6.1}$$

$$\int \psi_{v_2} \psi_{el_2} \mu \psi_{v_1} \psi_{el_1} d\mathcal{T} \longrightarrow \Gamma_{v_2} \otimes \Gamma_{el_2} \otimes \Gamma \mu_{xyz} \otimes \Gamma_{v_1} \otimes \Gamma_{el_1} \tag{6.6.2}$$

The conversions of integration to direct products of symmetry as shown gives spectroscopists a short cut into deciding whether the transition will be allowed or forbidden. A transition will be forbidden if the direct products of the symmetries of the electronic states with the coupling operator is odd. More specifically, if the direct product does not contain the totally symmetric representation, then the transition is forbidden by symmetry arguments. If the product does contain the totally symmetric representation (A, A_1, A_{1g}...etc) then the transition is symmetry allowed.

Some transitions are forbidden by the Equation 6.6.1 and one would not expect to be able to see the band that corresponds to the transition; however, a weak absorbance band is quite clear on the spectrum of many compounds. The transition may be forbidden via pure electronic symmetries; however, for an octahedral complex for example since it has a center of inversion, the transition is weakly allowed because of vibronic coupling. When the octahedra of a transition metal complex is completely symmetric (without vibrations), the transition cannot occur. However, when vibrations exist, they temporarily perturb the symmetry of the complex and allow the transition by equation (2). If the product of all of these representations contains the totally symmetric representation, then the transition will be allowed via vibronic coupling even if it forbidden electronically.

Hot Bands

Some transitions are forbidden by symmetry and do not appear in the absorption spectrum. If the symmetries are correct, then another state besides the ground state can be used to make the otherwise forbidden transition possible. This is accomplished by hot bands, meaning the electrons in the ground state are heated to a higher energy level that has a different symmetry. When the transition moment integral is solved with the new hot ground state, then the direct product of the symmetries may contain the totally symmetric representation. If we employ the old saying, "You can't get there from here!" then we would be referring to the transition from the ground state to the excited state. However, if we thermally excite the molecules from out of the ground state, then, "we can get there from here!"

Knowing whether a transition will be allowed by symmetry is an essential component to interpreting the spectrum. If the transition is allowed, then it should be visible with a large extinction coefficient. If it is forbidden, then it should only appear as a weak band if it is allowed by vibronic coupling. In addition to this, a transition can also be spin forbidden. The examples below of excited state symmetries, give an indication of what spin forbidden means:

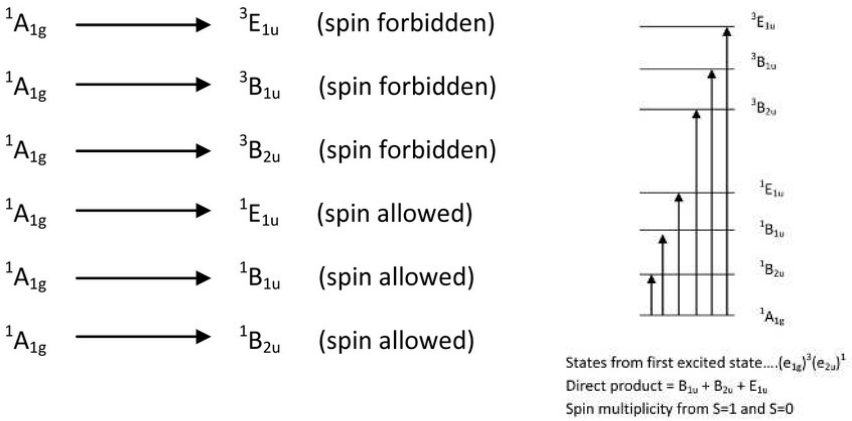
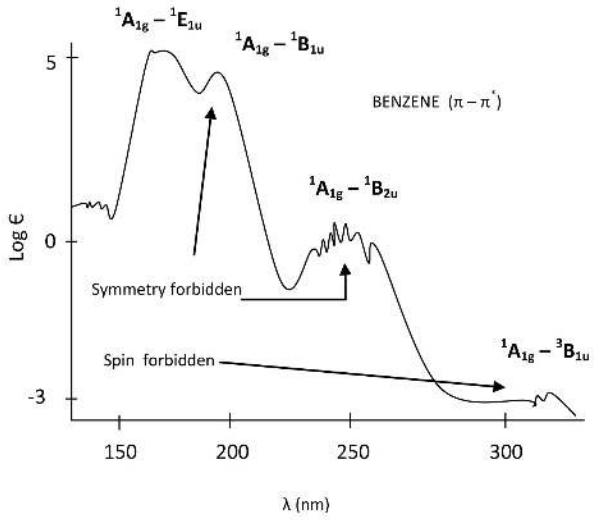


Figure **6.6.1**:

These states are derived from the electron configuration of benzene. Once we have the molecular orbital energy diagram for benzene, we can assign symmetries to each orbital arrangement of the ground state. From here, we can excite an electron from the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO). This is the lowest energy transition. Other transitions include moving the electron above the LUMO to higher energy molecular orbitals. To solve for the identity of the symmetry of the excited state, one can take the direct product of the HOMO symmetry and the excited MO symmetry. This give a letter (A, B, E..) an the subscript (1u, 2u, 1g...). The superscript is the spin multiplicity, and from single electron transitions, the spin multiplicity is 2S+1 = M, where S = 1 with two unpaired electrons having the same spin and S=0 when the excited electron flips its spin so that the two electrons have opposite spin. This gives M=1 and M=3 for benzene above. From the results above, we have three transitions that are spin allowed and three that are spin forbidden.

Once we take the direct product of the symmetries and the coupling operator for each of these states given above, we find that only the A_{1g} to E_{1u} transition is allowed by symmetry. Therefore, we have information regarding spin and symmetry allowedness and we have an idea of what the spectra will look like:

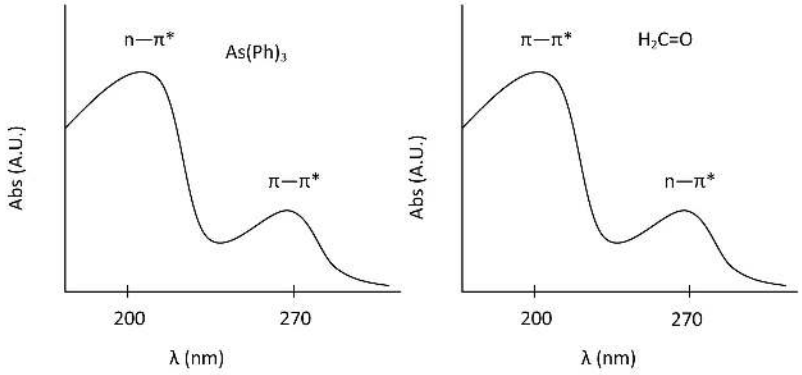


When interpreting the spectrum, it is clear that some transitions are more probable than others. According to the symmetry of excited states, we can now order them from low energy to high energy based on the position of the peaks (E1u is the highest, then B1u, and B2u is lowest). The A_{1g} to E_{1u} transition is fully allowed and therefore the most intense peak. The A_{1g} to B_{1u} and $A_{1g}$to B_{2u} transitions are symmetry forbidden and thus have a lower probability which is evident from the lowered intensity of their bands. The singlet A_{1g} to triplet B_{1u} transition is both symmetry forbidden and spin forbidden and therefore has the lowest intensity.

This transition is forbidden by spin arguments; however, a phenomenon known as spin-orbit coupling can allow this transition to be weakly allowed as well. If spin-orbit coupling exists, then the singlet state has the same total angular momentum as the triplet state so the two states can interact. A small amount of singlet character in the triplet state leads to a transition moment integral that is non-zero, so the transition is allowed.

Organic Molecule Spectra

From the example of benzene, we have investigated the characteristic pi to pi* transitions for aromatic compounds. Now we can move to other organic molecules, which involves n to pi* as well as pi to pi*. Two examples are given below:



The highest energy transition for both of these molecules has an intensity around 10,000 cm^{-1} and the second band has an intensity of approximately 100 cm^{-1}. In the case of formaldehyde, the $n \rightarrow \pi^*$ transition is forbidden by symmetry where as the pi to pi* is allowed. The opposite is true for $As(Ph)_3$ and the difference in molar absorptivity is evidence of this.

$n \rightarrow \pi^*$ transitions

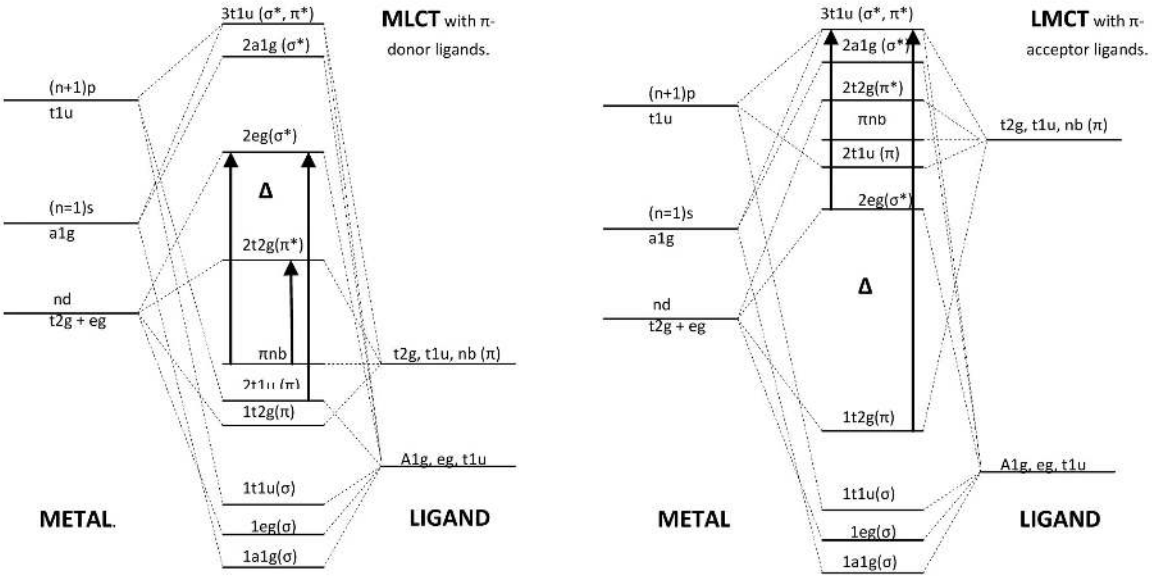
These transitions involve moving an electron from a nonbonding electron pair to a antibonding π^* orbital. They tend to have molar absorbtivities less than 2000 and undergo a blue shift with solvent interactions (a shift to higher energy and shorter wavelengths). This is because the lone pair interacts with the solvent, especially a polar one, such that the solvent aligns itself with the ground state. When the excited state emerges, the solvent molecules do not have time to rearrange in order to stabilize the excited state. This causes a lowering of energy of the ground state and not the excited state. Because of this, the energy of the transition increases, hence the "blue shift".

$\pi \rightarrow \pi^*$ transitions

These transitions involve moving an electron from a bonding π orbital to an antibonding π^* orbital. They tend to have molar absorptivities on the order of 10,000 and undergo a red shift with solvent interactions (a shift to lower energy and longer wavelengths). This could either be due to a raising of the ground state energy or lowering of the excited state energy. If the excited state is polar, then it will be solvent stabilized, thus lowering its energy and the energy of the transition.

Inorganic Molecule Spectra

Speaking of transition probabilities in organic molecules is a good introduction to interpreting the spectra of inorganic molecules. Three types of transitions are important to consider are Metal to Ligand Charge Transfer (MLCT), Ligand to Metal Charge Transfer (LMCT), and d-d transitions. To understand the differences of these transitions we must investigate where these transitions originate. To do this, we must define the difference between pi accepting and pi donating ligands:



d-d Transitions

From these two molecular orbital energy diagrams for transition metals, we see that the pi donor ligands lie lower in energy than the pi acceptor ligands. According to the spectral chemical series, one can determine whether a ligand will behave as a pi accepting or pi donating. When the ligand is more pi donating, its own orbitals are lower in energy than the t2g metal orbitals forcing the frontier orbitals to involve an antibonding pi* (for t2g) and an antibonding sigma* (for eg). This is in contrast to the pi accepting ligands which involve a bonding pi (t2g) and an antibonding sigma* (eg). Because of this, the d-d transition (denoted above by delta) for the pi acceptor ligand complex is larger than the pi donor ligand. In the spectra, we would see the d-d transitions of pi acceptor ligands to be of a higher frequency than the pi donor ligands. In general though, these transitions appear as weakly intense on the spectrum because they are Laporte forbidden. Due to vibronic coupling; however, they are weakly allowed and because of their relatively low energy of transition, they can emit visible light upon relaxation which is why many transition metal complexes are brightly colored. The molar extinction coefficients for these transition hover around 100.

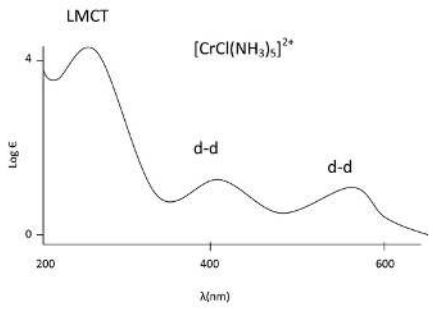
LMCT Transitions

At an even higher energy are the LMCT which involve pi donor ligands around the metal. These transitions arise because of the low-lying energy of the ligand orbitals. Therefore, we can consider this as a transition from orbitals that are ligand in character to orbitals that are more metal in character, hence the name, Ligand to Metal Charge Transfer. The electron travels from a bonding pi or non-bonding pi orbital into a sigma* orbital. These transitions are very strong and appear very intensely in the absorbance spectrum. The molar extinction coefficients for these transitions are around 10^4. Examples of pi donor ligands are as follows: F^-, Cl^-, Br-, I^-, H_2O, OH^-, RS^-, S_2^-, NCS^-, NCO^-,...

MLCT Transitions

The somewhat less common MLCT has the same intensity and energy of the LMCT as they involve the transition of an electron from the t2g (pi) and the eg (sigma*) to the t1u (pi*/sigma*). These transitions arise from pi acceptor ligands and metals that are willing to donate electrons into the orbitals of Ligand character. This is the reason that they are less frequent since metals commonly accept electrons rather than donate them. All the same, both types of Charge Transfer bands are more intense than d-d bands since they are not Laporte Rule forbidden. Examples of pi accepting ligands are as follows: CO, NO, CN^-, N_2, bipy, phen, RNC, $C_5H_5^-$, C=C double bonds, C≡C triple bonds,...

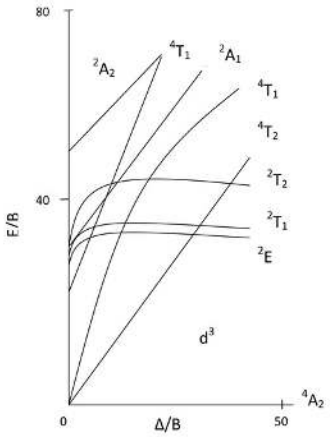
From this spectra of an octahedral Chromium complex, we see that the d-d transitions are far weaker than the LMCT. Since Chlorine is a pi donor ligand in this example, we can label the CT band as LMCT since we know the electron is transitioning from



a MO of ligand character to a MO of metal character. The Laporte forbidden (symmetry forbidden) d-d transitions are shown as less intense since they are only allowed via vibronic coupling.

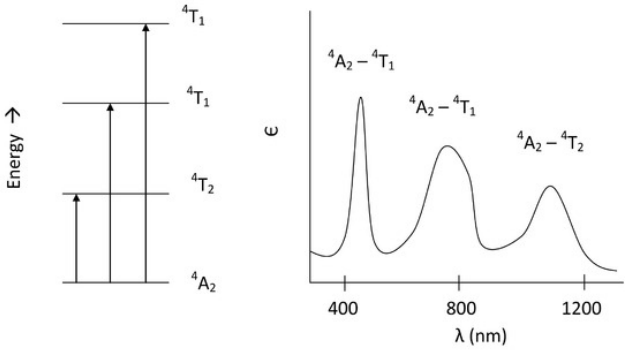
In addition, the d-d transitions are lower in energy than the CT band because of the smaller energy gap between the t2g and eg in octahedral complexes (or eg to t2g in tetrahedral complexes) than the energy gap between the ground and excited states of the charge transfer band.

These transitions abide by the same selection rules that organic molecules follow: spin selection and symmetry arguments. The Tanabe and Sugano diagrams for transition metal complexes can be a guide for determining which transitions are seen in the spectrum. We will use the [CrCl(NH3)5]2+ ion as an example for determining the types of transitions that are spin allowed. To do this we look up the Tanabe and Sugano diagrams for Octahedral fields. Since Cr in the complex has three electrons, it is a d3 and so we find the diagram that corresponds to d3 metals:



Based on the TS diagram on the left, and the information we have already learned, can you predict which transition will be spin allowed and which ones will be forbidden? From the diagram we see that the ground state is a $^4A_2$. This is because of the three unpaired electrons which make M=2S+1= 4. The A comes from the fact that there is only one combination of electrons possible. With a spin multiplicity of 4, by the spin selection rules, we can only expect intense transitions between the ground state $^4A_2$ and $^4T_2$, $^4T_1$, and the other $^4T_1$ excited state. The other transitions are spin forbidden. Therefore, we would expect to see three d-d transitions on the absorption spectra.

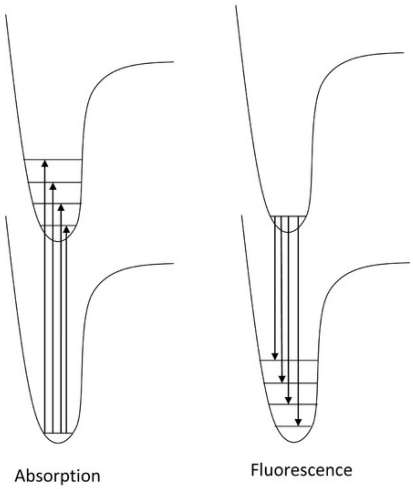
For us to visualize this, we can draw these transitions in order of increasing energy and then plot the spectrum as we would expect it for only the d-d transitions in a d^3 octahedral complex:



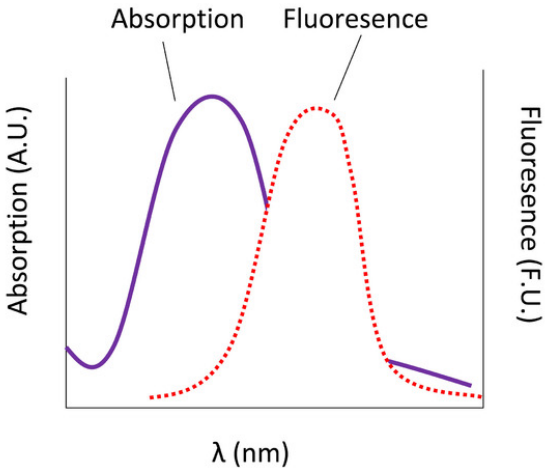
From three spin allowed transitions, we would expect to see three d-d bands appear on the spectrum. In addition to these of course, the LMCT band will appear as well.

Fluorescence

Now that we have discussed the nature of absorption involving an electron absorbing photon energy to be excited to a higher energy level, now we can discuss what happens to that excited electron. Due to its higher potential energy, the electron will relax back to its initial ground state, and in the process, emit electromagnetic radiation. The energy gap between the excited state and the state to which the electron falls determines the wavelength of light that will be emitted. This process is called fluorescence. Generally, the wavelengths of fluorescence are longer than absorbance, can you explain why? Given the following diagram, one can see that vibrational relaxation occurs in the excited electronic state such that the electronic relaxation occurs from the ground vibrational state of the excited electronic state. This causes lower energy electronic relaxations than the previous energy of absorption.



Here we see that the absorption transitions by default involve a greater energy change than the emission transitions. Due to vibrational relaxation in the excited state, the electron tends to relax only from the v'=0 ground state vibrational level. This gives emission transitions of lower energy and consequently, longer wavelength than absorption. When obtaining fluorescence, we have to block out the transmitted light and only focus on the light being emitted from the sample, so the detector is usually 90 degrees from the incident light. Because of this emission spectra are generally obtained separately from the absorption spectra; however, they can be plotted on the same graph as shown.



Generally separated by ~10 nm, the fluorescence peak follows the absorption peak according to the spectrum. With that, we conclude our discussion of electronic spectroscopy interpretation. Refer to outside links and references for additional information.

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3. Harris, Daniel; Bertolucci, Michael. Symmetry and Spectroscopy. *An Introduction to Vibrational and Electronic Spectroscopy.* Dover Publications, Inc., New York, 1989.
4. Miessler, Gary; Tarr, Donald. Inorganic Chemistry. Pearson Education Inc., New Jersey, 2004.

Practice Problems!

1. From what we've discussed so far, if we change the solvent from non-polar to polar what effect will this have on the frequency of absorption if the ground state is non-polar and the excited state is polar? Will it increase or decrease?
2. What causes peak broadening in absorption spectra?

3. What are the little spikes in the more broad electronic transition bands? Draw potential energy wells to show their order and use the Frank Condon factor to describe your answer.
4. Why are fluorescence bands lower in energy than absorption bands?
5. If an electronic transition is symmetry forbidden and spin forbidden, list two ways of overcoming this to explain why the bands are still seen in the spectrum.
6. Define MLCT, LMCT, and d-d transitions and label the molar extinction coefficients associated with each.
7. How do the spectra of transition metal complexes differ with organic molecule?
8. What is a "blue shift" and a "red shift" and what solvent conditions would cause these to occur?
9. From the Tanabe Sugano diagram of a d2 metal complex, list all of the transitions that are spin allowed.
10. Define the coupling operator that sits between the excited state wave function and the ground state wave function in the transition moment integral!

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